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PETROLEUM REFINERY ENGINEERING

BY

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PREFACE

There are many valuable reference books pertaining to petroleum refining and the derivatives of petroleum, but as yet there has been no adequate presentation of the fundamentals of engineering design and processing. It is my hope that this book will aid in clarifying the many detail questions that arise during plant operation and that the book will encourage the refinery engineer to utilize the principles of chemical engineering more fully. The book should be of value to engineering students; to plant superintendents, engineers, chemists, and foremen; and to scientists who may wish to follow the application of their theoretical work. Aside from petroleum refining, the book should be of interest to chemical engineers because of refinery practice that may be applied to other industries.

I regret that much useful information could not be discussed. Subjects such as corrosion, pipe and fittings, pumping equipment, engineering and plant economics, control instruments, and structural features are of vital importance, and they deserve more attention than this volume permits.

Engineering involves the practical application of scientific knowledge, and hence I have made a conscious effort to emphasize the practical phases of engineering work. In so doing it has often been necessary to resort to empirical relationships. No apology is necessary for such a treatment, because engineers must build and operate plants regardless of inadequate information. In fact the history of industrial development shows that commercial plants are usually built before the theory of the process is fully understood. Scientific study follows the empirical development, and science finally administers those fine improvements that stamp the new process as truly great. The process of empirical growth will always be the lot of the practical scientist or engineer.

For the same reasons some handbook information has been introduced. Although such information is not profound, it is the tool by which theory can be put into action. Such information is also necessary in the solution of illustrative problems, and I believe that no method of engineering study is more effective than detailed examples. Furthermore, an engineer must spend more time applying information than deriving or finding it, and hence handbook information and comprehensive references are provided. The current literature contains much that is useful, but the literature is so voluminous that it may be useless to a busy engineer unless it is presented in an organized form. I have attempted to organize this contemporaneous literature, but I have refrained as far as possible from tiring the average reader with too many references and conflicting opinions.

By this practical approach I hope that the book will make our inadequate fund of information more useful to the engineer. The book deals mainly with design fundamentals, and it should complement and supplement other valuable petroleum books which deal with other phases of refining, such as Redwood's "Treatise on Petroleum"; Nash and Howes' "Principles of Motor Fuel Preparation"; "Petroleum Technology," by Gurwitsch; and "Chemical Refining of Petroleum," by Kalichevsky and Stagner. Doubtless, the design methods here outlined will not always coincide with the methods used by other engineers, but by means of this structure of design methods we should all be able to gain a larger insight into petroleum processing.

I find it difficult properly to acknowledge all of the contributions to this volume. I am particularly indebted to Professor A. H. White of the University of Michigan, for inspiration and an appreciation of engineering endeavor, to Dr. S. Born of the University of Tulsa for a close cooperation in many phases of the work, and to Dr. G. G. Brown of the University of Michigan, because of frequent references to his valuable work on natural gas and petroleum.

I am indebted to Dr. Gustav Egloff of the Universal Oil Products Company, Dr. R. J. Kaufmann of the University of Tulsa, Mr. L. L. Davis of the Continental Oil Company, and Professor Walter G. Whitman of the Massachusetts Institute of Technology, for advice concerning parts of the manuscript.

W. L. NELSON.

TULSA, OKLA.,
January, 1936.

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PART I

INTRODUCTION

CHAPTER I

CHEMICAL ENGINEERING AND PETROLEUM ENGINEERING

The refining of petroleum constitutes one of the important branches of chemical engineering. The industry utilizes most of the unit operations of chemical engineering, and much of the modernization of the industry during the past decade can be attributed to the adoption of chemical engineering principles. The chemical engineer differs from the industrial or plant chemist in that he is trained as an engineer in the construction and operation of commercial chemical equipment, and he differs from the mechanical engineer because he has a more thorough training regarding the chemical and physical changes that occur. Thus, chemical engineering deals with processing operations, and petroleum refining is a typical process industry. Among the unit operations that are most widely used are fluid flow, heat transfer, distillation, absorption, filtration, and extraction. Some of the purely chemical operations are treatment with sulfuric acid and with alkalies, percolation and contacting with fuller's earth, cracking or thermal decomposition of heavy oils into lighter ones, and hydrogenation. The number of chemical engineering graduates that enter the petroleum industry is clear proof of the close relation of chemical and petroleum refinery engineering. In recent years more chemical engineering graduates have found employment in the petroleum industry than in any of the other chemical industries, such as organic chemicals, heavy chemicals, rubber, iron and steel, fertilizers, and leather. The petroleum industry is also said to be the largest single market for chemicals. Considering the sale of sulfuric acid, alkalies, fuller's earth, tetraethyl lead, alcohol and other chemicals as antifreeze materials, organic liquids for solvent extraction, and the many other chemicals that are used, the total market at the present time amounts to more than $100,000,000 a year.

Design and Operation.—The chemical engineer, by virtue of his training, is particularly qualified to supervise the design and operation of manufacturing equipment. The fundamentals of design and the fundamentals of plant operation are the same, and hence a designer cannot hope to be entirely successful unless he is an experienced operator, and conversely a plant cannot be operated most successfully or economically without a knowledge of design. In fact the very methods by which a plant is designed are the same as those used by an operator when he analyzes the behavior of the plant.

In many ways the operation of an equipment may be more difficult than the design of the equipment. The designer is somewhat removed from many practical problems, and regardless of his ability he will be unable to anticipate all of the factors that may appear during operation. The operator cannot avoid these factors—he must meet them in actuality, and his task is an endless one. Thus, plant operators, superintendents, and even plant executives are interested in equipment design because it is so closely related to plant operation.

Plant Development.—The training of the chemical engineer also fits him for the economic study of processing operations and the development of new processes. Perhaps this accounts for the large number of chemical engineers that are employed as business executives. The development of a new process embraces the broadest type of knowledge. The process must be based on sound scientific principles; methods and equipment must be devised by which the process can be carried to a commercial scale; and—of prime importance—the process must be economically feasible. A knowledge of the unit operations of chemical engineering is the tool by which new processes may be transferred from the laboratory to full-scale commercial equipment.

CHAPTER II

HISTORY AND DEVELOPMENT OF REFINING

Coal oil for household lamps was already being manufactured in the United States when the Drake discovery well (1859) was drilled. In 1846 Dr. Abraham Gesner had prepared coal oil from coal by thermal decomposition, and he lectured upon its manufacture and use. The country was truly interested in coal oil because sperm oil was becoming more and more expensive. The number of coal-distillation plants in the United States during the years 1852 to 1859 has been estimated as 60. The largest of these was the Downer plant which involved an investment of $250,000. This industry was thrown into confusion by the discovery of petroleum in Pennsylvania, and within a few years most of the coal-distillation plants had been adapted to the processing of petroleum. Although records show that petroleum was distilled in Russia in 1735,[1] the first real refinery is generally conceded to be that of William Barnsdall and William H. Abbott. This plant was built at Titusville, Pa., in 1860 at a cost of $15,000. Hundreds of small refineries, having daily capacities of 10 to 500 bbl., and several larger ones were in operation by 1873.

Continuous Distillation.—All the earliest refineries operated by the batch system of operation. In this method a quantity of oil was charged into a vessel, and the products were distilled, one by one, by raising the temperature until a residue of heavy lubricating oil or tar remained in the still. Although the batch method survives even today in small plants, enterprising refiners soon recognized the advantages of continuous operation. In 1860 a patent was granted to D. S. Stombs and Julius Brace disclosing the essentials of a continuous system. In such a process the crude oil is admitted to the plant continuously, and

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[1] Herodotus (450 B.C.) and other historians report petroleum and tar (under other names) at dates before 1735, but they do not tell how the oil was refined.

the products are collected continuously therefrom. Batch or intermittent processing with a cycle consisting of (1) charging, (2) operation, and (3) shut-down is wasteful of labor, material, and fuel. Truly successful continuous plants were not in operation until after the patents of Hill and Thumm of Oil City, Pa., in 1870; of Van Syckles of Titusville, Pa., in 1877; and of Norman H. Henderson, an Englishman, in 1889. Although the M. J. Trumble patents (1911) are usually considered as an innovation in fractionation, nevertheless they involve the use of a continuous tubestill heater and disclose the conception of modern continuous distillation. The first successful Trumble plant was built at Vernon, Calif., in about 1912 by the General Petroleum Corporation. Since that time the tubestill or pipestill has been finding increasing usefulness. As will be discussed later, the pipestill is necessary if the principles of fractionation in a bubble-tower are to be completely utilized. The pipestill has the further advantage that it allows an absolute control of the velocity of the fluid past the heating surface. The advantages of circulation have long been recognized even in shellstill practice. The Hill and Thumm patent of 1870 specifies that the oil shall flow continuously in a thin stream over the heating surface, and more recently C. W. Stratford introduced a shellstill with a manifold of nozzles arranged along the bottom of the still. Modern distillation plants are completely continuous, with the exception of cokestills which are operated either as batch or as semi-continuous operations. In modern plants several distillation units are often connected together so that the hot product from one unit (usually the residue) is pumped directly to another. Also, several units may have a common heat-exchange system by which the charge stock for one unit is heated in other units. In other phases of refining, such as treating, dewaxing, compounding, and packaging, the processing is still partly batch or semi-continuous, but continuous operation is not of great value in these operations.

Cracking or Thermal Decomposition.—Even the phenomenon of cracking is not a modern development. True, the large plants and the wholesale manufacture of decomposition products are new, but thermal decomposition was actually practiced in the distillation of coal and oil shale even before the days of the oil industry. During the first years of the petroleum industry a "cracking distillation," in addition to the customary distillation with steam, was practiced. The cracking distillation is reported to have been discovered accidentally in 1861. A distillation in a 16-bbl. still had been half completed, and the stillman had built a strong fire. The stillman intended to be away an hour but was unable to return until 4 hr. later. He found that a light-colored distillate of a low specific gravity was being collected. The specific gravity was even lower than that of the product before he left. Upon investigation, it was found that a heavy oil was condensing on cooler parts of the equipment and dropping back into parts of the still which were at a temperature sufficiently high to cause decomposition of the heavy oil into lower boiling-point products. In the early days of the industry gasoline was of little value, and cracking was practiced for the purpose of producing more kerosene than could be obtained by steam or simple distillation. The first attempts to produce gasoline by cracking were by the decomposition of petroleum vapor. Although none of these first attempts were commercially successful, they are worthy of mention. Early patents in vapor-phase cracking are those of Greenstreet, Rittman, Alexander, Hall, Parker, the General Petroleum Corporation, the Texas Products Company, Ramage, and others. However, vapor-phase plants were not entirely successful until about 1925. At that time the Gyro and de Florez processes were being developed.

Refinery statistics	1931	1933
Total refining capacity of U.S....	3,913,180	3,696,410 bbl. per day
Cracking capacity of U.S.......	1,844,609	1,823,521* bbl. per day
Cracked gasoline, percentage of total gasoline................	40.3†	53.3†
Number of refineries having cracking plants....................	208	198
Number of cracking plants (some shut down)..................	....	1,303

* It is now common to rate the capacity of cracking plants on the barrels of raw stock, whereas in the past the recycle stock was counted as capacity.

† EGLOFF and NELSON, "Cracking Light and Heavy Oils," 3d Midyear Meeting A.P.I., Tulsa, Okla., May, 1933.

The liquid-phase cracking processes were the first to be commercially applied, and the Burton process was the first to be practiced on a large scale. Development began in 1910, a patent was issued in 1912, recognition of Dr. Burton by the Willard Gibbs Medal was given in 1918, and by 1921 over eight hundred Burton stills were said to be in operation. Other early liquid-phase processes were the Fleming, Isom, and Emerson processes.

The importance of cracking in the modern refinery may be emphasized by a few statistics as shown in the table on page 7.

A list of the various cracking processes and the approximate daily capacity in the United States follows:

Process	1931
Tube and tank	499,000
Cross	354,000
Dubbs	277,250
Holmes Manley	189,400
Isom	85,000
Pipestill or tubestill	66,600
Jenkins	55,750
Vapor-phase	23,650
Others	293,159
Total	1,844,609

The general scheme of processing is much the same in all modern cracking plants. The advantages of cracking only those stocks that contain no cracked tar is recognized by all. A residual charge-stock is often distilled in the cracking unit itself, but only the distilled part of the stock is exposed to cracking conditions. However, residual stocks are cracked directly in some processes. These processes usually produce a slightly larger yield of gasoline, but the length of time on stream may be short. Another generally recognized advantage is the use of a quench-stock to cool the cracked material rapidly from the cracking temperature to a temperature low enough to avoid the deposition of coke. All systems are continuous, unless coke is being produced.

The newest developments in cracking are "viscosity-breaking" plants and "reforming" plants. In the first of these only a mild decomposition takes place. The purpose is to decompose the oil just enough to lower its viscosity and pour-point, so that it can be pumped more easily. Little or no gasoline is produced. Reforming units are cracking plants that operate on naphtha or low-octane-number gasoline. The naphtha is decomposed into a large percentage of highly antiknock gasoline. These units were developed in response to the growing demand for the antiknock gasoline that is required for modern automobile engines. Although hydrogenation may not belong under the heading of cracking, it is so similar to cracking that it should be mentioned at this point. Since 1927 the process of hydrogenation, as developed by the Standard Development Company, has attracted much attention. This process differs from cracking mainly because of the introduction of hydrogen, in the presence of a catalyst, into the decomposition zone. Assimilation of hydrogen occurs at elevated pressures and temperatures. The process may be adapted to the manufacture of most of the commercial oil products, whereas cracking is practiced only for the manufacture of gasoline. In the future we may expect that the hydrogenation plant will be the very nucleus of refinery processing.

Fractionation.—The term fractionation refers to the separation of a liquid mixture into several products of shorter boiling-range by means of vaporization. In early refineries this separation was obtained by a series of distillations in which, first, an inaccurate separation was made, and then the partly separated products were redistilled several times, if necessary, until finally the product met market requirements. The next development was to fractionate by partial condensation; *i.e.*, a mixture of vapor was condensed in portions by successively cooling the vapor to lower and lower temperatures. An invention of this nature was that of Hugh L. Allen (Eng. Pat. 117,277–1918) in which the vapor was successively cooled by means of a series of air-cooled condensers into several liquid products. This type of separation, although it is practiced even today, has not proved to be widely useful.

The modern era of refining dates from the adoption of pipestills and bubble-towers. The name bubble-tower has become common because the vapor in the tower bubbles through the liquid on the plates in the tower. In bubble-tower fractionation, a mixture of ascending vapor is scrubbed by a descending flow of oil. Bubble-towers have been so universally adopted, all within a few years, that no one can be accredited with invention. In fact the fundamentals of fractionation were borrowed directly from the chemical distillation industries.

Bubble-tower fractionation is the standard method of separation used in all phases of modern refinery distillation. Bubble-towers are used in topping plants, rerun plants, vacuum plants, cracking plants, natural-gasoline stabilizers, absorption plants, and steam stripping operations.

Natural-gasoline Plants.—Natural gasoline attracted little attention until about 1912, at which time the demand for motor fuels became acute. Today more than 7 per cent of all of the gasoline produced is manufactured from natural gas. The first widely used method of recovery was the compression process. As gas is compressed, the dew-point is raised so that, upon cooling to the original temperature, a mixture of hydrocarbons condenses. The condensate contains a large percentage of volatile hydrocarbons, such as propane, which must be removed before the gasoline is a suitable motor fuel. The first method that was used to remove these hydrocarbons from the raw gasoline was called "weathering." Weathering was accomplished by allowing the "wild" gasoline to stand in an open vessel for a time. A large part of the gasoline was lost during this weathering.

In later processes, natural gas was passed through absorption chambers or packed columns, in which the gasoline was absorbed by naphtha. These naphtha-columns finally developed into the absorption process of today. In the absorption process, the natural gasoline is absorbed by a low boiling-range gas oil, and the gasoline is recovered from the rich gas oil by heating it and stripping the gasoline from it with steam.

For a few years following the World War the *adsorption* process received much attention, but since that time it has been almost abandoned. In this process the gasoline was adsorbed by charcoal and recovered from the charcoal by steaming.

The high-pressure absorber is one of the newest developments in natural-gasoline manufacture. Much smaller quantities of absorption oil are required. Usually it does not pay to compress the gas, so that high-pressure absorption is usually limited to the processing of those gases that are already at a high pressure at the field. Natural gasoline is no longer weathered. The wild gasoline is stabilized by fractionating it at a pressure of about 150 lb. per square inch in a fractionating or stabilizing column.

Dewaxing.—The filter-press method of dewaxing, as originally used in Scotland for shale oil before the development of the oil industry, is still the most widely used method (1935) of dewaxing the lighter wax-bearing oils. Heavy residual wax-bearing stocks were first dewaxed by cold-settling. The early refiners discovered that a waxy layer of oil was deposited in the bottoms of crude-oil storage tanks, if the tanks were allowed to stand full of oil through the winter. The cold-settling method was a development of this practice. The oil was chilled and allowed to stand in insulated tanks. The centrifuge process of dewaxing residual stocks was studied for many years before it was entirely successful. The difficulty had been the obtainment of sufficiently high centrifuge speeds and the removal of the petrolatum wax from the bowl of the machine. In about 1921, warm water was suggested as a carrying liquid to be injected at the edge of the bowl. The use of warm water was successful, and the centrifuge method of today is essentially the same process as was then used.

Recently, solvent dewaxing methods have become important. An important advantage of these processes is the ability to handle both light and heavy wax-stocks by a single process. Many different solvent processes are being practiced commercially, but as yet no one process has been accepted to the exclusion of others.

Chronology of Market Demands.—In the following outline no attempt has been made to set the date at which new processes were conceived. Developments are not mentioned until the time when they were generally accepted by the industry.

1860 to about 1885.—The major refinery product was kerosene or burning-oil. During this period disfavor was brought upon the industry by the sale of burning-oils that contained too much gasoline. Laws were enacted limiting their flash-point.

1885–1900.—Mineral lubricating oils gained favor with the public. Until this time vegetable oils were considered the best. Paraffin-base lubricating oils gained a favorable reputation which has been retained to this day.

1900–1914.—Shortly after 1900, gasoline began to be valuable, and within a few years it had grown to be the most useful refinery product. The demand became so great that many new oil fields were discovered, and fundamental improvements in refining methods ensued. The compression process for the recovery of natural gasoline was developed, and experiments were conducted concerning cracking.

1914–1925.—The ever increasing demand for gasoline caused the refiner to turn to methods of recovering more of it from crude oil. The cracking processes were brought to a high degree of perfection, and the fundamentals of heating, fractionation, heat transfer, and absorption were developed and put into practice. Continuous processing systems using fractionating towers, pipe- or tubestill heaters, and heat exchangers, were developed. Structural equipment was developed for high pressures and high temperatures. In 1920 a marked increase in the use of fuel oil for the generation of power was noted, and the tendency has continued until today.

1925–1929.—During this period the large profits from lubricating-oil processing attracted attention, and vacuum distillation was developed. Until this time vacuum distillation had not been truly successful, because batch or shellstill heating had to be used. The newly acquired knowledge of pipestill and fractionating-tower design made the development of continuous vacuum-distilling systems a logical step. Low cold-test oils were produced by direct expansion of ammonia rather than by the customary method of circulating brine. Continuous pipestill equipment was adapted to all distillation operations including the rerunning of pressure-distillate and lubricating-oil stocks. The Edeleanu method of solvent treating proved to be commercially successful.

1929–1935.—The demand for highly antiknock gasoline resulted in the development of vapor-phase cracking plants, gasoline-reforming units, and an ever increasing use of cracking plants. The hydrogenation process was developed, but it has not been widely used because of unfavorable economic conditions. Several successful solvent-dewaxing and solvent-treating methods were developed. High-viscosity-index lubricating oils are produced by solvent-treating methods. Vacuum distillation was widely applied to the manufacture of road oil and asphalt.

The Magnitude of the Industry.—The "Biennial Census of Manufacturers" and the "Statistical Abstract of the United States," both by the Department of Commerce, indicate that the manufacture of petroleum (and coal) products is of national importance. In the year 1927, by value of plant products, petroleum and coal products ranked eighth among the 16 major groups of industry.

Compared with individual manufacturing industries, petroleum refining commands an even more important position. By value of products in 1931, slaughtering and meat packing ranks first, at a value of over $2,000,000,000 a year; and second and third places go to motor vehicles and petroleum refining respectively, each at about $1,500,000,000.

In 1890 the value of refinery products was about $85,000,000 per year, and by 1931 about $1,500,000,000. In 1935 there were 496 operating refineries in the United States having a daily capacity of almost 4,000,000 bbl. per day. The industry grew rapidly from about 1912, at which time the demand for gasoline became important.

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CHAPTER III

INTRODUCTION TO PROCESSING

There are three general types of crude oil, *viz.*, *paraffin* base, *mixed* base, and *naphthene* (asphalt) base. These classes and their identification will be discussed in detail in Chap. VII. The student should beware of attaching too much importance to this classification, but it is useful to men of wide experience. Crude oil varies greatly in composition, so that no definite grouping is possible. In general the oils fall into the foregoing classes, but few oils are typically paraffin, naphthene, or mixed base.

Variety in Processing Methods.—Because of the differences in crude oils, we find that processing methods differ. We may safely say that no two plants are employing exactly the same processing scheme. What may be a perfect method of handling one oil may be inadequate for another. The refining of an oil is, of course, an economic problem. (1) What are the value and the accessibility of the raw stock; (2) what are the value of the products and the possibilities of marketing them; (3) what yields of products are to be expected; and (4) what will it cost to process the stock? These factors promote the use of many different processing plans.

Refinery Products.[1]—A study of the products of refining will help to show why so many different processing methods are used. The more important refinery products may be grouped as follows:

1. *Natural and refinery gas*—household and industrial fuel.
2. *Gasoline*—fuel for internal-combustion engines.
3. *Naphtha and benzene*—cleaner's solvents, paint thinners, chemical solvents, and stocks for the blending of motor fuels.
4. *Kerosene*—burning-oil for household lamps.
5. *Distillates and gas oil* (distilled products)—fuels for industrial and household furnaces, enriching agents in gas manufacture, and absorbents for hydrocarbon gases.
6. *Neutral oils*—light or low-viscosity lubricating-oil stocks for the compounding of motor oils.

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[1] See Chap. IX for details.

7. *Brightstock*—heavy or high-viscosity lubricating-oil stocks for the compounding of motor oils.
8. *Cylinder oils*—unfinished heavy-oil stocks used directly as lubricants for steam-engine cylinders or for the manufacture of brightstock. Usually filtered but not dewaxed.
9. *Paraffin wax*—used for the manufacture of wax paper, insulating material, package sealing, etc.

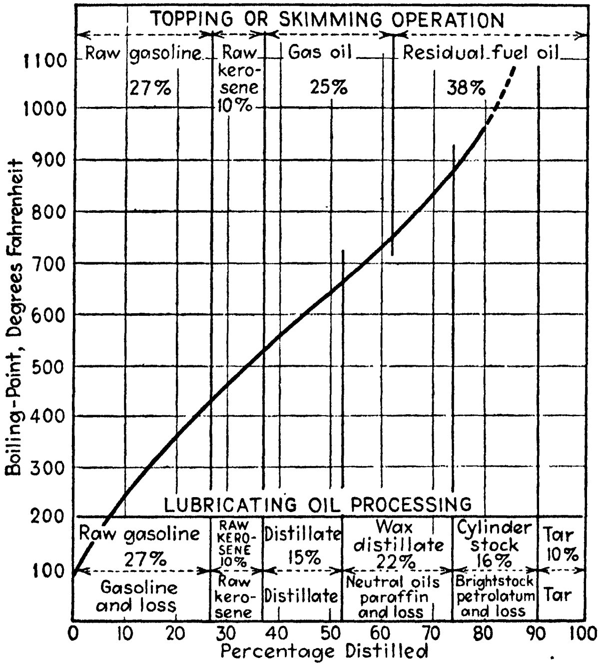

FIG. 1.—Boiling range of refinery products (31.7 A.P.I. Texas mixed-base crude oil).

10. *Petrolatum* (noncrystalline wax)—base material in the compounding of greases, salves, and ointments.
11. *Fuel oil* (residual product)—industrial fuel.
12. *Tar and asphalt*—asphalt, road oil, roofing materials, and protective coatings.
13. *Petroleum coke*—solid industrial fuel.

General Processing.—The most important method of separating petroleum products is distillation, and hence the products should be compared with one another in the order of their boiling-ranges. A mixed-base oil might yield products as indicated in Fig. 1. Figure 2 likewise indicates the relation among the raw materials, the intermediate refinery stocks, and the finished market products. The dotted lines indicate products obtained by cracking. The products obtained by distillation are called raw products, and most of them cannot be sold until they have been further refined.

Raw gasoline and raw naphtha are often treated with chemical agents such as sulfuric acid, sodium hypochlorite, or certain earths. Kerosene usually requires only a sweetening treatment; but for fine colors, acid treatment or filtration is used. The distillate fuels and gas oil are usually sold without being refined, but when used for special purposes they are also treated with sulfuric acid. *Pressure distillate* or pressure gasoline, obtained by cracking or thermal decomposition (Fig. 2), may be treated with acid and redistilled or treated in the vapor-phase with fuller's earth. *Natural gasoline*, obtained from natural gas, usually requires only a sweetening treatment for the removal of hydrogen sulfide.

Wax distillate, the raw stock for the manufacture of the light lubricating oils or neutral oil-blending stocks, contains crystalline wax. The wax is removed by chilling the distillate and filtering the wax from the oil in filter presses. Two unfinished stocks, *slack wax* and *pressed distillate,* are obtained in the pressing operation. *Neutral oils*[2] are produced from the pressed distillate by distillation and subsequent filtration through fuller's earth. Crude scale is produced from slack wax by "sweating" or, in other words, by slowly warming the chilled slack wax so that the oil and low-melting materials, which together are called *foots oil,* melt and drain from the slack wax. Crude scale is slightly yellow in color, and this coloration may be removed by treatment with acid or caustic or by filtering the melted wax through clay. Cylinder stock is another wax-bearing product, but the wax is such that it cannot be filtered from the oil in wax presses. This so-called amorphous wax or *petrolatum stock* may be removed by dissolving the oil in naphtha, filtering the solution to a proper color through fuller's earth, and centrifuging the chilled solution

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[2] The neutral oils are often referred to as pale or red oils. In the past it was thought that part of the wax distillate had to be cracked to produce a pressable material, and the neutrals from the cracked distillate, being a deep-red color, were called red oils. The terms have now lost their original significance, and the term red oil is usually reserved for any neutral oil that is darker than 3 N.P.A.

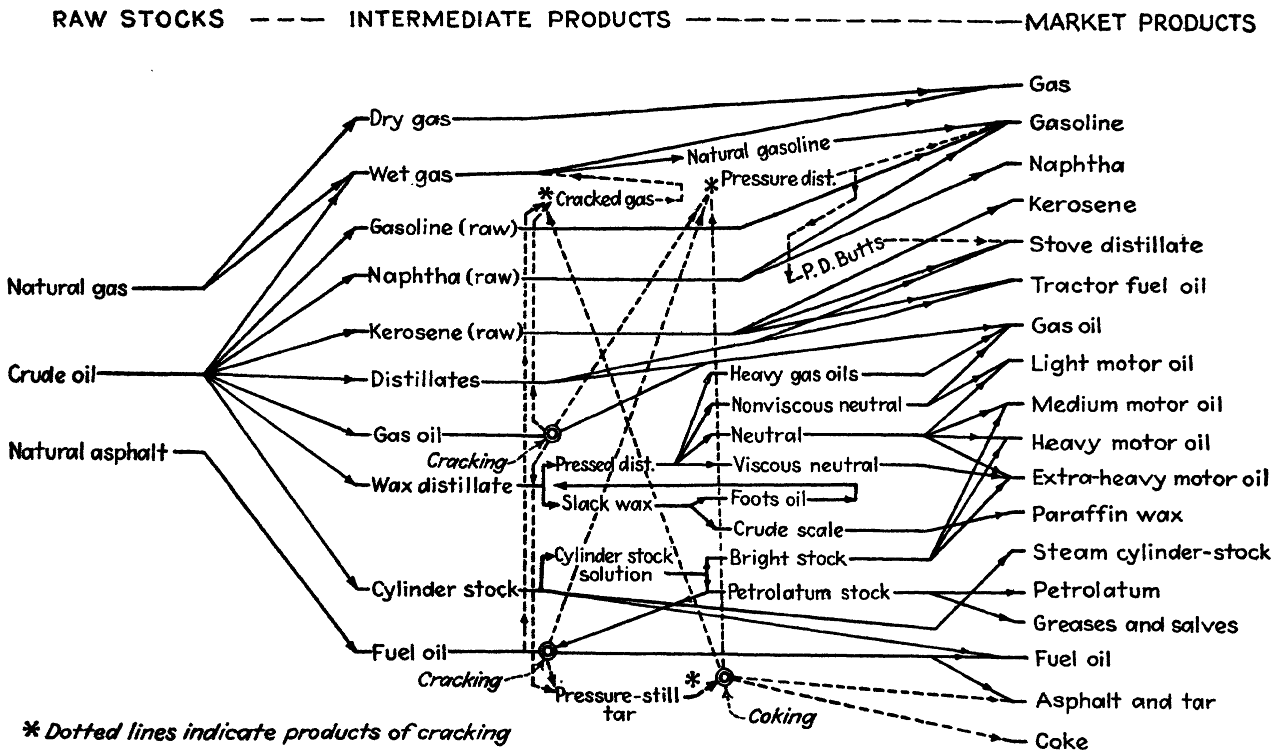


FIG. 2.—Relation between finished, intermediate, and raw products.

in high-speed centrifuges. The products from this separation are *brightstock* solution and petrolatum stock. The naphtha is removed from the solution by distillation, leaving finished brightstock.

Cracking Distillation.—Materials such as *cracking-still gas*, pressure distillate, *cracked gas oil*, and *pressure-still tar*, which are the products of cracking, have already been mentioned. By cracking we refer to the decomposition of heavy or high-boiling oils by heating. At temperatures exceeding about 680°F. materials such as gas oil, fuel oil, and tars are decomposed into (1) gas oil, (2) volatile materials (pressure distillate) having the same boiling-range as gasoline, and (3) a residue of heavy material (cracking-still tar) or coke. Pressure distillate receives its name by reason of the high pressures that are usually maintained in the cracking equipment. Cracked gasoline from pressure distillate is highly valued as an ingredient of the superior antiknock motor fuels. Likewise the residue, if cracking is not conducted to the ultimate formation of coke, is called pressure-still tar.

Recycle stock or cracked gas oil, an intermediate between the two foregoing products, is also produced. Recycle stock has about the same boiling-range and about the same physical characteristics as gas oil. This material is normally recycled through the cracking system so that it is completely used in the cracking reaction, but a part of it is sometimes sold as distillate or gas oil.

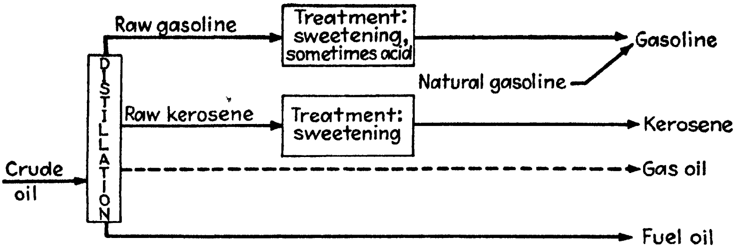
Summary.—In general the refining of petroleum is carried out as outlined in this chapter. However, crude oils vary widely in their properties, and some may not yield all the foregoing products or may contain such small amounts of certain of the products that their manufacture is not profitable. Likewise, certain oils are inherently superior to others and may not need the treating or finishing operations as outlined, but others may need an even more vigorous chemical treatment. Still further, the particular market conditions that each refiner must meet is an important factor in governing the extent of the refining operations. Certain localities have become accustomed to using discolored gasoline; others demand a white gasoline; and still others prefer a dyed gasoline, to which the coloring matter may have been added for the express purpose of masking the yellow color and simplifying the refinement. Likewise, in certain rural districts the customer will not buy a light-colored motor oil because he fears that the oil is not viscous, whereas in the city the darker colored oils may be considered as insufficiently refined. All of these factors tend to create a large number of different processing methods.

In general, paraffin-base raw products are the most easily treated, and the others follow in the order, mixed-base and naphthene-base. This applies to the light distillates such as gasoline, as well as to the heavy lubricating oils. Naphthene-base oils usually contain more *sulfur* than mixed-base oils, and paraffin-base oils may contain scarcely any sulfur. Paraffin- and mixed-base crude oils contain wax, and this must be removed in producing finished market products. The fact that a true naphthene-base oil contains *no wax* simplifies the manufacture of lubricants.

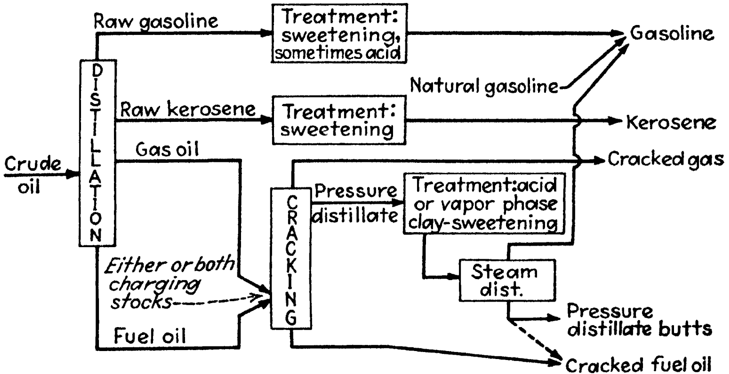
These characteristics govern the methods of processing that are used for the different bases of oils and the products that are manufactured. Paraffin-base oils are particularly suited for the manufacture of lubricating oils. However, the gasoline knocks badly in modern automotive engines. Lubricating oils are also produced from mixed-base oils, but acid treatment is usually necessary, and hence the expense of manufacture is greater. Vacuum distillation is particularly adapted to the processing of mixed- and naphthene-base oils because most of the asphalt or tarry material may be left as a distillation residue, and the distilled lubricating-oil stocks can be treated more easily than residual stocks. Naphthene-base oils produce good asphalt and usually in quantities large enough to justify its manufacture. The gasoline from naphthene crude oils is usually highly antiknock and may often be sold directly as premium-grade motor fuel. Large quantities of residual fuel oil and gas oil, of mixed- and naphthene-base origin, are sold, but most of the residue that remains after skimming the gasoline and kerosene is cracked. By cracking, the total yield of gasoline may be increased from about 30 per cent by simple topping, to as much as 70 per cent by topping and cracking.

The industry has adopted the following names for the general types of processing:

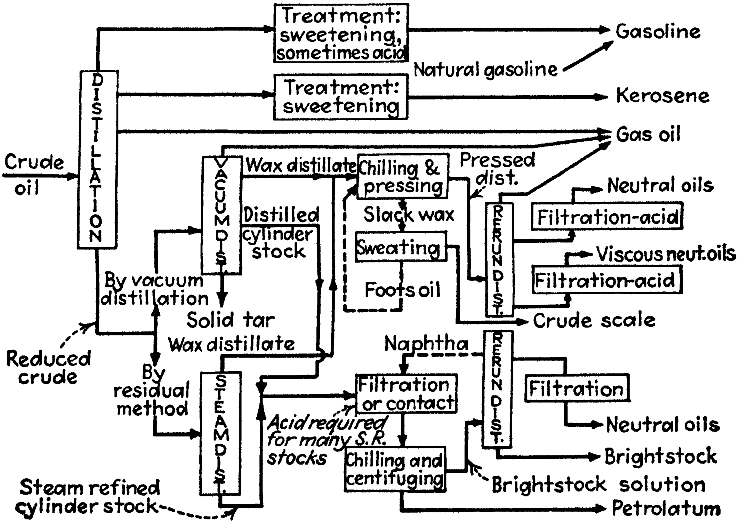
Skimming or Topping Processing.—By simple distillation the crude oil is separated into gasoline, kerosene, fuel oil, or reduced



(a) TOPPING OR SKIMMING PROCESSING



(b) CRACKING PROCESSING



(c) LUBRICATING-OIL PROCESSING

Fig. 3.—Types of refinery processing.

crude oil, and sometimes gas oil. Topping is practiced on all types of crude oils (Fig. 3*a*).

Cracking Processing.—This type of processing usually refers to a combined operation of skimming and cracking. No lubricating oils are produced in this type of operation. All bases of crude oil may be cracked, but the residual stocks from paraffin-base crude oils are seldom cracked (Fig. 3*b*).

Lubricating-oil Processing.—Skimming processing and the manufacture of lubricants are inferred by this type of processing, but no cracking is practiced. Paraffin-base crude oils are always processed for lubricants. Mixed-base oils are often processed thus, but naphthene oils are not processed for lubricants except under particularly favorable conditions (Fig. 3*c*).

Complete Processing.—Most of the larger plants practice skimming, cracking, and lubricant manufacture simultaneously, and this practice falls under the heading of complete processing.

The materials and methods outlined in this chapter constitute the most important ones. Many of the products found on the market are made by blending these stocks together to meet particular industrial requirements. As an example, the various grades of motor oil and machine oil are prepared by compounding different amounts and grades of the neutral oils and brightstock. Very heavy aero-oils, etc., consist mainly of brightstock, and sewing-machine oil consists mainly of nonviscous neutral oil. The details of the processing operations and the processing equipment will be enlarged upon in Part IV.

PART II

FUNDAMENTAL DATA

CHAPTER IV

COMPOSITION OF PETROLEUM

Most of the compounds found in petroleum are composed of hydrogen and carbon. In addition to these materials, called hydrocarbons, other compounds containing small amounts of sulfur, oxygen, and nitrogen are also present. The physical operations of refining, such as vaporization, fractionation, and cooling, are governed to a large extent by the properties of the hydrocarbons because they constitute the bulk of the petroleum, but the chemical operations, such as treating and filtering, are governed by the presence of sulfur, oxygen, and nitrogen compounds and, to some extent, by the small amounts of reactive hydrocarbons that may be present. Russian crude oils[1] and certain naphthene-base oils contain relatively large amounts of oxygen. The oxygen is often combined in the form of naphthenic acids. Nitrogen is most often found in naphthene-base oils and is generally supposed to be in the form of basic compounds similar to the alkyl quinolines.[2] Sulfur may be present as dissolved free sulfur, hydrogen sulfide, or as organic compounds,[3] such as the thiophenes, sulfonic acids, mercaptans, alkyl sulfates, and alkyl sulfides. Some of these sulfur compounds are not found in crude petroleum but they are produced from other compounds during distillation and refining. Only traces of sulfur have been found in typical paraffin-base oils. Sulfur compounds are particularly troublesome because they are usually foul smelling, and some of them are corrosive.

Many series of hydrocarbons are found in crude petroleum, and still other series are produced by cracking and hydrogenation. Among the series that are said to have been identified in petroleum are those having the type formulae C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, C_nH_{2n-8}, C_nH_{2n-10}, C_nH_{2n-14}, and C_nH_{2n-20}. Inasmuch as most of the higher members of these

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[1] VUISTAVKINA, T., *Neftyanoe Khozyaistvo*, **18**, 1000 (1930).

[2] SCHULZE, KING, and THOMPSON, *J. Am. Chem. Soc.*, **52**, 1239 (1930).

[3] EGLOFF and MORRELL, *Chem. Met. Eng.*, **28**, 633 (1923).

series have never been produced synthetically or prepared in sufficient quantity for study, we have few compounds with which to compare those that are isolated from petroleum. Furthermore, the isolation of pure compounds is extremely difficult because the properties of adjacent members of a series differ from one another only slightly and because constant-boiling mixtures, which cannot be separated by fractionation, are prevalent. These difficulties and the multitude of hydrocarbons which are present in petroleum[4] have discouraged the study of petroleum chemistry.

Hydrocarbon Series.—Of the many hydrocarbon series present in petroleum, only a few have been studied thoroughly enough to guide commercial development. The best known series are the paraffin, olefin, naphthene, aromatic, diolefin, and acetylene (Fig. 4*a* to *f* for examples of the structural formulae of these types of compounds).

The *paraffin series* (type formula C_nH_{2n+2}) is characterized by great stability. The name of each member ends in *-ane*—meth*ane*, eth*ane*, hex*ane*, and hexadec*ane*. At room temperatures the members, with the exception of those containing a tertiary carbon atom, are not acted upon by fuming sulfuric acid, concentrated alkalies, nitric acid, or even the powerful oxidizer chromic acid. They react slowly with chlorine in sunlight and with both chlorine and bromine if a catalyst is present.[5] Reaction usually occurs by the *substitution* of an element or a chemical group for a hydrogen atom. The lower members have been identified in most crude petroleums, but Mabery[6] reports that Mahoning County, Ohio, crude oil contains no paraffin hydrocarbons. The higher members of the paraffin series are probably present in most petroleums, although crude oils that are entirely free from wax may contain no high-boiling paraffin hydrocarbons. Paraffin wax probably consists of straight- or branched-chain paraffin hydrocarbons.[7] Egloff, Schaad, and Lowry[8] have made

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[4] Some authorities estimate that 3,000 compounds may be present in crude petroleum.

[5] EGLOFF, SCHAAD, and LOWRY, The Halogenation of the Paraffin Hydrocarbons, *Chem. Rev.*, **8** (1) (1931).

[6] *Ind. Eng. Chem.*, **6**, 101–107 (1914).

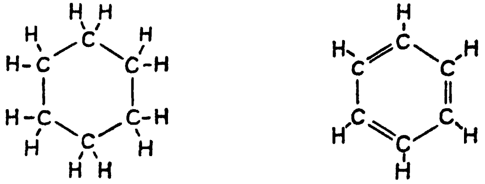
[7] BUCHLER and GRAVES, The Petroleum Waxes, *Ind. Eng. Chem.*, **19**, 718 (1927).

[8] The Decomposition of the Paraffin Hydrocarbons, *J. Phys. Chem.*, **34**, 1617 (1930).

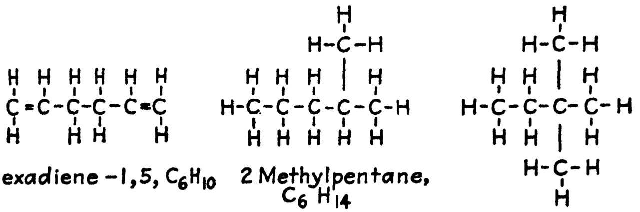
a thorough study of the decomposition of paraffin hydrocarbons (Fig. 4*a* and *f*).

The *olefin* or *ethylene series* (type formula C_nH_{2n}) is composed of unsaturated hydrocarbons; *i.e.*, the members of this series are capable of uniting directly with other materials such as chlorine, bromine, hydrochloric acid, and sulfuric acid, without displacing a hydrogen atom. The names of these hydrocarbons end in *-ene*, as eth*ene* (ethyl*ene*), prop*ene* (propyl*ene*), and but*ene* (butyl*ene*). Unsaturated compounds react with and dissolve in sulfuric acid and may thus be removed from petroleum oils. The low-boiling olefins are probably not present in crude petroleum but they are found in cracked products. Egloff, Schaad, and Lowry[9] have made an excellent study of the literature of the olefin hydrocarbons (Fig. 4*b*).

(*a*) Normal Hexane, C_6H_{14} (*b*) Normal Hexene, C_6H_{12}



(*c*) Cyclohexane, C_6H_{12} (*d*) Benzene, C_6H_6



(*e*) Hexadiene-1,5, C_6H_{10} 2 Methylpentane, C_6H_{14} 2-2 Dimethylbutane C_6H_{14}

(*f*) Isomeric Isoparaffin Compounds

Fig. 4.—Structural formulas of hydrocarbons.

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[9] The Decomposition and Polymerization of the Olefinic Hydrocarbons, *J. Phys. Chem.*, **35**, 1825 (1931).

The *naphthene series* (type formula C_nH_{2n}) has the same type formula as the olefin series but has greatly different properties. The naphthenes are ring or cyclic compounds, whereas the olefins are straight-chain compounds in which a double bond connects two carbon atoms. The naphthenes are saturated compounds and the olefins are unsaturated. Unsaturated compounds can react by direct combination with other materials, but saturated compounds can react only by the displacement of hydrogen by another material. In the older chemistry texts the naphthenes are called methylenes, *e.g.*, tetramethylene, pentamethylene, and hexamethylene, whereas the preferred names are now cyclobutane, cyclopentane, and cyclohexane. As an example of the relation of this series to other cyclic series, consider benzene and cyclohexane. Both compounds contain six carbon atoms per molecule, but six hydrogen atoms must be added to benzene to produce cyclohexane. The cyclohexane molecule is saturated but the benzene molecule is highly unsaturated because it has three doubly combined carbon atoms (Fig. 4*d*). The three double bonds are active so that benzene is an active material, but the cyclohexane contains no double bonds and does not react readily. However, most of the reactions of benzene are by substitution rather than combination. The naphthenes, unlike their isomers the olefins, are not easily soluble in sulfuric acid. They have been found in almost all crude oils, but again Mahoning County crude oil is an exception.[6] This crude oil contained the hydrocarbons of the C_nH_{2n-2} and C_nH_{2n-4} series but no paraffins or simple naphthenes. Egloff, Bollman, and Levinson[10] have studied the reactions of the cyclo hydrocarbons (Fig. 4*c*).

The *aromatic series* (type formula C_nH_{2n-6}), often called the *benzene series*, is chemically active. These hydrocarbons are particularly susceptible to oxidation with the formation of organic acids. The aromatics may form either addition or substitution products, depending upon the conditions of the reaction. Only a few petroleums contain more than a trace of the low-boiling aromatics such as benzene and toluene. Mabery[11] found

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[10] Thermal Reactions of Cycloparaffins and Cyclöölefins, *J. Phys. Chem.*, **35**, 3489 (1931).

[11] *Proc. Am. Acad. Arts Sci.*, **36**, 255 (1901).

relatively large quantities of aromatics in Ventura, Coalinga, and Puente Hills, Calif., petroleums. Some of the Sumatra and Borneo crude oils are rich in aromatics. This series is found in cracked distillates and is highly prized for its antiknock qualities (Fig. 4*d*).

The *diolefin series* (type formula C_nH_{2n-2}) is similar to the olefin series except that two hydrogen atoms are missing or two double bonds are present in each molecule. These double bonds cause the series to be extremely active. The diolefins tend to polymerize or combine with other unsaturated molecules forming high-molecular-weight gumlike solids. The diolefins and the gums from them are found in untreated cracked gasoline,[12] but they are probably not present in crude petroleum. They are polymerized and removed by sulfuric acid (Fig. 4*e*).

The *cyclic series* such as those having type formulae C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-8}, etc., are not well known. Nevertheless, the literature indicates that these series predominate in the higher boiling-point oils, such as gas oil and lubricating oils. Most of the hydrocarbons in lubricating oil are saturated, but Seyer[13] reports that about 20 per cent of a lubricating oil is soluble in sulfur dioxide. Doubtless the 20 per cent consists largely of unsaturated hydrocarbons.

Isomeric Compounds.—Confusion often arises because different compounds may have the same molecular formula. Isomeric compounds are those which have the same molecular formula but different internal structures. Compounds of the type formula C_nH_{2n} may be either saturated or unsaturated. The formulae of the saturated compound cyclohexane and the unsaturated compound hexene-1 may be compared in Fig. 4*b* and *c*. Likewise the formulae of *n*-hexane, 2-methyl pentane, and 2, 2-dimethyl butane, all having the type formula C_nH_{2n+2} or C_6H_{14}, may be compared in Fig. 4*a* and *f*. Groups of atoms such as the methyl groups in the compounds just referred to are called alkyl groups or radicals. These terms refer to a group of carbon and hydrogen atoms that may be conveniently considered as a unit, because they usually act as a unit in a chemical reaction. They may be defined as a monovalent hydrocarbon radical having

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[12] BRIDGEMAN and ALDRICH, *Oil Gas J.*, Jan. 29, 1931, p. 42.

[13] *Petroleum Equipment Exporter*, January, 1930, p. 65.

the general formula C_nH_{2n+1}. Common radicals are the methyl (CH_3), ethyl (C_2H_5), and propyl (C_3H_7) groups. Radicals are not individual compounds because they must always be attached to other radicals, elements, or groups of atoms.

There are two possible isomeric butanes, *viz.*, *n*-butane and 1-methyl propane; three pentanes; five hexanes; and nine heptanes. The number of possible isomeric hydrocarbons increases rapidly as the number of carbon atoms increases. Compounds of the type formula C_nH_{2n-4} present even more possibilities of isomerism than the foregoing. As an example, the saturated series might consist of three doubly combined rings or combined rings with alkyl side-chains; the unsaturated series might consist of numerous compounds having unsaturated carbon atoms in the rings, in the side-chains, or in both; and other series might exist having combinations of saturated or unsaturated rings with saturated, unsaturated, or acetylene side-chains. Consideration of the series that are even more deficient in hydrogen than the C_nH_{2n-4} series indicates that an enormous number of isomers is possible. Fortunately the number of unsaturated, high-molecular-weight hydrocarbons in petroleum are probably few, or the isolation of these complex compounds would prove an endless task.

Determination of Series.—Although chemists have not yet determined procedures and reagents for the isolation of each chemical series, a start toward this goal has been made.[14] The proposed methods do not indicate the exact series of hydrocarbons that are present, but they do indicate groups of compounds that behave chemically as the paraffin, olefin, aromatic, or naphthene series. All double-bonded hydrocarbons such as the olefins, diolefins, and double-bonded cyclics are classed together as one group, called unsaturates. The unsaturated group may be absorbed or polymerized by sulfuric acid; the aromatics may be nitrated or absorbed by fuming sulfuric acid or dissolved by dimethyl sulfate; the naphthenes may be determined by means of the aniline index; and the paraffins are found by difference. Such an analysis is perhaps just as valuable to the engineer as an exact one, because he is concerned with the retention or elimination of certain properties in the finished products rather than with a

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[14] EGLOFF and MORRELL, *Ind. Eng. Chem.*, **18**, 354 (1926).

detailed knowledge of exactly what compounds are present. By means of the foregoing analysis of chemical properties and the physical constants of each series, a reliable estimate or check of the physical constants for any petroleum oil is possible. Such an analysis, to be of most value, should be made on each of, say, 10 fractions of a crude oil, so that the change in the percentage of each series can be followed throughout the entire boiling-range of the oil. One of the first studies of this kind was made by Robinson,[15] and the results of his study have been presented in graphical form in "Motor Fuels," by E. H. Leslie.[16]

Composition of Petroleum.—In the past, petroleum has often been considered as a solution of the paraffin hydrocarbons, but a survey of the literature indicates that such an assumption is not justified. The paraffins predominate in most gasolines[13,14] and probably in kerosenes from paraffin- and mixed-base petroleum; the naphthenes predominate in most gas oils and lubricating oils from all bases of crude oils; and the naphthenes, aromatics, and unsaturated hydrocarbons constitute the bulk of the highest boiling or residual products. The only paraffins present in the higher boiling products appear to be those occurring in the wax, and the amount of wax in even paraffin-base petroleum is relatively small. Sachanen and Wirabian[17] present analyses of several Russian and American oils (Table 1).

TABLE 1.—CHEMICAL ANALYSES OF PETROLEUM, PER CENT

Fraction, °F.	1. Grozny ("high paraffin"), 45.3 per cent at 572°F.			2. Grozny ("paraffin-free upper level") 40.9 per cent at 572°F.			3. Oklahoma (Davenport), 64 per cent at 572°F.			4. California (Huntington Beach), 34.2 per cent at 572°F.		
	Aromatic	Naphthene	Paraffin	Aromatic	Naphthene	Paraffin	Aromatic	Naphthene	Paraffin	Aromatic	Naphthene	Paraffin
140–203	3	25	72	4	31	65	5	21	73	4	31	65
203–252	5	30	65	8	40	52	7	28	65	6	48	46
252–302	9	35	56	13	52	35	12	33	55	11	64	25
302–392	14	29	57	21	55	24	16	29	55	17	61	22
392–482	18	23	59	26	63	11	17	31	52	25	45	30
482–572	17	22	61	35	57	8	17	32	51	29	40	31

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[15] *Chem. Met. Eng.*, **11**, 389–394 (1913).

[16] Chemical Catalog Company, Inc., New York, 1923.

[17] *Petroleum Z.*, **25**, 867 (1929).

Table 2 shows a similar study of the composition of gasoline. Table 3 indicates in a general way the series of hydrocarbons that have been found in the Pennsylvania, Mid-Continent, and California oils. The C_nH_{2n-8}, C_nH_{2n-12}, C_nH_{2n-16}, and C_nH_{2n-20}

TABLE 2.—CHEMICAL ANALYSES OF GASOLINE*

Gasoline	Unsaturated	Aromatic	Naphthenic	Paraffinic
1. Cracked gasoline from Kentucky fuel oil	14.4	22.5	10.0	53.1
2. Cracked gasoline from Smackover fuel oil	14.7	27.5	21.2	36.6
3. Cracked gasoline from North Texas fuel oil	16.0	18.6	11.7	53.7
4. Cracked gasoline from Lost Soldier, Wyo	11.7	15.0	15.4	57.9
5. Cracked gasoline from Cushing, Okla.	10.9	19.8	18.0	51.3
6. Cracked gasoline from Somerset, Ky.	12.5	14.9	11.8	60.8
7. Straight-run gasoline, Cushing, Okla.	1.6	4.9	23.7	69.8
8. Straight-run gasoline, Somerset, Ky.	3.8	5.3	20.6	70.3
9. Commercial gasoline	4.5	12.1	17.6	65.8

* Egloff.

TABLE 3.—HYDROCARBON SERIES FOUND IN PETROLEUM

No. of carbon atoms	Pennsylvania	Mid-Continent	California and Gulf Coast
5	C_nH_{2n+2}	C_nH_{2n+2}	C_nH_{2n} and C_nH_{2n+2}
10	C_nH_{2n+2}	C_nH_{2n+2} and C_nH_{2n}	C_nH_{2n} and C_nH_{2n-6}
15	C_nH_{2n+2}	C_nH_{2n-2}	C_nH_{2n-2}
20	C_nH_{2n}	C_nH_{2n-4}	C_nH_{2n-4}
25	C_nH_{2n} and C_nH_{2n-2}	C_nH_{2n-4}	C_nH_{2n-4}
30	C_nH_{2n} and C_nH_{2n-4}	C_nH_{2n-8}	C_nH_{2n-8}
35	C_nH_{2n-4} and C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-12}
40	C_nH_{2n-4} and C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-12} and C_nH_{2n-16}
50	C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-16}
80	C_nH_{2n-8}	C_nH_{2n-16}	C_nH_{2n-20}

series were taken from Mabery's study of lubricant and asphaltic hydrocarbons.[18]

The ultimate composition[19] of a few petroleums is listed in Table 4.

TABLE 4.—ULTIMATE CHEMICAL ANALYSES OF PETROLEUM

Petroleum	Sp. gr.	At °C.	Per cent C	Per cent H	Per cent N	Per cent O	Per cent S	Base
Pennsylvania pipe line	0.862	15	85.5	14.2	....	...	....	Paraffin
Mecook, W. Va	0.897	0	83.6	12.9		3.6		Paraffin
Humbolt, Kans	0.912	..	85.6	12.4	....	...	0.37	Mixed
Healdton, Okla	.....	..	85.0	12.9	....	...	0.76	Mixed
Coalinga, Calif	0 951	15	86.4	11.7	1.14	...	0.60	Naphthene
Beaumont, Tex	0.91	..	85.7	11.0	2.61		0.70	Naphthene
Mexico	0.97	15	83.0	11.0	1.7		4.30	Naphthene
Baku, U.S.S.R	0.897	..	86.5	12.0	....	1.5		
Colombia, South America	0.948	20	85.62	11.91	0.54			

Vapor-pressure.—One of the most useful physical properties is the vapor-pressure temperature relation. The vapor-pressure of a liquid is a measure of the tendency of the liquid to vaporize. Thus the vapor-pressure is involved in problems of condensation, vaporization, fractionation, and the correction of boiling-points from one pressure to another. Figure 5 is a chart of the vapor-pressures of the normal paraffin hydrocarbons (horizontal lines) and of a few other compounds (sloping lines). The data for the paraffin hydrocarbons, and the convenient form of chart, were developed by Dr. G. G. Brown[20] of the University of Michigan. The acetylene and olefin curves were taken from Rechenberg's "Einfache und fractionierte Destillation," and the curves for the other hydrocarbons from the International Critical Tables. The curves for all of the compounds except the paraffins and acetylenes slope downward to the right, and the few data that are available concerning petroleum fractions indicate the same tendency.

Example 1. Use of Vapor-pressure Chart.—What is the vapor-pressure of *n*-butane at 77°F. (25°C.)?

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[18] *Ind. Eng. Chem.*, **15**, 1233 (1923).

[19] Int. Crit. Tables, II, 136–162 (1927).

[20] *Proc. 7th Ann. Convention Nat. Gaso. Assoc. America*, 1928.

Twenty-five degrees centigrade is located among the vertical lines. The vapor-pressure of butane is found as a horizontal line. These two lines intersect on the 1,800-mm. pressure-line. The vapor-pressure is 1,800 mm. What is the boiling-point of butane at atmospheric pressure?

Follow the butane line until it crosses the 760-mm. line. Reading directly below this point, the temperature is 0°C.

Compression Factor.—When gases or vapors are compressed or expanded under adiabatic conditions, the amount of work done and the amount of heat required are dependent upon the ratio of the specific heat at constant pressure to the specific heat at constant volume. The expansion of a gas can always be expressed by an equation of the form

TABLE 5.—COMPRESSION FACTORS

Gas	Temperature, °F.	$\gamma = C_p/C_v$	Pressure, atm.
Methane	−175	1.41	1
Methane	−112	1.34	1
Methane	−101	1.35	1
Methane	32	1.307	1
Methane	212	1.232	1
Methane	392	1.188	1
Methane	572	1.16	1
Methane	752	1.139	1
Ethane	−115	1.28	1
Ethane	59	1.22	1
Ethane	122	1.21	1
Ethane	212	1.19	1
Ethene (ethylene)	132	1.35	1
Ethene	212	1.18	1
Ethine (acetylene)	− 96	1.31	1
Propane	61	1.13	0.5
Isobutane	59	1.11	1
Pentane	187	1.08	1
Hexene	176	1.08	1
Hexane	176	1.08	1
Benzene	194	1.1	1

$$P_1V_1^n = P_2V_2^n = \text{a constant}$$

At adiabatic conditions the exponent n is referred to as gamma (γ) and is equal to the ratio of the specific heats as mentioned above. Table 5 is a list of the values of gamma for some of the

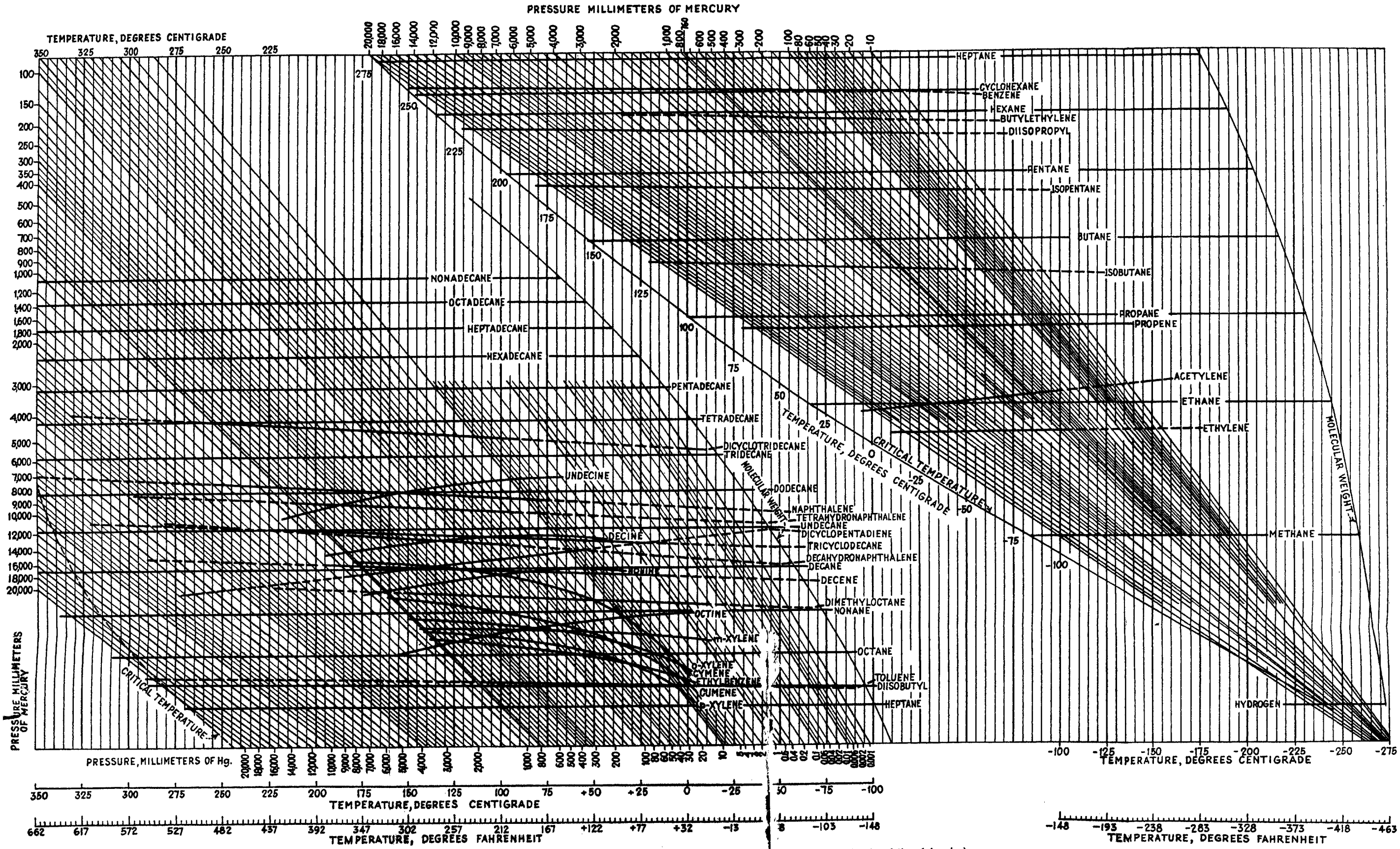

FIG. 5.—Vapor-pressures of pure hydrocarbons. (*Courtesy of Dr. G. G. Bro nd Natural Gasoline Association of America.*)

more common gaseous hydrocarbons. The value of gamma decreases at higher temperatures and also for high-molecular-weight materials. For hydrocarbons such as those in kerosene and heavier oils, the value of gamma approaches unity, and hence

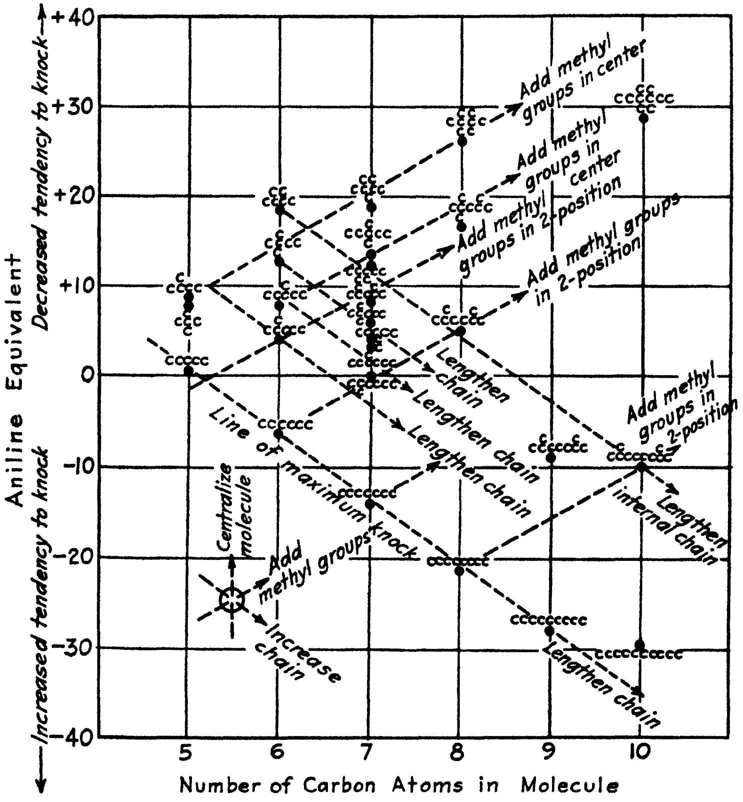

FIG. 6.—Detonation characteristics of the paraffin hydrocarbons. (*General Motors Corporation.*)

only a small refrigeration effect is noted when these vapors are expanded adiabatically. I. N. Beall[21] presents a working chart for the value of gamma for the low-molecular-weight paraffin hydrocarbons.

Detonation Characteristics.—The methods of determining the octane number or detonation characteristics of a motor fuel

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[21] The Compression of Hydrocarbon Gases, Part I, *Ref. Nat. Gaso. Mfr.*, February, 1931.

have been changed so frequently that octane numbers of the various hydrocarbons by the newest methods are not available. However, the relation between the detonation characteristics and the internal structure of many petroleum hydrocarbons has been given careful study. Lovell, Campbell, and Boyd[22] of the General Motors Corporation have presented several valuable papers concerning antiknock characteristics. Figure 6 summarizes their findings for the paraffin hydrocarbons. The relative knocking tendency is compared by means of the aniline equivalent. Positive aniline equivalents indicate compounds that knock less than the reference fuel (zero aniline equivalent) and negative equivalents indicate materials that knock more than the reference fuel. For the paraffin hydrocarbons the tendency to knock is decreased by

1. Shortening the main chain.
2. Introducing side-chain groups such as methyl groups.
3. Centralizing the molecule by adding methyl groups about the center of the main chain.

The tendency of the olefin hydrocarbons to knock is decreased by

1. The same three factors as for the paraffin hydrocarbons.
2. Moving the double bond toward the center of the chain.

The tendency of the naphthenes to knock is decreased by

1. Decreasing the size of the ring.
2. Decreasing the length of the longest unbranched side-chain.
3. Distributing the carbon atoms in the side-chains into many short chains rather than one long chain.
4. Centralization of the side-chains.

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CHAPTER V

ROUTINE LABORATORY TESTS

. A discussion of the large number of routine tests that are practiced today could easily fill an entire book. These tests were developed to provide simple methods of comparing products during their manufacture and as they appear on the business market. Although many companies have developed their own test methods, there are certain tests that have been accepted as standards. In this chapter emphasis will be placed on the engineering importance of these tests rather than upon the details of laboratory procedure. Those who are interested in laboratory manipulations may refer to the references at the end of the chapter and particularly to Petroleum Products and Lubricants,[1] a report by Committee D-2 of the American Society for Testing Materials (A.S.T.M.).

Routine or control tests are not satisfactory unless they can be (1) performed quickly, (2) easily duplicated by ordinary laboratory men, and (3) interpreted as a function of the performance of the material while in use. For these reasons routine tests may not be scientifically exact, but they are more valuable for general use than more elaborate tests would be. The procedures for such tests must be carefully specified and rigidly adhered to or the results will not be dependable. Because of the empirical nature of most routine tests, the results become intelligible only by comparison with a large number of similar tests and by a careful correlation with the performance of the product.

As an example, the A.S.T.M. distillation must be conducted in a flask having specified dimensions; the rate of heat input must be regulated so that the first drop of distillate is collected at a particular time and the rate of distillation thereafter is uniform; a special thermometer must be used; and the condenser must be held at a specified temperature. Even slight variations in the procedure, such as excessive drafts of air or an erratic rate of

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[1] *Report of Committee* D-2, A.S.T.M., Philadelphia, 1933.

distillation, will cause erroneous results. If the procedure of the test is carefully followed, the resulting distillation curve can be duplicated by other laboratories and will be a useful indication of the properties of the sample. However, in spite of the reliability of the test and its great value to the industry, it is not a true measure of the composition of the sample. The sample will contain material that boils below the initial boiling-point (I.B.P.), as recorded in the A.S.T.M. distillation, and will contain material that boils at a higher temperature than the end-point (E.P.) of the A.S.T.M. distillation.

Many articles have been published in which the A.S.T.M. distillation has been correlated with the performance of a motor fuel in an engine. The temperature at which various percentages of a motor fuel will distill have been found to bear a relation to the ease of starting, acceleration, losses of fuel, and vapor-lock tendencies of the fuel.

All of the design data that an engineer needs cannot be obtained from routine tests, and to obtain complete design data he must resort to special methods such as those outlined in Chaps. VI and VII. Nevertheless, routine tests are the common basis of understanding between the refiner and the business world. The engineer, although he may not use routine tests in design, must produce products that are ultimately compared with other commercial products by routine tests.

Refinery Control.—Routine tests are universally used as the basis for controlling refinery operations. During the first few months of the operation of a new equipment many of the products are tested at 2-hr. intervals. Soon certain of these tests begin to assume importance as criterions of the operation and by these tests the unit is controlled throughout its useful life. Products are periodically tested throughout the whole refinery. Not only are the raw materials and finished products examined but also the materials that are in the process of being finished. The finished products are often examined a second time after they have been loaded into cars and containers for the market. In filling such an extensive need, it is clear that routine tests must be simple and dependable.

A.P.I. and Specific Gravity.—The specific gravity and the A.P.I. (American Petroleum Institute) gravity are expressions of the density or the weight of a unit of material. The specific gravity is the ratio of the weight of a unit volume of oil to the weight of the same volume of water at a standard temperature. The specific gravity of an oil is always given at 60°F. referred to water at 60°F. Unless otherwise stated, both the specific gravity and A.P.I. gravity refer to these constants at 60°F. In plant practice the A.P.I. gravity is usually used. This scale is not directly related to the specific gravity. If the modulus of the American Petroleum Institute is used, the relation between the specific gravity and the A.P.I. gravity is

$$°\text{A.P.I.} = \frac{141.5}{\text{sp. gr.}} - 131.5 \tag{1}$$

or

$$\text{Sp. gr.} = \frac{141.5}{\text{A.P.I.} + 131.5}$$

The Baumé scale of gravity, which was previously used in the industry, is slightly different from the A.P.I. gravity. The constants in the foregoing equation are 140 and 130 rather than 141.5 and 131.5.

The specific gravity[1] (D287-33) or A.P.I. gravity is measured in the laboratory by means of hydrometers or the chainomatic specific-gravity balance. The latter is desirable if a larger number of exact determinations must be made or if very small samples (15 cc.) must be used. For viscous oils or semi-solid bitumens the pycnometer[1] (D70-27) or weighing bottle is used, and for solid materials an analytical balance[1] (D71-27), equipped with a pan straddle, may be employed.

In the past, Appalachian petroleums were the only widely known oils and the specific gravity was an important specification because it was directly related to other properties of the oil. Today, with the development of a large variety of crude oils, the specific gravity is much less important. However, the specific gravity does indicate the approximate boiling-range of an oil and to some extent the base of oil from which the product was produced. There is a relation between the gravity of a raw oil and the base of the oil, but the gravity is influenced by chemical treatment and by the boiling-range of the material.

A.S.T.M. Distillation.—In determining the boiling-range of gasoline and kerosene, the procedure and apparatus, as described in the Report of Committee D-2[1] (D-86-30 and D-216-32), is used. The name A.S.T.M. distillation is used because the method was first standardized by the American Society for Testing Materials. A somewhat similar test known as the "Engler distillation" has been used in the past, and often the A.S.T.M. distillation is referred to as "an Engler."

One hundred cubic centimeters of oil is distilled at a uniform rate of 5 cc. per minute. The distillate is condensed in a brass tube surrounded by cracked ice. The temperature of the vapor when the first drop of condensate drips from the condenser (in not less than 5 or more than 10 min.) is recorded as the "initial boiling-point." The vapor temperature is also recorded as each successive 10 per cent is collected. When 95 per cent has been distilled, the burner flame may need to be increased, and the maximum temperature is recorded as the "end-point."

Virtually no fractionation occurs in this distillation and the hydrocarbons in the oil do not distill one by one in the order of their boiling-points but as successively higher and higher boiling mixtures. The details of this inadequacy will be discussed under vaporization in Chap. XIV. Actually, the initial boiling-point, the end-point, and the intermediate vapor temperatures have little significance except when compared with corresponding points from other A.S.T.M. distillations. Material boiling below the initial boiling-point and above the end-point are present in the oil although these points are the extreme ends of the A.S.T.M. distillation range. In routine plant reports the loss is plotted at the end of the distillation curve, but for more scientific work it is usually plotted at the beginning of the curve. A comparison between the A.S.T.M. distillation and a true-boiling-point (T.B.P.) distillation is given in Figs. 71 and 72 (page 249).

Flash- and Fire-points.—The flash-point and the fire-point are further indications of the range and nature of the boiling-point curve. They designate respectively the temperature at which the vapor above an oil will momentarily flash or explode when in the presence of a flame and the temperature at which the vapors are evolved rapidly enough to burn continuously. These tests serve to indicate the temperature below which an oil can be handled without danger of fire. Certain high-boiling oils, such as lubricants, cannot be distilled at atmospheric pressure without thermal decomposition, and in such a case the flash-point helps to indicate the relative amount of low-boiling oil present in the material.

The two most common flash-point instruments are the *Cleveland*[1] (D92-33) open-cup and the *Pensky-Martens*[1] (D93-22) closed-cup testers. In both instruments the oil is heated at a constant rate of 10°F. per minute, and at intervals of 5° temperature rise a test flame is introduced into the vapor. The flash-point by the closed tester is approximately 10° lower than by the open tester; but if the flash-point is above 510°F. (Pensky-Martens), a larger difference exists between the flash-points by the two instruments. This discrepancy indicates the empirical nature of the flash and fire tests. The closed instrument is the more exact of the two but the open cup is used extensively because of its simplicity. The flash- and fire-points are important specifications of kerosene, fuel oil, and lubricating oil.

Color.—The color of an oil serves as an indication of the thoroughness of the refining process. True, oils of different boiling-range and from different crude oils may have different colors but, other things being comparable, the color indicates the degree of refining that the material has undergone. Distilled products that are discolored are an indication of (1) thermal decomposition, (2) the entrainment of dark-colored tarry material, or (3) materials that are inherently dark in color. Discoloration by decomposition is due to the use of too high temperatures, and discoloration by entrainment is usually due to "through-puts" above the maximum capacity of the equipment. The success of a chemical treating operation is often measured by the improvement in color.

The *Saybolt chromometer*[1] (D156-23T) is used to determine the color of gasoline and burning-oils, and the *Union colorimeter*[1] (D155-32T) for lubricating oils. Both of these instruments have empirical color scales which bear no direct relation to the Lovibond color analysis. For lubricating oil colors the *Tag Robinson* color instrument is also finding favor. The Saybolt chromometer color scale ranges from 30 for fine gasoline to 15 for mineral-seal burning-oil. Normally, one or two color disks are used, but a so-called "half-disk" is available for colors from +25 to +30. If the half-disk is used, the heights and colors are

Height, In.	Color
20	30
18	29
16	28
14	27
12	26

The A.S.T.M. color numbers are used almost universally in stating the color of lubricating oils. Table 6 presents a comparison of the A.S.T.M. numbers, the Lovibond colors (No. 500 series), and the National Petroleum Association or Union colorimeter letters.

TABLE 6.—COMPARISON OF COLOR SCALES

N.P.A. names	A.S.T.M. numbers	Union Petroleum Company letters	Lovibond color	Cell length, in.
1. Lily white	1	G	11	6
2. Cream white	1½	H	26	6
3. Extra pale	2	I	98	6
4. Extra lemon pale	2½	J	193	6
5. Lemon pale	3	K	290	6
6. Extra orange pale	3½	L	380	6
7. Orange pale	4	M	525	6
8. Pale	4½	N	65	½
9. Light red	5	O	80	½
10. Dark red	6	P	110	½
11. Claret red	7	Q	165	½
12.	8	R	205	½
13. Cylinder oil, extra light (filtered)	A	A	35	½
14. Cylinder oil, light (filtered)	D	D	70	½
15. Cylinder oil, medium (filtered)	E	E	170	½

Viscosity.—The viscosity of an oil is a measure of its resistance to internal flow and is an indication of its oiliness in the lubrication of surfaces. In the centimeter-gram-second (c.g.s.) system the unit of viscosity is the poise or centipoise (0.01 poise). Viscosity may be defined as the force in dynes required to move a plane of 1 sq. cm. area, at a distance of 1 cm. from another plane of 1 sq. cm. area, through a distance of 1 cm. in 1 sec.

The *relative viscosity* is the ratio of the viscosity of the liquid to that of water at 69.33°F. The viscosity of water at 69.33°F. is

1 centipoise, and hence the relative viscosity and the viscosity in centipoises are numerically equal. Two other common terms are *kinematic viscosity*, which is the viscosity in centipoises divided by the specific gravity at the same temperature, and *fluidity*, which is the reciprocal of viscosity.

The common viscosimeters do not read directly in centipoises. All employ arbitrary scales of viscosity. The *Saybolt Universal viscosity*[1] (D88-33) is the time, measured in seconds, required for the efflux of 60 cc. of oil from a container tube at a constant temperature through a calibrated orifice in the bottom of the tube. In the United States the usual temperatures for the measurement of viscosity are 70, 100, 122, 130, and 210°F. The procedure in determining the viscosity involves straining the oil to remove particles that might lodge in the orifice, bringing the oil to a constant temperature by means of a constant-temperature bath, and accurately measuring the time for efflux. The *Saybolt Furol viscosity*[1] (D88-33) is determined exactly as is the Universal viscosity except that a larger orifice is used. Both of these viscosities are determined with the same instrument, the Universal viscosimeter.[1] The viscosity of lubricants is usually reported as Saybolt Universal seconds at 100, 130, or 210°F., and of fuel oils as Saybolt Furol seconds at 122 or 210°F.

If t is the Saybolt Universal viscosity, and z and s respectively are the viscosity in centipoises and the specific gravity, all three factors taken at the same temperature, the relation[2] among these variables is

$$\text{Kinematic viscosity} = \frac{z}{s} = 0.220t - \frac{180}{t} \qquad (2)$$

The viscosity of gasoline and kerosene cannot be determined in the Saybolt viscosimeter because the large orifices result in turbulent rather than stream-line flow. The viscosity of such liquids is determined in the Saybolt *Thermoviscosimeter*.[3] The thermoviscosity of kerosene is sometimes specified because kerosene must be readily absorbed in a lamp wick. Figure 7[4] may be used to convert the viscosity by any one of the viscosim-

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[2] HERSCHEL, W. K., *Trans. Am. Soc. Civil Eng.*, **84**, 527–550 (1921).

[3] BENNETT, H. T., *Petroleum Age*, Dec. 15, 1921.

[4] *Lubrication*, May, 1921, published by the Texas Company.

eters to the viscosity by any of the other common instruments. Although Fig. 7 is useful for approximating the viscosity for design work or estimates, it should not be used for exact specifica-

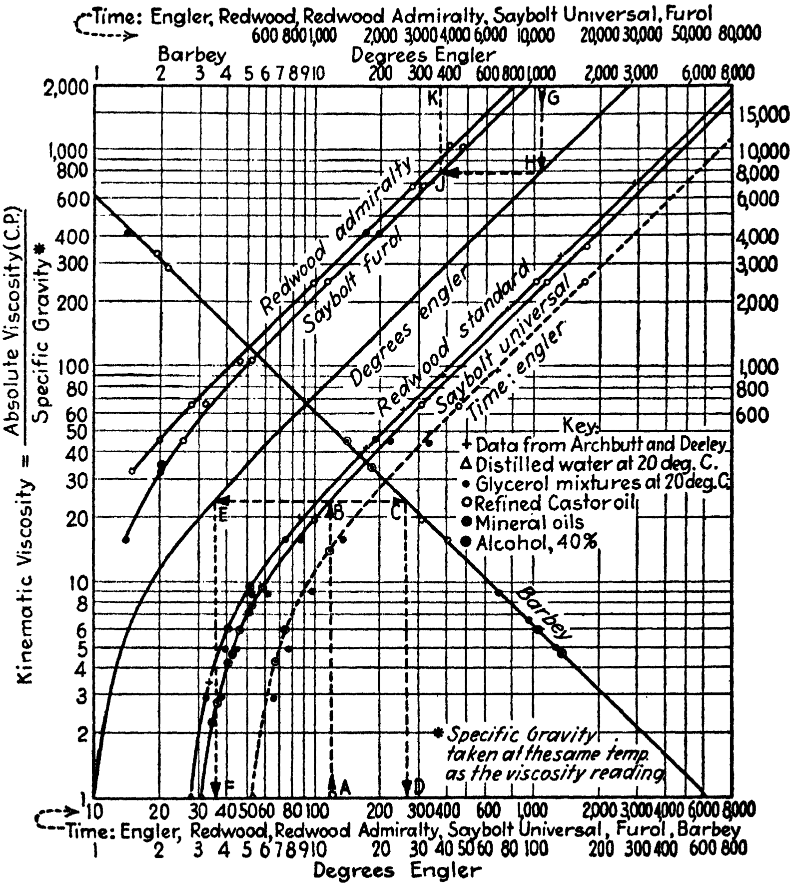

FIG. 7.—Comparison of viscosity by different instruments. (*The Texas Company.*)

tions. If the viscosity of a shipment of oil is specified in particular units, the viscosity should be determined in these units by using the proper instrument.

Example 2. Use of Viscosity Conversion Chart (Fig. 7).—The Saybolt viscosity is 1,000 sec. at 210°F. What is the Furol viscosity at 210°F.?

Trace the 1,000 time line to the intersection with the Saybolt Universal line. Follow the horizontal line (kinetic viscosity of approximately 215.0) to the Saybolt Furol line. Read down from the intersection. The Saybolt Furol time at 210°F. is approximately 103 sec.

The Engler time corresponding to the foregoing is 1,500 sec. The Engler degrees (or number) corresponding to the foregoing is 30.

The lower and left scales are used for Saybolt Universal viscosities up to 8,000. For higher viscosities the upper and right scales are used.

Cloud- and Pour-points.—The cloud- and pour-points are useful in estimating the relative amount of wax in an oil. However, all oils will solidify if cooled to a low enough temperature, and hence these tests do not indicate the actual amount of wax or solid material in the oil. They do indicate that most of the wax, melting above the pour-point, has been removed.

In the *cloud test*[1] (D97-33) the oil is cooled, from at least 25°F. above the cloud-point, in a specified test jar. The cooling bath is held between 15 and 30°F. below the cloud-point of the oil. At intervals the test jar is removed from the brine bath without disturbance to the oil, and the temperature at which a distinct cloudiness or haziness appears in the bottom of the jar is recorded as the cloud-point. The *pour test*[1] (D97-33) is conducted in much the same manner. However, the oil is first heated to 115°F., to be sure that all wax has dissolved, and cooled to 90°F. before the test. As in the cloud test the bath is held 15 to 30°F. below the estimated pour-point. At intervals of 5° the test jar is removed from the bath and tilted to ascertain if the oil will flow or move. If it shows no movement when the jar is held horizontal for 5 sec., it is said to be solid. The pour-point is taken as the temperature 5°F. above the solid-point.

The term *cold test* is used loosely and may refer to either the cloud or the pour test. Much confusion can be avoided if the proper term cloud test or pour test is used. Years ago the industry had a specified cold test which indicated the capacity of the oil to flow after vigorous stirring at a low temperature. This test proved to be inadequate and should not be confused with the cloud or pour tests of today.

These tests are for the purpose of ascertaining if an oil will function properly as a lubricant at low temperatures. Since 1929 effective methods for the removal of wax have been developed and the average specified pour-point for lubricating oils has been lowered from 30 to about 10°F.

Knock Testing.—Gasoline can be sold at a premium price if it does not "knock" in the automotive engine. Knocking does not appear greatly to decrease the power output,[5] but an antiknock fuel does permit a higher compression ratio and thus, indirectly, a greater efficiency. The problem of accurately determining the antiknock properties of a fuel has received much attention during the last 10 years. It involved the development of a standard test engine, the selection of a standard reference fuel, and the adoption of a standard test procedure. A standard engine,[6] called the *C.F.R. fuel-testing unit,* is manufactured by the Waukesha Motor Company. The engine and the motor-method test[7] were adopted by the D-2 Committee of the A.S.T.M. on Mar. 7, 1933. Iso-octane (2, 2, 4-trimethyl pentane) mixed with *n*-heptane[8] is the standard reference fuel. Since these hydrocarbons are expensive, reference gasolines that have been standardized against octane-heptane mixtures are used in commercial work. The *octane number* may be defined as the percentage by volume of iso-octane that must be mixed with normal heptane in order to match the knock intensity of the unknown fuel. In the past the antiknock value of a fuel has frequently been expressed as the *benzol equivalent. This* was the percentage of benzol that had to be mixed with a standard straight-run Mid-Continent or standard straight-run Pennsylvania gasoline in order to make a fuel that would match the knock intensity of the unknown fuel. The Mid-Continent gasoline standard had a higher antiknock value than the Pennsylvania standard, so that confusion arose. In other words a gasoline might have a high benzol equivalent measured by the Pennsylvania standard but a low value by the Mid-Continent standard.

Two methods of knock testing with the C.F.R. unit have been generally accepted. The *C.F.R. research-method* test is conducted at 600 r.p.m. and at a jacket temperature of 212°F. The *motor-method* test has been found more nearly to simulate the knock

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[5] Brown and Singer, Jr., *Oil Gas J.*, Feb. 15, 1934, p. 14.

[6] Boyd, T. A., The C.F.R. Research Apparatus and Method for Knock Testing, *Proc. A.P.I.*, Chicago, Nov. 11, 1931.

[7] "Methods of Test for Knock Characteristics of Motor Fuels," A.S.T.M., Philadelphia, 1933.

[8] Campbell, *et al.*, Standard Fuel for Antiknock Quality, *Oil Gas J.*, Jan. 23, 1930, p. 42.

tendency of fuels during road tests; the conditions are 900 r.p.m. and an inlet temperature of 300°F.[9]

The Series 30-B Ethyl knock-testing apparatus of the Ethyl Gasoline Corporation is still used by many refiners. Octane numbers obtained when operating at 900 r.p.m. and a jacket temperature of 345°F. with the Ethyl engine are approximately the same as by the C.F.R. motor method.

Sulfur Tests.—The sulfur[1] (D90-30T) content of gasoline and burning-oils is an important specification. Sulfur causes many corrosion difficulties. Twenty cubic centimeters of oil is burned in a small lamp, and the products of combustion are drawn through a sodium carbonate absorption solution. The sulfur is determined by titrating the unused sodium carbonate solution. Sulfur in residual fuel oil and crude oil is determined by the ordinary oxygen-bomb method[1] (D129-33).

The presence of corrosive materials such as free-sulfur and corrosive sulfur compounds is always objectionable. The test[1] (D130-30) consists in noting the effect of the heated oil on a strip of polished copper. More than a slight discoloration of the copper after heating for 3 hr. indicates that the oil is corrosive.

Tests for Bituminous and Semi-solid Materials.—The most common tests for asphaltic substances are the ductility, penetration, softening-point[1] (D36-26), and specific-gravity tests. The *ductility*[1] (D113-32T) of an asphalt is a measure of its capacity to elongate or stretch and is an indication of the ability of the material to flow and thereby mend a rupture in the surface of the material. A briquette of the asphalt is pulled apart at a uniform rate, and the elongation, measured in centimeters, that occurs before rupture takes place is called the ductility. The test is usually conducted at 77°F., and the briquette is pulled apart at a uniform rate of 5 cm. per minute. *Penetration* tests are made with a penetrometer which allows a needle or cone to penetrate the material without mechanical friction and is arranged to read the depth of the penetration in hundredths of a centimeter. A standard needle is used for asphalt materials[1] (D5-25), and the common test conditions are temperature, 77°F. (25°C.); time, 5 sec.; and load, 100 g. Other test conditions are

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[9] Correlation of Knock Ratings, *Ref. Nat. Gaso. Mfr.*, October, 1932, p. 536.

°F.	Load, g.	Sec.
32	200	60
115	50	5

For greases and petrolatum[1] (D217-33T) the needle is replaced with a standard cone. The procedure is the same as for asphalt materials except that the temperatures of 32 and 115°F. are seldom used.

Road oils are examined for their asphalt content; furol viscosity at 122 or 210°F.; and solubility in carbon disulfide,[10] carbon tetrachloride[1] (D165-27), and petroleum ether.[10] The asphalt content (D243-32T) is determined by an evaporation test. A 100-g. sample of the oil is heated at 480 to 500°F. until the residue has a penetration of 100 at 77°F. This test sometimes ruins the ductility of the asphalt, and hence the value of the test is being questioned.

Gum in Gasoline.—The determination of gum in gasoline has been a troublesome test. The copper- and porcelain-dish methods are rapidly being replaced by others. One of the most widely used new methods is the *accelerated aging test*[11] as developed by the U.S. Naval Experiment Station at Annapolis, Md. The test is conducted by heating a sample of the naphtha in an atmosphere of oxygen at 210 to 212°F. for 4 hr. The pressure of the oxygen is 100 lb. per square inch gage before the bomb is heated. A decrease in pressure at any time during the test indicates the formation of gum, but the gum content is actually measured by removing the sample after the 4-hr. heating period and determining the gum content by the porcelain-dish method using a steam bath and a jet of air. The length of time before the pressure starts to decrease is thought to bear some relation to the time required to produce gum when the gasoline is stored. Many refiners have used a 90-day storage period as an aging test for gum content, but the accelerated aging test is rapidly replacing storage tests.

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[10] Methods of Sampling and Testing Highway Materials, U.S. *Dept. Agr. Bull.* 1216, 1928.

[11] WARD, B.P., *Oil Gas. J.*, Aug. 11, 1932, p. 16.

	Procedures for Other Common Tests	Reference
1.	Burning quality of kerosene oils (D187-30)	1
2.	Burning quality of long-time burning-oils (D219-30)	1
3.	Carbon residue (Conradson carbon) of lubricating oils (D189-30)	1
4.	Distillation of tars or pitches (D20-27T)	10
5.	Doctor test	12, 13
6.	Emulsion, steam of lubricating oils (D157-28)	1
7.	Flash-point of volatile flammable liquids (D56-21), tag tester	1
8.	Float test for bituminous materials (D139-27)	1
9.	Gum in gasoline, glass dish and air jet (A.S.T.M. method A)	1
10.	Loss on heating asphalt or oil (D6-33)	1
11.	Melting-point of paraffin wax (D87-22)	1
12.	Melting-point of petrolatum (D127-30)	1
13.	Neutralization number (D188-27T)	1
14.	Vapor pressure of natural gasoline, Reid (D323-32T)	1
15.	Water and sediment by centrifuge (D96-30)	1

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[1] *Report of Committee* D-2, Petroleum Products and Lubricants, A.S.T.M., Philadelphia, 1933, published yearly.

[10] Methods of Sampling and Testing Highway Materials, *U.S. Dept. Agr. Bull.* 1216, 1928.

[12] *Nat. Petroleum News*, Atlantic Refining Co., Aug. 27, 1930.

[13] Cross, "Handbook of Petroleum Asphalt and Natural Gas," K. C. Testing Laboratory, Kansas City, Mo.

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CHAPTER VI

DESIGN DATA AND THE LABORATORY

From the discussion in the previous chapter it is apparent that routine tests are not always suitable as a basis for engineering calculations. In this chapter a general scheme of obtaining engineering design data is presented. In general, only the methods that are of broad applicability will be discussed. Engineering analysis methods must meet definite requirements. The most important of these are:

1. The results must represent yields and properties that can be duplicated in a modern, properly operated commercial equipment.
2. The method must be such that it can be reproduced easily and quickly.
3. The cost must not be excessive.
4. The equipment should produce fractions or products that are large enough for the determination of gravity, viscosity, flash-point, etc.
5. The data should be general in nature, if that is possible, so that many possible combinations of yields can be computed from a single analysis.

The true-boiling-point method of analysis meets most of these requirements but the Hempel distillation and other less elaborate distillations do not. Even a replica plant fails to meet the requirements of cost and of general usefulness.

Replica Plants.—As the first step in design calculations, the engineer must determine or estimate the yields and physical properties of the products that he hopes to produce. A direct means of obtaining such information is by the construction and operation of a laboratory-size apparatus which is a replica in all essential details of the proposed commercial installation. Excellent results can be obtained from a carefully built replica plant, but the plant is expensive and its operation demands more time than is usually available. Occasionally a complete study of the operating conditions of a process is desired, and in such an instance the replica plant is obviously useful. It must be designed so that it actually duplicates plant results, or its usefulness is lost. Compared with the cost of commercial operation, the operation of a replica plant is not expensive and the results obtained from one carefully operated are probably more accurate than those obtained in most commercial operating tests. However, the operation of a replica plant is even more difficult than commercial operation, and carelessness may result in misleading data.

Universal Design Data.—In the operation of the replica plant only one set of yields, properties, and conditions can be obtained during a single "run" or test, and hence several runs must be made in obtaining a complete set of results. For this reason many designers have adopted a more fundamental type of analysis which provides a more complete set of yields and properties. A discussion of the obtainment of this type of data is the purpose of this chapter. The extensive usefulness of this type of data, both in design and in operation, will be more apparent in Chap. VII. The methods outlined in this chapter provide a means of obtaining comprehensive design data but they do not provide complete operating data. The replica plant is perhaps the best method of obtaining operating data from laboratory tests.

A complete analysis, for design and operating purposes, should consist of the following data:

1. A distillation curve obtained by carefully fractionating the oil sample. This type of curve will be referred to as a *true-boiling-point curve.* The curve is obtained in a batch distillation in which each fraction or compound is carefully fractionated before it is allowed to leave the equipment.
2. A distillation curve obtained under equilibrium vaporization conditions. The vapor is not separated from the liquid until the desired equilibrium temperature is attained. This curve will be referred to as the *flash-vaporization curve.*
3. Mid per cent property curves which show the properties of the small amount of material that distills at any percentage. Common mid per cent curves are
    - *a.* Gravity mid per cent—specific gravity of fraction, versus mid per cent of fraction.
    - *b.* Viscosity mid per cent—viscosity at 100 or 210°F. of fraction, versus mid per cent of fraction.

These curves are called mid per cent curves because the property is plotted at the mid percentage of the fraction that it represents. This type of curve is sometimes referred to as a "stream" curve, *e.g.*, specific gravity (stream).

4. Cumulative property curves which show the average properties of the entire material distilling to a given percentage or, more often, the average

property of the residue at any percentage distilled. Common yield curves are

a. Viscosity yield—viscosity of residue versus per cent of residue.
b. Penetration yield—penetration of residue versus per cent of residue.
c. Flash-point yield—flash-point of residue versus per cent of residue.
d. End-point yield—end-point of gasoline versus per cent of gasoline.

The True-boiling-point Curve.—A true-boiling-point[1] curve is obtained by separating the liquid into nearly pure hydrocarbons[2] by distillation and fractionation and plotting the temperature of the vapor against the percentage. In order to obtain a thorough separation of hydrocarbons, an elaborate fractionating column is necessary. The best known of these types of columns are the Peters' true-boiling-point apparatus[1] for gasoline and heavier oils and the Podbielniak fractional-distillation apparatus[3] for heavy oils, gasoline, and natural gas. Many other equipments, which will accomplish practically the same results, are used by various refiners,[4] but they have not received names because they are not generally used. Several true-boiling-point curves are plotted in Fig. 8.

True-boiling-point Apparatus.—An apparatus of the Peters type is shown in Fig. 9. The fractionating column differs from most laboratory columns because it is completely insulated from the surroundings. The outer jacket *A*, through which heated air flows, is kept at substantially the same temperature as the temperature of the vapor within the column, so that no heat passes into or out of the fractionating column. The column is then said

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[1] PETERS and BAKER, *Ind. Eng. Chem.*, **18**, 69 (1926). The term true-boiling-point was first introduced by Peters in connection with the chemical distillation industries.

[2] The continuous character of the true-boiling-point curve for complex oils indicates that pure compounds are not produced. If pure compounds were produced, the curve would be made up of a series of steps, each flat step representing the boiling-point of a compound. Distillation curves of natural gas, natural gasoline, etc., by the Podbielniak fractional-distillation equipment do show these steps. However, crude oils are exceedingly complex materials and the quantity of any compound is so small that the flat step for each one of them is not evident.

[3] Apparatus and Methods for Precise Fractional Distillation Analysis, *Ind. Eng. Chem.*, anal. ed., **3**, 177 (1931). Apparatus for Precise High-temperature Fractionation of Complex Liquid Mixtures, *Ind. Eng. Chem.*, anal. ed., **5**, 119, 135 (1933).

[4] BEISWENGER and CHILD, True Boiling Crude Analysis, Petroleum Division, Am. Chem. Soc., Atlanta Meeting.

to operate under adiabatic conditions. Inasmuch as no heat is lost or gained by the column, the amount of reflux or cooling material that is introduced into the top of the column, by the reflux air-jacket *C*, is dependent only upon the composition of

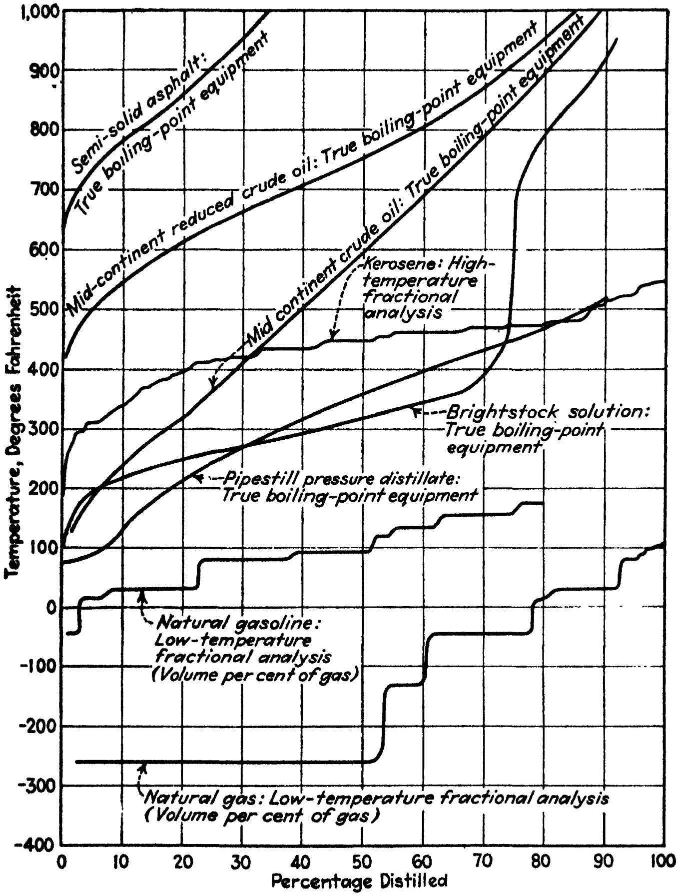

FIG. 8.—True-boiling-point distillation curves.

the vapor from the flask and the degree of separation desired. If the fractionating column is insulated with only an insulating material, the distillation and the amount of reflux required are directly subject to fluctuations in the condition of the environment, such as the room temperature and draughts of air, and to fluctuations in the rate at which heat is supplied to the flask or still. With the adiabatic jacket these fluctuations can be brought within control. The disturbing influence of changing room conditions is particularly important in the operation of laboratory equipment, because the heat losses, even though the equipment has been carefully insulated, are often larger than the useful heat input.

The true-boiling-point still consists of a flask *D* (Figs. 9 and 10) ranging in capacity from 1,000 to 5,000 cc. The larger still is advisable for the evaluation of heavy stocks, because fractions of 100 cc. are required for the determination of gravity, viscosity, flash-point, etc. However, the obtainment of very low pressures is difficult in the larger still unless a large vacuum pump is available. A vacuum pump having a displacement of 2 to 3 cu. ft. of air per minute is large enough for the 1,000-cc. still, but the larger still requires a pump having a displacement of at least 6 cu. ft. per minute. Heat is supplied throughout the entire apparatus by electrical resistance coils. The mixture of vapor that is generated in the flask ascends the adiabatic column *A* and is fractionated into pure compounds by the principles outlined in

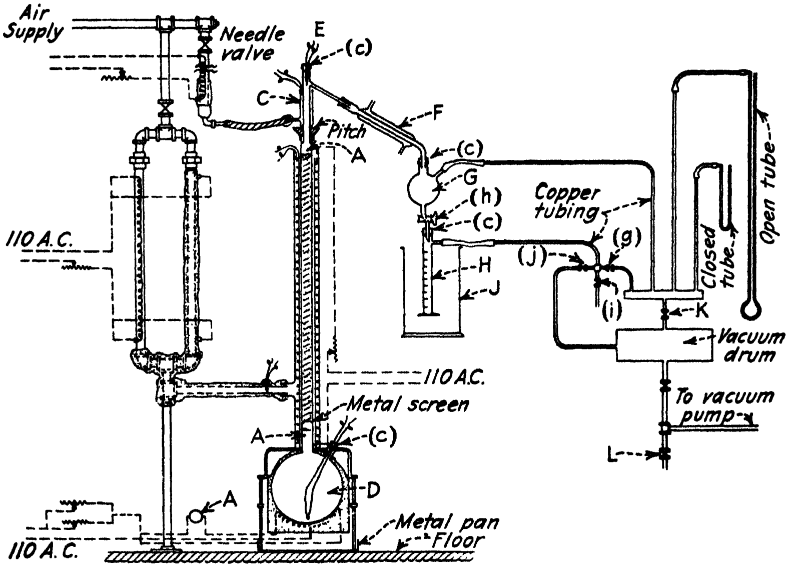

FIG. 9.—Diagram of a true-boiling-point apparatus.

Chap. XV. At the top of the column the vapor is cooled by the reflux air-jacket *C* so that most of it condenses and is returned to the column as reflux. The purified vapor passes the thermocouple *E* in the column head and is condensed in the water- or air-cooled condenser *F*. Near the end of the distillation the condensate may contain wax, and no cooling water is required for the condenser.

The temporary receiver *G* is for operation at reduced pressure. During vacuum distillation the product normally drips through the receiver *G* into the graduate *H*. When the graduate is full the stopcock *h* and the cock *g* are closed, and the graduate is removed by venting to the atmosphere through cock *i*. After an empty graduate is in position, the cock *j* is slowly opened so that the vacuum on the main system is not violently disturbed. An auxiliary vacuum pump may also be used to evacuate the graduate. After the graduate has been evacuated, cock *j* is closed and the cocks *g* and *h* may be opened again. Throughout the entire operation of changing the graduate, the pressure-regulation valve *K* need not be touched. Fine regulation of the pressure is obtained by means of the valve *K* but for large adjustments of the pressure, *i.e.*, at pressures above 50 mm., the valve *L* located near the pump may be used. A small amount of noncondensable vapor is always present during distillation, and this vapor passes through valve *K* causing the throttling action that is necessary for regulation of the pressure. Manometers are used to measure the pressure in the equipment and in the graduate while it is being evacuated. When the equipment is operated at atmospheric pressure the first product may be volatile and, if so, the graduate should be immersed in the removable ice-bath *J*. Many materials have been used for sealing the corks *c*, etc., but LePage's glue, although it must be frequently applied, appears to be most satisfactory.

The distillation may be conducted in two ways, *viz.*, at a constant or at a variable rate of distillation. The more common method of operation is to collect the distillate at a constant rate. The curve obtained by this manner of operation is smooth, with the exception of slight irregularities, and is more convenient for design purposes than one that shows flat steps for each component. The method does not accomplish such good fractionation as the second method of operation in which the rate of distillation is governed by the amount of material that boils at each temperature. If the amount of material that boils at a given temperature is great, the rate should be fast; but if little material boils at the temperature, the rate should be slow, so that a higher reflux ratio is maintained.

The curves in Fig. 8 by the Podbielniak equipment were obtained by the second method of operation. At present, our knowledge of the theoretical behavior of complex mixtures and of the individual components that constitute complex oils is so meager that the more exact curve, obtained by the variable rate of distillation, is almost useless. When our knowledge is extended, and this is rapidly taking place, the more exact curve showing the percentage of each hydrocarbon will be of great value. The variable rate of distillation is useful in the preparation of pure compounds.

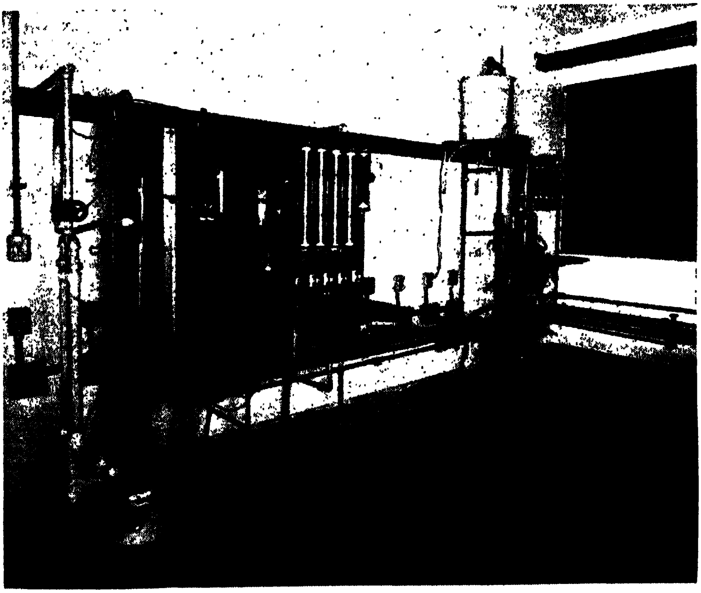

Fig. 10.—True-boiling-point vacuum still for charging 3,000 cc. The small still in the corner is a true-boiling-point still for distilling gasoline at atmospheric pressure. (*A. J. Smith Engineering Company.*)

When the column is operated by the constant-rate method, the rate of heating should be such that distillate is collected at the rate of 1 per cent in 2 min. for atmospheric distillations and

1 per cent in 3 to 5 min. for vacuum distillations. The temperature of the air that enters the bottom of the column jacket should be about 5° below the flask temperature, and the temperature of the air leaving the jacket should be about 5° higher than the vapor-temperature in the column head. If the air loses heat too rapidly in the jacket, more air may be used; and if this fails to sustain the temperature, the resistance wires, strung within the jacket, may be heated. The quantity of cooling material or reflux that is used should always be the maximum amount that the capacity of the column will permit. At all times the packing of Lessing rings in the column should be wet with liquid. However, if too much reflux is used, the column will "flood" or "prime," and reflux will accumulate in it to such an extent that vapor cannot pass up it without carrying the liquid with it. Finally, if flooding persists, the column fails to function as a fractionating device, and the reflux liquid is carried into the condenser.

High-boiling Materials.—Even though a pressure of 0.5 mm. of mercury may be maintained in the true-boiling-point column, the highest boiling oils, such as brightstock and tar, cannot be completely vaporized. The highest vapor-temperature that can be obtained in the true-boiling-point apparatus is approximately 1000°F. when corrected to atmospheric pressure (Fig. 45, page 127). However, when very short-boiling-range products (approximately 300°F.) are being distilled, a temperature of 1060 or even 1100°F. may be attained without decomposition. In evaluating heavy lubricating oil stocks, a narrow-boiling-range sample must be prepared, because a vapor-temperature of at least 1040°F. is necessary in order to evaluate heavy lubricating oils. To produce such a charge-stock, the volatile low-boiling and the tarry high-boiling portions of the lubricating oil sample must be removed. The light portions of the sample may be removed by a steam-atmospheric fractionating distillation in a laboratory shell-still. The residue from this "topping" operation may be separated into a narrow-boiling-range lubricating oil stock and a residual tar or "bottoms" product by a continuous vacuum-flash distillation. The "heart-cut" lubricating stock may be readily evaluated for lubricating oils by a true-boiling-point analysis. This heart-cut lubricating stock is particularly suitable for analysis because it contains no tarry material, and therefore the bottoms from the subsequent true-boiling-point analysis is a clean, heavy-cylinder stock.

As an example, we may wish to evaluate the lubricants in a Mid-Continent reduced or topped crude oil of 26 A.P.I. gravity. By a steam-atmospheric distillation in a small shellstill a 23 A.P.I. reduced crude-oil and a 32 A.P.I. gas-oil distillate may be produced. The 23 A.P.I. reduced crude oil is then distilled in the vacuum-flash vaporizer (Figs. 11, 12), leaving as a residue a 9 A.P.I. tar and obtaining as a distillate a 25 A.P.I. heart-cut lubricating-oil stock which is suitable for evaluation in the true-boiling-point column. The percentage "break-up" would be approximately as follows:

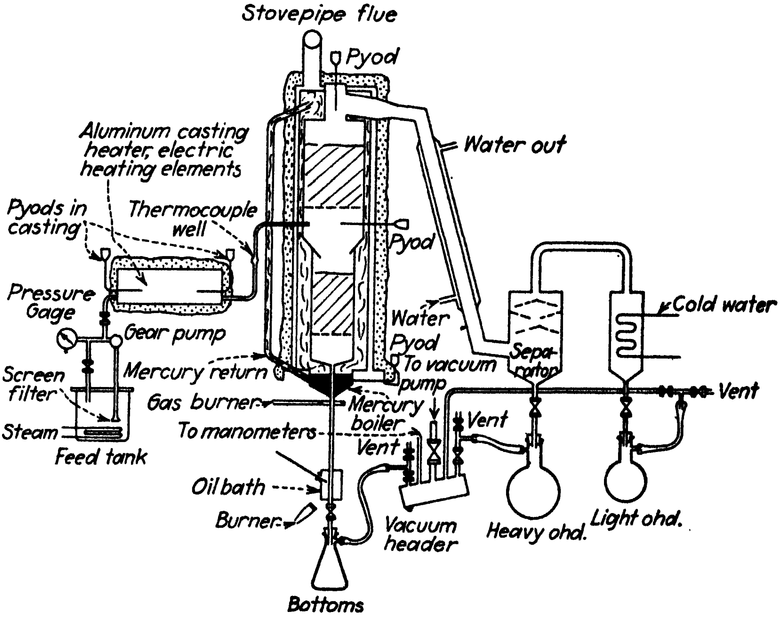

FIG. 11.—Diagram of continuous vacuum-flash equipment.

Material	Per cent	A.P.I.
Gas oil	20	32
Lube stock (heart-cut)	73	25
Tar	7	9
Reduced crude (charge-stock)	100	26

Continuous Vacuum-flash Vaporizer.—The flash vaporizer must be large, because small vaporizers cannot be easily controlled. However, a small one similar in principle to the equilibrium vaporizer shown in Fig. 13 might perform properly. A satisfactory flash vaporizer is shown in Figs. 11 and 12. In Fig. 12 it is situated to the right, and the control desk and panel are in the center.

The purpose of the flash vaporizer is to prepare a lubricating stock for evaluation purposes, and hence the residue of tar should be as small as possible and should contain no lubricants that can be removed from the tar in a commercial vacuum plant. For this reason the apparatus is always operated at the maximum allowable temperature of about 700°F.[5] and at as low a pressure as possible. With an almost leak-free apparatus and with a vacuum pump having a capacity of approximately 9 cu. ft. per minute the apparatus can be operated at a pressure of 7 mm. The capacity of the equipment ranges between 1 and 4 gal. per hour depending upon the character of the charging-stock. The aim is to vaporize as large a percentage of oil as possible, even though the fractionation is imperfect, and hence no more reflux

FIG. 12.—Continuous-flash vaporizer. (Two small shellstills are shown at the left.) (*A. J. Smith Engineering Company.*)

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[5] Decomposition or cracking starts at 680°F.

is used[6] than the small amount that is required to prevent entrainment of tar into the distillate.

The continuous vacuum-flash vaporizer is essentially a replica of a modern vacuum distillation plant, but its usefulness is not limited to such operations. The pipestill of the commercial unit is replaced by a coiled-steel heating-tube cast in aluminum. Insulated resistance heaters are also embedded in the casting, and they are connected to an automatic temperature controller. The use of a casting as a heating agent has several advantages. It serves as an excellent reservoir for heat so that large fluctuations in temperature are impossible; it facilitates the transfer of heat from the resistance heaters to the oil; and its temperature can be easily controlled by an automatic controller acting upon one of the resistance heaters. Heat losses are abnormally high in small equipment and hence the vacuum-tower is jacketed with mercury vapor and with flue gas. The temperature of the mercury jacket can be automatically controlled by regulating the pressure at which the mercury boils.

Equilibrium-flash Vaporizer.—If a liquid mixture is heated without allowing the vapor to separate from the unvaporized liquid until the final desired temperature is reached, and the two phases, liquid and vapor, are kept in intimate contact, the vaporization occurs by an equilibrium flash. By this method the temperature required to vaporize a given percentage is much lower than that required in vaporizing the same amount by a true-boiling-point or A.S.T.M. distillation. This difference may be explained by considering that the vapor acts as an inert gas and tends to vaporize the remaining liquid as does steam in a steam distillation.

Inasmuch as the continuous-flash process of vaporizing is used in almost all modern distillation plants, equilibrium-flash data are vitally important. Furthermore, as outlined in Chaps. XIV and XXI, such data are important in other phases of design work.

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[6] Operation with very little or no reflux at the vaporizer section of a tower is common commercial practice in the operation of atmospheric as well as vacuum plants. Usually very little reflux finds its way into the vaporizer section. However, a little fractionation does occur in the plates between the vaporizer and the first side-draw plate because of heat losses. This reflux is probably little more than that required to stop entrainment and to keep the plates sealed with liquid.

If the oil is "flashed" at one temperature, a certain percentage of it is vaporized; and by flashing at several temperatures a complete curve relating the flash temperature and the percentage vaporized may be obtained. Such a curve is called the flash-vaporization curve. Figure 13 is a sketch of a laboratory equipment for the determination of equilibrium-flash data. Successful flash-vaporization equipment must be capable of feeding a small amount of material at a constant rate and of heating it to a constant temperature. At the same time an equilibrium or intimate contact must be established between the liquid and the vapor at the flash temperature. The vaporizer *A*, packed with Lessing rings, is provided for establishing equilibrium. The rate of feed is regulated by the constant head device *D* and the orifice *E*. A constant rate depends upon a constant feed temperature, because the viscosity and the rate of flow through the orifice vary with temperature. Constancy of the flash temperature is maintained by the resistance coil which surrounds the heating tube and particularly by the glass heating tube in the vapor jacket. Should the temperature of the oil leaving the steel heating tube be slightly high, the oil will be cooled in the glass coil by the vapors, and vice versa.

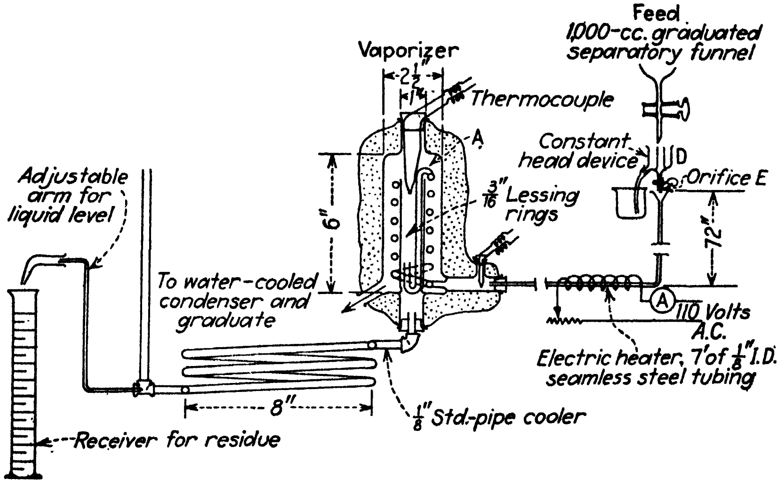

FIG. 13.—Equilibrium-flash vaporizer.

The apparatus described (page 66, Fig. 13) does not provide such exact results as do other types of equipment,[7,8] but the data are sufficiently accurate for most design work. The more exact equipments[7,8] consist of a large bath which keeps the heating coil and vaporizer at a constant temperature. The temperature of the bath can be controlled within ±0.5°F. The objection to such equipments for commercial work is the length of time required to make an analysis. The temperature of the bath changes very slowly, and a large sample of oil is required.

A series of orifices having holes ranging from ¼ to 2 mm. in diameter are necessary in order to handle the complete range of charging-stocks. The apparatus gives equilibrium conditions when operating at capacities of about 9 to 19 cc. per minute. A constant condition can be obtained in approximately 20 min. of operation but at least 40 min. is required for the determination of a single point on the flash-vaporization curve. In processing light materials such as gasoline, the distillate receiver should be immersed in a brine bath or even a carbon dioxide snow-container to condense the volatile hydrocarbons. Modifications can be made for the determination of flash-vaporization data at reduced pressures.

Fractional Analysis.—The Podbielniak low- and high-temperature precision fractional-distillation equipments[3] can be used to obtain this type of analysis. The fractional analysis may be defined as one that states the percentage of each compound in the sample. For relatively simple mixtures, such as natural gas, natural gasoline, lacquer thinners, and short-boiling-range petroleum fractions, the fractional analysis is of great importance (Fig. 8).

Figures 14 and 15 indicate details of the Podbielniak equipments. They are both essentially true-boiling-point equipments, but the low-temperature apparatus is modified so that it can be operated at temperatures far below zero. In the true-boiling-point apparatus discussed on the previous pages the pressure is usually not changed during the distillation, but in the fractional-analysis equipments the pressure and temperature may be

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[7] Leslie and Good, The Vaporization of Petroleum, *Ind. Eng. Chem.*, **19**, 453 (1927).

[8] Piromoov and Beiswenger, Equilibrium Vaporization of Oils . . . , *A.P.I. Bull.* 10, No. 2, Sec. II, p. 52, 1929.

changed simultaneously. In the low-temperature equipment the sample may be cooled with liquid ethylene, ethane, air, nitrogen, carbon dioxide, etc. Gas samples of 2,000 cc. are advisable, although samples of only 100 cc. have been successfully analyzed by the use of a microfractionating tube. Liquid samples of 50 cc. are desirable. The high-temperature equipment[9] may be obtained with flasks having capacities from 250 to 2,000 cc.

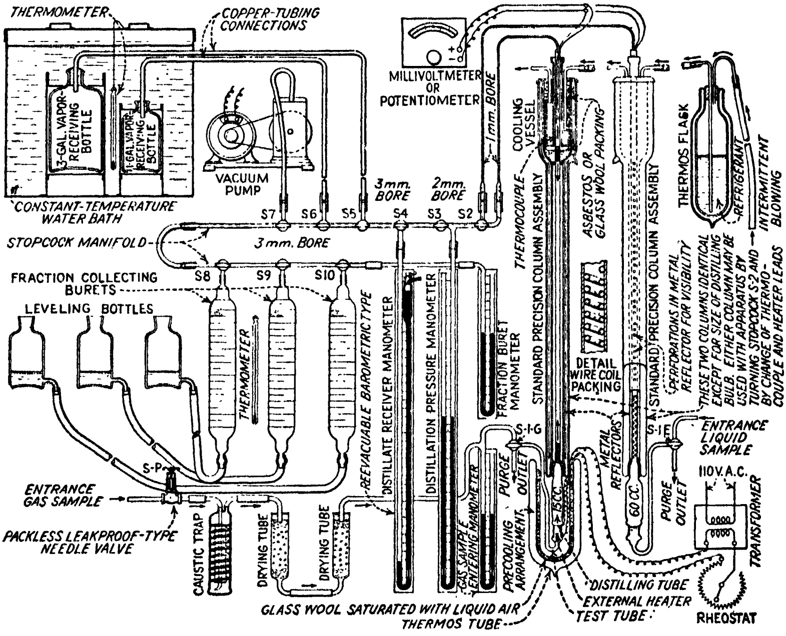

Fig. 14.—Podbielniak low-temperature precision fractional-distillation apparatus. (*Walter J. Podbielniak.*)

In analyzing gases (Fig. 14) the sample is introduced into the chilled distilling bulb and all gas except the air, hydrogen, and methane is condensed. These permanent gases are collected in an evacuated receiver and the pressure in the receiver is recorded. The condensed hydrocarbons are then allowed to warm and the components are fractioned and collected one by one in evacuated receivers. Heat may be required to vaporize the highest boiling part of the liquid. When a flat place occurs in the distillation curve or, in other words, material is collected at a constant temperature, the reflux is decreased by allowing the component

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[9] Podbielniak Industrial Research and Analytical Laboratories, Chicago.

to escape from the column more rapidly. As the temperature tends to rise, the reflux is increased by using a slower rate of distillation until finally little or no more material collects. At the same time the pressure in the column tends to drop. This condition indicates that one component has been removed. The

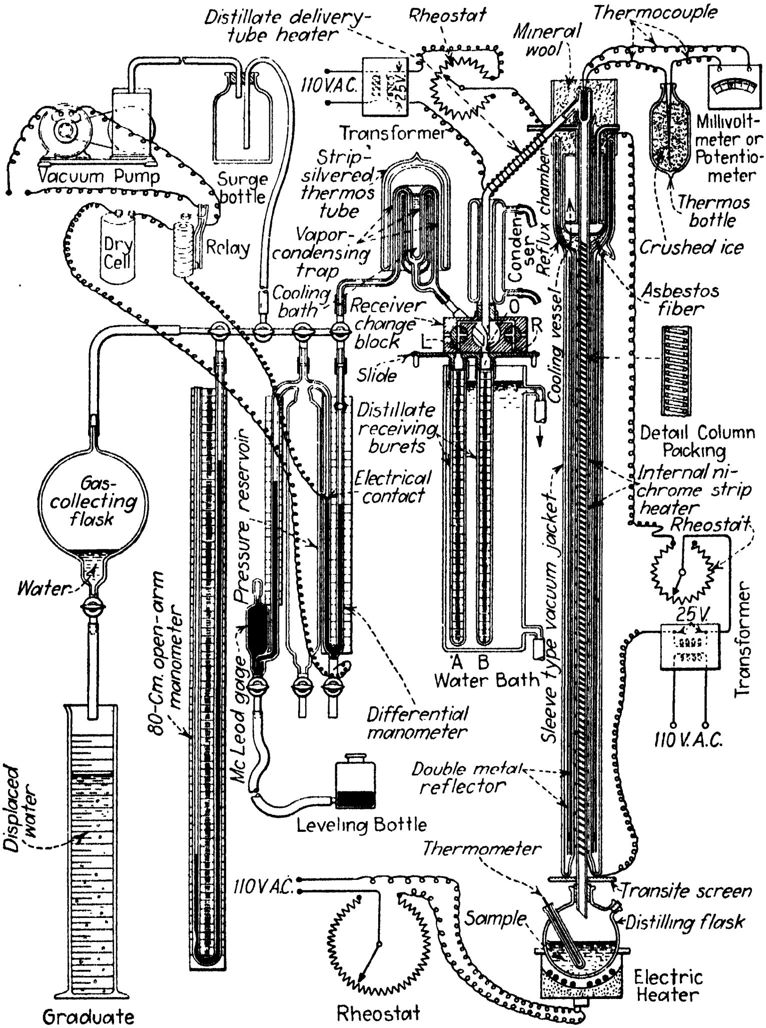

FIG. 15.—Podbielniak high-temperature precision fractional-distillation apparatus. (*Walter J. Podbielniak.*)

components may be collected in different receivers, but more often the gas is collected as a mixture, and the percentage of each component is determined by examining the distillation curve.

The volume of each component can be measured in mol or volume percentage by merely noting the change in pressure in the gas receiver, because the temperature and the volume of the receiver remain constant during the test.

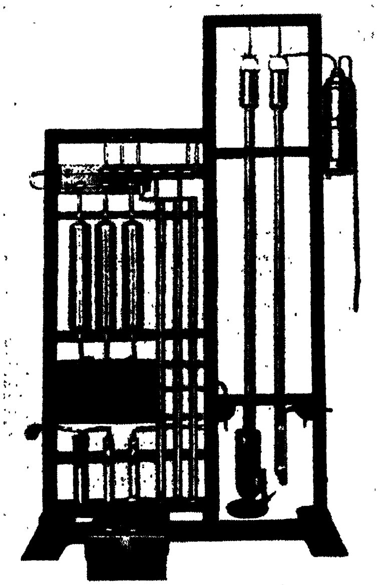

FIG. 16.—Standard Podbielniak equipment. (*Walter J. Podbielniak.*)

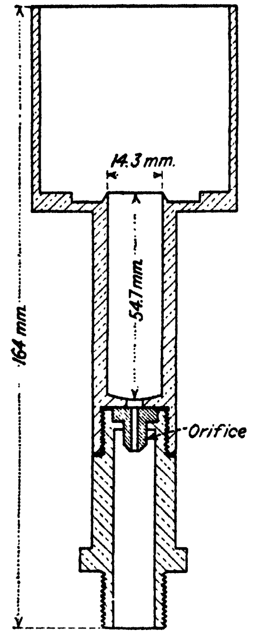

FIG. 17.—Microviscosimeter tube with standard Saybolt orifice.

Auxiliary Equipment.—In completing an evaluation of an oil stock, the fractions obtained in a true-boiling equipment are examined to determine their properties such as the gravity, viscosity, flash-point, and penetration (Chap. VII). The largest practical size of fraction is about 100 cc., and hence special microanalysis equipments are sometimes useful. The gravity may be obtained with 4-in. hydrometers and more accurately with a chainomatic specific-gravity balance. By careful management the standard viscosity equipment may be used, but viscosity pipettes[10] similar to the Ostwald pipette are useful.

The modified Saybolt tube for small capacity, as indicated in Fig. 17, is perhaps the most convenient type of microviscosimeter. A 15-cc. sample of oil is sufficient, and the results check those by the Universal Saybolt method within ±4 per cent. This accuracy is usually sufficient for the construction of the viscosity curves that will be discussed in the next chapter·

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[10] FERRIS, S. W., *Ind. Eng. Chem.*, **20**, 974 (1928).

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CHAPTER VII

THE EVALUATION OF OIL STOCKS

There are three general classes of crude oils: paraffin base, mixed base, and asphaltic base. In addition, Smith and Lane[1] have found that another distinct class exists. They have called this group of oils hybrid base because such oils partake of the properties of both the asphalt- and mixed-base oils. Hybrid-base oil differs from asphalt-base oil in that it contains wax. The four classes of oils by the Bureau of Mines are

1. Paraffin base.
2. Intermediate base (mixed base).
3. Hybrid base (asphalt base or mixed base).
4. Naphthene base (asphalt base).

Although the base of an oil indicates some of the general properties of the oil, no classification of crude oils can be entirely satisfactory. This is because few oils belong distinctly to any one group, and some oils have such intermediate properties that they are misfits in any group. Nevertheless, to experienced men, the base of an oil connotes certain distinctive properties. These are indicated in the following discussion.

The Base of a Crude Oil.—There are six common methods of determining the base of an oil. These tests or inspections should be used collectively because an oil may be of one base by one test and belong to another base by other tests. In other words, an oil may be on the border line between two bases, and the classification of it should depend somewhat upon the particular properties that are of greatest interest.

1. The Bureau of Mines "Key Fraction No. 1"[2] is the portion of a crude oil that boils between 482 and 527°F. If the gravity of this fraction is above 40 A.P.I., the oil is paraffin base; and if its gravity is below 33 A.P.I., the oil is naphthene base. In

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[1] Tabulated Analysis . . . Crude Oils . . . , *Bur. Mines. Bull.* 291, 1928.

[2] SMITH, N. A. C, The Interpretation of Crude Oil Analyses, *Bur. Mines Repts. Invest. Serial* 2806, 1927.

general this checks with the correlation of crude oils by gravity, as presented in Fig. 22.

2. The Bureau of Mines "Key Fraction No. 2"[2] is that portion of a crude oil that boils between 527 and 572°F. at 40 mm. pressure. By the correction chart (Fig. 45, page 127) the boiling-range at 760 mm. is 733 to 779°F. If the cloud-point of this fraction is below 5°F., the crude oil contains substantially no wax and is distinctly naphthene base. However, if the cloud-point is above 5°F., the oil may be hybrid, intermediate, or paraffin base.

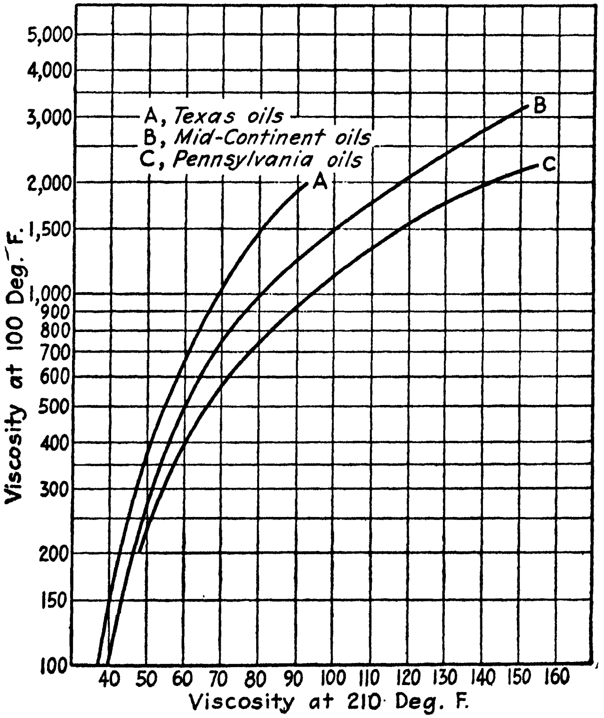

FIG. 18.—Relation of viscosity at 100°F. to viscosity at 210°F.

3. The viscosity-temperature relation of an oil is perhaps the most important property in the valuation of oil stocks. At high temperatures the viscosity of an oil and its ability to lubricate surfaces become less. Those oils whose viscosity decreases rapidly with temperature are not so desirable as oils that retain their viscosity. According to Fig. 18 the paraffin-base oils lose

less viscosity with an increase in temperature than do other types of oil. The viscosity-temperature relation is an important property and, inasmuch as the market price is largely determined by this property, it may eventually become of even more importance than the base of an oil. Recently, lubricating oils have been produced by the polymerization[3] of unsaturated light oils, by hydrogenation, and by solvent treating. Some of the oils by these methods exhibit viscosity-temperature relations that are superior to those of paraffin-base oils.

Dean and Davis[4] have suggested a useful constant, the *viscosity-index*, for comparing the viscosity-temperature relation of oils. A Pennsylvania or paraffin-base oil, with an arbitrary index of 100, was adopted as the standard high-index oil. At the other extreme is a naphthene-base oil with an index of 0. Figure 19 is a chart by which the viscosity-index may be computed. As an example, the viscosity-index of an oil having a viscosity of 90 at 210°F. and 1,200 at 100°F. is 79. The index was determined by following the oblique line marked 90 to the horizontal line marked 1,200. These lines intersect at the vertical line of 79 index.

The *viscosity-gravity constant*[5] is closely related to the viscosity-index. The constant can be obtained from the gravity at 60°F., and the viscosity at 100°F., and in turn the viscosity-index can be obtained from the viscosity-gravity constant. Thus the viscosity-index for light lubricating oils and distillates can be obtained without determining the viscosity at 210°F. The viscosity at 210°F. of such oils cannot be accurately determined.

The well-fractionated narrow-boiling-range fractions obtained in a true-boiling-point distillation seem to have slightly higher viscosity-indexes than regular blended oils. Figure 23 indicates higher indexes than those shown in Fig. 18.

4. The gravity versus gasoline-content of a crude oil is a further indication of the base of the oil. More than 130 crude-oil analyses were used in plotting Fig. 20. The percentage of

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[3] SULLIVAN *et al.*, Lubricants from Cracked Distillates, *Oil Gas J.*, June 4, 1931.

[4] Viscosity Variations of Oils with Temperature, *Chem. Met. Eng.*, **36**, 618 (1929); Applying Viscosity Index to the Solution of Lubricating Oil Problems, *Oil Gas J.*, Mar. 31, 1932, p. 92.

[5] MCCLUER and FENSKE, *Ind. Eng. Chem.*, **24**, 1371 (1932).

410 to 425°F. end-point gasoline was plotted against the A.P.I. of the crude oil. The comparison indicates three well-defined zones for the different bases of oils. For example, a 36 A.P.I. crude oil containing 30 per cent of 415°F. gasoline would be classed as a mixed-base oil.

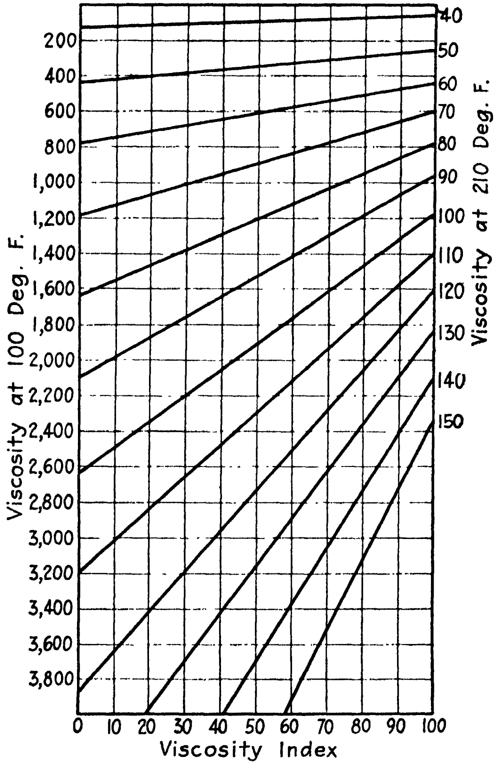

FIG. 19.—Viscosity-index. (*Dean and Davis, Chem. Met. Eng.*)

5. A comparison of the properties of an unknown oil with those of known oils is a common method of studying an oil. A comparison of only two or three oils is not satisfactory and may lead to erroneous conclusions. Hence the following comparison of more than 82 true-boiling-point analyses of crude oils is presented. In all cases the properties are those of raw products just as they were obtained from the true-boiling-point distillation equipment. A comparison of the properties of raw-oil samples is to be preferred to a comparison of finished-oil properties

because of the uncertainty introduced by laboratory treating and finishing operations.

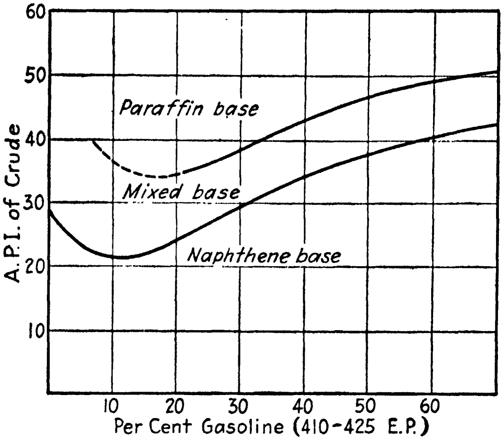

FIG. 20.—Base of a crude oil.

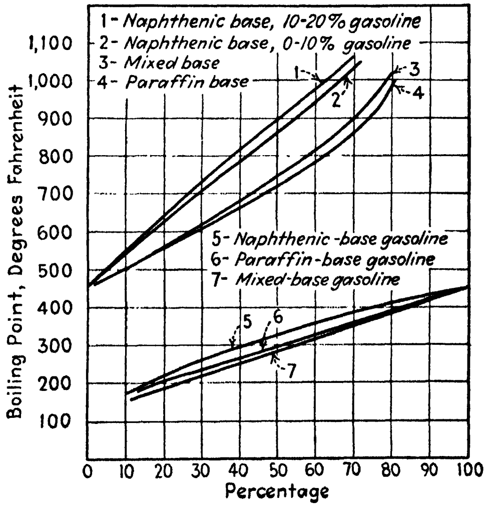

FIG. 21.—Correlation of the boiling-points of crude oils.

Figures 21, 22, and 23 are comparisons of the true-boiling-point distillation curves, the A.P.I. mid per cent gravity (see page 86), and the mid per cent viscosity (see page 86) of the various bases of crude oil. Figure 21 was obtained by plotting the boiling-

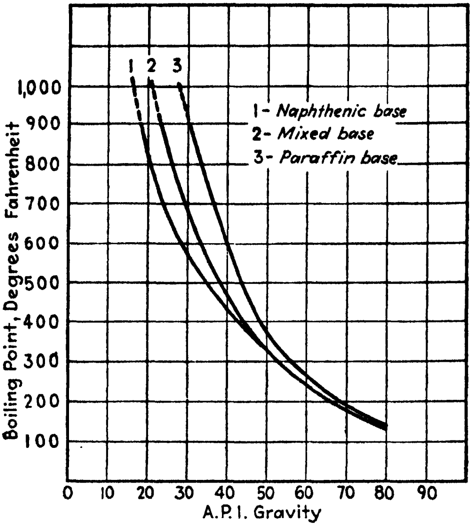

FIG. 22.—Correlation of A.P.I. gravity of crude oils.

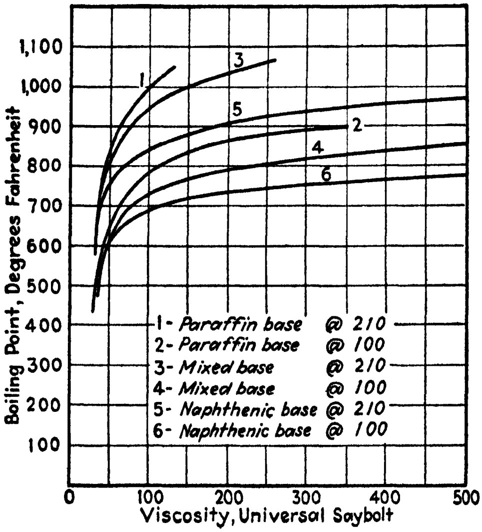

FIG. 23.—Correlation of viscosity of crude oils.

range of the material boiling up to 450°F. as 100 per cent and the boiling-range of the remaining material, or base of the oil, as 100 per cent. By a reverse operation, an approximate true-boiling-point distillation curve can be computed if the percentage of 450°F. (about 428°F. A.S.T.M. end-point) material and the base of the oil are known. Figure 22 was obtained by plotting the A.P.I. gravity of the fractions of crude oil at their mid or 50 per cent boiling-points. A large change in the boiling-point of the higher boiling oils causes only a small change in the gravity, and hence the upper parts of the curves are not entirely dependable. Figure 23 was plotted similarly to Fig. 22, *i.e.*, by plotting the viscosities at 100 (and 210)°F. of the fractions at their mid boiling-points.

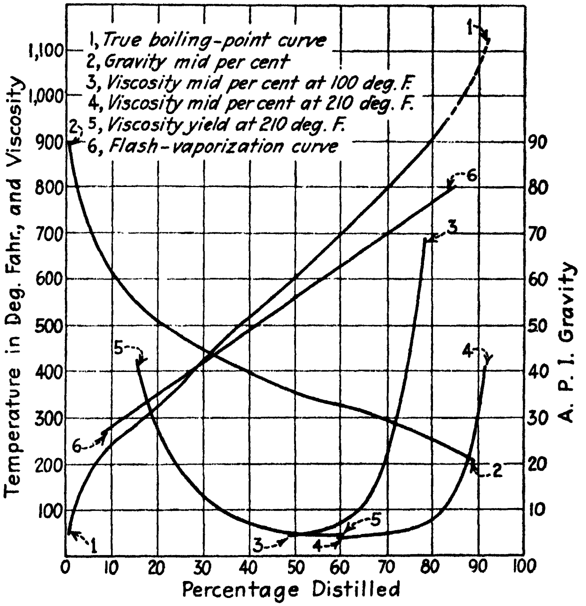

FIG. 24.—True-boiling-point evaluation curves for a 37.3 A.P.I. mixed-base crude oil.

These curves are merely averages of many crude oils, and perhaps no single crude oil will fall exactly on the average lines. As mentioned before, crude oils are seldom found that are typically paraffin, mixed, or naphthene base. Figures 24, 25, and 26 are analyses of typical crude oils.

Example 3. Construction of Average Crude-oil Curves without Analysis. A crude oil contains 40 per cent of gasoline and has a gravity of 38 A.P.I. According to Fig. 20 the oil is a typical mixed-base oil.

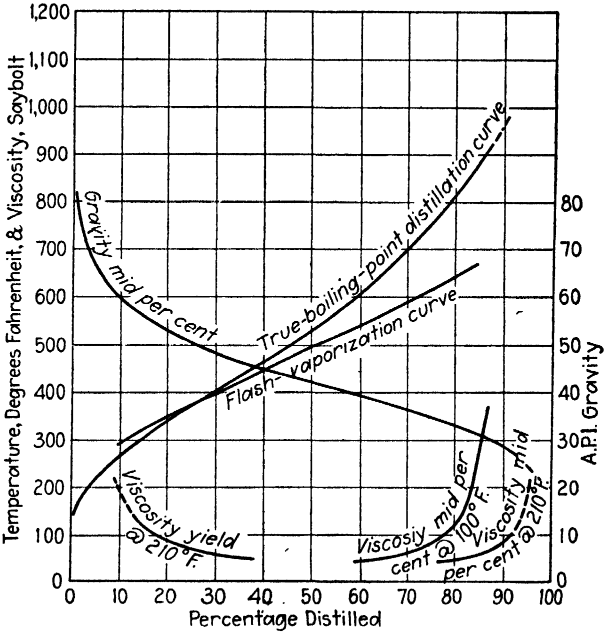

FIG. 25.—True-boiling-point evaluation curves for a 42.2 A.P.I. paraffin-base crude oil.

Computed data for true-boiling-point distillation curve (see curves 7 and 3, Fig. 21):

Per cent	Per cent of crude oil	Temperature, °F.
Gasoline:		
25	10	205
50	20	291
75	30	368
100	40	450
Base:		
20 40 + 60 ÷ 5 =	52	554
40	64	681
60	76	815
80	88	1020
100	100	

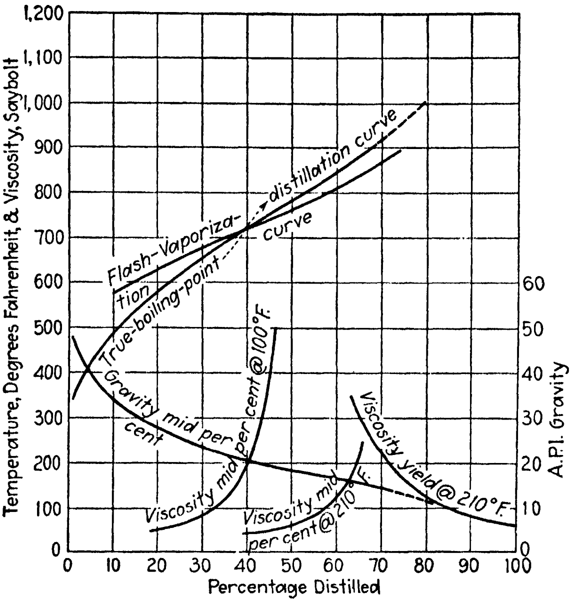

FIG. 26.—True-boiling-point evaluation curves for a 20.2 A.P.I. naphthene-base oil.

The gravity and viscosity data can be obtained from Figs. 22 and 23. The data for the mid per cent curves are as follows:

Temperature, °F.	Gravity, A.P.I.	Viscosity	
		At 100°F.	At 210°F.
150	75		
200	66		
300	52.2		
400	43.5		
500	38.5		
600	33.0	45	
700	29.3	76	
750	....	125	
800	26.0	233	48
850	....	490	63
900	22.7	...	76
950	....	...	105
1000	20.5	...	151
1050	....	...	238

6. Another indication of the base of an oil is the "cast" or "bloom" of the lubricating oil stocks. By transmitted light, the color of oils varies from a light yellow to a deep red. By reflected light, the oil may exhibit a blue- or yellow-green appearance at the surface, regardless of color. This appearance is due to fluorescence and is called the cast of the oil. It may be noted by looking at the oil at an angle rather than directly through the oil or, even better, by viewing the oil in thin layers on a black background. Properly refined paraffin-base oils and even some mixed-base oils have a yellow-green cast, but naphthene oils appear deep blue. The natural yellowish cast of paraffin-base or mixed-base oils may be spoiled by improper acid treatment.

Fundamental Mathematics.—The physical properties of an oil are found to vary gradually throughout the range of compounds that constitute the oil. Distillation is a means of arranging these chemical compounds in the order of their boiling-points. The properties such as color, specific gravity, and viscosity are found to be different for each drop or fraction of the material distilled. The rate at which these properties change from drop to drop may be plotted as mid per cent curves (page 86) such as curves 2, 3, and 4 in Fig. 24.

Calculus is the branch of mathematics that deals with the rate at which variables change. In the foregoing curves the percentage is called the independent variable and the property, such as gravity, is the dependent variable. In other words, the value of the property changes as the percentage is changed. The independent variable is usually plotted on the horizontal axis along the base of a chart, and the dependent variable on the vertical axis. As the percentage distilled is increased by, say, 5 per cent, the gravity also changes and by an amount that is specified by the curve. Mathematical equations of the mid per cent curves for oil are so complicated that they cannot be easily computed or handled by the formal methods outlined in calculus texts but they can be treated by the more simple and rapid methods of graphical calculus.

The refinery engineer is most often interested in determining the property of a commercial fraction such as the gravity or viscosity. In reality, the gravity or viscosity of a fraction is an average of the properties of the many drops that constitute the fraction. If each drop is equally different from the last drop and from the succeeding one, then the drop that distills at exactly half of the fraction has the same property as the average of all of the drops. This would be the condition for a mid per cent curve that is a straight line. Mid per cent curves are never exactly straight lines (Fig. 27) but they are substantially straight through any short range of percentage. For a short range of percentage the average property is equal to the property at the mid-point of the fraction. Each short range of percentage may be considered as a material, and the arithmetical average of the properties of these materials is the property of the total fraction. The mechanism of using the foregoing principles can be best illustrated by an example:

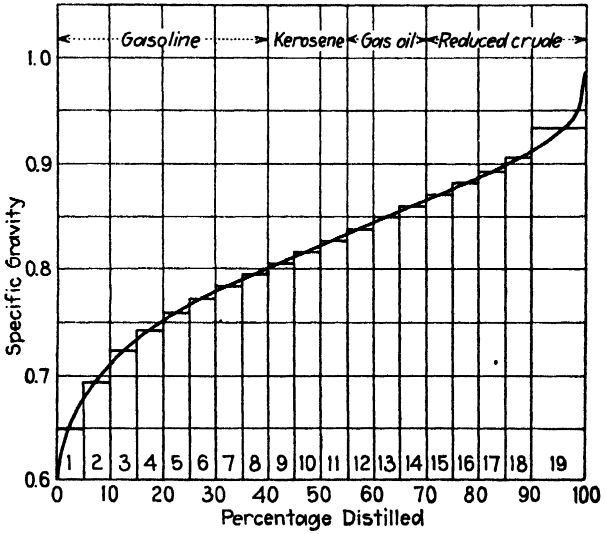

FIG. 27.—Mid per cent gravity curve.

Example 4. Use of Gravity Mid Per Cent Curve.—Compute the specific gravity of a 41.4 A.P.I. (0.8183 sp. gr.) mixed-base crude oil from the specific-gravity mid per cent curve. Figure 27 is the gravity mid per cent curve as determined in the laboratory.

Assume that the curve is broken up into 19 fractions as indicated in Fig. 27. The gravities of the 19 materials are indicated by the 19 short horizontal lines. The curve is substantially straight through fractions 5 to 18 inclusive, and the horizontal lines pass through the centers of these fractions. The horizontal lines (average gravities) for the other fractions

(1 to 4 and 19) do not pass through the mid-point but are so arranged that the triangular areas above and below the curve are equal. The gravities of the 19 fractions are as follows:

Fraction No.	Range of percentage	Sp. gr.
1	0–5	0.6506
2	5–10	0.6936
3	10–15	0.7227
4	15–20	0.7420
5	20–25	0.7583
6	25–30	0.7720
7	30–35	0.7844
8	35–40	0.7958
9	40–45	0.8067
10	45–50	0.8170
11	50–55	0.8280
12	55–60	0.8388
13	60–65	0.8498
14	65–70	0.8602
15	70–75	0.8713
16	75–80	0.8827
17	80–85	0.8939
18	85–90	0.9065
19	90–100	0.9340

The gravity of the crude oil is equal to five times that of each of the fractions 1 to 18 inclusive plus ten times the gravity of fraction 19, all divided by 100. The computed gravity is 0.8171, and the actual gravity of the crude oil was 0.8183. This is a reasonable check and is sufficiently accurate for most engineering design work.

This crude oil contains 40 per cent of gasoline, 15 per cent of kerosene, 15 per cent of gas oil, and 30 per cent of reduced crude oil. The gravity of the gasoline equals five times the gravity of fractions 1 to 8 inclusive divided by 40 and numerically is 0.7399 (59.8 A.P.I.). In a similar manner the gravity of the kerosene is equal to five times the gravity of fractions 9, 10, and 11 divided by 15 and is 0.8172 (41.6 A.P.I.). Likewise the gravity of the gas oil and reduced crude oil are respectively 0.8496 (35 A.P.I.) and 0.9037 (25.1 A.P.I.).

In this example the actual fractions that were produced in the laboratory were used. In the usual case only the curve is available and it is arbitrarily broken up into suitable fractions.

By inspecting the specific gravities computed in Example 4, it will be noted that the gravities of the kerosene and gas oil are the same as the gravities at the 47.5 per cent and the 62.5 per cent points respectively. More generally, they are the same as the gravity at the mid percentage points of these two cuts. Such might have been expected because the curve is nearly a straight line throughout these materials. Following this reasoning we may say that, if the property curve is nearly a straight line between the limits of the fraction, the average property of the fraction is equal to the value of the property at the mid percentage point of the fraction, and the laborious method of integral-averaging by graphical methods, as in Example 4, does not need to be used except throughout sharply curving sections of the curve.

Application of Graphical Integration.—Graphical integration cannot be used in obtaining an average unless the property is an additive property. In other words, if 10 volumes of an oil of specific gravity 0.8 is mixed with 10 volumes of an oil of specific gravity 0.9, the resultant 20 volumes must have a gravity of 0.85, if the specific gravity is an additive property. Most properties are not additive. As an example, if two equal volumes of oil having different viscosities are mixed together, the resultant oil has a lower viscosity than the arithmetic (or integral) average would indicate (see blending charts, Figs. 40, 41, and 42, Chap. VIII). Although specific gravity is additive, the A.P.I. gravity is not additive because it is not a direct function of specific gravity.

The boiling-point is not an additive property because the vapor-pressures of the compounds determine the boiling-point curve and vapor-pressure is not a direct function of temperature and is not additive (see Fig. 45, Chap. VIII) unless a mol basis is used.

Property Curves.—The most important curves for engineering evaluation purposes are the true-boiling-point distillation curve (see Chap. VI), the gravity mid per cent curve, the viscosity mid per cent curves at 100 and 210°F., the viscosity yield curve, and the flash-vaporization curve. The mid per cent curves are so named because they are curves which can *usually* be integrally averaged by merely noting the mid percentage point between the limits of a fraction. However, if a sharp curvature exists at the ends of the curves, the fractions containing the curvature must be integrally averaged. Other properties, such as the flash- and fire-points and the carbon residue, are sometimes plotted as mid per cent curves, but they are not usually necessary.

Figure 25 is an analysis of a paraffin-base crude oil showing these curves. These curves are dependable only when they are obtained from well-separated fractions such as those from a true-boiling-point distillation.

Gravity Mid Per Cent Curve.—This curve is obtained by plotting the gravities of the fractions of oil as shown in Fig. 27. The gravities of the fractions are plotted as a series of horizontal lines and the curve is drawn by balancing the triangular areas against each other. Throughout the middle of the curve, the curve usually passes directly through the mid percentage point of each of the fractions because the property increases evenly, but at the ends the triangular areas must be balanced. Any point on the curve is the mid-point for any width of fraction except when the limits of the fraction include a sharply sloping portion of the curve.

Viscosity Mid Per Cent Curves.—These curves are obtained by plotting the viscosity of each fraction at the mid percentage point of the fraction. The triangular areas need not be balanced against one another as in the case of the specific-gravity mid per cent curve. There is no theoretical background for the use of these curves in this manner but the results are accurate. Apparently the effect of the sharp curvature of these curves and the fact that viscosity is not an additive property counterbalance one another. Regardless of reasons, the curve may be used by noting the viscosity at the mid-point of the fraction. As an example, the following four (or more) fractions, each having a viscosity of 215 at 100°F., can be obtained from the oil shown in Fig. 24.

1. A 5 per cent fraction from 67.5 to 72.5 per cent.
2. A 10 per cent fraction from 65 to 75 per cent.
3. A 15 per cent fraction from 62.5 to 77.5 per cent.
4. A 20 per cent fraction from 60 to 80 per cent.

Since the curves slope steeply at higher percentages (88 to 92 per cent on curve 4, Fig. 24), they cannot be accurately read and hence the viscosity of the residual product should be obtained from the viscosity yield curve.

Beiswenger and Child[6] by correlation with plant results have found that the pressability of a wax distillate may be estimated

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[6] True Boiling Crude Analysis, Petroleum Div., Am. Chem. Soc., Atlanta Meeting (not for publication).

from the viscosity mid per cent curve at 100°F. If the upper end of a wax distillate (from a Mid-Continent crude oil) does not exceed a boiling-point of about 870°F. and the viscosity of the last drop is not over 600 at 100°F., the distillate will be pressable. With paraffin-base oils the cut-point may be somewhat higher.

Viscosity Yield Curve.—This curve shows the total percentage of residual or bottom product of a given viscosity that can be produced. Since residual products are usually viscous, the viscosity yield curve is determined at 210°F. The curve indicates the integral-average viscosity of any of the many possible bottom products. The curve can be obtained by sampling the residue remaining in the flask as various percentages of product have been collected as distillate, and determining the viscosities of these samples of bottom. However, such a method is awkward and a simpler and sufficiently exact method is to blend the *final bottom product* (such as fraction 19, Fig. 27) with the last fractions that have been collected as distillate, to make other bottom products. This is not possible if decomposition has occurred during distillation. In order to have enough oil for the compounding of several bottom products, the final bottom and the fractions are blended in aliquot parts rather than by using all of each fraction.

Example 5. Construction of Viscosity Yield Curve.—This method applies in general to all yield curves.

Consider 19 fractions of oil obtained by a fractionating type of distillation. The properties such as gravity and viscosity of the fractions have already been recorded so that the fractions can be used in the following blends. Fractions 1 to 18 inclusive consist of 100 cc. each and the last or bottom fraction (not distilled) amounts to 200 cc. The fractions can be blended in aliquot parts to make several bottom products as follows:

Per cent residue or bottom	Blend of fractions	Total quantity of blend, cc.
10	No. 19, 75 cc.	75
20	No. 19, 40 cc.; No. 18 and 17, 20 cc. each	80
30	No. 19, 30 cc.; No. 18, 17, 16, and 15, 15 cc. each	90
45	No. 19, 20 cc.; No. 18 to 12 incl., 10 cc. each	90
60	No. 19, 14 cc.; No. 18 to 9 incl., 7 cc. each	84

The viscosity of each blend is determined, and the four blends, along with fraction 19, constitute five points on the viscosity yield curve; also refer to Table 7, page 91.

The viscosity yield curve would not be necessary if accurate viscosity mid per cent curves could be obtained for the entire percentage range of the sample. These curves cannot extend entirely to the end of most samples because the distillation cannot be conducted to a flask temperature higher than 680°F. Even at low pressures such a temperature does not vaporize the heavy lubricating oil stocks. Furthermore, the mid per cent curves slope so sharply at the higher percentages that they cannot be accurately plotted. The viscosity yield curve is used only in the determination of the quantity of bottom product.

The several property curves tend to be confusing when plotted on a single sheet of paper (Fig. 24). For this reason the meaning of the percentage scale has been changed in plotting the viscosity yield curve. Normally the percentage scale denotes the total percentage of material that has been distilled, but for the viscosity yield curve the scale denotes the percentage of bottom product.

Often the stock contains black asphaltic material and is unsuitable as a lubricating oil stock because the removal of asphalt by treating or filtering is costly. Such stocks are evaluated by conducting a vacuum-flash vaporization which leaves a residue of solid tar. The overhead distillate is then analyzed in the true-boiling-point column and the property curves are drawn for this heart-cut material (see page 94).

The Flash-vaporization Curve.—This curve has been discussed in Chap. VI. A method for drawing the curve empirically is presented in Chap. XIV, but the curve is so important that it should be determined experimentally. In a sense, the flash-vaporization curve is a yield curve and is often called the flash yield curve. The curve is always given at 760 mm. pressure unless the pressure is specifically stated as otherwise. A point on the curve represents the temperature at which a given amount can be vaporized or distilled if the vapor and remaining liquid are kept in equilibrium with each other until the final high temperature is attained.

A.S.T.M. End-point of Distillates.—The A.S.T.M. end-point is an important specification of such distillates as gasoline and kerosene. What is the relation of the A.S.T.M. end-point to the cut-point by a true-boiling-point distillation? No all-comprehensive relation exists because of the wide variety of different petroleum stocks. Nevertheless, Fig. 28 is an approximation that will hold in most cases. The true-boiling-point cut-point is obtained by adding a correction, in degrees Fahrenheit, to the A.S.T.M. end-point. The four curves are for

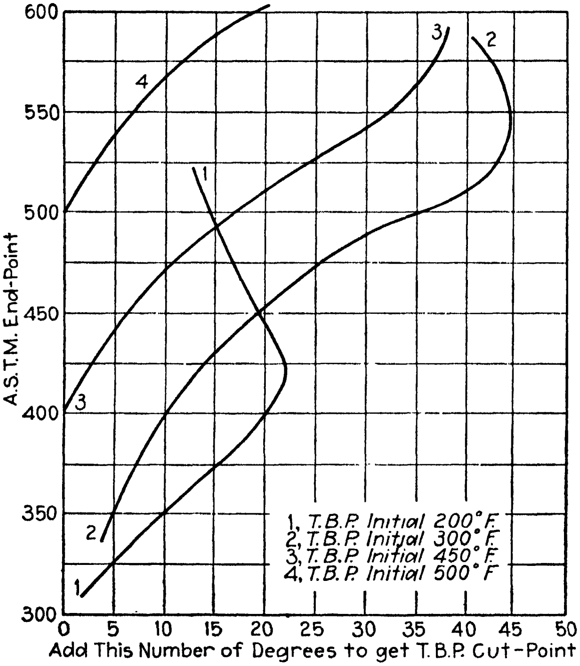

FIG. 28.—Correlation of A.S.T.M. end-point and true-boiling-point cut-point.

different initial boiling-points. This relationship should be determined for each distillation equipment because it may vary depending upon the design and method of operation.

Example 6. A.S.T.M. End-point and T.B.P. Cut-point.—It is desired to determine the cut-point on a true-boiling-point analysis curve that will give a product having an A.S.T.M. end-point of 437°F. At an end-point of 437 (curve 1, Fig. 28) the true-boiling-point cut-point is 21° higher than the A.S.T.M. end-point. The cut-point is 437 plus 21 or 458°F. The following tabulation indicates approximate end-points as well as cut-points for other distillates:

Material	Initial boiling-point	End-point	Correction	True-boiling cut-point	Curve
Gasoline	Less than 200	437	21	458	1
Gasoline	Less than 200	390	18	408	1
Naphtha	300	460	21	481	2
Kerosene	450	530	26	556	3
Distillate	500	590	16	606	4

Evaluation of Stocks.—The property curves that have been discussed heretofore are of general usefulness. In the following pages the necessary laboratory procedure, the construction of the curves, and the evaluations of several stocks will be discussed.

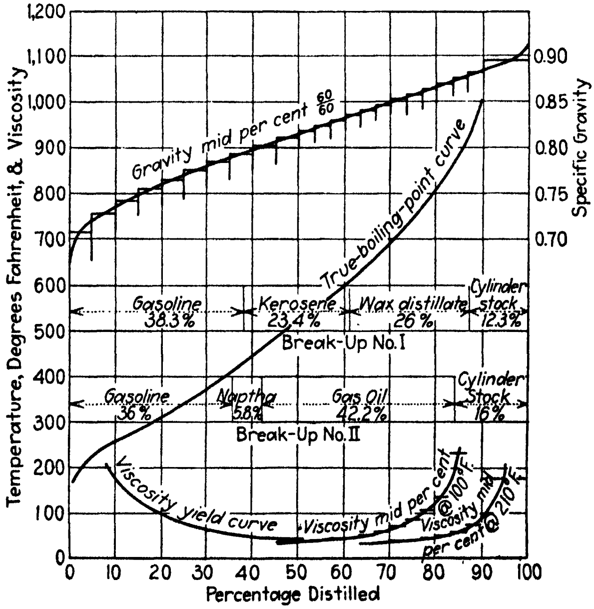

FIG. 29.—Evaluation curves from Table 7.

The evaluation of a *paraffin-base crude oil* is particularly simple because the oil contains no asphalt. Only a true-boiling-point distillation, conducted at first at atmospheric pressure and later at a low pressure, is necessary. Of course, the fractions from the distillation must be examined by routine tests. Table 7 is a log sheet of the data obtained in the analysis of a typical

TABLE 7.—TRUE-BOILING-POINT ANALYSIS

Sample____________________ Job No.____________________
From____________________ Sample No.____________________
Quantity of Charge—3000cc @ 60°F. A. P. I.–43

Time	Vapor temperature at 760 mm., °F.	Cumulative per cent	Fraction No.	Per cent in fraction	Sp. gr. 60/60	Viscosity		Notes
						100	210	
1. 9:06 A.M.	170	1	..	....	.....	...	....	Atmos.
2. 9:15	210	3.33						
3. 9:22	227	5	1	5	0.706			
4. 9:30	238	6.67						
5. 9:38	248	8.33						
6. 9:46	256	10	2	5	0.728			
7. 9:53	262	11.67						
8. 10:00	270	13.33						
9. 10:07	279	15	3	5	0.739			
10. 10:13	288	16.67						
11. 10:19	297	18.33						
12. 10:26	306	20	4	5	0.751			
13. 10:33	315	21.67						
14. 10:39	327	23.33						
15. 10:45	338	25	5	5	0.763			
16. 10:51	348	26.67						
17. 10:57	359	28.33						
18. 11:03	370	30	6	5	0.775			
19. 11:09	380	31.67						
20. 11:15	393	33.33						
21. 11:21	405	35	7	5	0.784			
22. 11:28	416	36.67						
23. 11:36	430	38.33						
24. 11:43	444	40	8	5	0.793	...	....	Rate slow
25. 11:51	455	41.67		....	.....	...	....	Rate slow
26. 12:01 P.M.	465	43.33						
27. 12:10	485	45	9	5	0.801			
28. 12:17	496	46.67						
29. 12:24	510	48.83						
30. 12:30	523	50	10	5	0.809	35		
31. 2:01	536	51.67						
32. 2:11	550	53.33	11	3.33	0.815	...	....	10 mm. pressure
33. 2:19	562	55						
34. 2:26	575	56.67	12	3.33	0.820			
35. 2:32	590	58.33						
36. 2:38	604	60	13	3.33	0.825	42		
37. 2:44	619	61.67						
38. 2:50	633	63.33	14	3.33	0.829			
39. 2:56	649	65						
40. 3:02	664	66.67	15	3.33	0.835	50	33	
41. 3:08	682	68.33						
42. 3:14	698	70	16	3.33	0.840	59		
43. 3:21	714	71.67						
44. 3:28	732	73.33	17	3.33	0.846	72	36.5	
45. 3:37	750	75						
46. 3:44	768	76.67	18	3.33	0.851	87		
47. 3:51	784	78.33						
48. 3:57	812	80	19	3.33	0.857	107	42	
49. 4:03	836	81.67						
50. 4:07	870	83.33	20	3.33	0.865	132	46	1 mm. pressure
51. 4:12	903	85	..	....	.....	...	....	Fast rate
52. 4:20	925	86.67	21	3.33	0.875	230	54	
53. 4:29	970	88.33						
54. 4:39	1025	90	22	3.33	0.884	...	70	Rate slow
Blend Data								
55.			23	10	0.900	...	178	Residue
56. 36cc., No. 23; 12cc., each No. 22, 21, and 20			24	20	.....	...	100	Blend
57. (21cc., No. 23; 7cc., each No. 22–17, incl.)			25	30	.....	...	62	Blend
58. (15cc., No. 23; 5cc., each No. 22–11, incl.)			26	50	.....	...	42	Blend

paraffin-base crude oil. Figure 29 is a graphical presentation of the data tabulated in Table 7. The vapor-temperature or true-boiling-point curve was plotted directly from the data. The gravity curve was drawn by plotting the specific gravity of each fraction as a horizontal line throughout the limits of the fraction, and then drawing the curve by balancing the triangular areas against one another. The highest gravity, extending through 90 to 100 per cent, is the gravity of the residue. The viscosity mid per cent curves were drawn by plotting the viscosity of each of the fractions at the mid percentage points of the fractions. The highest viscosity on the 210°F. curve is the viscosity of the bottom. The viscosity yield curve was plotted directly from the blend data given in Table 7 with the final bottom from the distillation as the 10 per cent bottom product.

Example 7. Evaluation of Paraffin-base Crude Oil.—The following sets of yields of raw stocks can be computed from the property curves of Fig. 29:

Raw stocks	Per cent	Sp. gr.	A.P.I.	Notes
Break-up 1:				
(1) 409 E.P. gasoline..	38.3	0.753	56.4	430°F. cut-point
(2) 42 A.P.I. kerosene.	23.4	0.815	42	Mid-point 50 per cent
(3) 85 Visc. at 100 wax distillate*..........	26.0	0.859	33.2	Mid-point 74.7
(4) 150 Visc. at 210 cyl. stock..............	12.3	0.892	27.1	Visc. yield curve
Break-up 2:				
(1) 391 E.P. gasoline..	36.0	0.751	56.9	410°F. cut-point
(2) 450 E.P. naphtha.	5.8	0.795	46.3	458°F. cut-point
(3) Gas oil (by difference)..............	42.2	0.837	37.4	Mid-point 62.9 per cent
(4) 120 Visc. at 210 cyl. stock..........	16.0	0.89	27.5	Visc. yield curve

* Will not be a pressable stock unless some of the heavy material is removed.

In obtaining Break-up 1 the percentage of 409°F. end-point gasoline was obtained by referring to Fig. 28 which indicates that the true-boiling-point cut-point is 21°F. higher than the A.S.T.M. end-point. The 42 A.P.I. kerosene was evaluated by noting that the mid per cent point of 0.815 (or 42 A.P.I.) gravity occurs at 50 per cent on the distillation curve. Since the kerosene starts at 38.3 per cent, the end-point must be at 61.7 and the total yield is 23.4 per cent. The cylinder stock of 12.3 per cent was obtained directly from the viscosity yield curve. Twenty-six per cent of material remains, and this material is the wax distillate. The gravities of the gasoline and cylinder stock were obtained by integral-averaging but the other gravities were obtained by noting the gravity at the mid percentage points of the cut or at 50 per cent and at 74.7 per cent respectively. The mid per cent viscosity at 74.7 per cent is 85 sec. at 100°F.

Evaluation of Dark-colored Stocks for Lubricants.—The evaluation of stocks that contain asphalt demands a more elaborate laboratory procedure. Such a stock must be subjected to preliminary distillations. The stock is first reduced by a steam distillation at atmospheric pressure to approximately 26 A.P.I. (Fig. 30). The removal of gasoline and kerosene is necessary because these materials cannot be condensed in the subsequent vacuum-flash distillation which is necessary for the removal of tar. The reduced crude is then flashed under vacuum, distilling a clear lubricating oil stock and leaving solid tar. The lubricating oil stock can then be evaluated in the true-boiling-point apparatus. A true-boiling-point analysis of the crude oil is also necessary if the light stocks are to be evaluated.

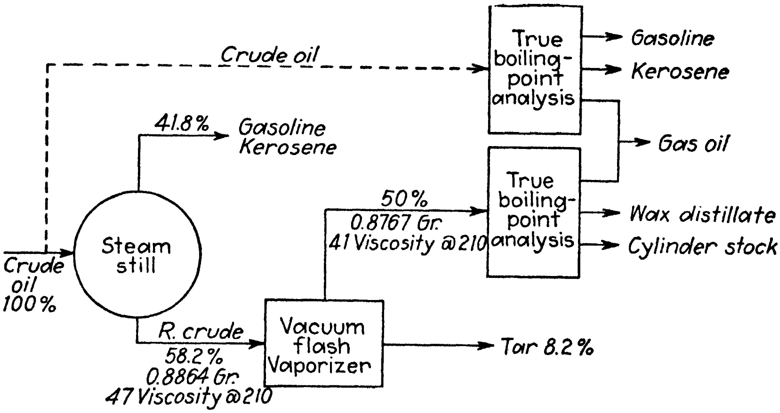

FIG. 30.—Laboratory processing scheme for evaluating heavy lubricating oil stocks.

The curves for such a laboratory procedure are given in Figs. 31 and 32. The viscosity yield curve is plotted separately (Fig. 32) because it was obtained for the heart-cut lubricating oil stock which does not contain the 8.2 per cent of tar. This viscosity yield curve (Fig. 32) is not general in usefulness because the plant must operate making exactly 8.2 per cent of tar bottoms or the yields will be inaccurate.

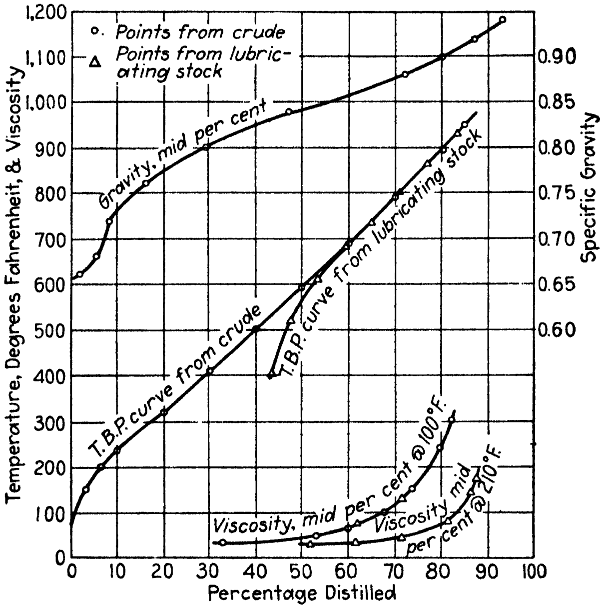

Fig. 31.—Curves for evaluating a dark-colored stock for lubricants.

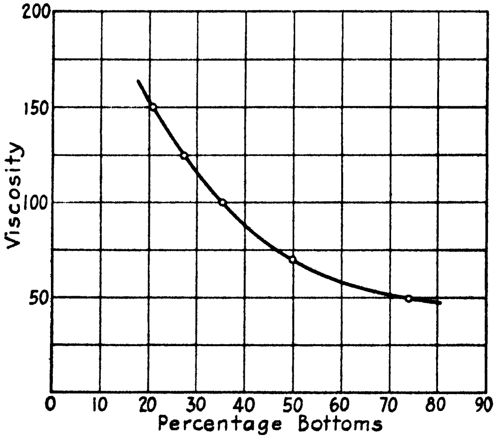

Fig. 32.—Viscosity yield curve for a heart-cut lube stock.

Dependability of Evaluation.—As an indication of the dependability of such laboratory data, consider some yields obtained from the crude oil shown in Figs. 31 and 32. Actual yields were 39.5 per cent of 69 viscosity at 100 wax distillate, 0.8654 gravity; and 10.5 per cent of 146 viscosity at 210 cylinder stock, 0.923 gravity. Computed from the curves, these yields are 40.2 per cent and 10.7 per cent respectively. Numerous other data are available and with few exceptions the yields by these evaluation methods are as dependable as the foregoing.

The preceding method of evaluation is conducted with a minimum of decomposition and hence the yields are the maximum that may be expected. If the designer expects to get such yields in a commercial plant, the plant must be properly designed and operated. Many poorly designed or carelessly operated plants fail to give the maximum yields but other plants produce even larger yields than indicated by the evaluation.[7]

Many refiners are obtaining much smaller yields than those found in the examples above. Nevertheless, these are typical yields if the plant processing is conducted properly.[8] The destruction of lubricants by shellstill distillation is a common occurrence.

Evaluation of Other Stocks.—Most clean stocks can be evaluated by the same procedure as that outlined for paraffin-base crude oil. Stocks that can be evaluated in this manner are

1. Light-colored crude oils.
2. Pressed distillate.
3. Wax distillate.
4. Brightstock.
5. Light-colored cylinder stocks.
6. Heart-cut lubricating oil stocks.
7. Distillates from cracking, etc.
8. Reduced crude oil for asphalt.

The viscosity curves are of little interest unless lubricating oils are to be manufactured.

In evaluating stocks for the asphalt contained in them, the same general procedure can be used but other curves are of inter-

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[7] The author has seen a modern vacuum plant produce 18 per cent of 200 viscosity at 210°F. brightstock, while only 10 per cent was previously manufactured by residual methods. This yield was 0.5 per cent more than indicated by the analysis.

[8] A Pennsylvania refiner was producing 22 per cent of a 220 viscosity at 100 viscous neutral oil from a pressed distillate by shellstill operation. The same stock yielded 45.5 per cent of the same neutral oil when processed in a steam atmospheric pipestill unit. The increase in yield came largely from the two other stocks that were being produced, so that doubtless a serious amount of decomposition had been occurring in the shellstill.

est. The most useful curves are the (1) specific-gravity mid per cent curve, (2) penetration yield curve, and (3) float-test yield curve. The final residue and the last fractions are blended, in determining the two yield curves.

In order to leave a solid residue, a very high vapor-temperature (about 1200°F., converted to atmospheric pressure) may be necessary. This precludes the use of the true-boiling-point type of distillation because of the big difference between the still- and vapor-temperature. A Hempel type of distillation is generally used but even with this type of distillation the liquid temperature usually reaches about 750°F. and some decomposition occurs. If the material is not held at the high temperature for too long a time, little harm results.

Treating and Dewaxing.—These operations are always troublesome. Most refinery laboratories have conducted hundreds of laboratory treats but with few exceptions they do not check with plant operations. The treating of light distillates, such as pressure-still distillate and kerosene, is most successful, but even in these the color seldom checks with the color of the plant product and the losses in the laboratory are large. In the acid treating of lubricating oil stocks the results are even less satisfactory. However, by conducting a large number of treats over a period of years, it is possible to say whether a stock can be successfully treated in the plant, even though the laboratory and plant results do not check. Difficulty arises because the treating operation cannot be controlled and because the sludge cannot be properly separated. Usually the engineer can obtain satisfactory evaluations of the yields of raw stocks but he must depend, to a large extent, upon plant operations for the losses during processing and for the color and properties of the finished products.

Light oils, such as gasoline and pressure distillate, are usually treated in the laboratory by placing the sample in a bottle or jug and agitating it with sulfuric acid for 10 to 20 min. The sludge is allowed to settle for several hours and is separated by decantation or by means of a separatory funnel. The settling time is sometimes shortened by centrifuging the "sour" oil for 2 or 3 min. at a speed of 1,500 revolutions per minute. The oil is then neutralized with caustic soda and washed with water. Treated pressure distillate must be distilled with steam or in a vacuum. The temperature is not allowed to exceed about 225°F. during the distillation. If many treats are conducted, special glass or iron stills may be built. These are usually of the batch type. An equipment for redistillation is discussed by Dailey, Meier, and Shaffer,[9] and a comparison of laboratory and plant results is given. A continuous-treating apparatus for light distillates is described by Zublin.[10]

The laboratory treatment of lubricating oil stocks cannot be so easily systematized. However, Weir, Houghton, and Majewski[11] have developed a standard method of treating lubricating oil stocks. The oil is measured directly into a 100-cc. centrifuge tube and acid is added from a small graduated pipette. The tube is stoppered and shaken either by hand or in a mechanical shaking device. The shaker can be placed in a heated cabinet if the treating is to be conducted at a high temperature. The time for shaking ranges from 10 min. for diluted samples to 40 or 60 min. for viscous oils. Next the sludge and "pepper" sludge are removed by centrifuging the tube for about one hour at 1,500 r.p.m. The sour oil is then neutralized with ammonia gas, caustic soda, or contact clay.

Most laboratories finish their lubricating oils by contact treatment with fuller's earth. Contacting is usually conducted on oils that have been treated with acid or "acid-stage" oils. About 10 per cent by weight, or less, of 200-mesh fuller's earth is mixed with the oil and heated to 450°F. for about 10 min. For neutral oils a temperature of 300° may be used. The mixture is agitated with steam or by a shaking device, and better color is obtained if the surface of the oil is protected from the air by a blanket of steam or inert gas. The clay is then filtered from the oil, while hot, by means of a Büchner funnel connected to a vacuum system.

Lubricating oil stocks are frequently diluted to allow more intimate mixing, to facilitate settling of the sludge, and to hasten filtration of the contacted oil. The material, usually naphtha,

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[9] Correlate Plant and Laboratory Procedures for Distilling Acid Treated Cracked Naphtha, *Oil Gas J.*, May 3, 1934, p. 11.

[10] Continuous Treating of Oils in the Laboratory, *Oil Gas J.*, November, 1932.

[11] Control of Color of Petroleum Oils by Acid Treating, *Ref. Nat. Gaso. Mfr.*, December, 1930, p. 89.

that is used as a diluent, must be removed by distillation. Steam or a vacuum may be used, and the temperature should be kept as low as possible.

In the study and treatment of oil stocks it is convenient to use a color scale that is directly proportional to the depth of color. The Atlantic Refining Company has developed such a color scale.[11] For stocks that are not diluted the relation between the true color scale and the N.P.A. scale is

$$\text{N.P.A. color} = 1.08C^{0.384}$$

in which C denotes the true or Optical Density color.

The usefulness of such a scale is at once apparent. It may be used to compare crude oils or black cylinder stocks for the degree of blackness. It thus indicates the power of these materials to spoil the color of distillates by entrainment. It also provides a means of comparing the actual decolorization during treatment. Thus, a 20 true color is twice as dark as a 10 true color. Finally, it allows the color scale to be rationally extended into the color range that is too dark for the ordinary scales, by diluting with a colorless material.

The dewaxing of oil in the laboratory is also a troublesome operation. A common method is to dilute the oil (about 3 to 1) and chill it in packed ice and salt to about 30° below the desired pour-point. About 1 oz. of filter-aid per 100 cc. of oil is added, and the mixture is filtered through a Büchner funnel provided with an ice-packed jacket and a cover. A vacuum is applied to the filter. A convenient method of chilling the oil is to use an ice cream freezer. Filter leaves are also widely used. These are constructed of very fine-mesh monel-metal screen and connected to a receiver and vacuum pump. Laboratory methods of dewaxing are troublesome because filtration occurs so slowly, because a low temperature is hard to maintain, and because it is difficult to obtain a low pour-point.

Davis and Campbell[12] have developed a systematic method of studying wax distillate in the laboratory to determine its pressing characteristics. The examination consists of a vacuum distillation at 40 mm. pressure, a determination of the viscosity at 100, and an examination of the crystal formation with a microscope.

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[12] Laboratory Control of the Quality of Paraffin Distillate, *Oil Gas J.*, May 25, 1933, p. 49.

Their data indicate that material boiling up to about 650°F. at 40 mm. pressure can be successfully incorporated in a wax stock. This corresponds to a temperature of about 885°F. at 760 mm. pressure. They made a complete study of a wax distillate by analyzing it in a true-boiling-point column and examining the wax fractions and blends of them.

Evaluation of Cracking-stocks.—No truly satisfactory method of estimating the yield of cracked gasoline that can be produced from a stock has been developed. Pressure-bombs have been widely used in the past but the yields by such tests bear little relation to the yields that are obtained in commercial operation. In commercial operation the stock is partially cracked, and the recycle stock from it is cracked over and over again until all of the material is decomposed into gas, tar, and cracked gasoline. This cycle cannot be easily duplicated in the laboratory except by the use of a replica plant or semi-plant scale equipment. Gary and Ward[13] describe such an equipment. However, the cost of a replica plant is so great that its usefulness is generally limited to research work and the design of new cracking plants.

For mild cracking operations, such as viscosity-breaking tests or cracking for lowering the pour-point of fuel oils, the bomb equipments are satisfactory. The common procedure is to heat the oil in a pressure-bomb to 820 to 860°F. for 10 to 30 min. The pressure rises as the oil is heated, and when the pressure reaches 200 lb. per square inch a relief valve is opened a little so that the gas and some distillate can escape through a condenser. After cracking is complete, the distillate is redistilled and the material that is not in the boiling-range of gasoline is mixed with the cracked stock that remains in the bomb.

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CHAPTER VIII

PHYSICAL PROPERTIES OF PETROLEUM OIL

The discussion in Chap. IV indicated that petroleum and petroleum products are complex materials. At present the chemical and physical laws that govern the behavior of mixtures of hydrocarbons are not adequate for most calculations and hence the engineer must base many of his computations on the average physical properties of petroleum oil cuts. It has often been necessary to resort to empirical equations of these properties for ease in correlation and to permit extrapolation to conditions for which data are lacking.

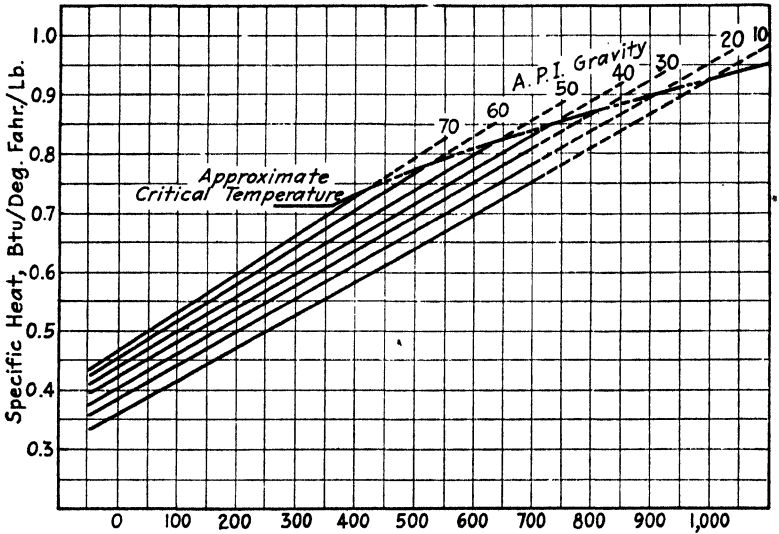

FIG. 33.—Specific heat of Mid-Continent oils (liquid).

Specific Heat.—The specific heat of a material is defined as the quantity of heat required to raise the temperature of a unit weight of material through a temperature difference of 1°. Universally the oil industry uses the English system in which the specific heat is defined as the number of British thermal units (B.t.u.) required to raise the temperature of 1 lb. of oil 1°F. and is expressed as B.t.u. per pound per degree Fahrenheit.

The specific heat increases with temperature but usually not as a linear function of temperature. However, the specific heat of petroleum oils, by the information now available, is a linear function. The specific heat also depends upon the gravity of the oil so that it is a function of both temperature and gravity.

Figure 33 is a chart of the specific heats of Mid-Continent petroleum oils. The data of Fortsch and Whitman[1] and of Weir and Eaton[2] were used. The two sets of data do not agree exactly but an average was used in constructing Fig. 33. The curves for 70 and 10 A.P.I. material are not so exact as the other curves because not many oils of these gravities were studied. The critical line indicated in Fig. 33 is not exact because the critical temperature is governed more by the boiling-range than by the gravity. Nevertheless, it is included in the figure as a warning that liquids cannot exist above the critical point.

Example 8. Heat Required to Raise the Temperature of Oil.—How much heat is required to raise the temperature of 1,000 lb. of a 40 A.P.I. oil from 100 to 600°F.?

$$\begin{aligned}\text{Specific heat at } 100 &= 0.48\\ \text{Specific heat at } 600 &= 0.775\\ &\overline{\;1.255}\end{aligned}$$

$$\text{Average specific heat from 100 to 600} = \frac{1.255}{2} = 0.627$$

$$\text{Also note the specific heat at 350} = 0.627$$

$$1{,}000\,(600 - 100)\,0.627 = 313{,}500 \text{ B.t.u.}$$

The data of Bahlke and Kay[3] for petroleum vapors from Mid-Continent oils are presented in Fig. 34. Data on vapors are not extensive but specific heats can be obtained from Weir and Eaton's[2] data. From their data the specific heats are slightly higher than those shown in Fig. 34 but they check remarkably well. The specific heats of gases are taken from the work of Watson and Nelson.[4]

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[1] Specific Heats of Oils, *Ind. Eng. Chem.*, **18**, 795 (1926).

[2] Heat Content of Petroleum Oil Fractions at Elevated Temperatures, *Ind. Eng. Chem.*, **24**, 210 (1932).

[3] *Ind. Eng. Chem.*, **21**, 942 (1929).

[4] . . . Approximating Critical and Thermal Properties of Petroleum Fractions, *Ind. Eng. Chem.*, **25**, 880 (1933).

Watson and Nelson[4] have devised a factor, the characterization factor, which has been of assistance in correlating the thermal properties of different bases of oil. This factor is defined as the cube root of the absolute temperature in degrees Fahrenheit divided by the specific gravity at 60°F. For typical stocks the factor has about the following values:

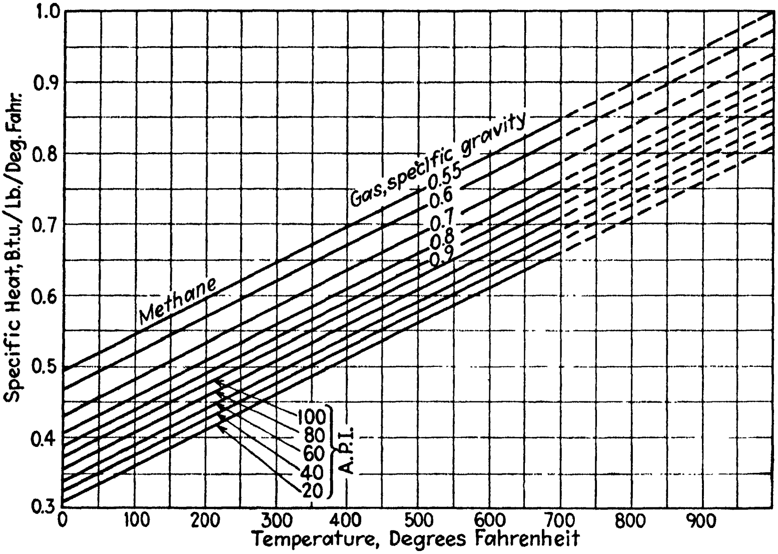

FIG. 34.—Specific heat of Mid-Continent oil vapors.

Stocks	Characterization Factor
Paraffin hydrocarbons	12.7
Paraffin-base oils	12.5
Mixed-base oils	11.8
Cracked material	10.5
Asphalt-base oils	10.2
Benzene	9.8

These authors[4] find that the specific heat of other oils than Mid-Continent oils can be found by means of the following equation:

$$\text{Specific heat} = \text{sp. ht. for Mid-Continent oil } (0.055k + 0.35)$$

The symbol k refers to the characterization factor. This correction indicates that typical naphthenic stocks will have liquid specific heats about 9 per cent lower than those given in Fig. 33 and paraffinic stocks about 4 per cent higher.

A similar equation is suggested for the specific heats of vapors:

$$\text{Specific heat} = \text{sp. ht. for Mid-Continent vapor } (0.12k - 0.41)$$

Thus the specific heats for paraffinic vapors should be about 9 per cent higher than those shown in Fig. 34 and for naphthenic vapors about 19 per cent lower.

Latent Heat.—The heat of vaporization, commonly referred to as the latent heat, is usually defined as the B.t.u. required to vaporize 1 lb. of a liquid at its atmospheric boiling-point. If vaporization takes place at another pressure (or temperature), the latent heat should be specified as such. The latent heat varies with the temperature (or pressure) at which vaporization occurs and with the gravity of the oil.

Cragoe[5] has made a study of the experimental determinations of the latent heat of oil. Laboratory measurements of latent heat are not easy to conduct and at the time of Cragoe's investigation only about 84 determinations of latent heat were to be found in the technical literature. The data were not consistent and all of the determinations were conducted at atmospheric pressure. The only extensive experimental data on the variation of the latent heat with temperature are the data of Young[6] for several of the normal paraffin hydrocarbons.

The data of Weir and Eaton[2] provide an accurate method of estimating latent heats. They determined the total heat for various Mid-Continent oils and vapors. The difference between the total heat of the vapor and the total heat of the liquid, at the same temperature, is the latent heat. An equation for latent heat obtained from their data is

$$\text{Latent heat} = 241 - 102d - t(0.396 - 0.361d) - t^2(0.000078d - 0.00002)$$

where t = temperature, °F.
d = sp. gr. at 60°F.

This equation gives latent heats as shown in Table 8.

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[5] Thermal Properties of Petroleum Products, *Bur. Standards Misc. Pub.* 97, 1929.

[6] *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

TABLE 8.—HEAT OF VAPORIZATION

Temp., °F.	Latent heat, B.t.u. per lb. for the following A.P.I. gravities				
	60	50	40	30	20
200	138.2	136.9			
300	123.3	123.3	123.4		
400	107.7	109.0	110.5	111.8	
500	.....	93.8	96.7	99.3	103
600	.....	.....	82.0	86.1	91.3
700	.....	.....	.....	73.8	78.5
800	.....	.....	.....	.....	64.7

Although Cragoe's latent heats[5] are considered as standard, the latent heats as given in Table 8 are worthy of attention. They were obtained from dependable data[2] and they are consistent with the specific-heat data as given in Figs. 33 and 34, whereas Cragoe's data are not entirely consistent with the specific-heat data.

The latent heat decreases with temperature until it has a value of zero at the critical temperature. Furthermore, the critical temperatures of high A.P.I. materials are lower than for low A.P.I. materials, and hence the latent-heat curves, when plotted as functions of gravity and temperature, should cross each other at some point. Table 8 indicates that they do cross.

Several methods have been proposed for computing the magnitude of the effect of pressure (or temperature) on the latent heat but most of these methods yield computed latent heats that are too high. However, a method based upon a corollary of the first law of thermodynamics gives values in fair agreement with Table 8 and is a sound method. When necessary, this method as outlined in Example 9 may be used and it will yield dependable results if accurate physical data are available. The first law of thermodynamics states that energy may be converted from one form to another without increasing or decreasing the total amount of energy. A corollary of this law states that a change within a system from one set of conditions to another set of conditions involves a constant difference in energy content, regardless of the path followed in performing the change.

Example 9. Computation of Latent Heat by First Law of Thermodynamics.—The latent heat of a narrow boiling-range product is 71.5 at 670°F. and 1 atm. pressure. Its molecular weight is 280 and its gravity is 30. Its boiling-point at 50 lb. per square inch gage pressure is 800°F. Assume no decomposition. What is the approximate latent heat at 800°F.?

In Fig. 35 points *A* and *C* represent the liquid at 670 and 800°F. respectively, and points *B* and *D* represent the vapor. The latent heat at 50 lb. or at 800°F. is represented by the total difference in the energy content of 1 lb. of the material at *A* and at *B*.

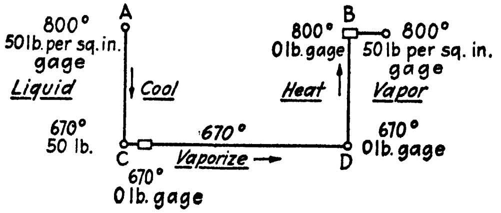

FIG. 35 —Cycle for computing the heat of vaporization at 800°F.

Basis: 1 lb.

The following series of steps is necessary:

(1) *A-C*. Cool liquid from 800 to 670°F. at 50 lb. pressure.

(2) *C*. Reduce pressure to atmospheric pressure (negligible).*

(3) *C-D*. Vaporize at 670°F. at atmospheric pressure.

(4) *D-B*. Heat vapor from 670 to 800°F. at atmospheric pressure.

(5) *B*. Isothermal compression to 50 lb. per square inch gage at 800°F.

Heat balance about the datum of 800°F.:

	B.T.U.
(1) $-1(800 - 670)\,0.83$ (liquid)	$= -108.0$
(2) Negligible.	
(3) 1×71.5	$= +\ 71.5$
(4) $1(800 - 670)\,0.685$ (vapor)	$= +\ 89.0$

$$\text{(5)}\qquad \text{Work of compression} = -W = -P_1V_1\ln\frac{V_2}{V_1} = P_2V_2\ln\frac{V_1}{V_2}$$

Volume of 1 lb.-mol of gas at 32°F. = 359 cu. ft.

$$V_2 = \text{volume at 14.7 lb.} = \frac{1}{280} \times 359\frac{800 + 460}{32 + 460} = 3.28 \text{ cu. ft.}$$

$$V_1 = \text{volume at 64.7 lb. abs.} = 3.28 \times \frac{14.7}{64.7} = 0.745$$

$$\ln\frac{V_2}{V_1} = \ln 4.4 = 1.48$$

$$-W = -64.7 \times 144 \times 0.745 \times 1.48 = -10{,}300 \text{ ft.-lb.}$$

$$\text{Work of compression in B.t.u.} = \frac{-10{,}300}{778} = -13.2$$

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* The modulus of elasticity for oils is high, and hence little expansion occurs.

Latent heat at 800°F. $= -108 + 71.5 + 89 - 13.2 = 39.3$

The critical-point of such a material is about 930°F.
Latent heat at 930°F. by the same method $= 8.5$

There is some question as to the validity of the equation for isothermal compression at conditions which approach the critical. Nevertheless, the method used in this example gives latent heats that are nearer to what theory requires than most other methods.

The average boiling-point of mixtures is defined with difficulty. An arithmetic average, from the distillation curve, does not completely describe the vaporization properties because the vapor-pressure is not directly proportional to temperature. A logical average boiling-point is the 100 per cent point on the flash-vaporization curve because the material cannot be completely vaporized at any lower temperature. For batch distillation the arithmetic average temperature should be used for computing the latent heat, but for continuous distillation, as in a pipestill, the 100 per cent point on the flash-vaporization curve should be used. The temperature at the 100 per cent point on the flash-vaporization curve is approximately the same as the temperature at the 70 per cent point of the material on the true-boiling-point curve. For some other purposes, such as estimating the molecular weight, gravity, or viscosity, the 50 per cent boiling-point should be used.

The heat of fusion of paraffin wax as reported by various experimenters, ranges from 63 to 78.5 B.t.u per pound, and perhaps the best data indicate 72.5.

Total Heat.—The quantity of heat required to heat and vaporize an oil can be most conveniently computed by the use of total heats. The heat required to raise the temperature of an oil from a given temperature datum to another temperature is called the heat of the liquid. If vaporization also occurs, the total quantity of heat that is required is called the heat of the vapor. Weir and Eaton[2] have determined heat equations for Mid-Continent oils:

$$H_L = 15d - 26 - (0.465d - 0.811)t + 0.000290t^2 \qquad (3)$$

$$H_v = 215 - 87d + (0.415 - 0.104d)t + (0.00031 - 0.000078d)t^2 \qquad (4)$$

where H_L = heat of the liquid above 32°F.
d = sp. gr. at 60°F.

t = temperature, °F.
H_v = heat of the vapor above 32°F.

When more data are available, tables of the total heats, etc., as found in tables for steam, will be useful. Watson and Nelson[4] suggest a means of computing the effect of pressure on the total heats of liquids and vapors.

Specific Volume.—The volume occupied by 1 lb. of vapor is called the specific volume. According to the laws governing the behavior of perfect gases, the volume varies inversely as the pressure (Boyle's law) and directly as the absolute temperature (Gay-Lussac's or Charles's law) or

$$\frac{PV}{T} = \frac{P'V'}{T'} = R \text{ (the gas-law constant)} \qquad (5)$$

where P and P' = lb. per sq. in. abs. (14.7 + gage pressure).
V and V' = volume, cu. ft.
T and T' = absolute temperature or (°F. + 460).
R = 10.7 when considering 1 lb.-mol of gas.

At standard conditions of 32°F. and a pressure of 1 atm. or 760 mm., the volume of 1 lb.-mol of a perfect gas is 359 cu. ft. At 60°F. and 760 mm. the volume is 379.4 cu. ft. (379 is commonly used).

The volume of 1 lb.-mol of a perfect gas, *viz.*, 359 cu. ft., is the factor which relates the volume of a gas to its weight. The foregoing laws are sufficiently exact for engineering calculations involving such gases as air, nitrogen, oxygen, flue gas, and natural gas, unless the pressure exceeds about 200 lb. per square inch. For high pressures and for the vapors handled in the refinery, the laws are not exact but they are used extensively.

Example 10. Volume of Flue Gas.—A flue gas consisting of N_2, O_2, CO_2, and water vapor has a molecular weight of 30. What is the volume of 100 lb. of this gas at 200°F. and a barometric pressure of 740 mm.?

$$\text{Volume at 200°F.} = \frac{100}{30} \times 379 \times \frac{760}{740} \times \frac{(460 + 200)}{(460 + 60)} = 1{,}648 \text{ cu. ft.}$$

What is the volume of 100 lb. at 1000°F. and 10 lb. per square inch gage?

$$\text{Volume at 1000°F.} = \frac{100}{30} \times 379 \times \frac{14.7(460 + 1{,}000)}{24.7\ (460 + 60)} = 2{,}110 \text{ cu. ft.}$$

also

$$\text{Volume} = \frac{100}{30} \times \frac{10.7 \times 1{,}460}{24.7} = 2{,}110$$

Pressure-volume-temperature Relations of Vapors.—Petroleum vapors do not follow the gas laws. In general, low-molecular-weight vapors such as natural gasoline and gasoline vapors may be handled as perfect gases up to gage pressures of 35 lb. per square inch without introducing great errors. For heavier vapors the laws are not exact but they are widely used because no other convenient laws are available. However, Dr. G. G. Brown[7] of the University of Michigan has studied the behavior of the normal paraffin hydrocarbons. His work is useful but an element of uncertainty exists because only a small amount of experimental data were available.

TABLE 9.—CRITICAL DATA FOR PARAFFIN HYDROCARBONS

Material	Critical temp.		Critical pressure, lb. per sq. in. Abs.	Critical volume		Reference
	°R	°K		Cu. ft. per mol	Cc. per g. mol	
Methane	344	191	673	1.59	99.3	Int. Crit. Tables
Ethane	550	305	709	2.19	136.0	Int. Crit. Tables
Propane	664	369	632	3.04*	190.0*	Int. Crit. Tables
Isobutane	733	407	544	4.00*	250.0*	Int. Crit. Tables
n-Butane	767	426	529	4.00*	250.0*	Int. Crit. Tables
Isopentane	830	461	484	4.85	303.0	Young—*Sci. Proc. Roy. Soc. Dublin*, **12**: 374 (1909–1910)
n-Pentane	847	470	485	4.97	310.0	Young—*Sci. Proc. Roy. Soc. Dublin*, **12**: 374 (1909–1910)
Di-isopropyl	901	501	452	5.72	357.0	Young—*Sci. Proc. Roy. Soc. Dublin*, **12**: 374 (1909–1910)
n-Hexane	914	508	435	5.88	367.0	Young—*Sci. Proc. Roy. Soc. Dublin*, **12**: 374 (1909–1910)
n-Heptane	972	540	396	6.85	428.0	Young—*Sci. Proc. Roy. Soc. Dublin*, **12**: 374 (1909–1910)
Diisobutyl	990	550	361	7.73	482.0	Young—*Sci. Proc. Roy. Soc. Dublin*, **12**: 374 (1909–1910)
n-Octane	1025	569	362	7.86	490.0	Young—*Sci. Proc. Roy. Soc. Dublin*, **12**: 374 (1909–1910)

* Interpolated values.

The theorem of corresponding states[7] affords a method of correlating the scattered data. This theorem postulates that all similar substances have corresponding volumes at corresponding temperatures and pressures, if the reference point of correspondence is the critical-point. Thus, instead of using pressure,

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[7] BROWN, SOUDERS, and SMITH, Pressure-volume-temperature Relations . . . , *Ind. Eng. Chem.*, **24**, 513 (1932).

volume, and temperature directly, the ratio of each of these to their value at the critical-point is used. These ratios are called reduced pressures, temperatures, or volumes.

$$V_R = \text{reduced volume} = \frac{\text{volume at a specified condition}}{\text{volume at critical-point}} = \frac{V}{V_c}$$

$$T_R = \text{reduced temperature} = \frac{\text{absolute temperature}}{\text{absolute critical temperature}} = \frac{T}{T_c}$$

$$P_R = \text{reduced pressure} = \frac{\text{absolute pressure}}{\text{absolute critical pressure}} = \frac{P}{P_c}$$

Table 9 gives critical values as published by Brown.[7]

The relation of reduced temperatures, pressures, and volumes is given in Fig. 36. The same relations may be handled more conveniently, for most computations, by means of the compressibility factor Z. Perfect gases behave as follows:

$$PV = nRT \text{ (Ideal)}$$

R = gas constant = 10.7 for the following units: 1 mol of gas, volume in cu. ft., pressure in lb. per sq. in. abs., and temperature °F. abs.

n = number of mols of gas.

Other gases deviate from the foregoing by the factor Z:

$$PV = ZnRT \qquad (6)$$

Values of Z may be obtained from Fig. 37.

Example 11. Pressure-volume-temperature Relations of Gases That Are Not Ideal.—*A*. One pound-mol of C_3H_8 (44 lb.) is held in a container having a capacity of 30.4 cu. ft. The temperature is 280°F. What is the pressure? (See Table 9.)

$$T_c = 664\text{°F. abs.}$$

$$P_c = 632 \text{ lb. per sq. in.}$$

$$V_c = 3.04 \text{ cu. ft.}$$

$$T_R = \frac{460 + 280}{664} = 1.115$$

$$V_R = \frac{30.4}{3.04} = 10$$

By Fig. 36 the reduced pressure = 0.372.

$$P_R = 0.372 = \frac{P}{632}$$

$$P = 235 \text{ lb. abs.}$$

As a check, the original volume can be computed from Fig. 37.

$$P_R = 0.372$$
$$Z = \text{approximately } 0.905$$
$$PV = ZnRT$$
$$V = \frac{0.905 \times 1 \times 10.7 \times 740}{235} = 30.5 \text{ cu. ft.}$$

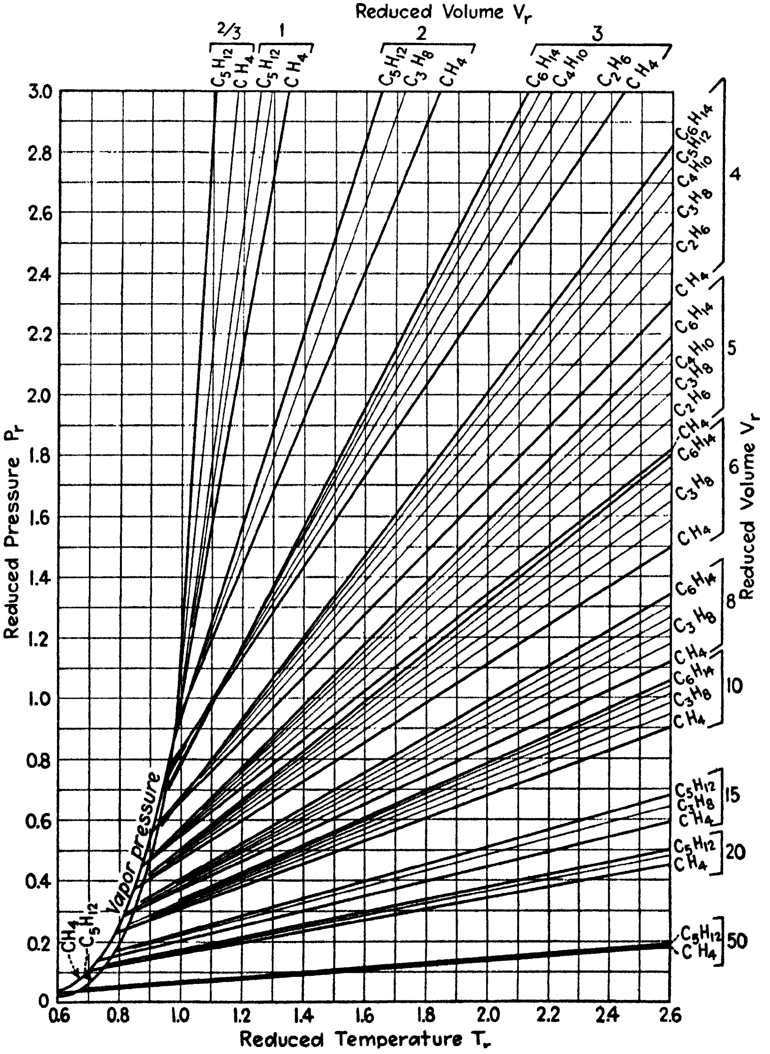

FIG. 36.—Relation of pressure, volume, and temperature for the normal paraffin hydrocarbons. (*Dr. G. G. Brown and Ind. Eng. Chem.*)

By the gas laws, the computed pressure would be

$$P = \frac{1 \times 10.7 \times 740}{30.4} = 260 \text{ lb. abs.}$$

B. One thousand cubic feet of methane is to be compressed from 60°F. and atmospheric pressure to 500 lb. per square inch gage and a temperature of 50°F. What volume will it occupy at these conditions?

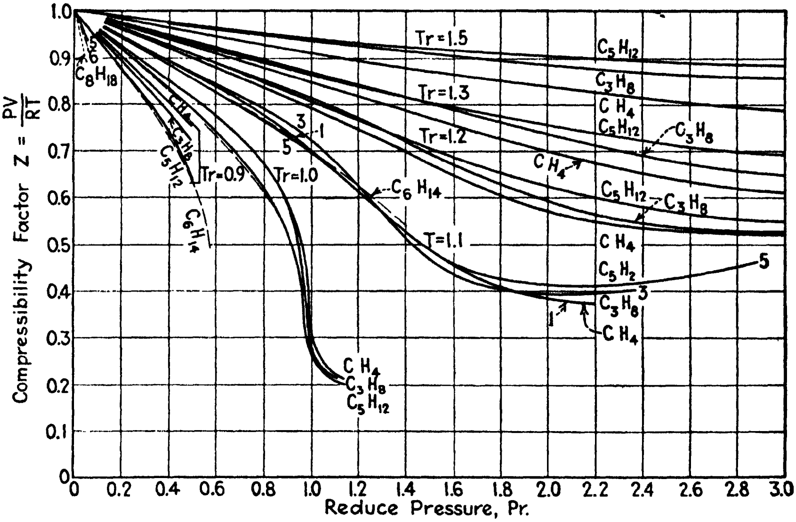

FIG. 37.—Compressibility factor as a function of reduced pressure. (*Dr. G. G. Brown and Ind. Eng. Chem.*)

$$\text{Mols } CH_4 = \frac{1{,}000}{379} = 2.64$$

At final conditions,

$$T_R = \frac{460 + 50}{344} = 1.48$$

$$P_R = \frac{500 + 14.7}{673} = 0.765$$

From Fig. 37

$$Z = 0.925$$

$$PV = ZnRT$$

$$V = \frac{0.925 \times 2.64 \times 10.7 \times 510}{514.7} = 25.9 \text{ cu. ft.}$$

By the gas laws the volume is 28.1 cu. ft.

Molecular Weight.—At present, experimental data regarding the molecular weight or apparent molecular weight of petroleum fractions are not extensive. Little order appears to exist even in considering the four variables molecular weight, specific gravity, boiling-point, and base of oil. Most success has been attained by plotting the molecular weight versus the average boiling-point; but if a sufficient amount of accurate data were available, doubtless the specific gravity would appear as an important factor.

The determination of the molecular weight of mixtures is a difficult laboratory operation and perhaps this accounts, at least in part, for the scattering of the results. Molecular weights are usually determined by the cyroscopic method which depends upon the lowering of the freezing-point of the solvent by the sample of oil. However, it has been found that a different apparent molecular weight is obtained for each concentration of solvent that is used, and hence a number of determinations must be made and the results extrapolated to obtain the molecular weight at zero concentration.

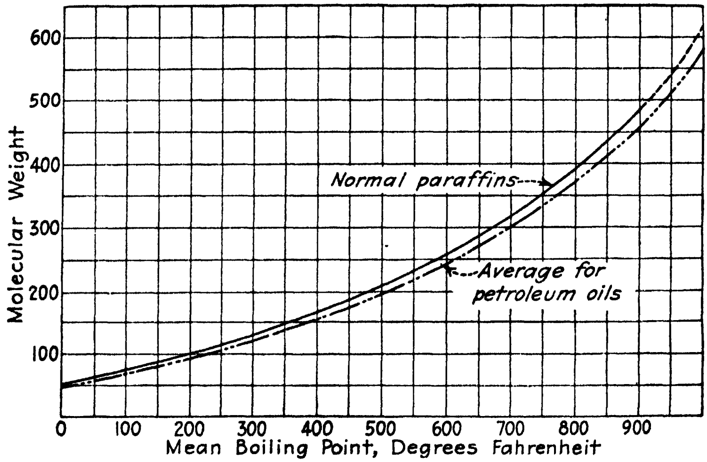

FIG. 38.—Average molecular weight of Mid-Continent oils.

For most design work the molecular weights of the normal paraffin hydrocarbons decreased by 5 per cent may be used[8] (Fig. 38). However, low-specific-gravity materials such as cracked distillates and certain naphthene-base products have a lower molecular weight than indicated in Fig. 38. The molecular weight for a given boiling-point is approximately inversely proportional to the specific gravity. As an example, an average straight-run oil which boils at 600°F. has a gravity of approxi-

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[8] FITZSIMONS and BAHLKE, Properties of Mid Continent Crude Oil, *Am. Petroleum Inst. Proc.*, 10th Ann. Meeting, **11** (1), Sec. III, 70 (1930).

mately 0.86. A recycle stock having a boiling-point of 600°F. may have a gravity of 0.922 (22 A.P.I.). The molecular weight of the straight-run stock is about 240, whereas the molecular weight of the recycle stock is

$$\text{Approximate mol. wt. of recycle} = \frac{0.86}{0.922} \times 240 = 224$$

Watson and Nelson[4] present a chart of molecular weights which indicates about the same influence of gravity.

In estimating the molecular weight, the mid per cent (50 per cent) boiling-point of the cut is used as the average boiling-point. When a fractional analysis of the material is available, the molecular weight may be computed by employing mol percentages as in Example 13.

Example 12. Estimation of the Molecular Weight of Oil.—See Fig. 29 (page 90). What is the molecular weight of the kerosene fraction in Break-up I?

The kerosene extends from 38.3 to 61.7 per cent. 50 per cent boiling-point is at $\frac{38.3 + 61.7}{2} = 50.0$ per cent on crude oil.

Temperature at 50.0 per cent = 522°F.
Mol. wt. at 522°F. (Fig. 38) = 203

Example 13. Determination of the Molecular Weight of a Gas Mixture.—A gas has the following composition (by volume):

Gas	Per Cent
Methane	75
Ethane	10
Propane	6
Isobutane	3
Butane	2
Isopentane	2
Pentane	1
Hexanes (and higher)	1
	100

What is its apparent molecular weight?
Basis: 1 mol of gas.

$$
\begin{array}{lrcl}
CH_4 \ldots\ldots\ldots\ldots & 0.75 \times 16.03 & = & 12.02 \\
C_2H_6 \ldots\ldots\ldots\ldots & 0.10 \times 30.05 & = & 3.00 \\
C_3H_8 \ldots\ldots\ldots\ldots & 0.06 \times 44.06 & = & 2.64 \\
C_4H_{10} \ldots (0.03 + 0.02) & \times 58.08 & = & 2.90 \\
C_5H_{12} \ldots (0.02 + 0.01) & \times 72.10 & = & 2.16 \\
C_6H_{14} + \ldots\ldots\ldots & 0.01 \times 90. & = & 0.9 \quad \text{(assumed mol. wt.)} \\
\hline
 & \text{Mol. wt.} & = & 23.62
\end{array}
$$

Critical Data.—When a compound is heated at atmospheric pressure, it eventually reaches its boiling-point and is completely vaporized at a constant temperature unless the pressure is increased. If the pressure is increased, the compound is completely condensed and cannot be vaporized again unless the temperature is also increased. This mechanism, alternately increasing the pressure and temperature, functions until at some high temperature and pressure it is found, regardless of the amount of pressure applied, that the material cannot be condensed. This point is called the critical-point and the temperature and pressure at the critical-point are called the critical temperature and pressure respectively. The liquid phase and vapor phase merge at the critical-point so that one phase cannot be distinguished from the other. No volume change occurs when a liquid is vaporized at the critical point and no heat is required for vaporization, but the coefficient of expansion has become large (Fig. 39).

The critical temperatures and pressures of some pure compounds are given in Table 9. Table 10 presents critical-temperature data for commercial mixtures.[9]

Eaton and Porter[10] present an equation by which the critical temperature may be computed from the A.S.T.M. distillation curve and the specific gravity.

$$t_c = 180 + 1.75a - 0.00088a^2 \qquad (7)$$

t_c = critical temperature, °F.

$a = (t_b + 100)s$

t_b = 50 per cent point on A.S.T.M.

s = sp. gr. at 60°F

The use of the 50 per cent boiling-point is not so satisfactory as the use of the molal average boiling-point[4] but for most design work it is sufficiently accurate. Furthermore, the distillation curve for high-boiling materials is seldom available through the entire boiling-range and hence the molal average boiling-point cannot be easily determined.

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[9] McKee and Parker, Critical Temperatures and Oil Cracking, *Ind. Eng. Chem.*, **20**, 1169 (1928).

[10] Critical Temperatures of Petroleum Oils, *Ind. Eng. Chem.*, **24**, 819 (1932).

Data concerning the critical pressures of petroleum mixtures are not extensive. As an approximation, the 30 per cent point on the distillation curve at atmospheric pressure may be corrected to the critical temperature of the material by means of Fig. 45.

TABLE 10.—CRITICAL DATA FOR PETROLEUM OIL

Oil	Origin	A.P.I.	Critical temperature, °F.
1. Petroleum ether	California	80.9	412
2. Gasoline	California	53.9	568
3. Gasoline	Bradford, Pa.	61.3	568
4. Gasoline	Burbank, Okla.	57.2	590
5. Gasoline	Pioneer, Tex.	56.3	585
6. Gasoline-1	New York City	54.5	574
7. Gasoline-2	New York City	59.5	568
8. Gasoline-3	New York City	60.5	576
9. Gasoline-4	New York City	58.0	585
10. Gasoline	Utah shale	47.4	676
11. Naphtha	California	48.2	656
12. Naphtha	Vinton, La.	50.3	612
13. Turpentine substitute	Vinton, La.	39.4	682
14. W. W. distillate	California	40.8	709
15. Kerosene	Burbank, Okla.	42.1	765
16. Kerosene	Bradford, Pa.	45.3	761
17. Kerosene	Pioneer, Tex.	42.9	765
18. Kerosene	Vinton, La.	33.5	752
19. Kerosene	Utah shale	34.0	811
20. "300" oil	Burbank, Okla.	37.0	847
21. "300" oil	Bradford, Pa.	40.5	855
22. "300" oil	Pioneer, Tex.	38.1	851
23. Gas oil	Bradford, Pa.	38.2	892
24. Gas oil	Vinton, La.	28.0	878
25. Gas oil	California	27.8	858
26. Gas oil	Utah shale	26.6	820
27. Transformer oil	Vinton, La.	24.0	865

Coefficient of Expansion.—The coefficients of expansion have been presented in government bulletins.[11] These bulletins present volume-correction tables for (1) straight-run products (10 to 95 A.P.I.), (2) volatile products (95 to 150 A.P.I.), (3) asphalt and fluxes (0 to 15 A.P.I.), (4) mixtures of gasoline and

[11] *Bur. Standards Misc. Pub.* 97; *Bur. Standards Circ.*, 154 and its supplement; *Bur. Standards Tech. Paper* 77.

benzol (0–50 per cent), and (5) cracked gasoline. The mean coefficients of expansion for different gravity materials are approximately as follows:

Gravity Range	Mean Coefficient of Expansion
79 and lighter	0.0008
78.9–65.0	0.0007
64.9–51.0	0.0006
50.9–35.0	0.0005
34.9–15.0	0.0004
14.9–0	0.00036

The coefficient of expansion may be defined as the fraction of unit volume that a unit of material will expand if it is heated through 1°.

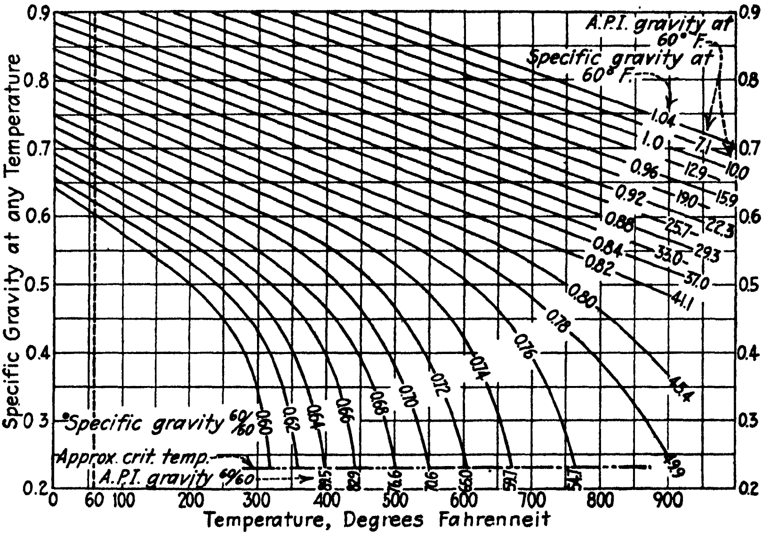

FIG. 39.—Change of specific gravity with temperature.

Example 14. Coefficient of Expansion and Fig. 39.—One barrel of a 19 A.P.I. oil is to be heated from 60 to 400°F. What volume will it occupy?

Coefficient of expansion = 0.0004 approximately
Increase in volume = 1(400 − 60).0004 = 0.136 bbl.
Total volume = 1.136 bbl.

Using Fig. 39,

Sp. gr. at 60°F. (19 A.P.I.) = 0.9402

Follow 0.94 line to 400°F.

Sp. gr. at 400°F. = 0.817

$$\text{Volume at }400°\text{F.} = 1 \times \frac{0.94}{0.817} = 1.15 \text{ bbl.}$$

The volume by Fig. 39 is probably the more accurate.

Density and Specific Gravity.—The density of petroleum products at elevated temperatures can be obtained from Fig. 39 (see Example 14). The figure relates the specific gravity at 60°F. with the specific gravity at other temperatures. The number accompanying each line indicates the gravity of the material at 60°F.

Density is defined as weight per unit of volume. In the petroleum industry, density is usually expressed as pounds per gallon. Since 1 gal. of water at 60°F. weighs 8.328 lb., the density is

$$\text{Density, lb. per gal.} = \text{sp. gr.} \times 8.328$$

The relation among A.P.I. gravity, specific gravity, and density are given in extensive tables in *Circular* 154 of the Bureau of Standards.[12] The density of gases can be computed by the mol volume relation discussed on page 109.

Example 15. Density and Specific Gravity.—What is the density of a 29.3 A.P.I. material at 60 and at 600°F.?

At 60°F.

$$\text{Sp. gr.} = 0.88;\ \text{density } 7.328$$

Refer to Fig. 39 and follow 0.88 line to 600°F.

$$\begin{aligned} \text{Sp. gr. at } 600°\text{F.} &= 0.678 \\ \text{Density at } 600°\text{F.} &= 0.678 \times 8.328 = 5.65 \text{ lb. per gal.} \end{aligned}$$

What is the density at 60°F., in pounds per cubic feet, of pure methane, and of a flue gas having a molecular weight of 30?

$$\begin{aligned} \text{Mol. wt. of } CH_4 &= 16 \\ \text{Density of } CH_4 &= {}^{16}/_{379} = 0.0422 \text{ lb. per cu. ft.} \\ \text{Density of flue gas} &= {}^{30}/_{379} = 0.0792 \text{ lb. per cu. ft.} \end{aligned}$$

Since 1 cu. ft. of water at 60°F. weighs 62.37 lb.,

$$\text{Sp. gr. of flue gas referred to water at } 60°\text{F.} = \frac{0.0792}{62.37} = 0.001271$$

Since mol. wt. of air = about 28.8,

$$\text{Sp. gr. of flue gas at } 60°\text{F. referred to air} = \frac{30}{28.8} = 1.04$$

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[12] National Petroleum Oil Tables, *Bur. Standards Circ.* 154, May 1924.

Viscosity of Blends.—Viscosity is not an additive property. When one volume of a 500 viscosity oil is mixed with one volume of a 100 viscosity oil of the same base, the resultant mixture has a viscosity of 209 rather than 300. When oils of a different base are mixed, the deviation is even greater. Figures 40, 41, and 42 were published by O. G. Wilson[13] and are perhaps the most convenient charts that have been published.

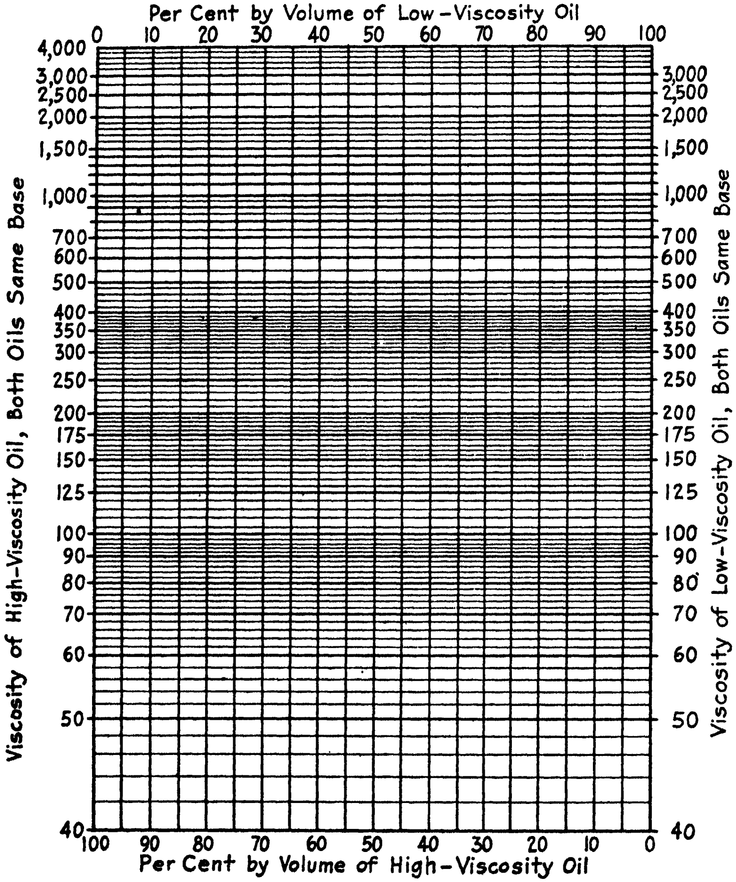

FIG. 40.—Viscosity blending chart for oils of the same base. (*O. G. Wilson, Nat. Petroleum News.*)

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[13] Chart Method of Predicting Viscosity, *National Petroleum News*, May 22, 1929, p. 87.

Figure 40 is for oils of the same base.
Figure 41 is for high-viscosity paraffin oils and lower viscosity naphthene oils.
Figure 42 is for high-viscosity naphthene oils and lower viscosity paraffin oils.

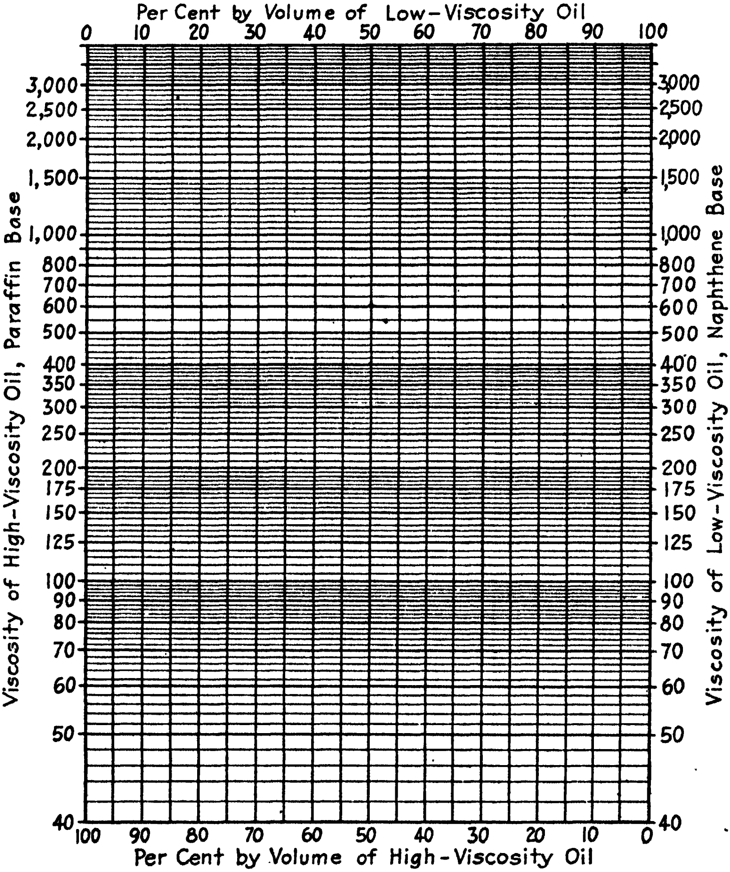

FIG. 41.—Viscosity blending chart. High-viscosity paraffin oil and low-viscosity naphthene oil. (*O. G. Wilson, Nat. Petroleum News.*)

The viscosity of the high-viscosity oil is used on the left axis of the charts and the lower viscosity oil on the right axis.

Example 16. Blending Lubricating Oils.—It is desired to produce an S.A.E. 30 (lowest viscosity 384) motor oil by blending 600 viscosity at 100 paraffin stock and 200 viscosity at 100 naphthene stock. In what proportions should they be mixed? (Refer to Fig. 41.)

A straight line is drawn across the chart from 600 on the left to 200 on the right. This line intersects the 384 viscosity line at about 40 per cent of low-viscosity oil. (Read at top.)

Change of Viscosity with Temperature and Pressure.—The engineer must frequently estimate the viscosity of an oil at another temperature than 100 or 210°F. This may be done by means of Fig. 49 (page 164), but it is usually more convenient to use the Herschel viscosity diagram (Fig. 43). In order to use this chart it is necessary to know the viscosity at one temperature and

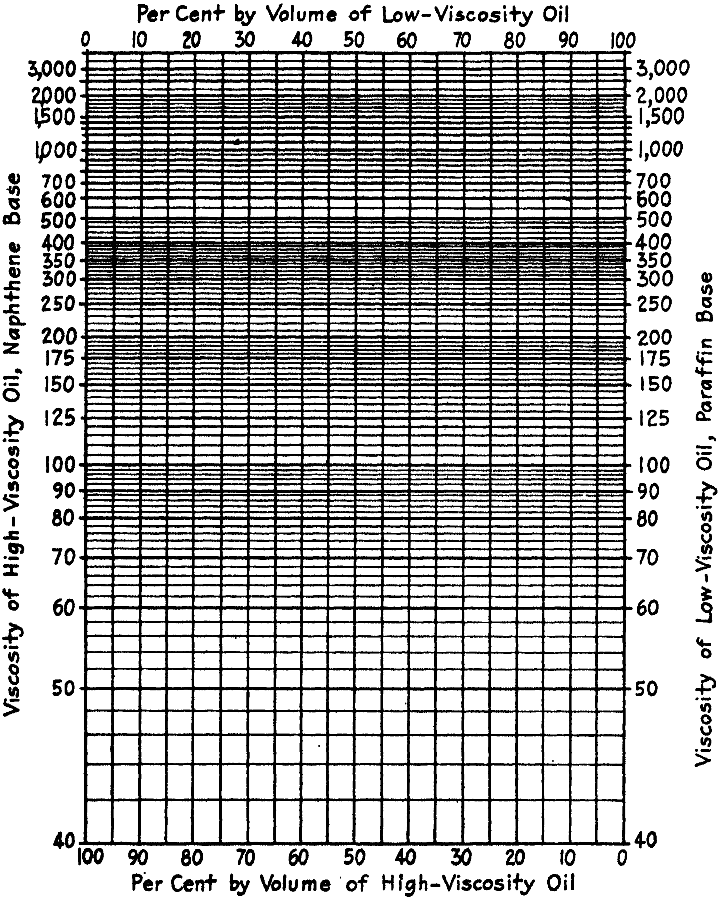

FIG. 42.—Viscosity blending chart. High-viscosity naphthene oil and low-viscosity paraffin oil. (*O. G. Wilson, Nat. Petroleum News.*)

the base of the oil. The kinematic viscosity and the viscosity in centipoises can be obtained by the use of Eq. (2), page 46.

Example 17. Viscosity at Different Temperatures.—A paraffin-base oil has a viscosity of 90 at 210°F. What is its viscosity at 160°F.?

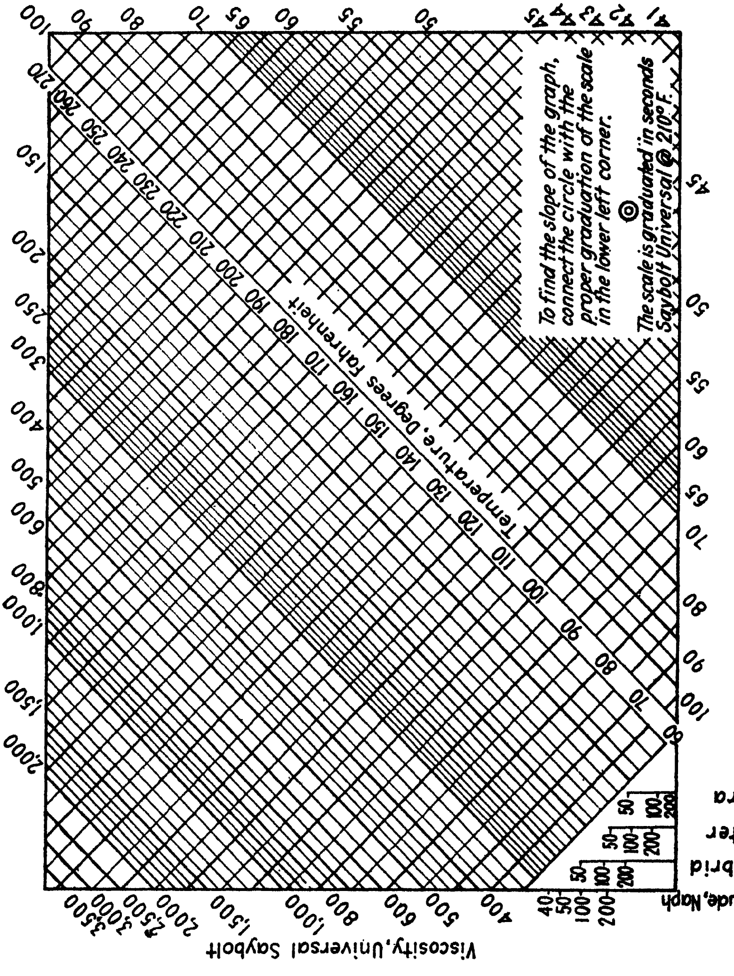

FIG. 43.—Herschel viscosity diagram. (*The American Instrument Company.*)

In using Fig. 43 a line must be drawn across the diagram. The slope of this line is determined by connecting the circle in the lower right corner with a point on one of the scales in the lower left corner. In this problem the 90 point on the Paraffin scale should be used.

A line is drawn through the point for 90 viscosity at 210°F., having a slope as indicated above. Follow this line until it crosses the 160°F. line. This point is located among the viscosity lines and is found to be 195 Saybolt seconds at 160°F.

If the specific gravity of the oil is 0.865 at 160°F., the viscosity in centipoises can be obtained by Eq. (2), page 46.

$$\frac{z}{s} = 0.22t - \frac{180}{t}$$

$$z = 0.865(0.22 \times 195 - {}^{180}\!/\!{}_{195}) = 36.3$$

The influence of pressure on viscosity is not great.[14] Except at very high pressures, such as those found in bearings, the effect of pressure may be neglected.

Recently it has become common to measure the rate at which viscosity changes with temperature by means of the viscosity-index. This relation is discussed on page 75 (see also Figs. 18 and 19, Chap. VII).

Vapor-pressures of Oil Fractions.—A study of mixtures requires a revision of our conception of vapor-pressure. Every material, by virtue of the movement of molecules within it, exerts a tendency to vaporize, even though it is far below its boiling-point. In the case of a single compound, the tendency to vaporize or to project molecules of itself into the surroundings becomes greater and greater as the temperature is raised, until it is equal to the pressure of the system, and the material is said to boil. At temperatures above the boiling-point the vapor-pressure is greater than atmospheric pressure and a convenient method of measuring such vapor-pressures is to apply enough pressure to suppress boiling.

A mixture tends to behave differently because it does not boil at one temperature. The vapor-pressure of a mixture is usually defined as the pressure exerted by the material when no vaporization occurs. If vaporization occurs, the composition of the material is no longer the same. The vapor-pressure of a mixture is a summation of the vapor-pressures of each of its components (Raoult's law, page 244) and hence the vapor-pressure should be a function of the slope of the distillation curve.

An excellent correlation of the vapor-pressures of gasoline is presented by Meyer,[15] and Bridgeman[16] presents the dew-points of gasolines as a function of the A.S.T.M. distillation curve.

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[14] "International Critical Tables," vol. II, p. 148, 1927.

[15] The Vapor Pressure Curves of Petroleum Spirits, *J. Inst. Petroleum Tech.*, **17**, 42 (1931).

[16] Dew Points of Air-gasoline Mixtures from Distillation Curves, *Ind. Eng. Chem*, **20**, 821 (1928).

Boiling-point Corrections.—The conversion of boiling-points from one pressure to another is of prime importance to the designer. A distillation conducted at a constant pressure is equivalent to changing the temperature and composition of the material simultaneously so that the vapor-pressure always equals the pressure at which the distillation is being conducted. If several distillations of the same material are conducted at different pressures and the same degree of fractionation is maintained throughout all of the distillations, we have a means of plotting vapor-pressure curves. If any percentage distilled is selected, the residue in the flask exerts a vapor-pressure that is equal to the pressure in the flask. Thus boiling-point corrections involve vapor-pressure and may be correlated by the same methods as those used in correlating vapor-pressures. However, the correlation of boiling-point corrections is involved because (1) the slope or distillation range of commercial products varies, (2) the manner of vapor formation may differ, and (3) the chemical composition of oils differs. Figure 44 presents a series of distillations of Mid-Continent kerosene. The circle points were computed by using the vapor-pressure chart for the paraffin hydrocarbons (Fig. 45).

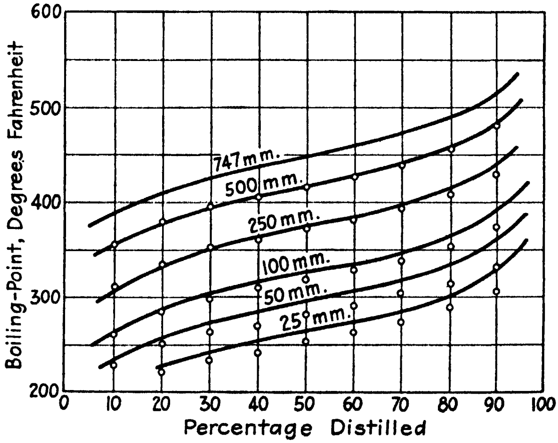

FIG. 44.—Vacuum distillations of kerosene.

Inherently the true-boiling-point curve should be most easily correlated because it consists of the boiling-points of nearly pure compounds as they distill one by one. The equilibrium-flash curve illustrates the other extreme type of distillation and corrections of this curve from one pressure to another should not be exactly the same as the correction for fractionating distillations. Nevertheless, a large difference does not seem to exist between these two extremes of boiling-point corrections, nor does the slope of the distillation curve seem to alter the vapor-pressure or boiling-point corrections to a great extent.

Piromoov and Beiswenger[17] find that the slopes of flash-vaporization curves are practically independent of pressure so that the correction of the boiling-point or flash-vaporization point is a constant number of degrees throughout the entire curve. They suggest that the correction should be determined by correcting the intersection point between the true-boiling-point curve and the flash-vaporization curve by the vapor-pressure data of the paraffin hydrocarbons. The intersection point is used because the true-boiling-point curve and the flash-vaporization curve intersect at approximately the same percentage point regardless of pressure.

A study of several distillations similar to Fig. 44,[18] as well as some scattered data on boiling-point corrections in the technical literature, has failed to reveal all of the factors that are involved

TABLE 11.—REDUCTION OF BOILING-POINT BY VACUUM, DEGREES FAHRENHEIT

Pressure, mm.	For oils which boil at the following atmospheric boiling-points:						
	300	400	500	600	700	800	900
760	0	0	0	0	0	0	0
500	25	29	32				
200	74	82	90	96	101	107	
100	106	117	130	137	143	153	161
50	137	151	167	179	186	196	208
20	...	190	215	227	238	254	270
10	...	...	252	267	280	298	316
5	...	...	...	305	323	342	364

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[17] Equilibrium Vaporization of Oils and the Carrying Effects of Light Ends, *A.P.I. Bull.* 10, No. 2, Sec. II, p. 52, 1929.

[18] Samples of Mid-Continent crude oil, gasoline, kerosene, gas oil, wax distillate, pressed distillate, lubricating oil, Gulf Coast crude oil, and cracked gas oil have been examined.

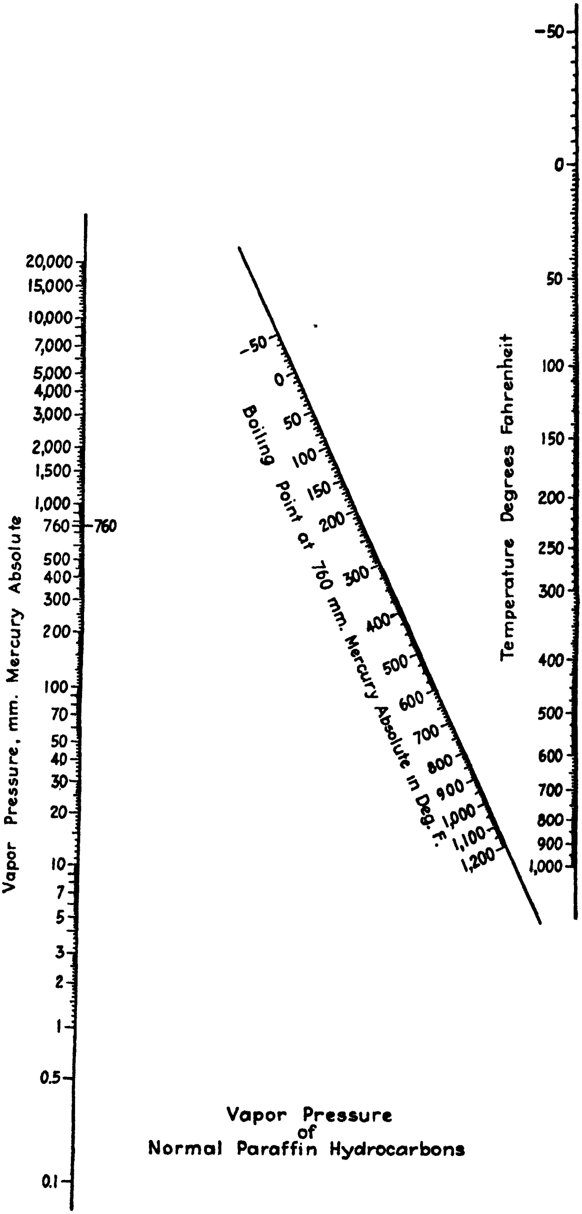

FIG. 45.—Vapor-pressure and boiling-point corrections for the normal paraffin hydrocarbons.

in correcting boiling-ranges from one pressure to another. However, Table 11 shows the approximate change in boiling-point that is caused by distillation at a reduced pressure, as obtained from distillations[18] such as the one shown in Fig. 44.

Obviously the correlation of vapor-pressures and boiling-point corrections for commercial mixtures is still in a formative stage. Apparently the vapor-pressures of the normal paraffin hydrocarbons are our most dependable data but they are not exact when applied to oils. However, if the laboratory data are converted from vacuum conditions to atmospheric pressure by means of Fig. 45 and the same chart is used during design calculations in determining boiling-points under vacuum, errors are eliminated to a large extent by the two operations. Figure 45 will be used throughout this book for boiling-point corrections.

Example 18. Correction of Boiling-point to Another Pressure.—An oil has a boiling point of 500°F. at atmospheric pressure. At what temperature will it boil if the pressure is 50 mm.? (Refer to Fig. 45.)

A line is drawn across the chart connecting 50 on the left scale with 500 on the center scale. The temperature may be noted on the right scale.

B.P. at 50 mm. = 329°F.

Discussion.—The rapid rate at which data regarding petroleum mixtures are being accumulated should always be borne in mind. Much of the data in this chapter will soon need to be revised. Much of the data are still in a poor state of correlation. Nevertheless, the use of the data such as they are is necessary, and judgment must be used accordingly. The oil industry should cooperate in determining the true properties of petroleum hydrocarbons and oil mixtures. Such a program would doubtless result in a new and astounding petroleum chemical industry.

There is hardly an end to the properties of petroleum oil that might be discussed in this chapter but many of them can be better presented as they are needed in definite problems.

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CHAPTER IX

REFINERY PRODUCTS

The underlying purpose of all refinery processing is the production of marketable products. Because of this fundamental purpose, a study of the uses and specifications of finished refinery products provides a broad understanding of the necessity for the various refining operations.

The large number of compounds constituting petroleum permits a single product to exhibit a wide range of physical properties. The boiling-range of crude petroleum ranges evenly from less than −100 to perhaps 1300°F., and the specific gravity from 0.6 for the lightest fractions to more than 1 for the highest boiling portion. During processing, the crude oil is separated into products, each product embracing a certain range of the foregoing physical properties. Obviously many different products can be made, depending upon the uses for the product and upon the limiting market specifications. Petroleum oil specifications usually allow a relatively wide range of physical properties. As an example, consider gasoline. Gasoline is not a distinct, uniform product. Depending upon the sales region and upon its use, gasoline may have an end-point between 320 and 437°F. and may vary in gravity between 50 and 70 A.P.I. Thus the amount of gasoline that may be produced from crude oil will vary widely not only because of differences in crude oils but also because many different gasolines may be produced. The same condition exists regarding many other refinery products.

In general, finished refinery products may be grouped as follows:

1. *Light oils*—gasoline, naphtha, solvents, and burning-oils.
2. *Distillates*—fuel oil, diesel fuel, tractor fuel, and gas oil.
3. *Lubricating oils*—motor oils, engine oils, machine oils, etc.
4. *Greases and waxes*—cup grease, salve bases, and paraffin wax.
5. *Residues*—fuel oil, coke, asphalt, carbon black, etc.
6. *Specialties*—medicinal products, insecticides, alcohols, etc.

Light Oils.—Gasoline is perhaps the most important petroleum product. The United States Government[1] specifies four gasolines. Two of these are used as motor fuels, *viz.*, United States Government Motor Fuel and Motor Fuel V; and two are for aviation purposes, *viz.*, Aviation Gasoline, fighting grade and domestic grade. Motor Fuel V is a special grade used by the government for ambulances, fire engines, emergency vehicles, etc. Some of the specifications of some standard and average fuels are tabulated in Table 12.

TABLE 12.—GASOLINE SPECIFICATIONS

Name and grade	Darkest color	Corrosion test	Maximum distillation range				E.P., °F.	Maximum sulfur, per cent	Vapor-pressure (Reid)	Octane No.
			5%	10%	50%	90%				
Government:										
1. Aviation, fighting	25	Required	122–149	....	203	257	329	0.1		
2. Aviation, domestic	25	Required	122–167	......	221	311	374	0.1		
3. U. S. Motor	..	Required	....	149–167	284	392	.....	0.1	12	
4. Fuel V	..	Required	....	158	257	356	.....	0.1	10	
W.P.R.A.*										
5. No. 1, low bracket	..	Required	....	167	284	392	.....	0.1	....	59 down
6. No. 2, middle bracket	..	Required	....	130–145	265	365	.....	0.1	....	60–66
7. No. 3, top bracket	..	Required	....	130–145	265	365	.....	0.1	....	67 up
Average motor fuels:										
8. 1928	..	....	....	....	265	380	424	0.08	....	56
9. 1930	..	....	....	....	260	370	420	.....	....	60
10. 1931 competitive	..	....	....	138	252	365	.....	0.072	9.1	62
11. 1931 premium	..	....	....	131	244	352	.....	0.072	8.5	77
12. 1934 summer†	..	....	132	148	247	351	397	.....	8.1	
13. 1934–1935 winter†	..	....	122	138	240	349	391	.....	9.2	
Aviation fuels:										
14. Wright Aero. Corp.‡	..	....	....	167–	202–	275–	.....	0.1	7.0	87
15. T.W.A.	..	....	....	167–	202–	311–	356–	0.1	7.0	80–87
16. British Air Ministry	..	....	....	167–	202–	302–	356–	0.15	7.0	77

* Western Petroleum Refiners Association, proposed April, 1933.

† Atlantic Coast.

‡ Wright Corp. also specifies 73 and 80 octane-number fuels.

The most significant properties of motor fuels may be summarized as follows:

1. Antiknock quality.

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[1] Gasoline, Motor, U.S. Government VV-G-101 and Motor Fuel V, VV-M-571, Superintendent of Documents.

2. Volatility.
3. Vapor-pressure.
4. Amount of sulfur and gum.

Other properties such as color, gravity, initial boiling-point, and end-point have been found to be of secondary importance. *Volatility* measures the ease with which a cold engine can be started and also the rate at which the engine will respond to the use of the throttle during acceleration. The curvature of the A.S.T.M. distillation curve is considered as the best indication of the volatility. The 10, 35, 65, and 90 per cent points are particularly significant.[2] The 10 per cent point must be low enough to allow sufficient vaporization to start the cold engine with a minimum number of revolutions of the motor and at the same time must not be so low as to promote vaporization in the gasoline feed system. The 35 and 65 per cent points are related to the performance of the car after the motor is started, and the 90 per cent point must not be too high or crank-case dilution and a loss of power will result. The *vapor-pressure* is a check on the possibility of vapor-lock in the feed system. The percentage of propane in the fuel is important in governing the tendency for vapor-lock. One per cent of propane increases the vapor-pressure of most fuels by about 2 lb. The vapor-pressure should be as low as possible, retaining at the same time a suitable volatility.

With the advent of high compression motors, the tendency of a fuel to *spark-knock* or *detonate* violently has attracted much attention. Knocking is characterized by a loss in power and a strain on the engine mechanism. Although little progress has been made in determining the exact nature of detonation or knocking, progress has been made in manufacturing antiknock fuels. Certain substances such as lead tetraethyl[3] and iron carbonyl[4] tend to prevent knocking. All hydrocarbons have different antiknock properties and certain of these, such as benzol[5] and those in cracked gasoline, are useful in suppressing

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[2] Brown, G. G., The Volatility of Motor Fuels, *Eng. Res. Bull.* 14, p. 7, University of Michigan, 1930.

[3] Midgley, Jr., Tetraethyl Lead Poison Hazard, *Ind. Eng. Chem.*, **17**, 827 (1925).

[4] "Motalin," a blending compound of the I. G. Farbenindustrie A.G.

[5] Campbell, Lovell, and Boyd, Standard Fuel for Anti-knock Quality, *Oil Gas J.*, Jan. 23, 1930, p. 42.

knocking. Standard ethyl gasoline has an octane-number of 76 (1934) and the Q grade of ethyl gasoline must have an octane number of at least 60 (1934). Cracked gasoline often contains *gumlike materials* that are deposited upon evaporation on the glasses of filling-station pumps and on the walls of the intake manifold and valves[6] of an engine. No universal specifications for gum content have been adopted but the gum content is always considered. Gasolines containing from 10 to 50 mg. of gum per 100 cc. by the accelerated porcelain-dish method are being marketed.

The amount of *sulfur* that can be safely allowed in gasoline has been a much discussed question. Quantities as high as 0.2 per cent usually will not cause serious corrosion difficulties. Nevertheless, owing to disastrous results with certain high-sulfur oils, the quantity of sulfur is usually limited to 0.1 per cent.

The *color* of gasoline indicates little about its quality although it is an indication of the thoroughness of the refining operation and of the tendency to produce gum. The highly desirable antiknock compounds are partly removed by treating, and hence the specification of color has become less and less important. Many refiners resort to the use of oil-soluble dyes to mask the color of the natural product. Dyes ranging in color from yellow to dark purple are available.[7] These dyes also serve (1) to identify a gasoline and thus promote confidence in its advertised quality, (2) to preserve the antiknock properties that would be partly lost during chemical treatment, and (3) to reduce the cost of refining.

The demand for volatile and antiknock fuels has promoted the development of the natural-gasoline industry and cracking processes. Our motor fuels consist of natural gasoline for volatility, cracked gasoline or antiknock substances for allaying the tendency to knock, and straight-run gasoline which usually constitutes the main bulk of the product.

The term *naphtha* is used to refer to any light oil product having properties intermediate between gasoline and kerosene. The various solvents, in general called *industrial naphthas*, are special

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[6] VOORHEES and EISINGER, The Importance and Significance of Gum in Gasoline, *Oil Gas J.*, Dec. 20, 1928, p. 152.

[7] EGLOFF *et al.*, Dye Saves Dollars in Treating Gasoline, *Oil Gas J.*, Mar. 5, 1931, p. 133.

products sold in small quantities and at special prices. In Table 13 are listed some common naphthas and their uses. In general, all industrial naphthas must meet the same special tests. Unsaturated and aromatic compounds are undesirable and are usually limited to 2 and 0 per cent respectively. The naphthas must be free from acidity, noncorrosive by the copper-strip test, free from gums or suspended matter, sweet smelling so that a petroleum odor is not imparted to the manufactured products, and well fractionated to eliminate as much of the fire hazard as possible. The color of Stoddard's or cleaners' naphtha is usually between 25 and 30, but rubber solvents and varnish makers' and painters' naphtha may have a color as low as 21.

Recently the art of distillation and fractionation has been developed to such a degree that pure compounds or nearly pure compounds can be prepared from petroleum. Among these compounds are propane, butane, pentane, hexane, heptane, and octane. Several of these have already been offered on the market, and doubtless during the next few years they will find a widespread use as commercial solvents. Commercial butane is

TABLE 13.—PETROLEUM SOLVENTS

Name and use	A.P.I.	I.B.P.	10%	50%	90%	E.P.	Rec., per cent
1. Tire manufacture, rubber cement solvent, trade name "Rub-Sol".......	78	82	111	147	191	222	98
2. Tire manufacture, rubber cement solvent, trade name "Rub-Sol".......	70	90	131	193	243	272	95
3. Tire manufacture, rubber cement solvent, trade name "Rub-Sol".......	69	104	143	197	245	278	99
4. Tire manufacture, rubber cement solvent, trade name "Rub-Sol".......	66	124	165	202	241	285	99
5. Same as above, also rubberizing solvent for spreader machines. No static fire hazard. "Rubberlene"........	64	136	166	198	240	274	99
6. Rubber-dipped goods solvent. "Dip-Sol"............................	60	193	212	228	257	289	99
7. Same as 6, also lacquer thinner. "Dryolene".........................	58	200	210	228	258	294	99
8. V. M. and P.* naphtha, cleaners' naphtha, paint remover................	57	200	229	262	285	312	99
9. V. M .and P.* naphtha, mineral spirits, turpentine substitute, Stoddard's solvent..........................	49	300	318	343	385	415	99
10. Heavy spirits, V. M. and P.* naphtha.	48	304	326	356	406	438	99

* Varnish Makers' and Painters' naphtha.

knocking. Standard ethyl gasoline has an octane-number of 76 (1934) and the Q grade of ethyl gasoline must have an octane number of at least 60 (1934). Cracked gasoline often contains *gumlike materials* that are deposited upon evaporation on the glasses of filling-station pumps and on the walls of the intake manifold and valves[6] of an engine. No universal specifications for gum content have been adopted but the gum content is always considered. Gasolines containing from 10 to 50 mg. of gum per 100 cc. by the accelerated porcelain-dish method are being marketed.

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7. Same as 6, also lacquer thinner. "Dryolene".........................	58	200	210	228	258	294	99
8. V. M. and P.* naphtha, cleaners' naphtha, paint remover................	57	200	229	262	285	312	99
9. V. M .and P.* naphtha, mineral spirits, turpentine substitute, Stoddard's solvent.........................	49	300	318	343	385	415	99
10. Heavy spirits, V. M. and P.* naphtha.	48	304	326	356	406	438	99

* Varnish Makers' and Painters' naphtha.

sold for gas manufacture and nearly pure propane is sold as a bottled gas for cooking purposes.

The mineral-oil solvents should not be considered as substitutes for other solvents that are now used because mineral solvents possess properties that are unique and useful, and for many purposes they can be selected because of their own merits.

The *burning-oils* represented by kerosene, long-time burning-oil, lighthouse kerosene, and 300°F. mineral seal oil, as their names imply, are used as fuels in household, marine, passenger-coach, and railroad illuminating lamps. Kerosene is the common household, marine, and government burning-oil. The 300° mineral seal oil is a high-grade oil having a Cleveland open-cup flash-point of not less than 250°F. Signal oil for railroad lamps is compounded from 300° mineral seal oil and lard or sperm oil. Long-time burning-oil is the finest grade and in the burning test 650 cc. of oil must not be consumed in less than 120 hr.

The value of kerosene is directly dependent upon its behavior in the burning or lamp test. The Saybolt thermoviscosity is also a good indication of the behavior of the oil in a lamp. The viscosity usually ranges between 325 and 450. However, an oil may have a proper viscosity and yet fail to burn satisfactorily. Kerosenes may have a gravity of 38 to 48 A.P.I. and a flash-point (Tag) of 120 to 180°F. The initial boiling-point is usually about 370°F. and the end-point about 540°F., although the government allows an end-point of 620°F. Although the gravity is not important, many refiners strive to produce a 41.5 to 43 A.P.I. kerosene and hence most of the kerosene on the market has this gravity. A small amount of light material (naphtha) is necessary in order to produce a high-quality burning-oil. For this reason a little heavy gasoline must always be present in the kerosene, and hence the boiling-ranges of kerosene and gasoline (or naphtha) overlap to some extent. If the gasoline (or naphtha) and kerosene are too well fractionated, the flash-point and initial boiling-point of the kerosene will be so high that it will not burn properly. This overlapping of cuts must always be considered when the gasoline and kerosene are evaluated from a crude-oil distillation curve.

Distillates.—Among the so-called distillates are included domestic fuel oils (stove distillates), diesel fuel oil, tractor oil, spray oils, insecticides, smudge oil, straw oil, absorption oils, industrial (distilled) fuel oils, and gas oil. Table 14 presents the properties of some of these distillates. This table indicates that the properties of distillates are not closely specified. Distillates are cheap and hence they are given little attention in the refinery. Although gas oil, which may include the domestic distillates, may be cracked for the production of antiknock gasoline, the distillate portion is exceedingly hard to crack and only small yields of gasoline can be obtained at ordinary cracking conditions. Often the refiner blends his distillates, along with other similar products such as pressure distillate "butts," with heavy tar to reduce the viscosity of the tar so that it can be marketed as a fuel oil.

All of the distilled industrial fuels come from this group. Usually none of the properties is specified except the open-cup flash-point (approximately 170°F.) and the corrosive action of the oil. Originally, gas oil was widely used for enriching artificial gas but today most of it is used as a fuel or cracked into gasoline. Distillates are also being used as insecticides in swamps and for spraying trees although residual fuel oils are more generally used.

TABLE 14.—DISTILLATE FUEL OILS

Grade	Flash-point, °F.	A.P.I.	Pour-point max., °F.	Distillation range			Vis-cosity at 100	Water and sedi-ment
				I.B.P.	10%	Max.		
1. Light domestic fuel oil	110–165	42	15	....	420	600	....	0.05
2. Medium domestic fuel oil................	125–190	39	15	....	440	620*	....	0.05
3. Heavy domestic fuel oil................	150–200	36	15	....	460	675*	....	0.1
4. Diesel fuel oil (aero)..	150–180 (O.C.)	38–43	30	380	490	600	32	None
5. Gas oil (gas manufacture)............	195	36	..	302	460	700+	35	
6. Industrial fuel oil (straight run)......	175–265	26–35	35	420–480	450–500	800+	41–50	
7. Absorption oil........	265	35.5	..	536	572	698	41	0.05
8. Straw oil............	275 and higher	34+	30	530	....	....	70 or less	
9. Tractor fuel oil†......	110	.....	..	250	347	465*		

* 90 per cent point.

† Western Petroleum Refiners Assoc., 1934.

Lubricating Oils.—The wide usefulness of mineral lubricating oils does not permit a discussion of all of the oils. Among these oils are motor oils, tractor oils, motorcycle oils, aero oils, engine and machine oils, locomotive and car oils, aircraft and machine-gun oils, gun and ice-machine oils, recoil oils, gear, chain and wire-rope oils, penetrating oils, transmission oils, putty oils, wool oils, spindle oils, thread-cutting oils, tempering and quenching oils, insulating oils, stainless oils, harness oils, floor oils, furniture and automobile polish, cutting oils, buffer oils, denaturing oils, medicinal mineral oils (white), and technical white oils. Technical white oil is particularly interesting because it is used to lubricate the machinery in food-manufacturing plants, such as bakeries and candy factories, and for lubrication in certain textile work.

The government specifies four classes of lubricating oil:

Class A.—For lubricating machinery and engines when a highly refined oil is not necessary. Not for steam-engine lubrication. Five grades: extra light, light, medium, heavy, and extra heavy.

Class B.—For lubricating turbines, dynamos, and high-speed steam engines using circulating or forced-feed lubricating systems. Five grades of viscosity.

Class C.—For lubricating when service conditions necessitate an oil suitable for both turbine and internal-combustion engine lubrication. Five grades of viscosity.

Class D.[8]—For lubricating internal-combustion engines except aircraft and diesel engines (special oils required). Nine grades of viscosity including those in Classes *A*, *B*, and *C* and in addition ultra heavy, tractor, tractor heavy, and motorcycle.

The characteristic differences in the four classes are Class *A*, reaction and corrosion; Class *B*, emulsibility and demulsibility; Class *C*, neutralization, demulsibility, and carbon residue; and Class *D*, neutralization, viscosity-temperature relation, and, for the heavier oils, carbon residue.

This somewhat elaborate system of classification has been replaced in the industry by the viscosity classification proposed by the Society of Automotive Engineers.[9] See tabulation, page 141.

The important common tests for an oil are (1) flash- and fire-points, (2) viscosity and viscosity-index, (3) color, (4) pour-point,

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[8] Oil, Lubricating, Class *D* VV-O-496, Superintendent of Documents.

[9] *Soc. Automotive Eng.*, p. 49, February, 1932.

(5) corrosion, (6) emulsibility and demulsibility, (7) carbon residue, and (8) precipitation.

The *flash-* and *fire-*points indicate the amount of light material (gas oil) in the lubricating oil. Naphthene-base oils usually have lower flash-points than other oils. Low-flash oils tend to be distilled into the exhaust of an automotive engine. However, the effect of the flash-point on lubricating ability should not be overemphasized because a low-flash oil always exists in the engine after a few miles of operation because of crank-case dilution. Thus a high-flash oil soon becomes no better than any other oil except for the smaller consumption of oil. The flash-point is widely used as an indication of the degree of fractionation that the oil has undergone and the base from which it was derived. The Standard Oil Company of Indiana markets a motor oil under the name of "Isovis." This oil is diluted with a lighter oil at the refinery so that it already has the composition of an oil that has been diluted by crank-case dilution.

S.A.E. No.	Viscosity, Saybolt Universal sec., °F., at		
	100	130	210
10	....	90–120	
20	231–384	120–185	50–60
30	384–550	185–255	60–69
40	550–652	255–293	69–75
50	652–1244	293–397	75–105
60	....	....	105–125
70	....	....	125–150

At present the importance of the *viscosity-temperature* relation seems to overshadow all other physical properties. As an oil is heated, its viscosity decreases so that it may be unsuitable as a lubricant at the temperature at which the engine operates. Furthermore, even though the oil has a proper viscosity at the high temperature, it may be so viscous at starting temperatures that it fails to lubricate properly.[10]

The major usefulness of determining the *color* is to indicate the nature of the refining operation. Nevertheless, some companies

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[10] See Fig. 18 (p. 74) for the relation of the viscosity of finished oils at 210°F. to the viscosity at 100°F.

have so improved the color that the costs of refining have been needlessly increased.[11] The *pour-point* indicates the tendency of an oil to congeal at low temperatures and thus fail to lubricate. Recent refinements in the art of dewaxing have led to the manufacture of zero[12] and lower pour-point products. Low pour-point oils are uniquely valuable for certain purposes such as for airplane oils, aircraft machine-gun oil, recoil oil, ice-machine oil, and motor oils in cold climates. *Emulsibility* and *demulsibility* are particularly important for oils that must be used in the presence of water or steam and for lubricating high-speed machines such as turbines. The *carbon residue* supposedly measures the tendency of an oil to deposit carbon in the internal-combustion

TABLE 15.—RANGE OF PHYSICAL PROPERTIES OF LUBRICATING OILS

Name of oil	Used for	A P.I.	Viscosity at		Flash (O.C.)	Pour-point	Carbon residue
			100	210			
1. Light motor	Automobiles	21–30	150– 330	43– 50	300–405	0–30	0.03–0.12
2. Medium motor	Automobiles	21–28	225– 450	47– 58	340–430	0–40	0.06–0.38
3. Heavy motor	Automobiles	20–27	300– 650	52– 77	360–450	0–40	0.1 –1.2
4. Extra heavy motor	Automobiles	18–26	500–2,100	70–125	370–470	0–45	0.2 –2.3
5. Diesel engine	Diesels	22–25	....	55– 70	370–450	10–50	0.3 –0.8
6. Tractor	Tractors	22–25	....	66–155	380–500	10–50	0.4 –1.8
7. Aero	Airplanes	23–26	....	75–125	400–475	0–45	1.0 –2.5
8. Transmission	Automobiles	20–23	....	90–175	440–515	40–60	2.5 –4.6
9. Cylinder (S.R.)	Steam engines	19–27	....	90–330	415–630	35–70	1.5 –4.5
10. Engine	Heavy bearings	21–27	150– 330	.....	350–550	0–35	
11. Crank case	Steam engines, crank case, splash, etc.	22–27	190– 330	......	400–550	0–35	
12. Turbine	Steam turbines, dynamos	26–32	90– 285	......	320–420	10–30	
13. Cold test	Ice machines, recoil aircraft, machine guns, etc.	25–33	50– 400	......	90–450	–50 to –5	
14. Spindle, etc	Light machines, weaving, spinning, automatics, etc.	26–35	90– 150	......	340–390		
15. Black	Rough, slow-speed bearings, crushers, etc. (cheap work)	16–28	....	95–160	375–450	15–40	
16. White	Machines in food plants, etc.	29–32	87– 140	......	290–380		

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[11] Some performance data indicate that the most valuable lubricants are removed by extensive treatment but this is a problem that is far from settled.

[12] LEDERER and ZUBLIN, Manufacture of Low Pour Point Oils, *Ref. Nat. Gaso. Mfr.*, January, 1931, p. 73.

engine. Wilson and Barnard[13] conclude that the carbon residue indicates the amount of carbon formation that will occur but that the amount that is formed is not directly (much less) proportional to the carbon residue. "Of course if the oils have different viscosities at the operating temperature, the one with the lower viscosity tends to pass the rings in larger quantities and thus affect the amount of carbon formation."

Unfortunately, even a complete laboratory examination in which all of the foregoing tests are employed does not always indicate the true usefulness[14] of an oil when in service. For this reason, a work-test[15] has been adopted by the United States Navy for evaluating an oil under conditions similar to those which it must meet in actual service. Tests of this nature will doubtless become more and more important.

In 1930 the production of lubricating oils was about 34,201,000 bbl.[16] About 57 per cent of the total domestic demand was used for automotive lubrication and the rest was for industrial lubrication. The following tabulation gives some interesting data regarding the production of lubricating oil in 1930.

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[13] *Proc. A.S.T.M.*, **28**, Part 2 (1928).

[14] The industry has apparently conceded that high-viscosity-index oils, such as Pennsylvania oils, are greatly superior and has attempted to make all oils meet the specifications of paraffin-base oil. Although high-index oils are necessary for certain exacting duties, the less-valued oils fill the need for a cheap grade of oil and are certainly good enough for most purposes. Doubtless the use of the so-called inferior oils is more economical for certain services than high-index oils. After all, lubrication is an economic problem, not a scientific novelty. Perhaps a comparison of oils based upon a purely cost basis, consisting of (1) cost of lubricant, (2) expenses and inconveniences involved in overhauling the engine, (3) cost of replacements and repairs directly due to a faulty lubrication, and (4) performance, may lead to a public favor of mixed- and naphthene-base oils. Without doubt the mixed-base oils do not give so much trouble by sticking valves or by hard carbon deposits. Few complete tests of this nature have been conducted and those that are available do not definitely indicate that high-index oils are superior. Note Cross, "Handbook," *Bull.* 25, p. 426, 1928; Livingston and Gruse, *Ind. Eng. Chem.*, **21,** 904 (1929); O'Neill and McGeary, *Nat. Petroleum News*, June 11, 1930, and Born and Harper, *Oil Gas J.*, Nov. 1, 1934, p. 12.

[15] O'Neill and McGeary, Evaluation of Lubricating Oils by the Work-factor Method, *Nat. Petroleum News*, June 11, 1930, p. 63.

[16] Reid, G., Source and Distribution of Lubricating Oil, *Ref. Nat. Gaso. Mfr.*, May, 1931, p. 110.

Type of crude	Per cent of production	Average per cent recovery from crude	Per cent of crude processed for lubricants
1. Mixed base	32	20	9.1
2. Paraffin base	30	30	100.
3. Coastal crude	31	30	32.4
4. California crude	7	20	5.

Greases and Waxes.—Greases and waxes also constitute a large group of different materials. Among the greases are recuperator, crank-pin, rod, cup, graphite, driving journal compound, axle, and fiber greases. Petrolatum stock is also used in the manufacture of shoe polish, medicinal salves, hair pomades, vaseline, cosmetics, etc. Paraffin wax is used as a sealing and insulating material, in candle manufacture, as a compounding material in the manufacture of waxes and salves, and in the manufacture of wax paper and matches.

The compounding of greases, etc., is often considered as an art and few "grease-makers" use the same process of manufacture. Greases may be grouped into three classes.[17]

1. Admixtures of mineral oil and solid lubricant. Some of the common solid lubricants are graphite, mica, talc, sulfur, and asbestos fiber. These greases are invaluable in the lubrication of ill-fitting machine parts functioning under heavy or intermittent loads. Examples of this type are tractor-roller lubricants, lubricants for concrete mixers, ditch-digging equipment, and railroad-car unloading devices.

2. Blends of residuum, waxes, uncombined fats, rosin oils, and pitches. This group is particularly suited to the lubrication of rock bits, steel cables, water pumps, dredges and chains, and gears operating under water or under exposed weather conditions.

3. Soap-thickened mineral oils. Common thickeners are sodium, calcium, aluminum, and lead soaps. The soaps of these metals are prepared by saponification of a fatty glyceride of either animal or vegetable origin. This group is widely useful because a large variety of different-consistency greases can be

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[17] SIMPSON and WELCH, Manufacture of Grease, *Ref. Nat. Gaso. Mfr.*, March, 1931, p. 77.

produced by selecting various metallic soaps, fatty glycerides, and mineral oils.

Paraffin wax is marketed according to the melting-point. The melting-point ranges from 105 to 140°F. Crude wax is sold in two common grades having melting-points of 118 to 120°F. and 124 to 126°F. Crude wax is used in the manufacture of matches, as a stuffing or loading material for leather goods, and in the textile industry for softening and lubricating yarn during winding. *Refined wax* must be free from odor or taste and usually a white wax is required. A large quantity of refined wax is used in the water-proofing of food containers. It is also used industrially as a lining for vats, tubs, containers, etc., in food-manufacturing plants. The highest grade of wax, having a melting-point of approximately 140°F., is used for the manufacture of wax paper, and the most common low-melting (110 to 112°F.) wax is used in manufacturing matches. Much of the high-melting-point wax is imported and is prepared from East Indian petroleum.

Residues.—The residual petroleum products usually do not command a high market price. Often they are merely by-products of the regular refining operation. Some of the residual products are residual fuel oil, fuel oil for diesel power engines, road oil, spray oil, coke, and paving, roofing or paint asphalts.

The United States Government specifies six fuel oils.[18] Three of these are distillate fuels (see oils 1, 2, and 3, Table 14) and three are residual fuel oils. Table 16 indicates the properties of these oils.

TABLE 16.—RESIDUAL FUEL OILS

Fuel oil	Flash-point, °F.	Water and sediment, maximum per cent	Pour-point, minimum °F.	Maximum viscosity, sec.
4. Low-viscosity fuel..	150–250	1	15	125 Saybolt at 100
5. Bunker "B".......	150	1	..	100 furol at 122
6. Bunker "C".......	....	2*	..	300 furol at 122

* Sediment alone not over 0.25 per cent.

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[18] *Bur. Standards C S* 12–33, effective May 1, 1933.

All of the oils must be free from grit, acid, and fibrous or other foreign matter that might clog or injure burner valves. The main difference in the specifications of the three government fuel oils is the viscosity. Residual fuel oils usually have a flash-point (O.C.) higher than 200°F., a furol viscosity of about 100 sec. at 122°F., a pour-point not exceeding 40°F., and the gravity ranges between 6 and 27 A.P.I. Sulfur is usually limited to 1.5 per cent and water and sediment to 1 per cent. Cracked fuel oils are desirable[19] as fuels because they usually have a lower pour-point, lower viscosity, and a slightly higher heating value than the residues from which they are produced. By law, the flash-point is usually limited to a minimum of 110°F. Perhaps the most common method of grading fuel oils is by gravity.

Petroleum coke is used commercially as follows:[20] as a refinery and commercial fuel (often powdered), in the manufacture of carbon electrodes, brushes, plates, etc., in the manufacture of abrasives and artificial graphite, in the manufacture of calcium carbide, as a metallurgical fuel, in paints and pigments, in gas manufacture, and in the ceramics industries. The high heating value and freedom from clinker-forming substances, the small quantity of ash, and the low-sulfur content of some petroleum coke make it a desirable fuel in metallurgical processes. Below are listed the average physical properties of common petroleum cokes:

Apparent density	0.9–1.1
Structure	Cellular to granular
Color	Dark brown to grayish black
Moisture	0.2–0.4
Ash	0.1–2.0
Sulfur	0.5–1.3
Volatile matter	5–16 per cent
Fixed carbon	80–90 per cent
Heating value	15,000–15,500 B.t.u. per lb.

In the past, the term *road oil* has been used carelessly by the refiner. The term has been used to designate a fluid residual oil for the purpose of "laying" the dust on dirt or gravel roads. Gradually the meaning of the term road oil has been revised so

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[19] MORRELL and EGLOFF: The Congealing Temperature . . . of Cracked Residue, *Ref. Nat. Gaso. Mfr.*, April, 1923, p. 17.

[20] SWANSON, E. B., Petroleum Coke, *Bur. Mines Econ. Paper* 9, 1930.

that now (1934) it refers to the more viscous grades of oil. These oils contain a high percentage of solid asphalt, and upon exposure the more volatile portion of the oil evaporates, leaving a solid tar which acts as a binding material for earth or aggregate. *Cutback* road oils are maufactured by blending gas oil and asphalt. Table 17 indicates the ranges of composition and properties of road oils. The many state specifications vary so widely that only the limits of the properties are given in Table 17. The table should not be used as a set of specifications.

TABLE 17.—PROPERTIES OF ROAD OILS

Property	Usual range	Limiting property which may be difficult to obtain
Specific gravity at 77°F	0.95–1.03	0.95+
Asphalt content (100 penetration at 77°F.)	40–85 per cent	85+
Asphalt content (80 penetration at 77°F.)	35–94 per cent	94+
Furol viscosity at 210°F	Wide range	
Solubility in carbon disulfide	99–99.5	99.5+
Percentage asphaltenes	4–15	Either extreme
Flash-point (O.C.)	120–400	400+
Evaporation loss:		
Residue oils	1–15 per cent	1−
Cut-back oils	2–40 per cent	2−
Ductility of asphalt content	1–100	100+

Table 18 likewise indicates the more important properties of asphalts. Many other specifications for asphalts are usually required but those in Table 18 serve to classify asphalt materials.

Asphalt finds many uses other than as a road material. Among these are: water-proofing of concrete and reservoirs, water-proofing paints, roofing material, asphalt shingles, rubber filler or substitutes, saturant for felting, as a briquette binder, and in the prevention of corrosion. In 1930 the sales of petroleum asphalt in the United States amounted to 3,326,378 tons valued at $35,380,620.

Petroleum Specialties.—During the last decade refiners have developed a large number of specialty products. More and more research work on the constitution of petroleum is being conducted and soon we may expect to have a purely chemical petroleum industry for the manufacture of chemical products that are far different from the petroleum products of today.

TABLE 18.—ASPHALT MATERIALS

Materials	Penetration at 77°F.	Ductility at 77°F.	Melting point, Ring and Ball
Paving binders:			
Mastic foot pavements and floors	10–15	.....	180–220
Asphalt blocks	10–25	20+	
Sheet asphalt pavement	25–40	40+	105–140
Grout filler	40–70	50+	113–140
Grout filler (blown type)	30–50	3+	150–230
Asphalt concrete (aggregate sand, etc.)	30–70	45+	113–150
Asphalt macadam	70–150	90+	104–113
Roofing asphalts:			
Saturant for felt or paper	75–140	100+	110–120
Heavy saturant for felt and rugs	28–32	40+	140–150
Roof coatings (blown)	10–50	1+	160–260
Sealing:			
Pipe sealing (sewers, etc.)	40–60	1+	200–225
Pipe coatings	10–15*	1+	200–215
Water-proofing	25–50	15+	140–170

* Consistency.

Among the many special products from petroleum, natural gas, etc., are the following: liquefied petroleum gas for domestic use, medicinal white oil, medicinal and dental wax, printer's ink, shoe polish, insecticides, furniture and automobile polish, dripless oils, and brick molding oils. The field of petroleum chemistry has hardly been touched and among the many possible petroleum derivatives are explosives, dye intermediates, pure hydrocarbons (paraffin, naphthene, and aromatic), soaps, antiseptics, anesthetics, wood preservatives, antifouling paints for ship bottoms, chemical alcohols, lacquers, varnishes, chlorinated products such as chloroform, carbon tetrachloride, and alkyl chlorides, organic acids, refrigerants, and rubber substitutes. Indeed, the possibilities are so many that the products cannot be predicted.

The production of specialty products, defined as products other than gasoline, kerosene, gas oil, fuel oil, lubricants, wax, coke, and asphalt, amounted to more than 9,900,000 bbl. in 1929. These specialties were probably sold, at the refinery, for an average of at least $4 a barrel.

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PART III

PRINCIPLES OF DESIGN

CHAPTER X

HYDRAULICS

The processing of petroleum consists primarily of three operations—heating, distillation, and transferring fluids. In spite of the basic importance of a knowledge of pumping, the refinery industry has not greatly enriched our knowledge of hydraulics. Rather, the refiner has turned to the comprehensive literature on the hydraulics of water and has adapted this information to the handling of petroleum. Although this practice has not led to serious difficulties, there are two important differences between oil and water that must be recognized—oils exhibit a wide range of viscosity and they are sensitive to the action of heat.

Mechanism of Fluid Flow.—By definition a fluid tends to assume the shape of the receptacle in which it is contained. When a solid moves through a fluid, force is delivered to the fluid and currents are set up in the body of the fluid. These forces are transmitted through the fluid because of its viscosity. Reynolds[1] demonstrated these currents by a series of elaborate experiments.

Flow within a tube or pipe is divided into two types of motion: stream-line flow and turbulent flow. Stream-line flow occurs at low velocities whereas turbulent flow occurs at higher velocities. In stream-line flow, through a circular conduit, the fluid travels as a series of cylinders which slip past one another. Flow at the center of the pipe progresses at the greatest velocity and the cylindrical film at the wall is almost stagnant. The wall of a pipe is relatively rough compared with the thickness of the film and the irregularities in the surface are effective in trapping part of the fluid and retarding its flow. Reactions are communicated to the body of the fluid by the viscosity or drag between particles. In small tubes or containers the condition of the surface is vitally important but in conduits having diameters of 6 to 12 in. the

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[1] REYNOLDS-OSBORNE, *Phil. Trans. London*, 1883.

condition of the surface is much less important.[2] The condition of the surface is more important at stream-line conditions than at turbulent conditions. The distribution of velocity across the diameter of a pipe is indicated in Fig. 46. The maximum velocity (at center) for turbulent flow is approximately 25 per cent greater than the average velocity, and for stream-line flow about 90 per cent greater than the average velocity.

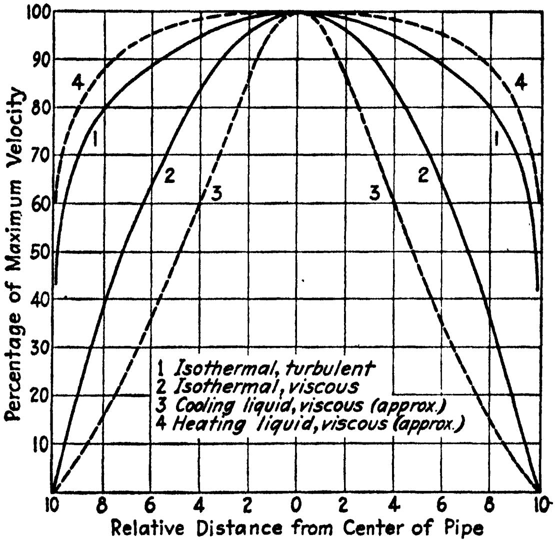

FIG. 46.—Distribution of the velocity of a fluid across a pipe.

The distribution of velocity across a pipe is due to the viscosity of the fluid. If the fluid is being heated or cooled, the viscosity is not constant throughout the fluid and hence the distribution of velocity is different. Curves 3 and 4 (Fig. 46) indicate the general effect upon the velocity gradient of heating or cooling the fluid.[3] If the fluid is heated, a temperature gradient exists through the film and the viscosity in the film will be less than in the body of fluid. For this reason the velocity of the material near the surface is greater if the fluid is being heated than if isothermal conditions are maintained.

Friction Losses.—When a fluid moves through a constriction in the passage through which it flows, a loss of energy occurs.

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[2] HELTZEL, W. G., Fluid Flow and Friction in Pipe Lines, *Oil Gas J.*, June 5, 1930, p. T203.

[3] KEEVIL and MCADAMS, *Chem. Met. Eng.*, **36**, 484 (1929).

This occurs to some extent even in a circular conduit such as a pipe. Loss is caused by the impact of fluid particles upon the walls of the conduit and by friction between particles of fluid as they move past one another. Fanning's equation for the pressure loss due to turbulent flow within a circular conduit may be expressed in English units as follows:

$$\Delta P_f = \frac{0.323 fsu^2L}{D}; \qquad \text{or} \qquad \frac{1.488}{100{,}000}\,\frac{Q^2}{D^5}fsL \tag{8}$$

where ΔP_f = pressure loss, lb. per sq. in.
s = sp. gr. referred to water at 60°F.
u = velocity, ft. per sec.
L = equivalent length of pipe, ft.
D = diameter of pipe, in.
Q = discharge, gal. per hr.
f = friction factor, a function of Dus/z (Fig. 47).
z = absolute viscosity, centipoises.

Throughout years of industrial development this equation has been found to be valid for the flow of all kinds of fluids in circular conduits. Comprehensive experimental data for sections other than circular are not available. However, the friction loss for other sections is usually computed by using the hydraulic radius

$$\Delta P_f = \frac{0.08075 fsu^2L}{m} \tag{9}$$

The hydraulic radius m is defined as the cross-sectional area divided by the wetted perimeter.

The equivalent length L is equal to the total length of straight pipe plus the lengths of pipe that are equivalent to the restrictions caused by elbows, valves, bends, etc. Equivalent lengths are usually expressed as diameters of straight pipe. Table 19 gives commonly accepted equivalent lengths at turbulent conditions of flow. Equivalent lengths for viscous or stream-line flow are so small that they are usually neglected.[4] Fanning's equation is not valid for the flow of gases if the pressure-drop is more than 10 per cent of the downstream pressure.

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[4] WILSON, MCADAMS, and SELTZER, *Ind. Eng. Chem.*, **14**, 105 (1922).

TABLE 19.—EQUIVALENT LENGTHS OF FITTINGS

Fittings	Nominal size, in.	Diameters of straight pipe
90 deg. elbows	1–2½	30
	3–6	40
	7–10	50
Return bends:		
Stream-line	2–4	40
Square block	2–4	80
Pipe bends	90-deg. center line radius, 2–6	10
	Larger radius	None
Tees	1–4	60
Valves:		
Globe	1–2½	45
	3–6	60
	7–10	75
Gate	1–2½	12
	3–6	16
Entry*	Sharp edge (flush with container wall)	20
	Sharp edge (extending into reservoir)	40
	Rounded	None
Meters	....	135–600

* These losses can be computed more accurately by use of the enlargement loss equation (p. 170).

The Fanning equation is usually used for both turbulent and stream-line conditions but the friction factor is much larger for stream-line conditions (Fig. 47). The Poiseuille equation, which does not involve a friction factor, may also be used for stream-line flow.

The Friction Factor.—The friction factor f in Fanning's equation has always been troublesome to engineers. Reynolds in 1883 recognized the relation between the friction factor and the dimensionless group Dus/z, but extensive data with which to check the relationship were not available until later. The group Dus/z is known as Reynolds' criterion. This factor can sometimes be handled more easily as $0.00682Qs/Dz$ in which Q equals gallons per hour.

The relation between the friction factor and Dus/z for an isothermal system is shown in Fig. 47. Keevil and McAdams[3] have determined the effect of heating or cooling on the friction factor and their conclusions are presented in Fig. 48. This

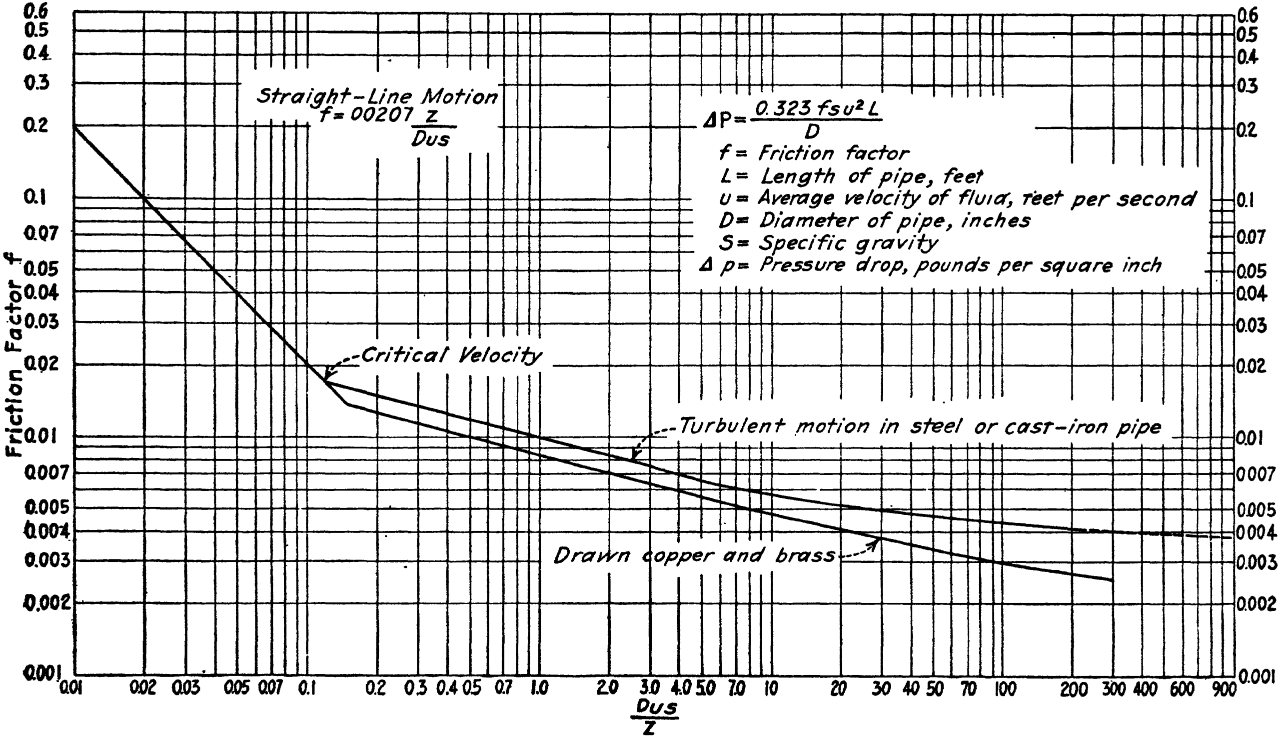

FIG. 47.—Friction factor for isothermal conditions as a function of Reynolds' criterion.

figure applies only to viscous flow, and for turbulent conditions the change in the friction factor is much less. It should be noted that Fig. 48 was obtained by a study of only two oils (70 and 150 viscosity at 100°F.).

The relation shown in Fig. 47 has been repeatedly checked[2,4,5,6] by numerous experimentors using a variety of materials, including water, air, natural gas, steam, oils, and solutions. Many empirical formulae for the pressure required to pump oil have been proposed. When these formulae are analyzed and inserted in the Fanning equation, they yield friction factors that are in close agreement with those given in Fig. 47.[7] In general, the friction factor should be slightly higher than that shown in Fig. 47 for small pipe sizes (less than 1½ in.) and slightly less for pipe exceeding 8 in. in diameter. The value of Dus/z when pumping natural gas in commercial lines is very high[6] and cannot be found

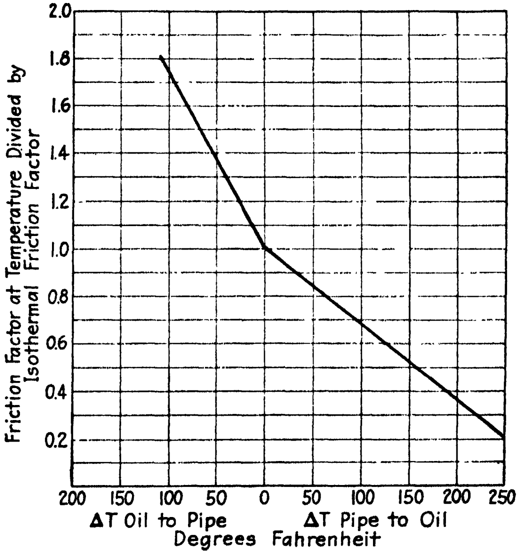

Fig. 48.—Correction for friction factor when the fluid is being heated or cooled. (*Keevil and McAdams, Chem. Met. Eng.*)

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[5] McAdams and Sherwood, Flow of Air and Steam in Pipes, *Mech. Eng.*, October, 1926.

[6] Berwald and Johnson, Factors Influencing Flow of Natural Gas . . . , *Bur. Mines Repts. Invest. Serial* 3153, 1931.

[7] The equations and data of Danforth, Twel, A. F. L. Bell, and McGregor have been checked in this manner.

on Fig. 47. The value of the friction factor is between 0.0033 and 0.0045 for pumping natural gas at high pressures.

Condition of Pipe Surface.—The friction factors shown in Fig. 47 are for commercially clean new pipe and are smaller than those usually obtained in practice. The smaller the pipe the greater is the effect of the surface in increasing the friction loss. For very large pipe the condition of the surface may be neglected entirely. The friction loss in old or corroded small pipes may be twice as great as for new clean pipe. The factors shown in Table 20 are considered safe.

TABLE 20.—EFFECT OF SURFACE CONDITION

Conditions	Correction for Surface Condition (multiply pressure drop by these factors)
New or clean, smooth pipe	None
Oil:	
Size 1–6 in.:	
Noncorrosive, no moisture	1.10
Corroded (after 3 years)	1.30
Corroded (after 10 years)	1.5
Size 8 in. and larger:	
Normal crude oil	None
Corrosive crude oil	1.1
Water:	
15-year-old pipe	1.4
25-year-old pipe	1.7
Badly corroded (tuberculated)	2.2
Gas, large lines	None

Absolute Viscosity.—The absolute viscosity z, expressed as centipoises (numerically the same as relative to water at 69.33°F.), is used in determining the friction factor. Water, common gases, and most oils have been studied completely and viscosity data are available, but the viscosity of (1) petroleum vapors and (2) mixtures of vapor and oil have not been determined experimentally and hence the usefulness of the formulations for friction losses, as outlined heretofore, is limited by a lack of viscosity data.

The average viscosities of oils are presented in Fig. 49. The chart is complicated by the fact that the curves for paraffin-base

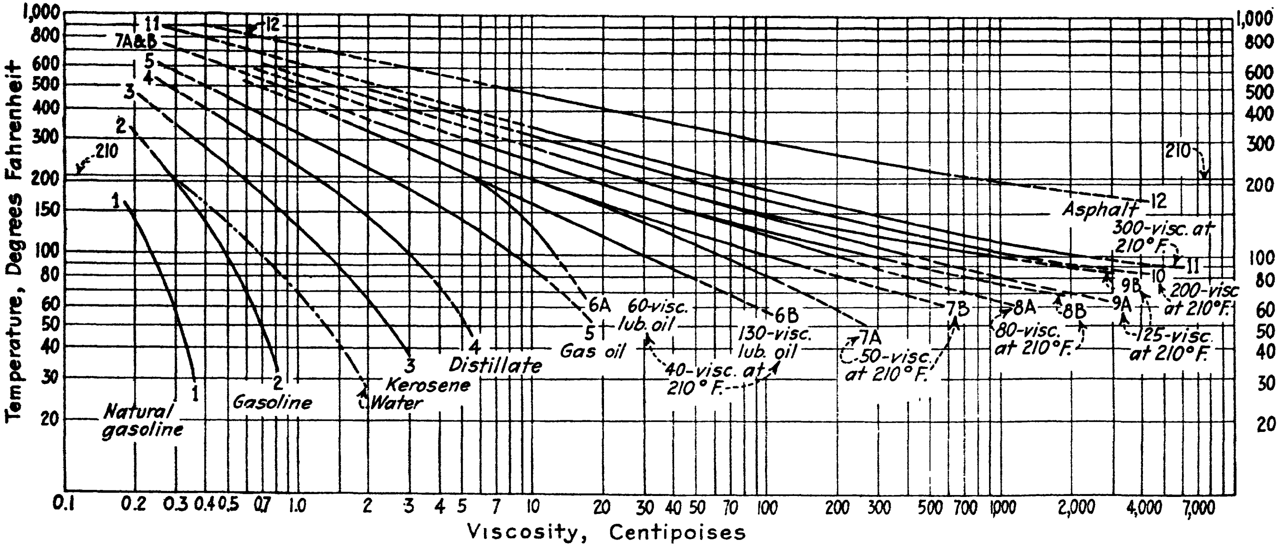

FIG. 49.—Change of viscosity of petroleum oils with temperature.

and naphthene-base oils have different slopes. The properties of the materials used in plotting Fig. 49 are shown in Table 21.

TABLE 21.—OILS USED IN PLOTTING FIG. 49

Curve No.	Material	A.P.I.	Viscosity at		Viscosity-index
			100	210	
1	Natural gasoline	76.5			
2	Gasoline	57.0			
3	Kerosene	42.0			
4	Distillate	35.0	35		
5	Gas oil	28.0	50		
6*A*	Lube oil	37.0	60	40	100
6*B*	Lube oil	22.0	130	40	0
7*A*	Lube oil	32.0	255	50	100
7*B*	Lube oil	21.0	420	50	0
8*A*	Lube oil	28.5	780	80	100
8*B*	Lube oil	20.0	1,640	80	0
9*A*	Lube oil	26.5	1,730	125	100
9*B*	Lube oil	18.5	4,400	125	0
10	Lube oil	20.5	....	200	70
11	Residuum	19.8	....	300	70
12	Asphalt	....	(50 penetration)		

The viscosities of several hydrocarbon gases and an approximate curve for petroleum vapors are shown in Fig. 50. Millikan and others[8] have found that the viscosity of gases is substantially independent of pressure or density, and exactly independent if a correction is applied for slip past the containing surfaces. The viscosity is also independent of the molecular weight, except for the first few members of a series, but it is greatly affected by the

Material	Formula	Centipoise
Alcohols	$C_nH_{2n+1}OH$	0.0142
Ethers	$C_nH_{2n}O_2$	0.0155
Chlorides	$C_nH_{2n+1}Cl$	0.0150
Bromides	$C_nH_{2n+1}Br$	0.0182
Iodides	$C_nH_{2n+1}I$	0.0210

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[8] MILLIKAN, *Phys. Rev.*, **21**, 250 (1923); VAN DYKE, *Phys. Rev.*, **21**, 217 (1923); and STATES, *Phys. Rev.*, **21**, 662 (1923).

molecular structure. Meyer[9] reports the data as shown at the bottom of page 165 for the viscosity of several chemical series, in the vapor state. With the exception of the first few members the viscosity of each series is a constant for a given temperature.

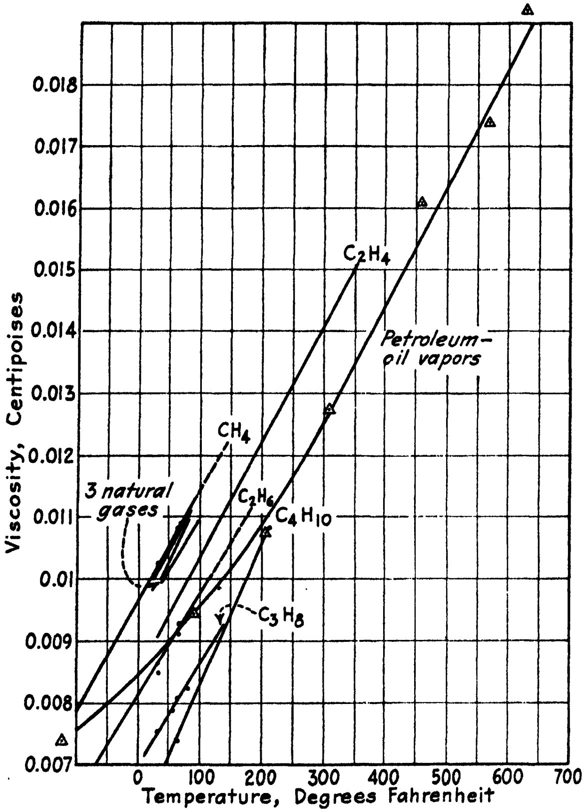

FIG. 50.—Viscosity of hydrocarbon gases.

Thus the temperature and the kind of a material are the only two factors that need be considered in determining the viscosity of a gas. Note that the viscosity of a gas increases with temperature whereas the viscosity of a liquid decreases with temperature.

Sutherland[10] finds that the viscosity at the critical temperature of the rare gases, argon, neon, etc., is directly proportional to

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[9] MEYER, O. E. "Kinetic Theory of Gases," 2d rev. ed., p. 122, Longmans, Green & Company, New York, 1899.

[10] *Phil. Mag.*, **36**, 507 (1893).

the square root of the atomic weight. Similarly, the viscosity of the normal paraffin hydrocarbons at their critical-points are almost proportional to the square root of the molecular weight. This method of correlation was used in drawing the curve for petroleum vapors as shown in Fig. 50. Although the triangular points through which the curve is drawn are the viscosities at the critical-point, nevertheless they should be approximately correct for all hydrocarbons of the normal paraffin series because of the work of Meyer[9] which shows that the viscosity of a series of hydrocarbons is a constant, regardless of molecular weight. Inasmuch as the only viscosity data that are available are for the hydrocarbons up to pentane, the curve had to be extrapolated far beyond the range of the experimental data.

The viscosity of natural gas has been studied by Berwald and Johnson.[11] The natural gases that they studied all had about the same viscosity except for those gases that contained large amounts of nitrogen, oxygen, and carbon dioxide. For practical purposes the viscosity of natural gas, at room temperatures, can be considered as 0.0105 centipoise.

The viscosity of mixtures of oil vapor and oil is a particularly pertinent problem because such mixtures are so frequently handled in the refinery. Whenever a material is continuously heated in exchangers or tubular heaters, vaporization occurs and the viscosity of the resulting mixture of vapor and oil governs the pressure-drop. Apparently only one article pertaining to this important problem has been published. Uren[12] has conducted experiments regarding the mechanics of flow in columns of mixtures of oil and air. By assuming that Reynolds' criterion was valid for such a case, he was able to compute values of the viscosity of these mixtures. The viscosities that he obtained in this manner were not a simple function of the viscosity of the gas and of the oil but were approximately a linear function of the arithmetic mean density.[13] The mechanics of fluid flow indicates

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[11] Viscosity of Natural Gas, *Bur. Mines, Tech. Paper* 555, 1933.

[12] URBN, GREGORY, HANCOCK, and FESKOV, Flow Resistance of Gas Oil Mixtures, *Oil Gas J.*, Oct. 3, 1929, p. 148.

[13] According to the data, the viscosity is related to the density approximately as follows: $z = -0.00055 + 0.00032s$. Doubtless this relation is not of a general nature and is not valid for other gases than air and for other oils than the one they studied. The relation holds between limits of 24 and 120 cu. ft. of air per gallon of oil.

that the viscosity of the liquid will be more important than the viscosity of the gas, in governing the behavior of the mixture. The liquid will be thrown to the walls of the conduit and will not travel at the average velocity of the mixture. Likewise the specific gravity used in determining the friction factor should be nearly the gravity of the oil, but the specific gravity used in the Fanning equation should be the gravity of the mixture.

Many formulas, charts, alignment charts, and tabulations have been presented for the rapid solution of friction-loss problems. These have been developed to meet special needs and, although they are useful if a particular type of fluid is handled day after day, there are so many special cases that they cannot all be presented.[14]

TABLE 22.—STANDARD FULL-WEIGHT WROUGHT-IRON AND STEEL PIPE

Nominal diameter, in.	Diameter, approx. internal, in.	Diameter, external, in.	Thickness, in.	Circumference, in.		Transverse internal area, sq. in.	Ft. of pipe per sq. ft. of external surface	Nominal weight per ft.-lb.
				Internal	External			
⅛	0.27	0.405	0.068	0.85	1.27	0.06	9.44	0.24
¼	0.36	0.54	0.083	1.14	1.70	0.10	7.08	0.42
⅜	0.49	0.675	0.091	1.55	2.12	0.19	5.66	0.57
½	0.62	0.84	0.109	1.95	2.63	0.30	4.55	0.85
¾	0.82	1.05	0.113	2.59	3.30	0.53	3.64	1.13
1	1.05	1.315	0.134	3.29	4.13	0.86	2.90	1.68
1¼	1.38	1.66	0.140	4.34	5.22	1.50	2.30	2.27
1½	1.61	1.9	0.145	5.06	5.97	2.04	2.01	2.72
2	2.07	2.375	0.154	6.49	7.46	3.36	1.61	3.65
2½	2.47	2.875	0.204	7.75	9.03	4.78	1.33	5.79
3	3.07	3.5	0.217	9.63	11.00	7.39	1.09	7.57
3½	3.55	4.0	0.226	11.15	12.57	9.89	0.96	9.11
4	4.03	4.5	0.237	12.65	14.14	12.73	0.85	10.79
6	6.07	6.625	0.280	19.05	20.81	28.89	0.58	18.97
8	8.07	8.625	0.276	25.35	27.10	51.15	0.44	24.69
8	7.98	8.625	0.322	25.07	27.10	50.02	0.44	28.55
10	10.19	10.75	0.278	32.01	33.77	81.55	0.36	31.20
10	10.14	10.75	0.306	31.86	33.77	80.75	0.36	34.24
10	10.02	10.75	0.366	31.47	33.77	78.82	0.36	40.48
12	12.09	12.75	0.328	37.98	40.06	114.8	0.30	43.77
12	12.00	12.75	0.375	37.70	40.06	113.1	0.30	49.56

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[14] In the author's experience he has found that for general work the use of Fanning's equation and the friction factor chart Fig. 47 is the most satisfactory method of computing pressure-drops. Question as to the reliability of the many charts to be found in the literature is a bothersome worry.

Example 19. Friction Loss in an Oil Line.—One thousand six hundred gallons per hour of a 15 A.P.I. ($s = 0.966$) fuel oil at a temperature of 200°F. is to be pumped through a distance of 1,700 ft. in a 3-in. well-insulated pipeline. Two gate valves and six elbows are in the line and the oil enters a tank through a sharp-edge entry flush with the side of the tank. The Saybolt viscosity of the oil is 300 at 210°F. What is the total friction loss in the line? Assume no change in temperature.

The viscosity of the oil at 200°F. (Fig. 49) is approximately 80 centipoises. The specific gravity at 200°F. (Fig. 39) is 0.916. The 1,600 gal. is the volume at 60°F.

$$\text{Volume at 200°F.} = 1{,}600 \times \frac{0.966}{0.916} = 1{,}688 \text{ gal. per hr.}$$

$$\text{Velocity} = \frac{\dfrac{1{,}688 \times 231}{3{,}600}}{\dfrac{(3.07)^2 \times 3.14}{4}} \times \frac{1}{12} = 1.21 \text{ ft. per sec.}$$

L, the equivalent length (Table 19):

$$\begin{array}{lcrl}
\text{Straight pipe} \ldots\ldots\ldots\ldots\ldots\ldots & & 1{,}700 & \text{ft.} \\
\text{Elbows} \ldots\ldots\ldots\ldots & \dfrac{6 \times 40 \times 3.07}{12} = & 61.4 & \\
\text{Gates} \ldots\ldots\ldots\ldots & \dfrac{2 \times 16 \times 3.07}{12} = & 8.2 & \\
\text{Entry} \ldots\ldots\ldots\ldots & \dfrac{20 \times 3.07}{12} = & 5.1 & \\
\hline
 & & 1{,}774.7 & \text{ft.} = \text{total equivalent length}
\end{array}$$

Using Fanning's equation, Eq. (8):

$$\frac{Dus}{z} = \frac{3.07 \times 1.21 \times 0.916}{80} = 0.043$$

The friction factor f from Fig. 47 = 0.047

$$\Delta P_f = \frac{0.323 \times 0.047 \times 0.916\,(1.21)^2 \times 1{,}774.7}{3.07} = 11.82 \text{ lb. per sq. in. for clean new pipe}$$

Check with the equation

$$\Delta P_f = \frac{1.488}{100{,}000}\,\frac{Q^2}{D^5}\,fsL$$

$$\Delta P_f = \frac{1.488 \times (1{,}688)^2 \times 0.047 \times 0.916 \times 1{,}774.7}{100{,}000 \times 273} = 11.87$$

Example 20. Friction Loss in Vapor Line.—Four thousand pounds per hour of a 55 A.P.I. naphtha vapor at a temperature of 300°F. passes through a 4-in. vapor line that is 130 ft. long. The molecular weight is 110. The pressure is 5 lb. gage. What is the pressure drop?

Volume of vapor

$$\frac{4{,}000}{110} \times 379 \times \frac{760}{520} \times \frac{14.7}{19.7} = 15{,}000 \text{ cu. ft. per hr.}$$

Viscosity at 300°F. (Fig. 50) = 0.0125 centipoise

$$\text{Specific gravity} = \frac{4{,}000}{15{,}000 \times 62.4} = 0.00427 = s$$

$$u = \frac{15{,}000}{3{,}600} \times \frac{144}{12.73} = 47.0 \text{ ft. per sec.}$$

$$\frac{Dus}{z} = \frac{4.03 \times 47 \times 0.00427}{0.0125} = 64.8$$

$$f = 0.00459 \text{ (Fig. 47)}$$

$$\Delta P_f = \frac{0.323 \times 0.00459 \times 0.00427 \times (47)^2 \times 130}{4.03} = 0.449 \text{ lb. per sq. in.}$$

Other Pressure Losses.—The losses due to increasing or decreasing the cross-sectional area of a conduit suddenly are sometimes relatively large. The loss due to a sudden enlargement of the cross section may be expressed as follows:

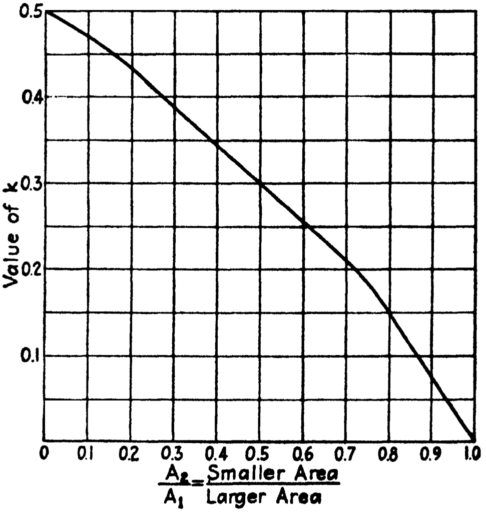

FIG. 51.—Constant for contraction losses.

$$\Delta h_e = \frac{(u_2 - u_1)^2}{2g}; \qquad \text{or} \qquad \Delta P_e = 0.00673s(u_2 - u_1)^2 \quad (10)$$

where Δh_e = pressure drop expressed as ft. of fluid.
ΔP_e = pressure drop, lb. per sq. in.
s = sp. gr.
u_2 = velocity, ft. per sec. at smaller section.
u_1 = velocity, ft. per sec. at larger section.

The loss due to a sudden contraction in the cross section is

$$\Delta P_c = 0.00673ksu_2^2 \tag{11}$$

where P_c = pressure drop, lb. per sq. in.
k = a constant (Fig. 51).
u_2 = velocity, ft. per sec. at the smaller section.

The relation among specific gravity, head of liquid, and pressure pounds per square inch is presented in Fig. 52.

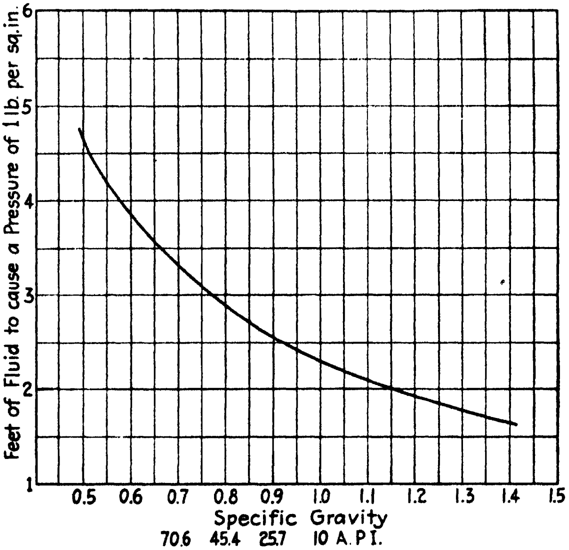

FIG. 52.—Relation of fluid head and pressure head.

Example 21. Contraction and Enlargement Losses.—*A*. Sixteen hundred gallons per hour of a 15 A.P.I. oil at a temperature of 60°F. is pumped through a 3-in. pipeline. A contraction to a 1-in. pipe occurs. What is the loss in pressure due to the contraction?

$$\Delta P_c = 0.00673ksu_2^2$$

$$u_2 = \frac{\dfrac{1{,}600}{3{,}600 \times 7.48}}{0.86/144} = 9.95 \text{ ft. per sec. (downstream)}$$

$$\text{Ratio of } \frac{A_2}{A_1} = \frac{0.86}{7.39} = 0.116$$

k from Fig. 51 = 0.465

$$\Delta P_c = 0.00673 \times 0.465 \times 0.966 \times (9.95)^2 = 0.299 \text{ lb. per sq. in.}$$

B. The oil then flows back to a 3-in. pipe from the 1-in. pipe. What is the loss in pressure?

$u_2 = 9.95$ (upstream)
$u_1 = 0.116 \times 9.95 = 1.15$ ft. per sec. (downstream)
$\Delta P_e = 0.00673(9.95 - 1.15)^2 \times 0.966 = 0.503$ lb. per sq. in.

Orifice Coefficients.—The standard sharp-edge orifice is the most common instrument for the measurement of oil flow. The formula for flow through such an orifice is

$$\sqrt{u_2^2 - u_1^2} = c\sqrt{2g\Delta h} \tag{12}$$

where u_2 = velocity, ft. per sec., through the orifice port.
u_1 = velocity, ft. per sec., in the line.
g = gravity constant or 32.2.
Δh = observed decrease in static pressure expressed as ft. of fluid flowing at the downstream density.
c = constant—the discharge coefficient.

If the ratio of the diameter of the pipe to the diameter of the orifice is large, the u_1^2 term may be neglected. The formulation does not hold if (1) the pressure-drop through the orifice is large compared with the absolute pressure and (2) the taps or connections for measuring the static pressure-drop are not properly located. The fluid as it approaches the orifice plate is contracted, and as it leaves the orifice plate it continues to contract for a short distance. The maximum contraction occurs at the *ventura contracta*. The upstream tap should be situated just above the first contraction of the fluid and the downstream tap should be situated at the center of the *ventura contracta*.

The discharge coefficients for water have been carefully determined and are given in Fig. 53. The coefficients for other materials than water have not been completely studied. Professor Daugherty[15] of the California Institute of Technology finds that the discharge coefficient is a function of *Dus/z*. Others[16] suggest that the viscosity is not an important factor and that *c* is independent of the viscosity of the fluid up to several hundred times the viscosity of water. Since the problem of

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[15] DAUGHERTY, R. L., "Investigation of the Performance of Centrifugal Pumps when Pumping Oil," Goulds Pumps, Inc., 1925–1926.

[16] WALKER, LEWIS, and MCADAMS, "Principles of Chemical Engineering," 2d ed., p. 55, McGraw-Hill Book Company, Inc., New York, 1927.

determining the discharge coefficient is not entirely settled, it is usually necessary to calibrate the orifice (in place) unless approximate or comparative measurements are satisfactory.

The head that is permanently lost by flow through an orifice is governed by the ratio of the diameter of the chamber to the diameter of the orifice. The losses are approximately as follows:

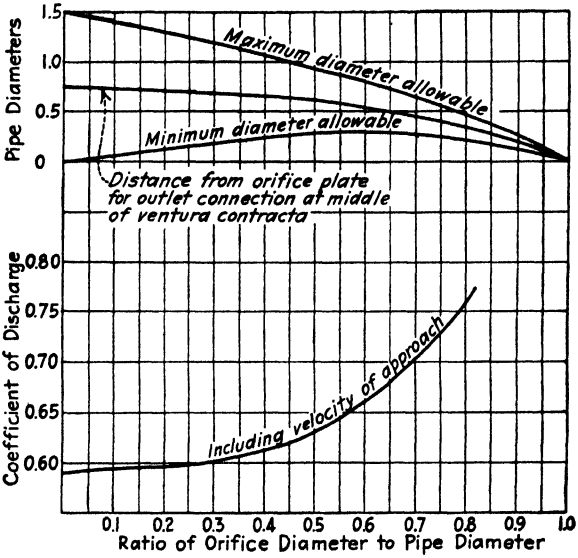

FIG. 53.—Coefficients for sharp-edge orifices and distances to tap connections.

$\frac{\text{Chamber Diameter}}{\text{Orifice Diameter}}$	$\frac{\text{Lost Head}}{\text{Drop in Pressure Head}}$
1.2	0.30
1.5	0.55
2.5	0.8
4.0	0.91
6.0	0.95

Example 22. Orifice Calibration Curve.—A 1-in. sharp-edge orifice is inserted in a 6-in. line. Where should the taps be located and what will the reading on the manometer be if 3,000 gal. per hour and 1,000 gal. per hour of a 27 A.P.I. (0.893 specific gravity) oil flows through the line?

The ratio of orifice diameter to pipe diameter is 1.0/6.07 = 0.1648. The discharge coefficient c (Fig. 53) is 0.595. The downstream tap should be located (Fig. 53) at 0.7 dia. or $4\frac{1}{4}$ in. downstream and the upstream tap at about 2 dia. or 12 in. upstream (Fig. 54).

$$\text{Upstream velocity (3,000 gal.) } u_1 = \frac{\dfrac{3{,}000}{3{,}600 \times 7.48}}{28.89/144} = 0.555 \text{ ft. per sec.}$$

$$\text{Upstream velocity (1,000 gal.) } u_1 = 0.555 \times \frac{1{,}000}{3{,}000} = 0.185 \text{ ft. per sec.}$$

$$\text{Downstream velocity } u_2 = 0.555 \times \frac{(6.07)^2}{1^2} = 20.6 \text{ ft. per sec.}$$

$$\text{Downstream velocity } u_2' = 0.185 \times \frac{(6.07)^2}{1^2} = 6.85 \text{ ft. per sec.}$$

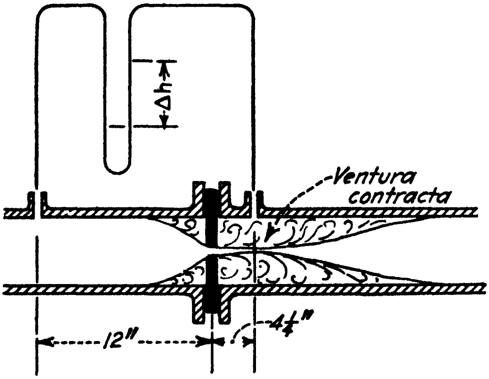

FIG. 54.—Arrangement of orifice and manometer.

$$\text{For 3,000 gal. per hour, } \sqrt{20.6^2 - 0.555^2} = 0.595\sqrt{2 \times 32.2\Delta h}$$

$$20.6 = 0.595 \times 8.03\sqrt{\Delta h}$$

$$\Delta h = \left(\frac{20.6}{0.595 \times 8.03}\right)^2 = 18.5 \text{ ft. of fluid}$$

From Fig. 52,

Ft. of fluid equivalent to 1 lb. per sq. in. = 2.58

$$\text{Manometer reading } \frac{18.5}{2.58} = 7.17 \text{ lb. per sq. in.}$$

Permanent loss in head = approximately 7.17 × 0.95 = 6.8 lb. per sq. in.
For 1,000 gal. per hour,

$$\Delta h = 2.05 \text{ ft. fluid}$$
$$= 0.795 \text{ lb. per sq. in.}$$

$$\text{Manometer reading in mm. of mercury} = \frac{0.795}{14.7} \times 760 = 41.1$$

The calibration curve plotted on logarithmic paper is a straight line.

Weirs.—In refinery design the two most important weirs are the rectangular or suppressed weir and the V-notch weir. Both are used in the design of the overflow dams in bubble towers. The formula for flow over a rectangular weir is

$$Q = 3L(h)^{3/2} \tag{13}$$

where Q = quantity of liquid, gal. per min.
L = perimeter of weir, in.
h = effective head above weir, in.

Francis (1851), Hamilton Smith (1886), and Bazin (1888) suggest constants between 3.33 and 3.7 for water but the value of 3 seems to represent more accurately the behavior of petroleum oils. The constant holds only up to heads of 5 or 6 in. and perimeters of 24 in. The formula for the triangular weir having an angle of 90 deg. is

$$Q = 2.3L(h)^{5/2} = 1.155L(h)^{3/2} \tag{14}$$

Triangular weirs are useful if the capacity of a rectangular weir must be increased without increasing the head or the perimeter.

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* Data on oil.

CHAPTER XI

COMBUSTION

The generation of power and the liberation of heat are important operations in almost all industries. The generation of heat in the petroleum industry is a somewhat different problem from that in other industries because fuel is abundant and cheap and because petroleum, the feed stock, is affected by high temperatures.

Heating Value.—The amount of heat that is liberated when a unit quantity of a fuel is burned is called the heating value or heat of combustion. The heat liberation, when 1 lb. of a fuel at 60°F. is burned and the products of combustion are cooled to 60°F., is called the *net heating value.* If the products are cooled to 60°F., and in addition the water vapor in the flue gas is condensed, the *gross* or *high heating value* is obtained. In most industrial processes the water vapor that is contained in the stack or flue gases is not condensed and hence the most logical basis for the design of equipment is the net heating value. Continental engineers use the net heating value but American engineers usually base their computations on the gross heating value. The reason for the general use of the gross heating value is probably due to the fact that the gross heating value is obtained in the laboratory directly, whereas a correction must be applied to obtain the net heating value.

The heat that is evolved when 1 lb. of water is condensed at 60°F. is 1058.2 B.t.u. or for 1 cu. ft. of water vapor (measured at 60°F.) 50.3 B.t.u. The net heating value can be computed from the gross heating value by subtracting the quantity of heat that is required to condense the water vapor in the flue gas.

Example 23. Calculation of Net Heating Value.—What is the net heating value of methane expressed as B.t.u. per cubic foot?

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

One cubic foot of methane burns and produces 2 cu. ft. of water vapor. The gross heating value of methane = 1009 (Table 24).

Net heating value = 1009 − 2 × 50.3 = 908.4 B.t.u. per cu. ft.

Compute the net heating value of fuel oil 1 in Table 23, page 180.

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

The molecular weight of hydrogen is 2 and of water 18. Two pounds of hydrogen burns, yielding 18 lb. of water.

$$\text{Water produced per lb. of fuel} = 0.12 \times {}^{18}\!/\!_{2} = 1.08 \text{ lb.}$$

Gross heating value from Table 23 is 19,376 B.t.u. per pound.

Net heating value = 19,376 − 1.08 × 1058.2 = 18,234 B.t.u. per lb.

The gross heat of combustion of pure compounds may be estimated[1] by a consideration of the structural formulae of the compounds. The following values for the various parts of structural formulae are suggested:

Bond	Heat Liberation, B.T.U. per Lb.-mol.
C—C	95,220
C—H	94,860
C═C	219,240
C≡C	365,760

Example 24. Heating Value of Pure Compounds.—Compute the gross heating value of methane (CH_4).

There are four C—H bonds.

$$4 \times 94{,}860 = 379{,}440 \text{ B.t.u. per lb.-mol.}$$

There are 379 cu. ft. of gas per lb.-mol at 60°F.

$$\text{Heating value, B.t.u. per cu. ft.} = \frac{379{,}440}{379} = 1001+$$

Experimental values range from 998 to 1,009.

Compute the gross heating value of *n*-pentane. There are four C—C bonds and 12 C—H bonds.

$$\begin{aligned} 4 \times 95{,}220 &= 380{,}880 \\ 12 \times 94{,}860 &= 1{,}138{,}320 \\ \hline \text{B.t.u. per lb.-mol} &= 1{,}519{,}200 \end{aligned}$$

$$\text{B.t.u. per lb.} = \frac{1{,}519{,}200}{72} = 21{,}377$$

Experimental value 21,100 B.t.u.

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[1] Some authorities believe that the computed heats of combustion are more accurate than most experimental data.

Refinery Fuels.—The heating value of petroleum-oil fractions increases with gravity. Figure 55 indicates the relationship between the gravity and the heating value of petroleum fuels.[2] The data are accurate within about 1 per cent if the percentage of water, ash, and sulfur is accounted for. In general, cracked fuel oils have a higher heating value than straight-run products.[3] Table 23 indicates the characteristics of the solid and liquid fuels that are used in the refinery. In this table the heating value, pounds air per pound fuel, and the per cent carbon dioxide were computed on the "as fired" basis. Although the heating value is of some importance in the selection of a fuel, the viscosity and atomizing properties of the oil are usually more important. Viscous fuel oils must be heated in order to obtain adequate atomization.

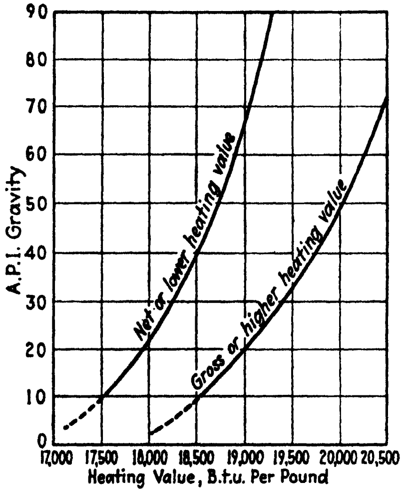

Fig. 55.—Relation of heating value and A.P.I. gravity. (*U. S. Bureau of Standards.*)

Natural gas and cracked gas are also used extensively as refinery fuels. Gas is more easily fired than solid or liquid fuels, but it has the minor disadvantage of producing a long flame, and a flame that is often deficient in its ability to radiate heat. Some of the characteristics and combustion constants for gaseous fuels are given in Table 24. The table is for gases that contain

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[2] Cragoe, C. S., *Bur. Standards Misc. Pub.* 97, 1929.

[3] Faragher, Morrell and Essex, *Ind. Eng. Chem.*, **21**, 933 (1929).

TABLE 23.—REFINERY FUELS

Fuel	A.P.I.	H_2O	Ultimate composition					Per cent undetermined, ash, etc.	Heating Value†		Lb. air per lb. fuel at 0 per cent excess air*	Per cent CO_2 at 0 per cent excess air*
			C	H_2	S	O_2	N_2		Gross	Net		
1. Mid-Continent topped crude	27.1	....	86.1	12.0	0.35	1.1		0.45	19,376	18,241	14.17	15.7
2. Topped crude, Calif	26.2	0.89	85.8	12.09	1.19	....	....	0.04	19.053	18,001	14.12	15.65
3. Mid-Continent topped crude	25.5	....	86.5	12.38	0.46	....	....	0.76	19,182	18,002	14.1	15.6
4. Mid-Continent topped crude	25.3	....	86.4	12.38	0.46	....	....	0.46	19,353	18,173	14.3	15.6
5. Mid-Continent topped crude	25.1	0.33	86.2	12.39	0.39	....	....	0.69	19,256	18,076	14.1	15.6
6. Topped crude, Ky	24.4	....	87.1	12.53	0.22	....	....	0.15	19,358	18,168	14.35	15.6
7. Mid-Continent residuum	22.0	0.05	87.4	11.1	0.42	....	....	1.03	18,778	17,723	14.0	16.0
8. Topped crude, Calif	18.7	0.05	85.6	11.4	1.6	....	....	1.35	18,607	17,522	14.0	15.8
9. Residual fuel oil, Calif	16.5	0.05	87.5	10.17	1.14	....	....	1.14	18,319	17,351	13.7	16.4
10. Fuel oil, Calif	15.6	....	84.0	12.6	0.75	2.55		0.10	18,910	17,720	14.25	15.4
11. Residual fuel oil, Ky	15.2	0.05	88.7	10.23	0.3	....	....	0.72	18,651	17,677	13.8	16.4
12. Mid-Continent residuum	14.3	0.05	87.6	10.27	0.70	....	....	1.38	18,454	17,479	13.7	16.4
13. Mexican crude	13.6	1.85	83.7	10.2	4.15	....	....	0.10	18,710	17,767	13.4	16.2
14. Cracked fuel oil, Calif	11.3	0.3	86.5	10.04	1.49	....	....	1.67	18,088	17.128	13.5	16.4
15. Mid-Continent cracked residuum	10.7	....	88.5	9.92	0.77	....	....	0.81	18.293	17,349	13.65	16.5
16. Mid-Continent cracked residuum	9.2	0.4	88.4	9.95	0.68	....	....	0.81	18,274	17,324	13.7	16.6
17. Mid-Continent cracked residuum	8.6	....	88.9	9.8	0.56	....	....	0.74	18,277	17,345	13.7	16.6
18. Mid-Continent residuum	8.1	0.25	88.5	9.07	0.67	....	....	1.51	18.077	17,212	13.4	16.9
19. Cracked residuum, Calif	8.0	0.05	88.3	9.5	1.2	....	....	0.95	18,084	17,179	13.5	16.7
20. Residual fuel oil, Calif	7.6	0.10	87.5	9.38	1.37	....	....	1.65	17,970	17,075	13.4	16.8
21. Cracked residuum, Ky	3.3	....	90.6	8.49	0.41	....	....	0.50	17,837	17,030	13.4	17.1
22. Bituminous coal, Pa	....	2.5	77.8	4.8	1.2	6.2	1.5	6.0	13.997	13.543	10.4	18.6
23. Bituminous coal, Mo	....	2.6	72.6	4.6	1.8	6.3	1.2	10.9	13.533	13.098	9.7	18.6
24. Petroleum coke	....	1.2	96.0	2.1	0.41	....	....	0.29	15,241	15.040	11.9	18.9

* On the "as fired" basis.

TABLE 24.—GASEOUS FUELS

Material	Mol. wt.	Density, lb. per cu. ft. at 60°F.	Analysis, volume per cent									Gross H.V., B.t.u. per cu. ft.	Cu. ft. air per cu. ft. gas at 0 per cent excess air	Per cent CO_2 at 0 per cent excess air
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}			
1. Methane	16	0.0422	100	...	.....	...	.....	...	.....	.....	.....	1,009	9.57	11.65
2. Ethane	30	0.0792	.....	...	100	...	.....	.....	.....	.....	.....	1.795	16.75	13.1
3. Propane	44	0.1162	.....	...	.....	...	100	...	.....	.....	.....	2.580	23.9	13.7
4. Butane	58	0.153	.....	...	.....	...	.....	...	100	.....	.....	3,350	31.1	14.0
5. Pentane	72.1	0.632*	.....	...	.....	...	.....	...	.....	100	.....	21,100†	37.9	14.2
6. Hexane	86.1	0.664*	.....	...	.....	...	.....	...	.....	.....	100	21,000†	45.5	14.3
7. Octane	100.1	0.687*	.....	...	.....	...	.....	...	.....	.....	100	20,800†	59.8	14.47
8. Natural gas, wet	21.8	0.0577	80	...	6.6	...	6.3	...	3.7	3.0	.....	1,360	12.58	11.99
9. Natural gas, wet	20.5	0.0541	81.3	...	9.8	...	5.6	...	1.7	0.9	0.5	1,253	11.85	11.96
10. Natural gas, dry	19.5	......	85.1	...	6.1	...	7.4	...	1.2	0.1	.....	1,200	11.34	11.9
11. Natural gas, dry	18.6	0.049	86.6	...	8.6	...	3.9	...	0.7	0.2	.....	1,160	10.95	11.89
12. Natural gas, dry	17.3	0.0458	90.7	...	6.2	...	2.1	...	1.0	....	.....	1,112	10.58	11.81
13. Cracked gas, wet	35.0	0.098	34.6	1.7	21.6	4.7	17.4	3.0	7.5	5.8	3.5	2,058	19.38	12.91

* Sp. gr. of liquid 60/60.

† B.t.u. per lb. of liquid.

no air or inert gases. Inert gases are usually present in amounts ranging from 1 to 10 per cent and hence the heating values of commercial gases will range from 11 to about 206 B.t.u. lower than shown in the table. The flames produced by wet gases, particularly wet cracked gases, are almost as luminous as oil flames and are good radiators.

Combustion Reactions.—The fundamental reactions which are involved in combustion are shown in Table 25. If the ultimate analysis of the fuel is available, these equations are all that are required to solve many combustion calculations.

An examination of these chemical equations yields information concerning, first, the weights of materials that react and, second, the volumes of gases that react. For example, reaction 1 indicates that 1 cu. ft. of hydrogen reacts with one-half of 1 cu. ft. of oxygen to produce 1 cu. ft. of water vapor. Likewise reaction 6 shows that one volume of methane requires two volumes of oxygen for combustion. One volume of carbon dioxide is produced and two volumes of water vapor. Volumes are directly proportional to mols, and hence the number of mols that react are directly proportional to the number of volumes that react. The molecular weight of methane is 16 and of oxygen 32. With reference to reaction 6, 16 lb. of methane reacts with 2 × 32 lb. of oxygen to produce 44 lb. of carbon dioxide and 2 × 18 lb. of water. A knowledge of these elemental combustion reactions, along with data on specific heats of the gaseous products, constitutes the bases for almost all combustion calculations.

TABLE 25.—COMBUSTION REACTIONS

Reaction	Fuel name	Mol. wt.	Heating value, B.t.u. per lb.	Lb. air per lb. fuel, no excess
1. $H_2 + \frac{1}{2}O_2 = H_2O$	Hydrogen	2	62,000	34.8
2. $C + O_2 = CO_2$	Carbon	12	14,600	11.6
3. $C + \frac{1}{2}O_2 = CO$	Carbon	12	4,440	5.8
4. $CO + \frac{1}{2}O_2 = CO_2$	Carbon monoxide	28	10,160	2.48
5. $S + O_2 = SO_2$	Sulfur	32	4,050	4.35
6. $CH_4 + 2O_2 = CO_2 + 2H_2O$	Methane	16	23,800	17.28
7. $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	Ethylene	28	21,600	14.81
8. $C_2H_6 + 5O_2 = 2CO_2 + 3H_2O$	Ethane	30	22,650	16.13

These reactions do not take place completely to the formation of the products indicated in Table 25 unless an excess of oxygen or air is present. The extent to which the reaction will be completed can be computed by applying the law of mass action, but such computations are of little value in commercial work. In firing a commercial furnace the use of too little excess air is evident at once by carbon monoxide or even smoke in the stack gas. Carbon monoxide is seldom found in the flue gas from oil stills because at least 30 per cent of excess air is normally used in order to keep a low furnace temperature, and no carbon monoxide is produced under these conditions if effective burners are used. High furnace temperatures tend to cause the formation of coke in the tubes or still. Not many years ago furnace designers felt that 75 per cent of excess air was necessary to keep the furnace cool, but modern methods of furnace design permit the use of as little as 20 per cent excess air.

The pounds of air required for the combustion of a pound of fuel can be stated as an equation by the use of Table 25. The symbols refer to the pounds of hydrogen, carbon, sulfur, and oxygen that are present in a pound of fuel.

$$\text{Lb. air required per lb. of fuel (no excess)} = 34.8H_2 + 11.6C + 4.35S - 4.31O_2 \quad (15)$$

The pounds of flue gas per pound of fuel can be obtained by adding 1 to the pounds of air per pound of fuel. The molecular weight of flue gas including the water vapor that it contains is approximately 30.

Example 25. Weight and Volume of Flue Gas.—Fuel 1 in Table 23 is to be burned with 40 per cent excess air. How many pounds of flue gas will be produced per pound of fuel and what will the volume of the flue gas be at 600°F.?

Assume half of the 1.1 per cent of N_2 and O_2 is oxygen.

$$\text{Lb. air (no excess)} = 34.8 \times 0.12 + 11.6 \times 0.861 + 4.35 \times 0.0035 - 4.31 \times 0.0055 = 14.171$$

$$\text{Lb. air at 40 per cent excess} = 14.17 + 0.4(14.17) = 19.84$$

$$\text{Lb. flue gas} = 19.84 + 1 = 20.84$$

$$\text{Volume at 600°F.} = \frac{20.84}{30} \times 379 \times \frac{1{,}060}{520} = 536 \text{ cu. ft.}$$

Specific Heats of Combustion Products.—The heat that is contained in the flue gas as it enters the stack is an important item in a heat balance. Figure 56 is a chart showing the sensible heat content of the several gases that are found in flue gas. The *sensible heat content* may be defined as the amount of heat required to change the temperature of a quantity of material

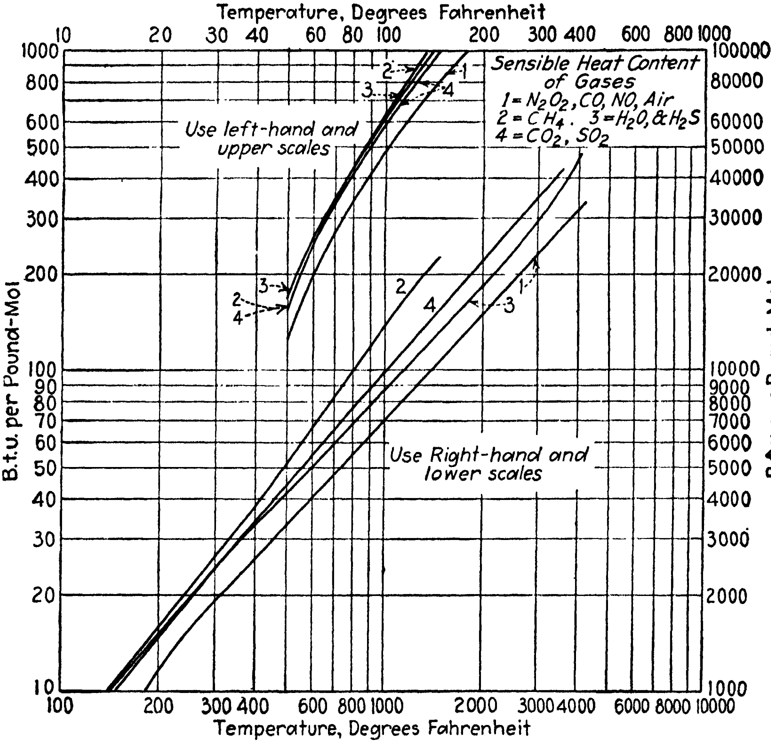

FIG. 56.—Sensible heat chart of common gases (basis 32°F.).

from one temperature to another by simple heating. No changes of state, such as vaporization or fusion, are involved.

$$\text{Sensible heat content} = W(T_2 - T_1)C_p$$

where W = lb. material (lb.-mols in Fig. 56).
T_2 = final temperature, °F.
T_1 = initial temperature, °F.
C_p = average sp. ht. at constant pressure, B.t.u. per lb. through the temperature range of T_2 and T_1.

Figure 56 is plotted on a mol basis because the diatomic gases—oxygen, nitrogen, carbon monoxide, air, etc.—can be represented by a single curve. The same applies to other groups of gases. The figure gives the number of B.t.u. required to raise the temperature of 1 lb.-mol of gas from 32°F. to the desired temperature. The upper and left scales are for temperatures up to about 150°F. and the lower and right scales are for higher temperatures.

Example 26. Use of Sensible Heat Chart for Gases (Fig. 56).—One thousand cubic feet of a flue gas is cooled from 1000 to 100°F. Analysis of gas: CO_2 10 per cent, H_2O vapor 12 per cent, O_2 3.7 per cent, and N_2 74.3 per cent. How much heat must be removed?

$$\text{Mols } CO_2 = \frac{1000 \times 0.10}{379} = 0.264$$

$$\text{Mols } H_2O = \frac{1000 \times 0.12}{379} = 0.316$$

$$\text{Mols diatomics} = \frac{1000 \times 0.743}{379} + \frac{1000 \times 0.037}{379} = 2.057$$

Sensible Heat, B.t.u. per Mol

Material	At 1000°	At 100°
CO_2.	9850	580
H_2O	8650	610
Diatomics.	7000	478

Heat removed from CO_2 = 0.264(9,850 − 580) = 2,445 B.t.u
Heat removed from H_2O = 0.316(8,650 − 610) = 2,540
Heat removed from diatomics = 2.057(7,000 − 478) = 13,400

Total heat removed = 18,385 B.t.u.

Although heat quantities must sometimes be computed as in Example 26, the charts (Figs. 57, 58) are more convenient and are sufficiently exact for most computations. These charts are based on the net heating value because the net heating value is a more honest basis for efficiency calculations than the gross heating value. Although these charts were computed for specific fuels, they can be used for other similar fuels without great inaccuracy. They should not be used for computations with fuels that are abnormal. The subject of heat balances and material balances will be discussed more completely in Chap. XII.

Example 27. Use of Combustion Charts (Fig. 57, 58).—A 20 A.P.I. fuel oil is burned and the gases are cooled to 300°F. The heating value of the fuel is 17,900 B.t.u. per pound net; carbon dioxide, 13 per cent. How

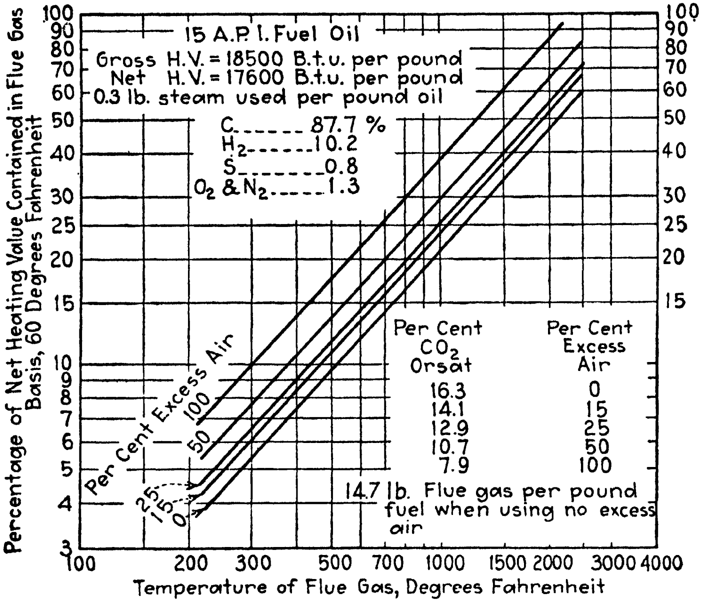

FIG. 57.—Fuel-oil combustion chart.

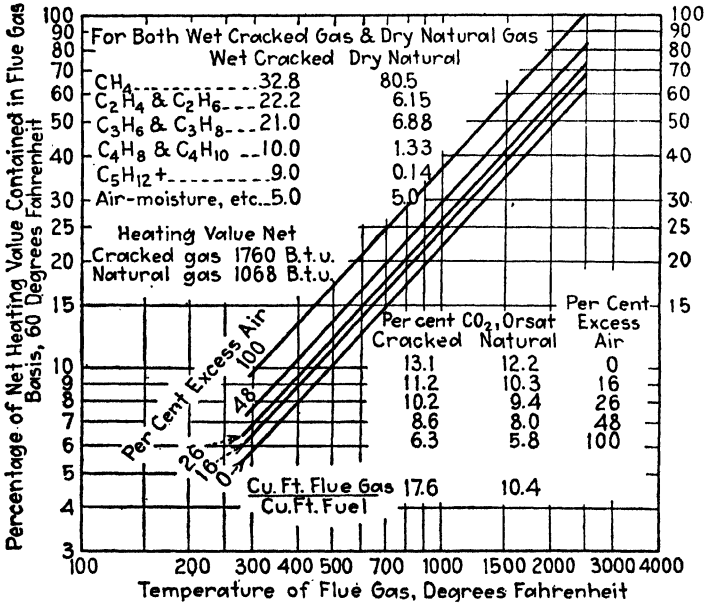

FIG. 58.—Gas combustion chart.

much heat is lost to the stack and how many pounds of flue gas are produced? Basis: 1 lb. of fuel and 60°F. (Fig. 57).

At 13 per cent CO_2 the per cent excess air is approximately 23. Reading between the 15 and 25 per cent excess air curves, the heat lost to the stack at 300°F. is about 6.3 per cent. This amounts to $0.063 \times 17{,}900$ or 1,130 B.t.u. per pound of fuel. Also, 14.7 lb. of flue gas or 13.7 lb. of air is required to burn 1 lb. of the fuel if no excess air is used (Fig. 57). At 23 per cent excess air the pounds of flue gas is

$$13.7 \times 1.23 + 1 = 17.9 \text{ lb. per lb. of fuel.}$$

The Burning of Oil Fuels.—In refineries or small boiler plants, fuel oil can usually be burned more efficiently than coal or gas. However, large stoker-fired coal furnaces or powdered-fuel furnaces are about as efficient as oil-fired furnaces. At low firing rates the steam-atomizing oil burner is most satisfactory but at high firing rates the mechanical-atomizing burners are preferred. Steam-atomizing burners are widely used in the refinery.

In order to fire an oil fuel successfully and economically, the following factors should be considered:

1. The burners must be designed so that the oil is effectively atomized.
2. During the atomization the droplets of oil must be brought into contact with enough air (primary air) to assure continuous combustion.
3. Immediately after atomization the oil spray must be heated to cause vaporization and to promote combustion throughout the entire volume of air-fuel mixture. This is usually accomplished by the use of a fire-clay firing-tunnel through which the flame passes into the combustion space. Failure to vaporize and ignite the flame rapidly, results in a long flame which tends to impinge on the heating surfaces or the furnace walls. Secondary air must be available to the flame as it leaves the firing-tunnel.
4. The furnace combustion space must be ample for a normal length of travel of the flame. The burners and heating surface must be arranged so that impingement does not take place and so that all parts of the heating surface are as nearly as possible at an equal distance from the flame. Flame impingement or local overheating is important in boilers but not so vital as in oil stills. Oils are sensitive to heat, and a condition of local overheating may cause (a) discoloration of the product and subsequent expensive treating operations, (b) a loss in viscosity of the lubricating-oil stocks, and (c) in extreme cases a serious decomposition with the formation of gas, lower boiling oils, and coke.

Atomizing.—The success of oil firing rests largely with the obtainment of proper atomization. The atomizing properties of an oil depend on the viscosity and to some extent the surface tension. In general, it appears that atomization is not effective unless the viscosity of the oil is below about 30 centipoises at the temperature at which the oil is fed to the burner. This corresponds to an approximate Universal Saybolt viscosity of 150 sec. at the firing temperature. In still a more general way the proper temperature can be estimated from the gravity of the oil. The Babcock and Wilcox Company suggest

A.P.I.	11–13	14–16	15–17	17–20	20–24	24–30
°F	220–240	200–220	180–190	140–180	100–140	80–100

This tabulation should serve only for estimates, because many 10 A.P.I. cracked fuel oils do not need to be heated and some 26 A.P.I. naphthene residues must be heated to 180°F.

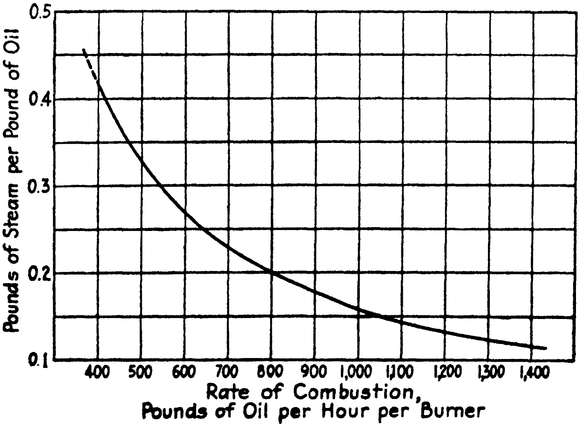

FIG. 59.—Steam required to atomize oil. (*Gebhardt*, "*Steam Power Plant Engineering*," *John Wiley & Sons, New York.*)

The amount of steam required for atomization is also dependent on the viscosity but it is influenced more by the care used by the fireman and by the rate of firing than by the viscosity. In modern pipestill practice the steam consumption usually amounts to about 0.4 lb. of steam per pound of oil. Surveys of boiler practice indicate that the steam consumption of burners amounts to from 0.5 to 8 per cent of the total steam that is generated. This corresponds to 0.1 to 1.2 lb. of steam per pound of fuel oil. Thus an important inefficiency can exist without attracting much attention. If the burners are carefully adjusted and a hot, clean fuel is available, the steam consumption can be kept to 0.15 lb. The steam consumption for different rates of firing can be estimated from Fig. 59. These data[4] were obtained with the use of Hammel oil burners. For steam-atomizing burners the oil should be at a pressure of 40 to 60 lb. per square inch at the burner. Figure 60 illustrates several types of steam-atomizing nozzles.

Mechanical-atomizing burners have not been generally used in the oil industry. However, a mechanical burner or a combination steam- and mechanical-atomizing burner is useful when firing inferior fuels, such as cracked residues that contain suspended carbon, or acid sludges from lubricating oil treating. These inferior fuels are supplied to the burner at 200 to 300°F. and at a pressure of 100 to 200 lb. per square inch. Acid sludge, without any treatment, can be burned in some mechanical burners but more often the sludge is hydrolized with water and allowed to settle. Acid sludge is often mixed with fuel oil and the mixture is burned. Acid sludge is not a good fuel but it must be disposed

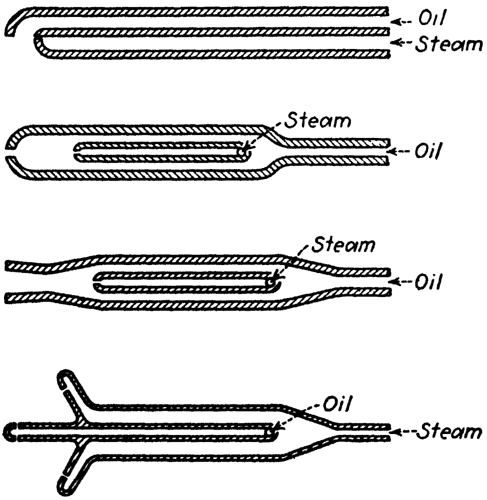

FIG. 60.—Nozzles for steam-atomizing burners.

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[4] GEBHARDT, G. F., "Steam Power Plant Engineering," 6th ed., p. 256, John Wiley & Sons, Inc., New York, 1928.

of, and burning is one of the simplest solutions to a troublesome problem.

Fuel Oil Circulating System.—The fuels that are burned in the refinery are often hardly more than waste products. Tars that are almost solid are common. Such fuels must be heated in order to pump them to the burners and they must be circulated continuously past the burner to prevent solidification in the line. The general method of circulation is indicated in Fig. 61. In large plants the circuit may be so long that a system of parallel flow must be used. In the parallel system a small flow of oil must be maintained in each of the parallel branches.

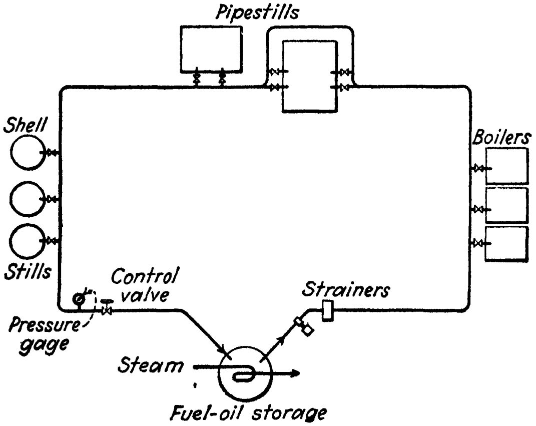

FIG. 61.—Circulating system for fuel oil.

Individual circulation systems are often maintained for each pipestill. With such an arrangement the rate of firing may be controlled by regulating the pressure in the fuel line without visiting the burner. The pressure may be conveniently regulated at a central control board. Such a system is not satisfactory unless clean, fluid fuels are available and unless minor adjustments of the firing rate are all that are necessary.

Combustion Data.—In computing an accurate heat balance as explained in Chap. XII, certain laboratory data are necessary. Among these data are (1) the heating value of fuel, (2) ultimate analysis of fuel, and (3) Orsat analysis of the flue gas. The heating value of a solid fuel may be determined by the bomb methods[5] using any of the common bombs such as the Atwater, Emerson, Parr, or Williams. The heating value of gaseous fuels is determined in Junkers-type calorimeters[6] such as the Sargent calorimeter. The ultimate analysis of fuels showing the percentage of carbon, hydrogen, etc., is determined by burning a sample of the fuel under controlled conditions and absorbing the various constituents of the combustion gas in chemical solutions.[7] These solutions are then analyzed by the regular quantitative chemistry methods.

The Orsat-type apparatus[6] for the analysis of flue gas is offered in many modifications such as the Hay's portable analyzer, Williams', Orsat-Lunge, etc. Carbon dioxide, sulfur dioxide, oxygen, carbon monoxide, and nitrogen (by difference) can be determined in these equipments. The carbon dioxide is absorbed by a solution of caustic soda and any other acid gases, such as sulfur dioxide and hydrogen sulfide, are absorbed with the carbon dioxide and are reported as carbon dioxide. The flue gas is cooled to room temperature during the analysis, and hence most of the water vapor which it contains is condensed. Thus the Orsat analysis is not the analysis of the gas that is present in the furnace or stack because the gas in the furnace contains water vapor. The analysis of the flue gas including the water vapor must be obtained by calculation.

Example 28. Analysis of Flue Gas from Fuel Analysis.—Fuel 1 in Table 23 is burned with 50 per cent excess air. Compute the Orsat analysis of the flue gas and the analysis of the flue gas including water vapor.
Basis: 1 lb. of Fuel 1.

$$\text{Mols C} = \frac{0.861}{12} = 0.0717$$

$$\text{Mols } H_2 = \frac{0.12}{2} = 0.0600$$

$$\text{Mols S} = \frac{0.0035}{32} = 0.0001$$

$$\text{Mols } N_2 \text{ and } O_2 = \frac{0.011}{30} = 0.0004 \text{ (assume half and half)}$$

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[5] Petroleum Products and Lubricants, *Report of Committee* D-2, A.S.T.M., 1933.

[6] WHITE, A. H., "Technical Gas and Fuel Analysis," McGraw-Hill Book Company, Inc., New York; GILL, A.H. "Gas and Fuel Analysis," John Wiley & Sons, Inc., New York.

[7] BORN, S., Combustion in the Petroleum Industry, *Petroleum Eng.*, October, 1931, p. 140.

Oxygen required (see Table 25):

Mol

For carbon: $0.0717 \times 1 =$ 0.0717

For hydrogen: $0.06 \times 0.5 =$ 0.0300

For sulfur: $0.0001 \times 1 =$ 0.0001

0.1018

Less oxygen in fuel: $\frac{0.0004}{2} = -0.0002$

Oxygen required (no excess) = 0.1016

Excess oxygen (or air) = $0.1016 \times 0.5 =$ 0.0508

Oxygen required at 50 per cent excess = 0.1524

Composition of air by volume is N_2 79.1 and O_2 20.9 per cent.

Nitrogen with this oxygen: $0.1524 \times \frac{79.1}{20.9} = 0.577$ mol

Nitrogen in fuel: $\frac{0.0004}{2} = 0.0002$ mol

Nitrogen in flue gas = 0.5772 mol

ORSAT ANALYSIS

Material	Number of mols	Per cent by volume
CO_2 (and SO_2)	0.0717 and 0.0001	10.25
O_2 (excess)	0.0508	7.26
N_2	0.5772	82.49
Total	....	100.00

ACTUAL ANALYSIS IN FURNACE

Material	Number of mols	Per cent by volume
CO_2 (and SO_2)	0.0718	9.4
O_2	0.0508	6.7
N_2	0.5772	76.0
H_2O*	0.0600	7.9
		100.0

* Table 25.

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CHAPTER XII

HEAT AND MATERIAL BALANCES

The computation of heat, material, energy, volume, and weight balances is doubtless the most important type of computation that is available to the engineer. Practical problems always involve energy or material balances in some phase of their solution. These computations are used so generally that they are not always recognized as such.

Basis for Computation.—The selection of the basis for computation is an important factor in the ease of solution of a problem. In the solution of gas problems the most common basis is 1 cu. ft. (or 100 cu. ft.), measured at 60°F. Oil computations are usually based on the gallons of oil per hour, measured at 60°F. Fractionating-tower heat-balances are computed about the temperature datum of (1) the temperature at the vaporizer section of the tower or (2) the temperature at the top plate. Volumes of oil, A.P.I. gravities or specific gravities, and heating values are usually stated at 60°F. Analyses of oils are usually stated as percentage by volume; gas analyses are given as percentage by volume or mol per cent; and analyses of solids are given in percentage by weight.

The molecular weight is a fundamental physical and chemical unit and computations may often be simplified by using the pound- or gram-mol as the basis. The number of computations is often cut in half by the use of the mol basis. This is particularly true if chemical reactions occur. Pound-mols of a gas (perfect) may be converted to volume, measured at 60°F., by multiplying by 379. Mols may be converted to pounds by multiplying by the molecular weight. The mol basis may be used during the calculation and the final quantities converted from mols to pounds or cubic feet as the final step in the calculation. By Avogadro's hypothesis, equal volumes of gases contain the same number of molecules or mols. Hence the number of mols that react together is directly proportional to the volumes of gases that react, and volume percentage is proportional to mol percentage. Likewise Dalton's law of partial-pressures states that the fraction of the total pressure that is exerted by a gas in a gaseous mixture is proportional to its volume percentage in the mixture. Thus the following useful generalization concerning gases is possible:

Volume per cent = mol per cent = pressure per cent (partial-pressure) (16)

Many of the difficulties in the solution of problems arise because of a hazy conception of the basis upon which the computation is based. This is particularly noticeable with students, but even practicing engineers are frequently confused over the basis of a problem. In order to clarify the sequence of thought in a computation, the basis should be clearly stated at the beginning of the calculation. If it becomes convenient to adopt a new basis during the calculation, a statement of the new basis indicating its relation to the old basis should be inserted.

Conversion Constants.—In the solution of energy and material balances it becomes necessary to convert energy or mass from one form to another. The following is a list of a few of the more important conversion constants:

1 in. = 2.54 cm. = 25.4 mm.
1 ft. = 0.3048 m.
1 lb. = 0.4536 kg. (1 kg. = 2.204 lb.)
1°C. change in temperature = 1.8°F. change in temperature
°Kelvin = °C. abs. = °C. + 273
°Rankin = °F. abs. = °F. + 460
°F. = (°C. + 40)1.8 − 40
°C. = (°F. + 40) ÷ 1.8 − 40
1 standard petroleum barrel = 42 U.S. gal. (sometimes 50, lubricating-oil barrel 55)
1 bbl. per day = 1.75 gal. per hr.
1 cu. ft. = 7.48 gal.
1 gal. = 3.786 l. = 3,786 cc.
Density of water at 60°F. = 8.328 lb. per gal.
= 62.37 lb. per cu. ft.
1 atm. at sea level = 760 mm. of mercury
= 29.92 in. of mercury
= 14.697 lb. per sq. in.
= 34 ft. of water
1 lb. per sq. in. = 2.31 ft. of water (Fig. 52)
= 51.7 mm. of mercury
= 0.0703 kg. per sq. cm.

1 g.-mol volume = 22.41 l. at 0°C. and 760 mm.
1 lb.-mol volume = 359 cu. ft. at 32°F. and 760 mm.
= 379.4 cu. ft. at 60°F. and 760 mm.
1 kg.-cal. = 3.968 B.t.u.
1 cal. per g. = 1.8 B.t.u. per lb.
1 B.t.u. = 777.5 ft.-lb.
1 kw.-hr. = 1.341 hp.

Conservation of Mass.—The familiar law of the conservation of mass forms the basis for material balance computations. This law is often stated as "The total mass of a system is the same before and after a chemical or physical change occurs." The application of this law to engineering problems is indeed simple and often the engineer applies the law without even recognizing it. Stated in perhaps a simpler way, it may be said that all that goes into a processing system must come out of the system.

The importance of the basis that is used in a calculation is illustrated by Example 29.

Example 29. Conservation of Mass.—One thousand pounds of a solid containing 25 per cent by weight of moisture is dried until it contains only 1 per cent by weight. How much water must be removed?
Basis: 1 lb. of dry solid.

Into processing system, 1.0 lb. of solid carries with it $1 \times 0.25/0.75$ or 0.333 lb. of water. One pound of solid must also leave the system.
Moisture leaving system,

$$\frac{1.0}{0.99} \times 0.01 = 0.0101 \text{ lb. of water}$$

$$\text{Water removed per lb. of dry solid} = 0.3232$$

Total water removed,

$$750 \times 0.3232 = 242 \text{ lb.}$$

Any other basis than the dry-solid basis would probably have led to undue complications and perhaps errors might have arisen because of a befuddled conception of the basis. In many processing systems the materials entering and leaving the system are measured by volume rather than by weight and in such cases it is always safest to convert all quantities to a weight basis.

Example 30. Gravity of Residue by Material Balance.—A 37 A.P.I. crude oil is being processed for the production of 30 per cent of 55 A.P.I. gasoline, 10 per cent of 42 A.P.I. kerosene, 15 per cent of 36 A.P.I. gas oil, and a residual stock. The percentages are by volume measured at 60°F. What is the A.P.I. of the residual stock?

Basis: 100 gal. of crude oil measured at 60°F.

Material	Per cent by volume	A.P.I.	Lb. per gal.	Lb.
Gasoline	30	55	6.316	189.5
Kerosene	10	42	6.790	67.9
Gas oil	15	36	7.034	105.3
Residue	45	?	?	?
Crude	100	37	6.993	699.3

Pounds residue stock,

$$699.3 - (189.5 + 67.9 + 105.3) = 336.6$$

Density of residue stock,

$$\frac{336.6}{45} = 7.48 \text{ lb. per gal.}$$

This corresponds to an A.P.I. of 26.

This method of solution is satisfactory because petroleum oils behave as almost pure solutions. In other words, if 1 gal. of oil A is mixed with 1 gal. of oil B, the resultant volume is 2 gal. Certain liquid combinations, such as alcohol-water and sulfuric acid-water, do not behave thus.

Conservation of Energy.—The law of conservation of energy is of more general usefulness than the law of conservation of mass. This law is also called the *first law of thermodynamics* and is stated in many different ways depending upon the use to which it is to be put. The following are perhaps the most common statements: (1) Energy in the form of heat may be converted into mechanical work and likewise energy in the form of mechanical work may be converted into heat; (2) energy may undergo change in form but not in amount.[1] Heat and mechanical work are the most common forms of energy and hence the law may be conveniently expressed as the following mathematical expression:

$$h = \Delta u + w \tag{17}$$

h = all energy absorbed by the system from the surroundings. Heat energy is often the only energy form that is added to the system although any other energy addition may be included in this term.

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[1] The author suggests: The energy that goes into a system is equal to the energy that leaves the system except for changes in the internal energy content.

Δu equals the increase in the internal energy content of the system. This increase may be evidenced in any form of energy such as an increase in pressure or temperature, in changes of phase such as vaporization, increases in surface energies, chemical energy, etc. In ideal gas cycles, in which no chemical reactions occur, no change in the internal energy is possible unless the temperature changes. In such special cases the change in internal energy is equal to the energy required to heat the gas at constant volume.

w equals all work done by the system on the surroundings. Usually only the mechanical work done on the surroundings is considered, but properly this term should include all forms of energy that might leave the system, including losses.

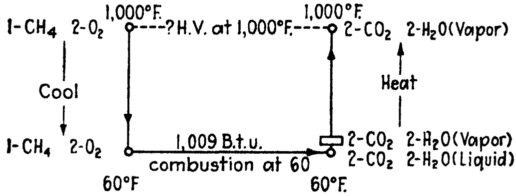

FIG. 62.—Thermodynamic cycle. Example 31.

An exceedingly useful corollary of the first law may be summarized as follows: The energy content of a system at a fixed and complete set of conditions is a constant and hence the difference in the energy content of a system between two sets of conditions is also a constant. Because energy cannot be destroyed, it appears that the algebraic sum (or difference) of the energy inputs and expenditures required to get from one condition to another will be a constant regardless of the sequence of the changes or the number of energy changes involved.

The two following examples and Example 9 (page 107) illustrate this corollary.

Example 31. Heating Value at Another Temperature Than 60°F.—The heating value of methane (CH_4) is 1009 B.t.u. per cubic foot at 60°F. What will its heating value be if the gas, along with its air, is burned at 1000°F. and the products are cooled to 1000°F.?

Basis: 1 cu. ft. of methane measured at 60°F. and 760 mm. pressure.

$$CH_4 + 2O_2 = CO_2 + 2H_2O - 1009 \text{ B.t.u. per cu. ft.}$$

Since the difference in energy content of CH_4 and O_2 at 1000°F. and the products of combustion, CO_2 and H_2O, at 1000°F. is a constant, we may complete the combustion reaction by any series of steps (Fig. 62).

The system is taken through the following particular series of steps because data are available for each of the operations.

Cool (sensible heat):

CH_4: $\frac{1}{379}(245 - 13{,}800) = -\ 35.8$ (Fig. 56)

$2O_2$: $\frac{2}{379}(200 - 7{,}000) = -\ 35.9$ (Fig. 56)

Gross heating value at 60°F. $1 \times (-1{,}009) = -1{,}009.0$

$-1{,}080.7$

Vaporize water at 60°F. $\frac{2 \times 18}{379} \times (1{,}058.2) = +\ 100.4$

Heat (sensible heat):

$2CO_2$: $\frac{2}{379}(9{,}850 - 245) = +\ 50.75$ (Fig. 56)

$2H_2O$: $\frac{2}{379}(8{,}650 - 270) = +\ 44.3$ (Fig. 56)

Heating value of CH_4 from and to 1000°F. $= -885.25$ B.t.u. per cu. ft. (measured at 60°F.)

Example 32. Total Heat Required to Vaporize Gasoline at Different Temperatures.—A 60 A.P.I. gasoline at 100°F. is to be heated, vaporized, and superheated to 500°F. at atmospheric pressure. How much heat is required per pound of gasoline?

The vaporization of complex mixtures differs from the vaporization of pure compounds because vaporization occurs throughout a range of temperature. According to the corollary to the first law, the temperature at which vaporization occurs can be any temperature at which the latent heat is known, provided all of the energy changes that are involved are properly considered.

For comparison, the total heat input will be computed for vaporization at the temperatures of 250, 300, 350, and 400°F.

Basis: 1 lb. gasoline (Figs. 33 and 34 and Table 8).

Vaporizing at °F.	Sensible heat of liquid		Latent heat		Sensible heat of vapor		Total heat, B.t.u. per lb.
250	1(250 − 100)0.563	+	130.8	+	1(500 − 250)0.53	=	347.4
300	1(300 − 100)0.58	+	123.3	+	1(500 − 300)0.541	=	347.5
350	1(350 − 100)0.595	+	115.5	+	1(500 − 350)0.554	=	347.6
400	1(400 − 100)0.61	+	107.7	+	1(500 − 400)0.568	=	347.5

The discrepancy of about 0.2 B.t.u. may be explained by inaccuracy of the data for specific heats and latent heats. Furthermore, the vaporization at 250°F. must take place at a reduced pressure, and vaporization at 400°F. at a pressure higher than atmospheric pressure (see Example 9, page 107).

Heat-balances.—Certain special cases arise in which the change in energy content of a system involves only heat energy and chemical energy, or at least other energy changes are negligiible. Such processes may be studied by means of the heat-balance. With reference to the mathematical expression for the first law, all three of the items will involve changes in heat energy and chemical energy.

The following examples serve to illustrate both heat and material balances.

Example 33. Heat-balance of a Furnace.—Fuel 12 (Table 23) is fired at 200°F. using 0.4 lb. (280°F.) of steam per pound of fuel. The flue gas has an Orsat analysis of 13.0 per cent of CO_2, 4.25 per cent of O_2, and 82.75 per cent of N_2. The heat gainfully used to heat oil amounts to 1,367,000 B.t.u. The stack temperature is 800°F. The air is at 80°F. and has a relative humidity of 50 per cent. The vapor-pressure of water at 80°F. is 26.6 mm. The still is operating in a continuous manner.

Basis: 100 lb. of oil 12, 60°F. temperature datum.

The ultimate constituents in the fuel undergo the following chemical reactions:

$$\begin{aligned} C + O_2 &= CO_2 \\ H_2 + \tfrac{1}{2}O_2 &= H_2O \\ S + O_2 &= SO_2 \\ H_2O \text{ (liquid)} &= H_2O \text{ (vapor)} \end{aligned}$$

Mols of combustion products:

Carbon............. $\frac{87.6}{12} = 7.3$

Sulfur.............. $\frac{0.7}{32} = 0.02$ (reported as CO_2 by Orsat)

Hydrogen........... $\frac{10.27}{2} = 5.14$

Water.............. $\frac{0.05}{18} = 0.003$ (neglect)

Undetermined....... $\frac{1.38}{30} = 0.05$ (considered as O_2 and N_2, equal parts)

Material balance of carbon:

Mols of dry flue gas from 100 lb. of fuel. Mol per cent = volume per cent (gases).

All of the carbon is found in the carbon dioxide (13 per cent).

$$\begin{aligned} &\text{Mols } CO_2 \text{ (and } SO_2) &&= 7.32 \\ &\text{Mols } N_2 = 7.32 \times \frac{82.75}{13} &&= 46.50 \\ &\text{Mols } O_2 = 7.32 \times \frac{4.25}{13} &&= 2.39 \\ &\text{Total mols of dry flue gas} &&= 56.21 \text{ mols} \end{aligned}$$

Material balance of oxygen:

Air required:

$$\text{Mols } N_2 \text{ from air} = 46.5 - \frac{0.05}{2} = 46.475$$

$$\text{Mols } O_2 \text{ used} = 46.475 \times \frac{20.9}{79.1} + .025 = 12.28$$

$$\text{Mols air} = 46.475 \times \frac{1}{0.791} = 58.7$$

Per cent of excess air:

$$O_2 \text{ required for C and S} = 7.32 \text{ mols}$$

$$O_2 \text{ for hydrogen} = \frac{5.14}{2} = 2.57$$

$$O_2 \text{ required} = 9.89 \text{ mols}$$

$$\text{Per cent of excess } O_2 \text{ or air} = \frac{12.28 - 9.89}{9.89} \times 100 = 24.2 \text{ per cent}$$

Material balance of water vapor:

Water in	Mols
Atomizing steam $= 100 \times \frac{0.4}{18}$	= 2.22
From H_2 in fuel (same number mols as H_2)	= 5.14
From air $= \frac{13.3}{(760 - 13.3)} 58.7$	= 1.04
Free moisture in fuel (negligible)	= 0.00
Total	= 8.40

The water vapor leaving the system in the flue gas must equal the water coming into the system or 8.4 mols.

Heat balance:

Heat Entering System		B.t.u.
Net heating value of fuel	17,479 × 100 =	1,747,900
Heat in air (note Fig. 56)	58.7(336 − 196) =	8,210
Heat in steam (see Fig. 56 or steam tables)	0.4 × 100(2,200 − 260) =	77,600
Sensible heat content of fuel oil	100(200 − 60)0.442 =	6,190
		1,839,900

All of this heat will be recovered from the system if the flue gas is cooled to 60°F.

Heat Leaving System

Sensible heat content (see Fig. 56) at 800°F.:

CO_2	7.32(7,600 − 245) =	53,900
Water vapor	8.4 (6,800 − 260) =	54,900
Diatomic gases (N_2 and excess O_2)	48.89(5,500 − 200) =	259,000
		367,800 B.t.u.

Summary of heat-balance:

Heat	B.t.u.	Per cent
Into system	1,839,900	100.0
Out of system:		
Useful heat (given)	1,367,000	74.25
Stack loss	367,800	19.9
Unaccounted for and losses	105,100	5.73
	1,839,900	100.0

Approximate stack loss using Fig. 57:

Stack loss at 800°F. and with 13 per cent of CO_2 in the flue gas (25 per cent of excess air) = 19.6 per cent (in foregoing, 19.9 per cent)

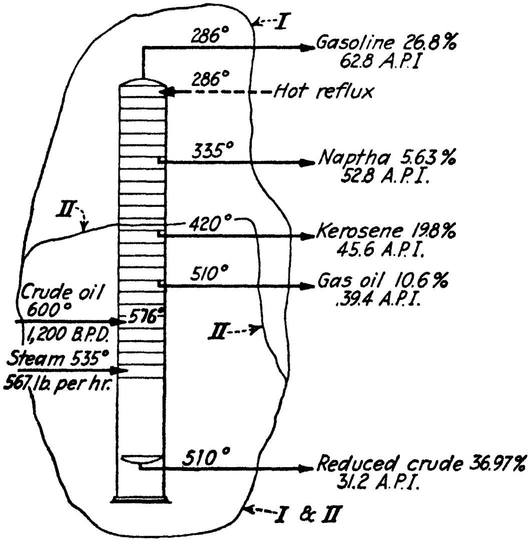

FIG. 63.—Simple tower system.

In this example the system consists of the fuel, air, steam, and the products of combustion. The products include the combustion gas, excess air, atomizing steam, and the water vapor from the air.

Applying the equation

$$h = \Delta u + w$$

the symbol h refers to the sensible heat content of the air above 60°F., the sensible heat content of the steam above 60°F., and the sensible heat content of the fuel above 60°F.

The change in internal energy (Δu) is represented by the decrease in chemical energy as the fuel burns. The system decreases in energy content by the amount of the net heating value of the fuel. In combustion calculations the heat input is considered as ($h + \Delta u$) which amounts algebraically to transferring the Δu term in the foregoing equation as follows:

$$h - (-\Delta u) = w = h + \Delta u$$

The work done or the heat added to the surroundings is represented by w. This term consists of the stack losses (eventually transferred from the system to surroundings), the heat lost to the furnace walls, air, soil, foundations, etc., and the useful heat.

Example 34. Heat-balance of a Fractionating Tower.—The simple tower system shown in Fig. 63 will be studied by means of a heat-balance to determine the amount of reflux (286°F.) that must be supplied in order to cause the tower to function as a fractionating device. Capacity, 1,200 barrels per day.

Basis: 1 hr., 2,100 gal. per hour.

The properties of the feed and products are as follows:

	Volume, per cent	A.P.I.	Lb. per gal.	Gal. per hr.	Lb. per hr.	50 per cent B.P.	Mol. wt.	Latent heat*
Gasoline	26.8	62.8	6.06	563	3,415	260	110	127.0
Naphtha	5.63	52.8	6.39	118	754	370	144	118.0
Kerosene	19.8	45.6	6.65	416	2,765	460	178	106.0
Gas oil	10.6	39.4	6.89	222	1,530	585	234	96.0
Reduced crude	36.97	31.2	7.24	776	5,610			
Loss	0.2	....	....	.....	96			
Crude	100.00	43.0	6.75	2,100	14,170			

* The latent heats (Table 8) were taken at the temperatures in the tower at which the materials condense, *i.e.*, 286, 335, 420, and 510°F. respectively, and not at the average atmospheric boiling-points of the products.

This problem might be analyzed as the preceding example, by using a temperature basis of 60°F. However, the solution is facilitated by selecting the vaporizer temperature as the temperature datum and computing directly the heat that must be removed from the system by the reflux.

Basis: Temperature datum 576°F.

The system consists of the crude oil and process steam. At 576°F. the gasoline, naphtha, kerosene, and gas oil are vapors and the reduced crude oil is a liquid. A sufficient quantity of heat must be removed from the vapors to cool them to the temperatures at which they are withdrawn from the tower and to condense the naphtha, kerosene, and gas oil at their withdrawal temperatures.

Heat to be removed by the reflux:
Sensible heat:

			B.t.u.
Gasoline	3,415(576 − 286)0.56	=	555,000
Naphtha	754(576 − 335)0.565	=	102,800
Kerosene	2,765(576 − 420)0.58	=	250,000
Gas oil	1,530(576 − 510)0.592	=	59,800
Reduced crude	5,610(576 − 510)0.722	=	268,000
			1,235,600
Steam	567(535 − 286)0.5	=	70,600
			1,306,200
Latent heat:			
Naphtha	754 × 118	=	89,000
Kerosene	2,765 × 106	=	294,000
Gas oil	1,530 × 96	=	147,000
Total heat to be removed		=	1,836,200

The gasoline, naphtha, kerosene, and gas oil were cooled as vapors and hence the specific heats of vapors (Fig. 34) were used but the reduced crude oil was cooled as a liquid (Fig. 33).

Bernoulli's Theorem.—Bernoulli's theorem is used in the solution of many hydraulics problems. This theorem is a special case of the first law of thermodynamics in which changes in the energy content of a fluid system are balanced against one another. Although friction losses are evident as heat, the theorem is concerned only with the pressure and energy changes, and heat is considered as lost energy. Bernoulli's theorem may be stated as follows:

$$\left.\begin{array}{r} X_a\ \text{(static head)}\\ +\dfrac{u_a^2}{2g}\ \text{(velocity head)}\\ +P_aV_a\ \text{(pressure head)}\\ +W\ \text{(mechanical work)}\end{array}\right\} = \left\{\begin{array}{l} X_b\\ +\dfrac{u_b^2}{2g}\\ +P_bV_b\\ +F\ \text{(friction)}\end{array}\right\} \tag{18}$$

Example 35. Hydraulic Energy Balance.—A tank of water at 150°F. (specific gravity 0.985, viscosity 0.433 centipoise) is discharging through a standard 2-in. pipe system at the rate of 120 gal. per minute by its own hydrostatic head. Figure 64 indicates the pipe system. What is the height of the water above the discharge point?

In this problem the only energy input to the system is the difference in the static head ($X_a - X_b$). This energy is dissipated as friction losses in the pipe and fittings, in the entrance to the line from the tank, and as kinetic energy in the fluid as it flows from the end of the pipe.

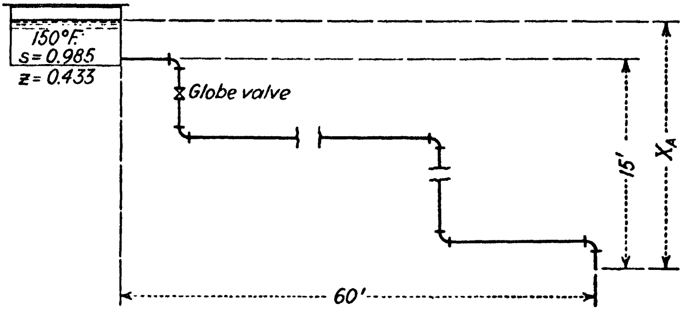

FIG. 64.—Simple hydraulic system. Refer to Example 35.

Basis: 1 sec., isothermal at 150°F.

$$\text{Velocity} = \frac{120 \times 144}{7.48(1.035)^2 \times 60 \times 3.1416} = 11.5 \text{ ft. per sec.}$$

$$\text{Velocity head} = \frac{u_b^2}{2g} = \frac{(11.5)^2}{2 \times 32.2} = 2.05 \text{ ft. of fluid}$$

Friction losses (see Fig. 51):

$$\text{Contraction loss at connection to tank} = \frac{ku_b^2}{2g} = 0.5 \times 2.05 = 1.025 \text{ ft. of fluid}$$

Loss in pipe and fittings (see Fig. 47):

$$\text{Equivalent length of pipe} = 60 + 15 + \frac{2.07}{12} \times 45 + \frac{5 \times 2.07 \times 30}{12} = 108.66 \text{ ft.}$$

$$\Delta P_f = \frac{0.323 f s u^2 L}{D} \qquad \frac{Dus}{z} = \frac{2.07 \times 11.5 \times 0.985}{0.433} = 54.1$$

Friction factor for new, clean pipe = 0.0046

$$\begin{aligned} \Delta P_f &= \frac{0.323 \times 0.0046 \times 0.985(11.5)^2 108.66}{2.07} \\ &= 10.1 \text{ lb. per sq. in.} \\ &= \frac{10.1 \times 144}{62.4 \times 0.985} = 23.8 \text{ ft. of fluid} \end{aligned}$$

Difference in head required $= X_a - X_b = 2.05 + 1.025 + 23.8 = 26.9$ ft.

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CHAPTER XIII

HEAT TRANSFER

The solution of problems that involve the transfer of heat is difficult because of the lack of adequate data. The film transfer rates can be computed with reasonable accuracy for clean or new pipe but the effect that dirty or corroded pipe surfaces will have on the transfer rate cannot be satisfactorily estimated. With the greatest possible care, the accuracy with which the rate of heat transfer can be computed is probably not better than ±10 per cent. Nevertheless, even this accuracy cannot be attained unless the designer thoroughly understands the fundamentals of heat transfer.

The dismaying lack of data on the effect of the surface condition has caused many engineers to turn to the use of over-all coefficients of heat transfer. Although the use of the over-all coefficient is convenient and sometimes necessary, most heat-exchange experts feel that the use of over-all coefficients is inaccurate and that an attempt to compute or estimate the individual film coefficients is always the safest method to use. In this chapter the film transfer coefficients for materials contained in clean or new equipment will be studied and in Chap. XIX transfer rates for commercial equipments will be discussed.

There are three common methods of transferring heat, *viz.*, radiation, conduction through solids, and conduction through fluids. In practice a combination of two or even all of these methods may take place simultaneously.

Radiation.—Although radiation is probably the most important method of transferring heat, the calculation of the rate at which radiation occurs in many commercial furnaces is impossible. In Chap. XX are examples of radiation calculations for the particular case of the tubestill heater.

Nevertheless, qualitative study of radiation theory leads to a clearer insight into this method of transferring heat. The transfer of heat by radiation is governed by Stefan's law:

$$Q = bAT^4$$

where A = area of radiating surface, sq. ft.
T = absolute temperature of the surface, °F.
Q = B.t.u. transferred per hr.
b = 1.72×10^{-9} B.t.u. per °F. (diff.) per sq. ft. per hr. at black-body conditions.

But a surface cannot radiate all of this heat to another surface because the cooler surface also radiates heat. For a small body completely surrounded by a hotter body the foregoing statement simplifies to

$$Q = \text{net heat transferred} = Q_2 - Q_1 = bA(T_2^4 - T_1^4) \quad (19)$$

This expression involves the assumption that all of the energy that is emitted by the hot body is absorbed by the cooler body, and that all of the energy emitted from the cooler body is absorbed by the hotter body. In practice most materials fail to absorb all of the radiant energy that falls upon them and hence the constant b is different for all materials.

Materials that have a rough or dull-finish surface absorb radiation almost as completely as perfect radiation absorbers (black bodies) but polished surfaces or even clean metallic rough surfaces reflect a large part of the radiation that falls upon them and hence require a corrected value of b. Furthermore, it appears that surfaces such as a brick wall at incandescent temperatures reflect much of the radiation that falls upon them. Table 26 gives common values of b.

TABLE 26.—RADIATION CONSTANTS

Material	$b \times 10^{-9}$
1. Perfect black body	1.72
2. Brass, matte	0.374
3. Cast iron, rough and highly oxidized	1.57
4. Clay	0.65
5. Copper	0.278
6. Ceramics ware, unglazed	1.34
7. Field soil	0.63
8. Granite, smooth but not polished	0.745
9. Lamp black	1.56
10. Lime mortar, rough	1.51
11. Sheet iron, matte oxidized	1.55
12. Sheet iron, polished	0.466

The differences in the fourth powers of the temperature are involved in this formulation and it becomes apparent that the higher temperature raised to the fourth power may be so large that the lower temperature may be neglected. Furthermore, the quantity of heat that is radiated increases very rapidly for small increases in temperature. The following tabulation indicates the rate of increase:

$1{,}000^4 = 1 \times 10^{12}$
$1{,}200^4 = 2.1 \times 10^{12}$
$1{,}400^4 = 3.9 \times 10^{12}$
$1{,}600^4 = 6.6 \times 10^{12}$
$1{,}800^4 = 10.5 \times 10^{12}$
$2{,}000^4 = 16.0 \times 10^{12}$

Thus the temperature was doubled but the radiation increased sixteen fold.

Another deduction of a qualitative nature but of great value regards the angle of vision or sight of a point radiation source. Radiation is a wave phenomenon and it travels through gaseous materials in a straight line without suffering much of a loss in intensity. It is unable to penetrate opaque or dark solid materials. Thus cooling surfaces cast what might be called radiation shadows behind them and the space shielded from radiation is not heated by radiation.

In most combustion problems the radiation of heat is practiced by allowing combustion to take place in proximity to cooled surfaces. Radiation from flames and gases cannot be easily handled by Eq. (19) because (1) the size of the flame cannot be accurately determined, (2) the flame has a thickness so that radiation from the center of the flame must penetrate the outer layers, and (3) the luminosity of flames varies with different fuels and conditions of combustion. In nonluminous flames, radiation is found to be dependent to a large extent on the percentage of carbon dioxide and water vapor that is present. However, radiation from such a flame is not effective and the presence of partially burned carbon particles (luminous flames) greatly increases radiation. The problem of radiation from flames is further complicated by the convection heat transfer that occurs by the circulation of gases within the furnace box.

CONDUCTION THROUGH SOLIDS

Conduction is the most simple method of heat transfer. Newton's fundamental law of resistances and driving forces, if applied to conduction, takes the following form:

$$Q = \frac{kA(T_2 - T_1)}{L} \qquad (20)$$

where Q = B.t.u. heat transferred per hr.
A = area of surface, sq. ft.
T_2 and T_1 = temperatures at hot and cold surfaces.
k = conductivity as B.t.u. per sq. ft. per hr. per °F. temperature difference for 1 ft. thickness.
L = thickness, ft.

The values of k for some common materials are given in Table 27.

TABLE 27.—THERMAL CONDUCTIVITY

Conductivity: B.t.u. per sq. ft. per hr. per °F. temperature difference for 1 ft. thickness

Material	70°F.	212°F.	500°F.	1800°F.
Brass (70–30)	63	72.5		
Copper	227	220.0		
Iron (wrought)	35	35.0		
Iron (cast)	22–36			
Steel (0.1 per cent carbon)	26.1	25.8	25.0	
Alloy steel, austenitic chrome-nickel	......	......	10.4	
Calcium carbonate (scale)	0.5–1.5			
Porcelain	0.6			
Magnesia (85 per cent)	......	0.04		
Asbestos (felt)	......	0.12		
Cork	......	0.03		
Portland cement	0.5			
Brick or mortar wall	0.4			
Concrete wall	......	......	0.505	0.70
Red brick	0.39	0.43	0.52	0.95
Firebrick and clay-bond silica	0.48	0.5	0.56	0.82
Sil-o-cel brick	0.125	......	......	0.125
Carborundum brick	......	......	5.6	6.4
Magnesite brick	......	......	3.5	2.3
Silica brick	......	......	0.7	1.15
Asbestos cement board (transite)	......	0.23	......	0.23

Table 28 presents the conductivities of petroleum oils.[1]

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[1] CRAGOE, C. S., *Bur. Standards Misc. Publ.* 97, 1929.

Table 28.—Thermal Conductivity of Petroleum Products and Water
B.t.u. per hr. per sq. ft. for 1 ft. of thickness per °F. temperature difference

Temperature, °F.	A.P.I. at 60°F.	Water	10	20	30	40	50	60	Asphalt	Wax
	Sp. Gr. 60/60		1.0	0.934	0.8762	0.8521	0.7796	0.7389		
0		0.322*	0.0683	0.0735	0.0783	0.0833	0.0875	0.0925	0.1	0.133
200		0.41	0.0642	0.0691	0.0735	0.0783	0.0825	0.0875	(Average from 32°F. to melting-point)	
400		......	0.06	0.0642	0.0691	0.0735	0.0775	0.0815		
600		......	0.0558	0.06	0.0642	0.0683	......	......		
800		......	0.0525	0.0558	0.0591	......	......	......		

* At 35°F., also 0.357 at 100°F.

In using Newton's law, the factor L/kA may be considered to be a resistance (R) to the driving force represented by the temperature difference $(T_2 - T_1)$. The equation may be rearranged as

$$Q = \frac{\Delta T}{L/kA} = \frac{\Delta T}{R} \tag{21}$$

When heat is transferred by conduction, several materials usually compose the vessel or wall through which heat is being conducted and hence conduction problems involve the conduction of heat through a series of resistances. The quantity of heat Q which passes through each material is the same, but the temperature difference across each material will be different for each material. Suppose a flat wall is composed of three materials having conductivities of k_1, k_2, and k_3, having thicknesses of L_1, L_2, and L_3, and having temperature differences of ΔT_1, ΔT_2, and ΔT_3. The heat that is conducted per square foot per hour is

$$Q = Q_1 = Q_2 = Q_3 \quad \text{and} \quad = \frac{\Delta T_1}{L_1/k_1A_1} = \frac{\Delta T_2}{L_2/k_2A_2} = \frac{\Delta T_3}{L_3/k_3A_3}$$

Also

$$\Delta T_1 = Q\frac{L_1}{k_1A_1}; \qquad \Delta T_2 = Q\frac{L_2}{k_2A_2}; \qquad \Delta T_3 = Q\frac{L_3}{k_3A_3}$$

The temperature difference across the three materials is the sum of the three individual differences and hence the following relation may be written:

$$Q\left(\frac{L_1}{k_1A_1} + \frac{L_2}{k_2A_2} + \frac{L_3}{k_3A_3}\right) = \Delta T_1 + \Delta T_2 + \Delta T_3 = \Delta T$$

and

$$Q = \frac{\Delta T}{\frac{L_1}{k_1A_1} + \frac{L_2}{k_2A_2} + \frac{L_3}{k_3A_3}} = \frac{\Delta T}{R_1 + R_2 + R_3} \qquad (22)$$

Thus we find that the resistance to the flow of heat corresponds exactly to the resistance to the flow of electricity through a series electrical circuit. The temperature differences are directly proportional to the resistances to flow, so that

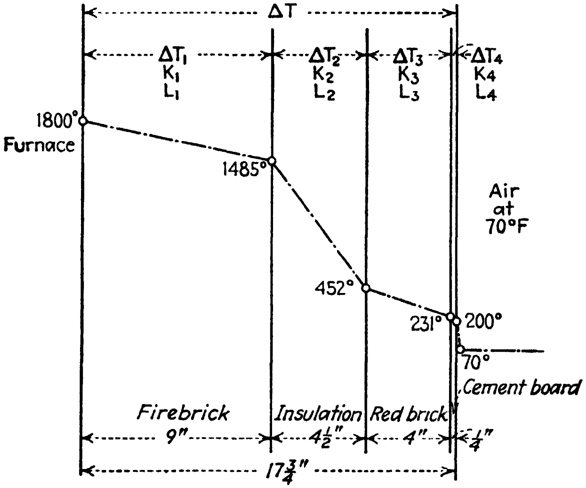

FIG. 65.—Temperature inside of a furnace wall. Refer to Example 36.

$$\Delta T : \Delta T_1 : \Delta T_2 : \Delta T_3 : : R : R_1 : R_2 : R_3 \qquad (23)$$

Example 36. Heat Loss through a Furnace Wall.—A furnace wall consists of 9 in. of firebrick, 4½ in. of sil-o-cel brick, 4 in. of red brick, and ¼ in. of transite board. The conductivity coefficients for these materials are given in Table 27. The inside wall of the furnace is at 1800°F. and let us assume that the outside of the wall is at 200°F.*

How much heat is lost per hour through a surface of 10 sq. ft.? (See Fig. 65.)

Basis: 1 sq. ft.

The surface is the same through each of the materials, and hence the area has been left out of all of the formulations [see Eq. (22)].

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* Since the outside temperature cannot be easily measured, the air temperature is usually used, but this involves the conductivity of a film of stagnant air at the wall (see Example 39, p. 222).

$$Q = \frac{\Delta T}{\frac{L_1}{k_1} + \frac{L_2}{k_2} \cdots} = \frac{1800 - 200}{\frac{9}{12 \times 0.82} + \frac{4.5}{12 \times 0.125} + \frac{4}{12 \times 0.52} + \frac{0.25}{12 \times 0.23}}$$

$$= \frac{1600}{0.915 + 3.0 + 0.641 + 0.0905} = \frac{1600}{4.646}$$

= 344 B.t.u. per sq. ft.

= 3440 B.t.u. through the 10 sq. ft.

The temperatures within the wall can be computed by Eq. (23).

$$\frac{\Delta T}{\Delta T_1} = \frac{R}{R_1}$$

Location	Temperature difference	Temperature °F.
Between firebrick and sil-o-cel	$\frac{1600}{4.646} = \frac{\Delta T_1}{0.915}$ $\Delta T_1 = 315$	1485
Between sil-o-cel and red brick	$\Delta T_2 = 1033$	452
Between red brick and transite	$\Delta T_3 = 221$	231
At outer wall (as a check)	$\Delta T_4 = 31$	200

Pipe Insulation.—In the case of pipe insulation the area through which heat is transferred is not constant. If the thickness of the material is small, compared with the diameter, the arithmetic average of the larger area and the smaller area may be

TABLE 29

Pipe size, in.	Standard insulation			High-temperature insulation*		
	Thickness, in.	Log mean area†	Approx. error, per cent	Thickness, in.	Log mean area†	Approx. error, per cent
½	⅞	4.9	10	1½	6.2	19.0
1	⅞	6.53	5	1½	7.95	11.5
1½	⅞	8.41	4	1½	9.9	7.5
2	1 1/32	10.4	4	1½	11.5	5.8
3	1 1/32	14.0	2	2½	17.65	6.3
4	1⅛	17.4	1½	2½	21.1	4.0
5	1⅛	20.8	1	2½	24.5	3.5
6	1⅛	.....	....	2½	28.0	2.0
8	1¼	.....	....	2½	34.6	1.0
12	1½	44.8	....	3	49.6	

* High-pressure steam lines, oil lines above about 400°F., etc.

† Square inches per inch of length.

used. The arithmetic mean area may be used for all cylindrical vessels and for pipe sizes down to about 2 in. if standard insulation is used and if an error of 4 per cent is permitted. If the thickness is great compared with the diameter, the logarithmic mean area must be used:

$$\text{Logarithmic area} = \frac{A_2\ (\text{large}) - A_1\ (\text{small})}{2.3 \log \dfrac{A_2\ (\text{large})}{A_1\ (\text{small})}} \qquad (24)$$

Table 29 shows the error if the arithmetic area is used instead of the logarithmic area.

CONDUCTION THROUGH FLUID FILMS

The heating of fluids through the walls of a metal container is at the same time an important and a most troublesome method of transferring heat. As indicated in Chap. X all fluids are bounded at the retaining walls by a film of stagnant fluid. Heat must be transferred through these films by conduction. The films are very thin, their thicknesses cannot be easily measured, and hence the thickness L which is involved in the resistance of the film cannot be determined directly. In order to avoid this difficulty, the resistances of fluid films have been correlated by expressing the resistance as $1/h$ in which h is the film coefficient of heat transfer. From commonly accepted heat-transfer coefficients the apparent film thickness varies from about 0.1 for gases to about 0.0001 in. for condensing steam. If the conduction equation is applied to the transfer of heat from a fluid into a solid partition wall and into another fluid, the conduction equation takes the following form:

$$Q = \frac{\Delta T}{\dfrac{1}{h_1 A_1} + \dfrac{L_2}{k_2 A_2} + \dfrac{1}{h_3 A_3} + R_D} \qquad (25)$$

In this equation h_1 and h_3 represent the film coefficients of heat transfer for the two fluids; L_2 and k_2 are the thickness and conductivity of the partition wall; and R_D is the resistance due to corrosion, dirt, or roughness of the surfaces. The resistances indicated in the denominator may, for convenience, be added, and the total equals $1/H$ in which H is the over-all rate of heat transfer. Returning to the first equation of conduction we see that it may be stated as follows:

$$Q = \frac{A\Delta T}{1/H} = HA\Delta T \tag{26}$$

Thus if an average area is used,

$$\frac{1}{H} = \frac{1}{h_1} + \frac{L_2}{k_2} + \frac{1}{h_3} + R_D$$

$$H = \frac{1}{\frac{1}{h_1} + \frac{L_2}{k_2} + \frac{1}{h_3} + R_D} \tag{27}$$

If one of the film coefficients is small compared with the other coefficients, the resistance $1/h$ which corresponds to it will be proportionally large. In such a case the value of the over-all coefficient will be nearly the same as the small film coefficient. For the same reason the resistance of the metal wall may often be neglected.

Example 37. The Over-all Coefficient of Heat Transfer.—Heat is being transferred from a gas through the walls of a standard 2-in. pipe, and into water which is flowing on the inside of the pipe. $h_G = 6$, $h_W = 500$, and k for the pipe wall is 25 [see Eq. (27)].

$$H = \frac{1}{\frac{1}{h_G} + \frac{L}{k} + \frac{1}{h_W}} = \frac{1}{\frac{1}{6} + \frac{0.154}{12 \times 25} + \frac{1}{500}}$$

$$H = \frac{1}{0.1667 + 0.00051 + 0.002} = 5.91$$

Thus the resistance of the metal wall and the water film could be neglected with an error of only 1.52 per cent.

Likewise, the pipe could be made of copper, which is an excellent conductor of heat ($k = 220$), and the over-all coefficient would be changed by only a small amount.

$$H = \frac{1}{0.1667 + 0.000058 + 0.002} = 5.93$$

Factors Which Affect the Film Coefficient.—Exactly as in conduction through solids, a temperature difference exists across fluid films. The temperature difference in the film causes convection currents which tend to decrease the thickness of the film, and forced circulation of the fluid past the heating surface has the same effect. Thus the numerical value of the film coefficient is directly dependent on the thickness of the film and the material which composes the film.

Some of the factors that affect the thickness of the film are

1. Viscosity.
2. Density.

3. Velocity in main body of fluid.
4. Conductivity.
5. Shape of retaining walls and turbulence caused by such disturbances as bends, etc.
6. Specific heat.
7. Latent heat, in the case of vaporization or condensation.
8. Materials or impurities, having low conductivities, that may accumulate in the film and retard mixing. Examples of this are (*a*) air in steam, (*b*) paraffin wax in oils, and (*c*) materials that may corrode the metal surface.
9. Temperature.

Temperature is not in itself important but it does affect the value of the other physical constants. For example, the viscosity changes rapidly with temperature and hence temperature becomes indirectly of great importance. An examination of these factors indicates why some coefficients are low and others are high. The coefficients for lubricating oils are low mainly because the viscosity is high; the coefficients for gasoline and water are high because of the high fluidity of these materials. However, the conductivity of water is much higher than the conductivity of oils and hence the coefficients for water are even higher than for gasoline. Similarly the viscosity of gases is low but the conductivity is extremely low, so that the coefficients for gases are low. Finally, paraffin-containing stocks when cooled to fluid-body temperatures of even 300°F. may deposit a thin but effective film of solid paraffin wax so that heat transfer is greatly retarded.

Film Temperature.—Obviously the several physical properties that are mentioned above should be taken at the mean temperature of the film. However, the effect of temperature on the value of these constants, except the viscosity, is not great. The arithmetic mean film temperature is usually considered as sufficiently accurate. Although the use of the film temperature is most exact, the computation of film temperatures is tedious and hence many of the formulae for transfer rates, as given in the following pages, are based on viscosities measured at the temperature of the main body of fluid. The film temperature may be computed by noting that the film resistances are directly proportional to the temperature drop across the film. If the area is the same at each film, the film temperature may be expressed in terms of the total temperature difference and the film coefficients as follows:

$$\Delta T:\Delta T_1:\Delta T_2:, \text{etc.}::\frac{1}{H}:\frac{1}{h_1}:\frac{1}{h_2}:, \text{etc.}$$

$$\frac{\Delta T_1}{\Delta T} = \frac{1/h_1}{\dfrac{1}{H}} = \frac{1/h_1}{\dfrac{1}{h_1} + \dfrac{1}{h_2}}$$

$$\Delta T_1 = \frac{\Delta T \dfrac{1}{h_1}}{\dfrac{1}{h_1} + \dfrac{1}{h_2}} = \Delta T \frac{h_2}{h_2 + h_1}$$

Let

$$\Delta T_1 = T_1 - T_2; \quad \Delta T_2 = T_2 - T_3; \quad \text{and} \quad \Delta T = T_1 - T_3$$

where T_1 = high temperature.
T_3 = low.

Film temperature in film 1 or hot film $= T_1 - \dfrac{\Delta T_1}{2} =$

$$T_1 - \frac{\Delta T}{2}\frac{h_2}{h_2 + h_1} \quad (28)$$

Film temperature in film 2 or cold film =

$$T_3 + \frac{\Delta T}{2}\frac{h_1}{h_2 + h_1} \quad (29)$$

For the simple case where $h_1 = h_2$

$$\text{Hot-film temperature} = T_1 - \frac{\Delta T}{4}$$

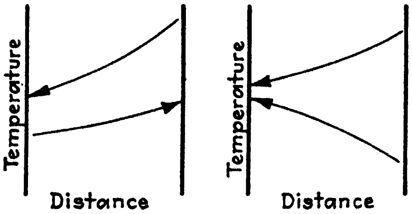
$$\text{Cold-film temperature} = T_3 + \frac{\Delta T}{4}$$

The Temperature Difference.—In the case of conduction through solids, the temperature difference ΔT is usually the same at all points but in the case of fluid systems, the temperature difference is not the same at all points because as one fluid is heated the other is cooled. In Fig. 66 the arrows indicate the direction of flow of the fluids with respect to one another for the common arrangements of flow. Almost all commercial equipments are designed for countercurrent flow or at least for conditions that approach countercurrent flow. The conditions indicated in *c* and *d* (Fig. 66) are closely simulated in steam heaters and in coil-in-box coolers.

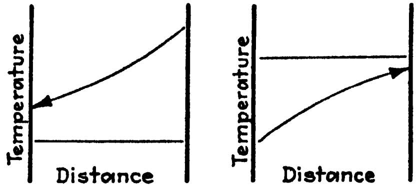
The temperature difference for a fluid system is an average quantity. For the simplified case of a constant transfer coefficient and constant specific heats for the two fluids, the logarithmic mean temperature difference is valid:

$$\theta = \text{log mean temp. diff.} = \frac{\text{larger temp. diff.} - \text{smaller temp. diff.}}{\log_e \dfrac{\text{larger temp. diff.}}{\text{smaller temp. diff.}}} \tag{30}$$

The logarithm to the base 10 may be converted to base e by multiplying by 2.3.



(a) Countercurrent (b) Parallel



(c) Constant Cooling Temperature (d) Constant Heating Temperature

FIG. 66.—Common arrangements of flow.

Example 38. The Logarithmic Mean Temperature Difference.—An oil is to be cooled from 200 to 100°F. by water which enters at 60 and leaves at 80°F. [see Eq. (30)].

$$\theta = \frac{(200 - 80) - (100 - 60)}{\log_e \dfrac{120}{40}}$$

$$= \frac{80}{1.1} = 72.8°\text{F.}$$

The arithmetic temperature difference would be in error by about 10 per cent.

$$\text{Arithmetic } \Delta T = \frac{120 + 40}{2} = 80°\text{F.}$$

If the ratio of the temperature differences is less than 2, the arithmetic average temperature difference may be used with an error of only 4 per cent. For convenience the logarithmic temperature differences are plotted in Fig. 67 as a function of the larger and smaller temperature differences.

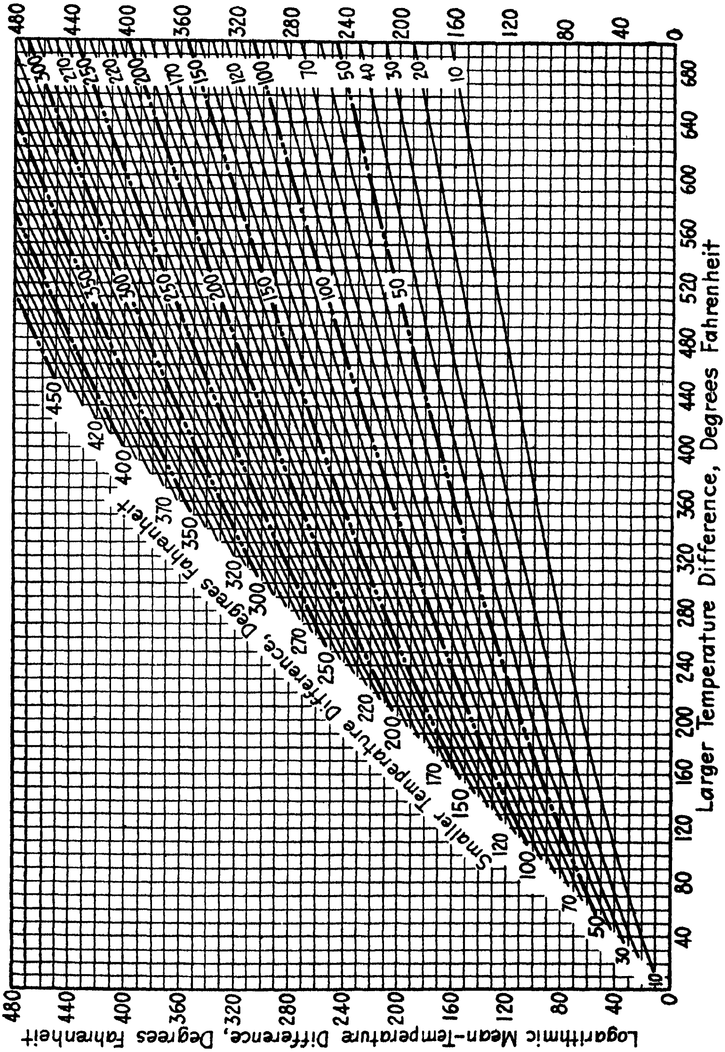


FIG. 67.—Logarithmic mean temperature difference.

The logarithmic temperature difference is accurate enough for materials such as air, water, and steam, whose viscosity does not change rapidly with temperature, but in the case of lubricating oils it may be far in error. Later in the chapter an example will be given to illustrate the use of the actual temperature difference. Suffice here to say that the logarithmic temperature difference may cause errors as high as 20 per cent when exchanging heat between two viscous petroleum oils.

NUMERICAL VALUE OF FILM COEFFICIENTS

The following formulations have been presented for the computation of film coefficients when the heating surfaces are clean. After even a few days of service the transfer rates may drop to values much lower than these equations indicate.

To facilitate the presentation of the equations the following symbols will be used:

h = film coefficient, B.t.u. per sq. ft. per hr. per °F. temp. diff.
c = sp. ht. at constant pressure.
T = temp., °F. abs.
t = temp., °F.
ΔT = temp. diff. °F. across film.
v = mass velocity, lb. of fluid per sec. per sq. ft. of free cross-section area. Is equal to $u\rho$.
u = velocity, ft. per sec.
U = velocity, ft. per hr.
s = sp. gr.
ρ = density, lb. per cu. ft.
D = diameter of pipe or tube, in.
d = diameter of pipe or tube, ft.
g = gravity constant, 4.18×10^8 ft. per hr.^{2}
k = conductivity, B.t.u. per sq. ft. per hr. per ft. thickness per °F. temp. diff.
z = viscosity, centipoises.
j = fluidity, reciprocal of viscosity, centipoises.
μ = viscosity, English units lb. per ft.-hr. = $2.42z$.

Subscripts:
f = film.
G = gas.
L = liquid.
V = vapor.

Gases (Permanent) in Forced Convection in Pipes.—Dixon and McAdams[2] suggest the following equation:

$$h_G = \frac{0.22c(T_f)^{0.667}v^{0.8}}{D^{0.2}} \tag{31}$$

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[2] WALKER, LEWIS, and McADAMS, "Principles of Chemical Engineering," 2d. ed., McGraw-Hill Book Company, Inc., New York, 1927.

For sections other than circular the equivalent diameter may be used for D. The equivalent diameter is equal to four times the heated radius (see page 224). Note that the temperature in Eq. (31) is the film temperature.

Petroleum vapors appear to have lower coefficients than the foregoing equation would indicate. The viscosity of the gas is not considered in the foregoing equation and perhaps this accounts for the lower rates with petroleum vapors.

Gases—Forced Convection, Outside Pipes, and at Right Angles to the Pipes.—Monrad[3] obtained the following equation by an examination of the existing literature:

$$h_G = \frac{1.75v^{0.667}T^{0.3}}{D^{0.333}} \tag{32}$$

The mass velocity is computed for the free area in a plane at right angles to the direction of gas flow.

The data used in formulating this equation covered the following ranges: mass velocity from 0.2 to 1.9, diameter from 0.59 to 1.3 in., and temperature from 560 to 920°F. He also presents data on the convection-section rates in modern pipestills and finds the same equation except that the constant is 1.6 rather than 1.75. The pipestill data covered temperatures from 1033 to 1675°F. and tube diameters from 3.75 to 5 in. Monrad found that the number of rows of tubes did not affect the results if there were more than four rows. These equations apply only to pure conduction through the gas film and hence radiation may constitute an additional transfer of heat.

Gases—Natural Convection and Radiation Combined.—Convection is always accompanied by radiation, and hence the most convenient method of computing heat losses from an exposed surface to air is by a coefficient that represents both the convection and radiation transfer of heat. A study of the literature on this subject shows that the coefficient is substantially the same for vertical brick, asbestos, metal, canvas, and wood surfaces. The following formula was obtained by using data for all of these materials between temperatures of 100 and 500°F. when the materials are in a vertical position.

$$h_G = 1.5 + 0.0058(\Delta t)_f \tag{33}$$

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[3] *Ind. Eng. Chem.*, **24**, 505 (1932).

When the surface is horizontal, the rate h_G is about 25 per cent lower for the upper surface than the values given by Eq. (33) and about 60 per cent lower for the under surface. Note that ΔT is the temperature difference across the air film.

Example 39. Natural Convection Film.—In Example 36 (page 212) the temperature of the wall was assumed to be 200°F. This temperature is dependent on the natural convection air film at the surface [Eq. (33)]. In Example 36 the air temperature was 70°F.

$$h_G = 1.5 + 0.0058(200 - 70) = 2.25$$

$$\text{Total } R = 4.646 + \frac{1}{2.25} = 5.091$$

$$\text{Heat loss through wall} = \frac{1{,}800 - 70}{5.091} \times 10 = 3400 \text{ B.t.u. per hr.}$$

Liquids—Water in Forced Circulation in Pipes.—For turbulent flow in clean pipes, the Frost[4] equation is the most generally known:

$$h_W = \frac{14.5k}{D}\left(\frac{Dv}{z_f}\right)^{0.8}\left(1 + \frac{50}{r}\right) \tag{34}$$

where r = ratio of length of pipe, in., to internal diameter of pipe.
k = conductivity of water, always used as 0.35 in this equation.

Since this equation was published, Lawrence and Sherwood[5] have shown that r, the ratio of the length to the diameter of the pipe, has little effect on the transfer rate so that the expression $(1 + 50/r)$, is unnecessary. Nevertheless, in the foregoing equation $(1 + 50/r)$ had a value of 1.5 for most of the experimental data so that the constant 14.5 should be multiplied by 1.5 and the $(1 + 50/r)$ factor omitted.

Liquids—Oil in Forced Circulation inside Pipes.—The Whitman and Morris[6] data are the most complete data for the computation of oil transfer rates. These investigators find (Fig. 68) that the coefficients for all oils may be correlated by an additional factor, *viz.*, cz/k. Figure 68 shows coefficients for heating petroleum oils. A value of k of 0.078 should be used for all oils. For cooling, their results indicated rates that are 25 per cent lower than for heating. The viscosity should be taken at the average temperature of the main body of oil. Perhaps the discrepancy

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[4] McAdams and Frost, *Refrigerating Eng.*, **10** (9) (1924).

[5] *Ind. Eng. Chem.*, **23**, 301 (1931).

[6] *Ind. Eng. Chem.*, **20**, 234 (1928).

in the heating and cooling data could be eliminated if the viscosity at the average film temperature were used. Coulthurst and Scoville[7] have published a similar chart for the heat transfer of oils in tubular exchangers. They find that an exponent of 0.37 for cz/k will not correlate all the data but that the coefficient is a function of cz/k.

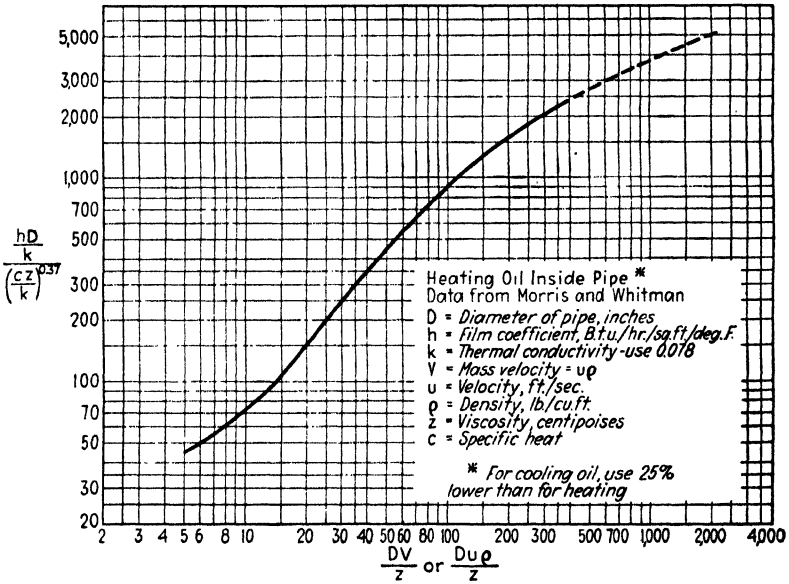

FIG. 68.—Film transfer rates for heating petroleum oils. (*Morris and Whitman, Ind. Eng. Chem.*)

Sherwood and Petrie[8] have developed an equation for the transfer coefficient for all materials flowing inside pipes. They suggest the following equation:

$$\frac{hd}{k} = 0.024\left(\frac{dU\rho}{\mu}\right)^{0.8}\left(\frac{c\mu}{k}\right)^{0.4} = 0.024\left(\frac{d^2U^2\rho^2c}{\mu k}\right)^{0.4} \qquad (35)$$

Data for air, acetone, benzene, water, kerosene, and the data of Morris and Whitman and of Dittus and Boelter were used in formulating the equation. In general the Morris and Whitman data (Fig. 68) are more exact for oils.

[7] *Petroleum Eng.*, May, 1931, p. 101.

[8] Heat Transmission to Liquids Flowing in Pipes, *Ind. Eng. Chem.*, **24**, 737 (1932).

Liquids—Circulated outside Tubes.—Experimental data for the film coefficients of liquids flowing outside tubes are scarce. Some authorities suggest that an equivalent diameter should be computed from the hydraulic radius. However, it would seem more logical to use the *thermal radius* which may be defined as the cross-sectional area divided by the *heated perimeter* or perimeter through which heat flows. The equivalent diameter is four times the thermal radius.

The only comprehensive experimental data are those of Perrone[9] for a small commercial exchanger having cut-out type baffles. Water was the only fluid that was studied. The film coefficients for the shell-side or for water on the outside of the tubes are given by the following equation:

$$\frac{hd_t}{k} = 0.73\left(\frac{d_tG}{\mu}\right)^{0.66}\left(\frac{c\mu}{k}\right)^{0.4}\left(\frac{d_sN_b}{L}\right)^{0.35}\frac{P^{0.95}}{d_t^{0.15}} \tag{36}$$

The special symbols that are used, are

d_t = dia. of tubes, ft.
G = mass velocity, lb. per sq. ft. per hr.
d_s = dia. of shell, ft.
N_b = number of baffles.
L = distance between inlet and outlet, ft.
P = tube pitch, ft.

The film rates are much higher than those obtained in commercial equipment because the experimental equipment was carefully cleaned after each run. Difficulty is encountered in determining the average mass velocity through the tube bundle and baffles.

Liquids—Natural Convection.—Stose and Whittemore[10] have derived the following formula for the heating of sugar solutions and molasses.

$$h_L = 50\sqrt[3]{j\Delta T} \tag{37}$$

In their experiments a 3/8-in. copper steam-heating coil was used. Scattered data in the literature reveal that lower rates are obtained with cast-iron heating coils. This may be explained by the rough surface of cast iron. However, in large equipment such as coil-in-box condensers or coolers the foregoing equation

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[9] Pressure Drop and Heat Transfer in Exchangers, *Oil Gas J.*, Mar. 28, 1935, p. 71.

[10] WALKER, LEWIS, and MCADAMS, "Principles of Chemical Engineering," 2d ed., p. 139, McGraw-Hill Book Company, Inc., New York, 1927.

probably holds even for cast-iron coils. Ribbed surfaces on the outside of natural-convection cooling coils apparently decrease the heat-transfer rate[11,12] although the total heat transferred, per unit of space occupied, may be larger owing to the larger surface of the ribbed equipment.

Liquids—Boiling on the Outside of a Tube.—The only comprehensive study of heat transmission from metal surfaces to boiling liquids is the work of Cryder and Gilliland.[13] They suggest the following equation:

$$\frac{hD}{k(\Delta T)^{1.2}_{f}} = 5.4\left(\frac{\Delta T s^2 D^2 k}{z^3}\right)^{1.2}\left(\frac{cz}{k}\right)^{0.4} \tag{38}$$

A single horizontal small heating tube was used. A variety of materials including water, solutions, methanol, kerosene, and gasoline were studied. In most of their experiments the temperature difference across the film did not exceed 10°F.

Condensing-vapor Film.—The films formed during the condensation of vapors are complex. Liquid droplets are formed upon the cooling surface and if the surface tension of the condensate is relatively low the droplets form a continuous liquid film. If the vapor contains a noncondensable gas, the fixed gas is carried to the surface by the condensation and remains there as a gas film. The effect of a noncondensable gas on the condensing rate is illustrated by the effect of air on the condensing rate for steam. Othmer[14] reports that the film coefficients between steam at 230°F. and a metal wall are about as follows:

Per cent air	Temperature difference across film, °F.		
	10	25	50
0.0	2800	1800	1400
1.07	1500	1000	780
1.96	900	700	570
2.89	740	600	490
4.53	490	420	370

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[11] BADGER, ROGERS, and DIAMOND, *Oil Gas J.*, Mar. 31, 1932, p. 100.

[12] OLSON and WENTWORTH, *Oil Gas J.*, June 30, 1932, p. 14.

[13] *Ind. Eng. Chem.*, **24**, 1382 (1932).

[14] BADGER, W. L., "Heat Transfer and Crystallization, Art. IV," Swenson Evaporator Co., 1928.

The marked influence of temperature difference on the condensing rate is also shown by Othmer.[15] As an example, at zero per cent air the condensing coefficient dropped from 10,000 at a ΔT of 1°F. to approximately 1000 at a ΔT of 80°F. For steam that contained air, the general effect of the temperature difference was the same. Apparently the adoption of a standard average condensation coefficient of 2,000 or 3,000 B.t.u., as recommended by many authorities, may be in error even for commercial work.

Kirkbride[16] has studied the condensation of pure hydrocarbons and mixtures on horizontal tubes. For a bank of tubes he recommends the equation by Merkel.[17]

$$h = 0.725\left(\frac{k^3\rho^2\lambda g}{\Delta T d\mu n}\right)^{0.25} \tag{39}$$

where λ = latent heat plus sensible heat of vapor through range of ΔT, B.t.u. per lb.

n = number of tubes in a vertical row.

For condensing two immiscible liquids simultaneously, Kirkbride[16] suggests that the average condensing coefficient should be computed by determining the condensing coefficient for each of the pure materials by the foregoing equation and then combining the two in proportion to the amount of heat that is delivered as each vapor is condensed, thus

$$h_{\text{ave}} = \frac{h_1Q_1 + h_2Q_2}{Q_1 + Q_2} \tag{40}$$

where Q_1 = B.t.u. per hour that is recovered from one of the materials.

Q_2 = heat recovered from the other.

Kirkbride also discusses the effect of permanent gases on the condensation coefficient and presents a method of computing such coefficients.

Corrosion, Dirt, and Fouling Resistances.—The practical usefulness of all of the foregoing coefficients is vitally dependent

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[15] *Ind. Eng. Chem.*, **21**, 576 (1929).

[16] Heat Transmission by Condensing Pure and Mixed Substances on Horizontal Tubes, *Ind. Eng. Chem.*, **25**, 1324 (1933).

[17] "Die Grundlagen der Wärmeübertragung," p. 140, T. Steinkopf, Leipzig, 1927.

upon the condition of the surfaces through which heat is being transferred. With few exceptions the over-all rates computed from the theoretical coefficients can always be reduced by a resistance of 0.0005 (1/2,000). Although this seems small, in certain cases it becomes of great importance. For example, consider heating water at a velocity of 3 ft. per second within tubes by condensing steam. Approximate values of the theoretical film coefficients for these conditions are

$$h_c = 2{,}500$$
$$h_w = 800$$

$$H = \frac{1}{\frac{1}{2{,}500} + \frac{1}{800}} = \frac{1}{0.00165} = 605$$

Inserting a dirtiness resistance of 0.0005,

$$H = \frac{1}{0.00165 + 0.0005} = 465$$

Except in rare cases, a resistance of 0.0005 is even too low and not infrequently the resistance caused by water-scale, mild corrosion, and dirty liquids amounts to 0.005 ($\frac{1}{200}$). For the foregoing case

$$H = \frac{1}{0.00165 + 0.005} = 150$$

When a definite corrosive action takes place or a solid is deposited at the surface by cooling, the resistance may reach a value of 0.033. This magnitude of fouling resistance often results when a cylinder stock is cooled if the average film temperature is below 300°F. Obviously, high velocities tend to keep surfaces clean and reduce the dirtiness factor.

No definite values of fouling resistance can be suggested because each design problem may involve new conditions. However, in Chap. XIX a tabulation of approximate fouling resistances is given for oil heating and cooling equipments.

Example 40. Transfer Rate in a Steam Heater.—A fuel oil is to be heated from 80 to 150°F. by steam. The oil flows through standard $1\frac{1}{2}$-in. pipe at an average velocity of 4 ft. per second and saturate steam at 220°F. condenses on the outside of the pipe.

A. What is the over-all coefficient of heat transfer?
B. How much surface is required to heat 5,000 lb. of oil per hour?

A. The properties of this fuel oil at the average oil temperature are

z = 200 (Fig. 49).
ρ = 58 lb. per cu. ft. (sp. gr. 0.931—A.P.I. 20.5).
k = 0.068 (Morris and Whitman use 0.078 for all oils).
c = 0.44 (Fig. 33).

Neglect the difference in area at the inside and outside of the pipe.

On a basis of 1 sq. ft. of surface,

$$H = \frac{1}{\frac{1}{h_o} + \frac{L}{k} + \frac{1}{h_s}}$$

Film coefficient for oil, h_o,

$$\frac{Du\rho}{z} = \frac{1.61 \times 4 \times 58}{200} = 1.865$$

$$\frac{cz}{k} = \frac{0.44 \times 200}{0.078} = 1{,}130$$

$$\left(\frac{cz}{k}\right)^{0.37} = 13.5$$

Using Fig. 68 and extrapolating

$$\frac{h_oD/k}{(cz/k)^{0.37}} = 33 \text{ approx.}$$

$$\frac{h_oD}{k} = 33 \times 13.5 = 445$$

$$h_o = \frac{445 \times 0.078}{1.61} = 21.6$$

But the Sherwood and Petrie equation,[8] Eq. (35), should be more accurate in this range and also more accurate because of the extrapolation that was necessary with the Morris and Whitman data.

$$\mu = 2.42z = 484 \qquad U = 4 \times 3{,}600 = 14{,}400 \text{ ft. per hr.}$$

$$\frac{dU\rho}{\mu} = \frac{1.61 \times 14{,}400 \times 58}{12 \times 484} = 232$$

$$\left(\frac{dU\rho}{\mu}\right)^{0.8} = 78$$

$$\left(\frac{c\mu}{k}\right)^{0.4} = \left(\frac{0.44 \times 484}{0.068}\right)^{0.4} = 25$$

$$\frac{h_od}{k} = 0.024 \times 78 \times 25$$

$$h_o = \frac{0.024 \times 78 \times 25 \times 0.068 \times 12}{1.61} = 23.7$$

The film coefficient for condensing steam is large and in this problem it is negligible.

$$h_s = 2{,}500 \text{ approx.}$$

$$\frac{1}{h_s} = \frac{1}{2{,}500} = 0.0004$$

Likewise the resistance of the pipe wall is negligible:

$$\frac{0.145}{12 \times 25} = 0.000484$$

Hence

$$H = \frac{1}{1/h_o} = h_o = 23.7$$

B. Amount of clean new pipe required.

$$Q = 5{,}000(150 - 80)0.44 = 154{,}000 \text{ B.t.u.}$$

$$\theta = \frac{140 - 70}{\ln {}^{140}\!/_{70}} = 101$$

$$Q = HA\Delta T = 154{,}000 = 23.7 \times A \times 101$$

$$A = 64.3 \text{ sq. ft.}$$

$$\text{Feet of } 1\tfrac{1}{2}\text{-in. pipe} = 64.3 \div \frac{5.06}{12} \times 1 = 152 \text{ ft. } 6 \text{ in.}$$

A dirtiness factor should be applied to care for the condition of the surface.

Example 41. Gasoline Condenser Cooled with Water.—A 56 A.P.I. gasoline is to be condensed in a condenser having ¾ by ⅞ in. tubes. The tubes are arranged in vertical rows, 10 to the row. Water flows inside the tubes at the rate of 5 ft. per second. The water enters at 80 and leaves at 120°F. The gasoline condenses at an average temperature of about 260°F. What is the over-all rate of heat transfer?

Data on the two fluids are

Water	Gasoline
$k = 0.35$	$k = 0.086$
$\rho = 62$	$\rho = 47$
$z = 0.68$	$z = 0.235$

$$H = \frac{1}{\frac{1}{h_1} + \frac{L}{k} + \frac{1}{h_3}}$$

Film coefficient for water, h_3 [see Eq. (34). Equation (35) could also be used].

Assume drop through water film = 20°F. (see check at end)
Film temperature = 100 + ²⁰⁄₂ = 110°F.

$$\frac{Dv}{z_f} = \frac{Du\rho}{z_f} = \frac{0.75 \times 5 \times 62}{0.68} = 342$$

$$h_3 = \frac{14.5 \times 0.35}{0.75}(342)^{0.8}(1.5) = 1{,}075$$

Film coefficient for condensing gasoline, h_1 [see Eq. (39)].

Assume ΔT through film = 140°F. (see check at end)

$$
\begin{aligned}
\mu &= 2.42 \times 0.235 = 0.568 \text{ at } 260\text{°F.}\\
\lambda &= 130 + 140 \times 0.565 = 209.0 \text{ (130 is latent heat)}\\
g &= 4.18 \times 10^8 \text{ ft. per hr.}^2\\
h_1 &= 0.725\left(\frac{k^3\rho^2\lambda g}{\Delta T d\mu n}\right)^{0.25}\\
&= 0.725\left(\frac{(0.086)^3(47)^2 \quad 209.0 \times 4.18 \times 10^8}{140 \times \frac{0.875}{12} \times 0.568 \times 10}\right)^{0.25}\\
&= 0.725\left(\frac{0.000636 \times 2{,}200 \times 209.0 \times 4.18 \times 10^7}{140 \times 0.0728 \times 0.568}\right)^{0.25}\\
&= 0.725(2{,}110{,}000{,}000)^{0.25} = 0.725 \times 215 = 156
\end{aligned}
$$

Check of the assumptions of the temperature drops:

$$\text{Total resistance } R = \frac{1}{156} + \frac{1/16}{12 \times 25} + \frac{1}{1{,}075}$$

$$= 0.00641 + 0.000208 + 0.00093 = 0.00755$$

Total temperature difference = 260 − 100 = 160°F. approx.

Drop through water film $= \frac{0.00093}{0.00755} \times 160 = 19.7$°F. (check)

Drop through gasoline film $= \frac{0.00641}{0.00755} \times 160 = 136$°F. (satisfactory)

$H = \frac{1}{0.00755} = 132.3$ B.t.u. for clean pipe

With a dirtiness resistance of 0.005,

$$H = \frac{1}{0.00755 + 0.005} = 79.$$

COMPUTATIONS WHEN THE LOGARITHMIC MEAN TEMPERATURE DIFFERENCE IS IN ERROR

The logarithmic mean temperature difference was based on the assumption of a constant heat-transfer coefficient. The transfer rate is greatly dependent on viscosity and hence the best method of ascertaining if the logarithmic mean temperature difference may be used is by an examination of the viscosity properties of the material. It appears that, if the viscosity of the oil varies greatly in the range of temperature through which it is being heated or cooled, then the transfer rate will not be a constant and the logarithmic mean temperature difference will not be an accurate average temperature difference.

In many cases the arithmetic temperature difference is more accurate then the logarithmic mean temperature difference. An oil whose absolute viscosity changes by four times as much as the lower viscosity, while being processed, results in errors of approximately 15 per cent if the logarithmic temperature difference is used. If heat is being transferred by using two such oils, then the error becomes even greater. Obviously, if the tubes are rough or dirty the over-all coefficient will not be so greatly affected by inaccuracies in estimating the temperature difference as when clean surfaces are used.

In case the logarithmic mean temperature difference cannot be used, the following arithmetic integration method will be satisfactory. Consider the proposed heat-exchange equipment to be broken up into a number of small sections of exchanger. In each of these the temperature of one of the fluids changes by a small increment of, say, 10°F. The temperature difference between the two fluids in each of these sections is nearly the arithmetic average temperature difference (Fig. 69).

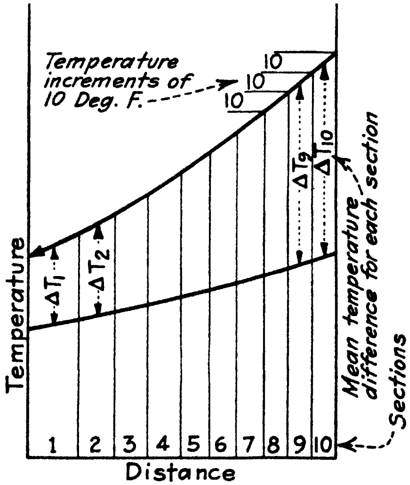

FIG. 69.—Actual temperature difference in countercurrent flow.

Assuming a constant specific heat, Q per small unit of exchanger equals, $H_1\Delta T_1A_1 = H_2\Delta T_2A_2 = H_3\Delta T_3A_3$, etc. The total area is equal to the sum of the areas A_1, A_2, A_3, etc. So many variables are involved in the heat-transfer coefficient that formal calculus methods are not practical, although several generalizations[18] of this kind have been made.

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[18] GARCIA, M., *Ind. Eng. Chem.*, **20**, 889 (1928) and BADGER and McCABE, "Elements of Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1930.

Example 42. Comparison of Methods of Obtaining the Temperature Difference.—Sixty thousand eight hundred pounds per hour of a heavy oil, specific gravity 0.93 at 60°F., viscosity 600 centipoises at 100°F. (Fig. 49), is to be heated from 120 to 200°F. with steam at 25 lb. per square inch gage pressure. $k = 0.08$, specific heat = 0.7, and $h_s = 2{,}500$; 1½-in. standard pipe, steam jacketed. How long a pipe is required?

Mass velocity: The mass velocity is a constant:

$$v = u\rho = \frac{\dfrac{60{,}800}{3{,}600} \times \dfrac{1}{62.4 \times 0.93}}{2.036/144} \times 62.4 \times 0.93$$
$$= 1{,}195 \text{ lb. per sq. ft. of cross-sectional area}$$

Steam temperature:

Saturate at 25 lb. = 267°F.

A. Using the Actual Temperature Difference.—Use 10 sections of exchanger with a temperature rise for the oil in each section, of 8°F. Use Morris and Whitman data (Fig. 68). Refer to Fig. 69.

TABLE 30.—TABULATED COMPUTATION FOR EXAMPLE 42

(1) Section	(2) Temp. range	(3) Aver. temp.	(4) ΔT 267−(3)	(5) z at ave. temp.	(6) $\frac{Du\rho}{z}$	(7) $\frac{hD/k}{(cz/k)^{0.37}}$ (Fig. 68)	(8) $\frac{cz}{k}$	(9) $\left(\frac{cz}{k}\right)^{0.37}$	(10) h solving (7)	(11) H over-all	(12) A $\frac{34 \times 10^4}{(11) \text{ and } (4)}$
1	120–128	124	143	200	9.6	68	1,750	15.9	53.6	49.8	46.8
2	128–136	132	135	155	12.4	85	1,360	14.4	60.5	57.6	42.9
3	136–144	140	127	120	16.0	112	1,050	13.1	73.0	68.7	38.2
4	144–152	148	119	100	19.2	142	875	12.3	87.0	80.9	34.7
5	152–160	156	111	83	23.2	184	725	11.4	104.0	95.6	31.4
6	160–168	164	103	70	27.5	223	613	10.8	119.0	108.0	30.9
7	168–176	172	95	59	32.7	270	516	10.1	135.0	119.0	29.6
8	176–184	180	87	50	38.5	330	438	9.5	156.0	137.0	28.0
9	184–192	188	79	42	46.0	410	368	8.9	181.0	157.0	26.9
10	192–200	196	71	36	53.5	475	315	8.4	198.0	169.0	27.8
Total surface											337.2 sq. ft.

$$Q = 60{,}800 \times 0.7\frac{(200 - 120)}{10} = 340{,}000 \text{ B.t.u. per hr. of each section}$$

Total duty, 10 sections = 3,400,000 B.t.u. per hr.
Total length = 2.37 × 337.2 = 800 ft. (Table 30)

B. Using Log Mean Temperature Difference.

$$\theta = \frac{147 - 67}{\ln {}^{147}\!/_{67}} = 102°\text{F.}$$

Average oil temperature = 165°F. $z = 70$

$\frac{Du\rho}{z} = 27.5$ $h = 119$ (Fig. 68)

$$H = \cfrac{1}{\frac{1}{119} + \frac{0.145}{12 \times 25} + \frac{1}{2{,}500}} = 108$$

$$A = \frac{3{,}400{,}000}{108 \times 102} = 309 \text{ sq. ft.}$$

Length = 2.37 × 309 = 732 ft.
Per cent error = 8.5

C. Using the Arithmetic Mean Temperature Difference.

$$\text{Temperature difference} = \frac{147 + 67}{2} = 107$$

$$\text{Average oil temperature} = 267 - 107 = 160$$

$$H = \frac{108 + 95.8}{2} = 101.9 \text{ (Table 30)}$$

$$A = \frac{3{,}400{,}000}{107 \times 101.9} = 312 \text{ sq. ft.}$$

Length = 740 ft.
Per cent error = 7.5

In this case the arithmetic temperature difference is more exact than the logarithmic mean temperature difference.

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CHAPTER XIV

VAPORIZATION AND CONDENSATION

The subject of distillation is usually referred to as a combination operation involving heating, vaporization, fractionation, condensation, and cooling. It is the purpose of this chapter to discuss the theory of vaporization and condensation, and particularly to discuss the equilibrium relations for vapor-liquid systems. Both vaporization and condensation are phenomena which involve vapor-pressure and the two operations can be conducted as analogous processes except that condensation is just the reverse of vaporization. The theory of vaporization must be developed for two component systems, but to be of real usefulness in petroleum refining the theory must be adapted to the treatment of systems involving many components. This is accomplished by the use of the equilibrium-flash-vaporization curve which has been introduced in Chaps. VI and VII.

The physical laws governing the distribution of a component between the liquid and the vapor above the liquid form the basis of many refinery operations. Among these processing operations are shell or pipestill vaporization, fractionation, and condensation. In addition, the vapor-pressure laws may be applied to the estimation of fractionating-tower temperatures, partial condenser temperatures, friction losses in tubular heaters and pipestills, and in computing the quantity of steam that is required for distillation and steam stripping.

Vaporization and Condensation.—Vaporization may be defined as the change from the liquid to the vapor state. This change absorbs energy. When heat is applied to a mixture of hydrocarbons under constant pressure, part of the energy is absorbed by the change of state and part is expended in raising the temperature of the remaining liquid. This rise in temperature increases the vapor-pressure or the tendency of all components of the mixture to leave the liquid and enter the vapor-phase. Therefore, the vapor from a liquid contains some of each of the components present in the liquid. However, rise in temperature increases the vapor-pressures of the lower boiling components more rapidly than the vapor-pressures of the higher boiling components. Thus the vapor will be richer in lower boiling and poorer in higher boiling components than the liquid that remains, and the residual liquid will be richer in higher boiling and poorer in lower boiling components than the original liquid. Moreover, the vapor will always be richer in lower boiling components than the original liquid, unless the mixture is heated to a temperature at which it is completely vaporized, in which case the vapor will have the same composition as the original liquid. The equilibrium diagram shown in Fig. 70 illustrates these principles. Below the liquid line the mixture is entirely liquid and above the vapor line a pure vapor-phase exists. Between the two lines a mixture of liquid and vapor is present. Raoult's law was assumed to be valid in computing Fig. 70.

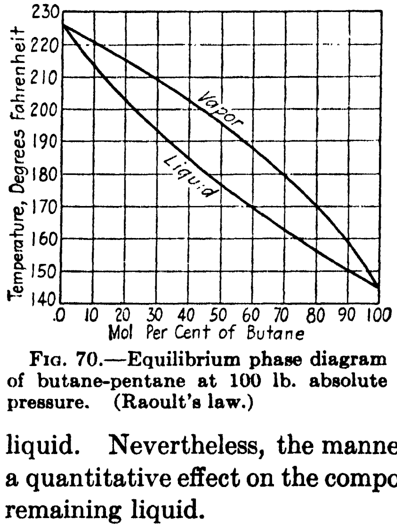

FIG. 70.—Equilibrium phase diagram of butane-pentane at 100 lb. absolute pressure. (Raoult's law.)

These generalizations are equally valid whether the vapor is removed continuously or remains in contact with the liquid. Nevertheless, the manner of separation of the vapor has a quantitative effect on the composition of the distillate and of the remaining liquid.

Condensation is essentially the inverse of vaporization. It follows therefore that the condensate will be richer in higher boiling and poorer in lower boiling components than the original vapor, and that the remaining vapor will be richer in lower boiling components than the condensate.

Mechanism of Vaporization.—The most common method of vapor formation is *batch vaporization* as conducted in the A.S.T.M. distillation or as practiced in early shellstill distillation. The mechanism is differential because, as the temperature is raised a small amount, a corresponding evolution of vapor takes place. As this vapor is removed and the temperature is again raised, another evolution of vapor occurs. The operation continues thus until finally the liquid is depleted or some extraneous operation such as thermal decomposition occurs. In distilling a liquid mixture thus, each component in the liquid exerts a partial-vapor-pressure or a part of the total vapor-pressure and every component tends to leave the mixture in proportion to its partial-vapor-pressure at that temperature. The lower boiling components, those with high vapor-pressures, compose the most of the first vapors, but some remain in the liquid and are distilled later with other components whose boiling-points are much higher. The reason for this strange behavior may be most easily pictured by conceiving that the high-velocity, low-boiling molecules bump into slower moving molecules and lose the energy content which would normally cause them to leave the liquid and enter the vapor. Some of the slower moving molecules may receive enough energy by these impacts to leave the liquid and this occurs because we find that high-boiling components are present in the first vapor even though the temperature is much lower than their boiling-points. Thus a mixture of vapors arises throughout the entire distillation.

Differential or batch vaporization may be mathematically formulated as follows. If L represents the liquid, x the percentage of a component in the liquid, and y the percentage of the component in the vapor, a material balance with respect to the component is

$$xL = (x - dx)(L - dL) + ydL$$
$$xL = xL - xdL - Ldx + dxdL + ydL$$

The second order differential $dxdL$ may be neglected:

$$(x - y)dL = Ldx$$
$$\frac{dL}{L} = \frac{dx}{x - y}$$

The quantity that must be distilled in order to cause a particular change in composition may be determined by integrating between L_0, the initial quantity of liquid, and L_1 the final quantity:

$$\ln\frac{L_0}{L_1} = \int_{x_1}^{x_0} \frac{dx}{x - y}$$

The value of the function $dx/(x - y)$ may be obtained by graphically integrating between the limits x_1 and x_0. The various values of x are plotted against the corresponding values of $1/(x - y)$, and the area under the curve is the integral of the function. The relation between x and y may be obtained by Henry's law or Raoult's law. Data on two component systems are all that are usually available.

Equilibrium-flash Vaporization.—The mechanism of this type of vaporization differs from differential vaporization in that the vapor is not removed as it is formed but is kept in intimate physical contact with the remaining liquid until the heating is completed. In the refinery such a method is practiced in the pipestill. Any vapor which is formed in the pipestill tubes is kept in contact with the remaining liquid until the mixture flows from the outlet of the still. Mechanical contacting is effected by the high velocity which results as soon as even a small quantity of vapor is produced.

The flash-vaporization curve may be drawn just as the batch-vaporization curve is drawn, *i e.*, by plotting the temperature against the percentage distilled (Fig. 71). The molecules that normally would be vaporized at a low temperature are unable to separate themselves from the liquid, and they lose much of their energy content to the high-boiling molecules. Thus vaporization does not start to occur at the boiling-point of the lowest boiling component, and at low percentages vaporized the equilibrium-flash manner of vapor formation requires a higher vapor-temperature than batch vaporization. However, after having vaporized a considerable percentage of liquid, the bombardment of the many high-velocity vapor molecules succeeds in vaporizing a part of the high-boiling material and the flash-vaporization curve crosses the differential-vaporization curve (Fig. 71). At percentages past the intersection, flash vaporization is highly advantageous because a relatively large amount can be distilled without heating to a high temperature.

The saving in heat is not the only advantage. Thermal decomposition halts all distillations at liquid temperatures of approximately 700°F. and thus by flash vaporization, the high-boiling part of a liquid may be vaporized whereas by batch vaporization this high-boiling part could never be vaporized. Of course, steam or a low pressure may be used to distill high-boiling oils but these modifications can be applied to either method of vapor formation.

Commercial Vaporization.—In practice, the foregoing methods are often used in combination. *Successive flash* vaporization occurs if two or more pipestills are used in series. The liquid residue from the first flash is further heated (or the pressure is reduced) and a second flash-operation is conducted. As an example, crude oil is often heated in an exchanger system and flashed into a fractionating tower. The remaining liquid is then heated in a pipestill and flashed in a second tower. The two-flash atmospheric and vacuum system is also becoming important. In this system the crude oil is heated and flashed at atmospheric conditions and the residue of reduced crude (already at a high temperature) is flashed under vacuum to recover gas oil and light lubricating oils. A two-flash system is sometimes used in rerunning brightstock solution. This material consists of approximately 70 per cent of a low-boiling naphtha and 30 per cent of finished brightstock. The naphtha is flashed in one operation and the remaining brightstock is further heated and flashed in the presence of steam. Other examples are the atmospheric-vacuum redistillation of pressure distillate and the production of well-fractionated solvents by the use of several heaters and fractionating towers.

The *continuous shellstill battery* is an operation involving flash vaporization but not flash vaporization alone. In pure flash vaporization the vapor is physically mixed with the remaining liquid, but in a shellstill battery the flash in each still occurs in the presence of an abnormally large quantity of residue liquid. Thus the concentration of slow-moving molecules is high and these molecules tend to absorb the energy content of the lower boiling molecules. However, some molecules have energy contents bordering between liquid and vapor and these molecules are vaporized. The equilibrium that is established is indeed complicated. In a sense, the laboratory batch distillation, with no fractionation, is equivalent to a shellstill battery having an infinite number of stills. Theoretically this method of vaporization seems to have no outstanding advantages. *Batch distillation* as practiced in a single shellstill has been discussed on page 237.

Distillation Curves.—As a summary, a comparison of distillation curves by various vaporization methods will be useful. Figure 71 shows the vapor-temperatures plotted against percentage distilled for (1) flash, (2) A.S.T.M., (3) Hempel, and (4) true-boiling-point distillations of a Mid-Continent pressure distillate. The same relations hold true for other stocks but to a lesser degree for wide-boiling-range materials.

Although the foregoing comparison is commonly used, it appears that the engineer should be more interested in the liquid temperatures required for a given vaporization than in the vapor-temperatures. Hence the same four curves are compared in

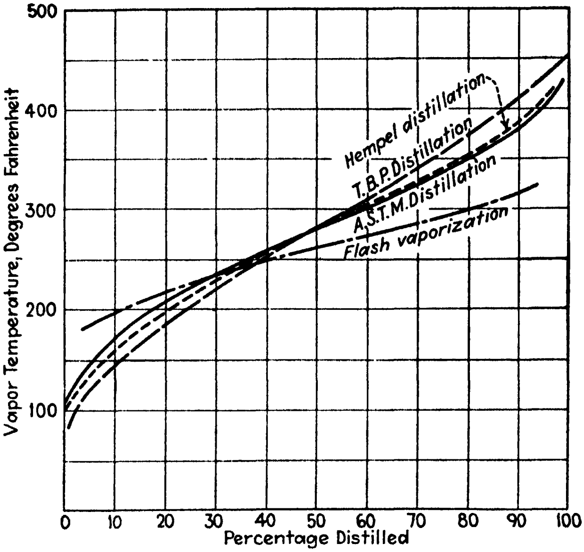

FIG. 71.—Vapor-temperatures for several kinds of distillation.

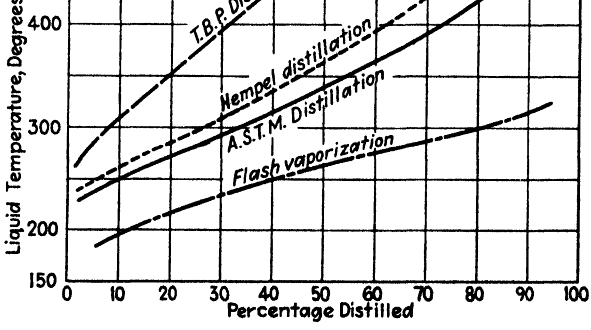

FIG. 72.—Liquid-temperature curves by several kinds of distillation.

Fig. 72, by plotting the liquid temperature against the percentage distilled. This figure clearly shows that vaporization can be conducted at lower liquid temperatures by flash vaporization than by any other method.

CONDENSATION

In many ways condensation is just the reverse of vaporization although some of the vaporization mechanisms cannot be mechanically duplicated in condensing equipment. Differential condensation, in which the condensate is removed as soon as it is formed, is not practiced commercially. Differential condensation may be mathematically formulated in an analogous manner to the formulation for differential vaporization (page 237).

Equilibrium Condensation.—The mechanism of equilibrium condensation is practiced in most commercial condensers. The condensed liquid is kept in contact with the remaining uncondensed vapor until the outlet of the condenser (or cooler) is reached. The *flash-vaporization* and the *equilibrium-condensation* curves are identical if intimate physical contacting is maintained during both operations.

In large condensers of the tubular type, the condenser is usually broken up into several separate condensing units and liquid is withdrawn from each. Each of these units is referred to as a *partial condenser*. However, partial condensation does not give an effective separation between products and hence it is not usually used as a method of fractionation. The partial condensers that are used in a modern vacuum plant for the separation of gas oil and wax distillate are an exception. This separation need not be exact and hence partial condensers are satisfactory (Fig. 113, Chap. XVIII). In the past, *dephlegmators*[1] or partial condensation towers, cooled either by air or water, were extensively used. Inasmuch as these equipments are not used now, they will not be discussed further.

In certain plant equipment the vapor is suddenly cooled under equilibrium conditions and such a process may be called *quench condensation*. Jet condensers embody this method but they are not widely used. However, barometric condensers, in which steam is condensed with water, are common. Of more impor-

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[1] The term *dephlegmator* is usually reserved for partial condenser towers but certain cracking processes have retained this name for their fractionating towers. They have changed the process of separation but have retained the older name.

tance is the condensation of vapor on each plate of a fractionating tower by reflux. In this case, the condensation may take place in the presence of other vapor which does not condense. As an example, kerosene is condensed on a "side-draw" plate of a bubble-tower. Gasoline vapor is also present at the plate but it does not condense. The details of the application of this phase of condensation will be discussed in Chap. XXI. The equilibrium-condensation curve also describes quench condensation.

EQUILIBRIUM

In order to use any of the aforementioned operations, the equilibrium relations between liquids and vapors must be ascertained. In other words, the distribution of a component in the two phases after no further interchange takes place must be known. For petroleum oil mixtures which contain only a few components, the distribution of a component is accurately described by Dalton's law of partial-pressures, by Henry's law, and in many cases by Raoult's law.

The change of state from liquid to vapor or from vapor to liquid is not unidirectional. Although the predominate tendency may be for the molecules to leave the liquid and enter the vapor, some of the gaseous molecules will reenter the liquid phase. This may be explained by the uneven distribution of energy among the molecules. That is, although all of the molecules of the vapor are in motion, some have greater energy than others as a result of collisions and other effects, so that the slower molecules fall back into the liquid. Conversely, when the predominant tendency is from the vapor to the liquid state, some of the liquid molecules, which have greater velocity than the average, break from the liquid surface and reenter the vapor phase.

When the rate at which molecules leave the liquid is equal to the rate at which vapor molecules reenter the liquid, the system is said to be in equilibrium and neither vaporization nor condensation appears to be taking place. In reality, both are occurring simultaneously but at equal rates so that the system is in dynamic balance.

Figure 70 shows the equilibrium relationships between liquid and vapor compositions for butane-pentane mixtures at 100 lb. absolute pressure. With the pressure fixed, temperature is the only variable; *i.e.*, there is a single composition of the liquid and of the vapor at each temperature. At equilibrium, a change in the liquid or vapor composition requires a change in temperature, and a change in temperature necessarily involves a change in liquid and vapor composition. For example, assume that a liquid containing 70 per cent of butane and 30 per cent of pentane is to be heated. No vapor will be formed until the liquid equilibrium line is reached at 163°F. At this point an infinitesimal quantity of vapor will be formed having the composition corresponding to 163°F. on the vapor curve, *i.e.*, 88 per cent of butane. If heating is continued, the composition of the liquid must necessarily change along the liquid curve with the production of increasing quantities of vapor, the composition of which follows the vapor curve. The change in liquid and vapor compositions will continue thus until the total vapor has the composition of the original liquid, and the liquid is completely vaporized. Further heating will merely superheat the vapor without changing its composition.

Partial-pressures of Vapor Components.—In a mixture of gases, each gas exerts a pressure equal to the pressure it would exert if it occupied the entire volume by itself, and the total pressure of the mixture is equal to the sum of the partial-pressures of the component gases (Dalton's law). The pressure exerted by each component is called the partial-pressure[2] of the component and is dependent on the total pressure and the volume or number of molecules of that component in the gas.

In the gas phase if π is the total pressure and y is the volume or mol fraction of an individual component in the mixture, the law of partial-pressures may be expressed as

$$p = \text{partial-pressure in vapor} = \pi y, \qquad \text{or} \qquad \frac{p}{\pi} = y$$

For example, in a vapor mixture composed of 70 per cent of butane and 30 per cent of pentane at 100 lb. per square inch absolute pressure, the partial-pressures are

$$\text{p.p. butane} = 100 \times 0.7 = 70 \text{ lb. per sq. in.}$$
$$\text{p.p. pentane} = 100 \times 0.3 = 30 \text{ lb. per sq. in.}$$

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[2] Confusion often arises over the term partial-pressure, because it is used in the same discussion both as it is above and also to denote the fraction of the total pressure.

Partial-vapor-pressures of Liquid Components.—Just as each component of a vapor exerts a partial-pressure, each component of a liquid exerts a partial-vapor-pressure. This is dependent upon the concentration of the component in the liquid and the vapor-pressure of the pure component. The escaping tendency of a component appears to depend upon the percentage of the surface area (mol fraction) covered by the component and the molecular energy (vapor-pressure) of the component. If P is the vapor-pressure of the pure component at a given temperature, and x is the mol fraction of this component in the liquid,

$$p = \text{partial-vapor-pressure in liquid} = Px$$

Expressed as a fraction of the total pressure,

$$\frac{p}{\pi} = \frac{P}{\pi}x$$

At equilibrium the partial-pressure of a component in the gas is equal to the partial-vapor-pressure of the component in the liquid. Inasmuch as p/π is equal to y, the mol fraction of the component in the gas is

$$y = \frac{p}{\pi} = \frac{P}{\pi}x \text{ (Raoult's law)} \tag{41}$$

Considering two components,

$$\pi y_1 = P_1x_1$$

and

$$\pi y_2 = P_2x_2$$

adding

$$\pi(y_1 + y_2) = P_1x_1 + P_2x_2$$

but

$$x_2 = 1 - x_1, \quad \text{and} \quad y_1 + y_2 = 1$$

$$x_1 = \frac{\pi - P_2}{P_1 - P_2}, \quad \text{and} \quad x_2 = \frac{\pi - P_1}{P_2 - P_1} \tag{42}$$

$$y_1 = \frac{P_1}{\pi}x_1, \quad \text{and} \quad y_2 = \frac{P_2}{\pi}x_2$$

Example 43. Raoult's Law.—A liquid consists of 42.5 per cent by volume of butane and 57.5 per cent by volume of pentane at 60°F. If the liquid is heated to 180°F. at 100 lb. per square inch absolute pressure, what will be the composition of the vapor that is produced? (See Example 1, page 33, or Fig. 5.)

Vapor-pressure of C_4H_{10} at 180°F. = 152 lb. per sq. in.
Vapor-pressure of C_5H_{12} at 180°F. = 56 lb. per sq. in.
Sp. gr. at 60°F. of C_4H_{10} = 0.585, and C_5H_{12} = 0.631

Basis: 100 gal. of the mixture. Assume Raoult's law is valid.

$$\text{Mols of } C_4H_{10} = \frac{42.5(8.33 \times 0.585)}{58} = 3.57$$

$$\text{Mols of } C_5H_{12} = \frac{57.5(8.33 \times 0.631)}{72} = 4.20$$

$$\text{Total mols} = 7.77$$

$$x_1 = \text{mol fraction } C_4H_{10} \text{ in liquid} = \frac{3.57}{7.77} = 0.46$$

$$x_2 = \text{mol fraction } C_5H_{12} \text{ in liquid} = \frac{4.20}{7.77} = 0.54 \text{ or } (1 - 0.46)$$

See Eq. (41):

$$y_1 = \text{mol fraction of } C_4H_{10} \text{ in vapor} = {}^{152}\!/_{100}\ 0.46 = 0.70$$

$$y_2 = \text{mol fraction of } C_5H_{12} \text{ in vapor} = {}^{56}\!/_{100}\ 0.54 = 0.30$$

Thus a liquid containing 46 per cent of butane and 54 per cent of pentane (mol per cent) at 180°F. and 100 lb. per sq. in. is in equilibrium with vapor containing 70 per cent of butane and 30 per cent of pentane (see Example 44 and also Fig. 70).

Raoult's law is a special case of the more general relationship known as Henry's law. For our purposes Henry's law may be stated as follows:

$$y = Kx \tag{43}$$

The constant K must be determined experimentally and it is a function of temperature just as vapor-pressure is a function of temperature. It is also dependent on the pressure. In the special case of Raoult's law the value of K is equal to the vapor-pressure divided by the total pressure [see Eq. (41)].

Equilibrium Data.—Henry's law of equilibrium is obviously applicable to all kinds of materials but the constant K must be determined experimentally for each material and for different conditions of temperature and pressure. The constant varies with the temperature and with the pressure (Figs. 73, 74). Dalton's law of partial-pressure is generally applicable to all materials if the critical condition is not approached. In other words, the law is valid if the pressure is well below the critical pressure and the temperature is several hundred degrees below the critical temperature. Nevertheless, no other simple relationship is available and hence Dalton's law is widely used even for conditions at which it is known to be in error.

Raoult's law is not so generally valid as the foregoing relation. For the normal paraffin hydrocarbons this law is valid up to pressures of approximately 60 lb. per square inch.[3] As the pressure approaches the critical pressure, the deviation from Raoult's law becomes great.[4] Although data concerning the equilibrium relations at or near the critical point are not extensive, enough is known to serve as a useful basis for engineering estimates and designs. Nevertheless, an element of uncertainty exists[4] because the experimental data are inadequate and the data had to be extrapolated.

Brown[4] correlates equilibrium data by the use of the reduced temperature concept which was introduced in Chap. VIII (page 110). Equilibrium data[4,5] are given in Figs. 73 and 74.

Example 44. Equilibrium Relations at High Pressures.—Example 43 will be repeated using the actual equilibrium constants rather than assuming that Raoult's law is valid. When the actual constants are used, the compositions of both the liquid and the vapor may be different from those in Example 43. An expression similar to Eq. (41), but using K's, is as follows:

$$x_1 = \frac{1 - K_2}{K_1 - K_2}$$

K_1 for butane (Fig. 73c) at 180°F. and 100 lb. $= 1.4$
K_2 for pentane (Fig. 74c) at 180°F. and 100 lb. $= 0.6$

$$\begin{aligned} x_1 &= \frac{1 - .6}{1.4 - .6} = 0.50 \\ x_2 &= 1 - 0.50 = 0.50 \\ y_1 &= K_1x_1 = 1.4 \times 0.50 = 0.7 \\ y_2 &= K_2x_2 = 0.60 \times 0.50 = 0.3 \end{aligned}$$

It is a coincidence that vapor composition is the same as in Example 43. Note that in this example the 70–30 vapor is in equilibrium with a 50–50 liquid whereas in Example 43 a 70–30 vapor was in equilibrium with a 46–54 liquid.

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[3] Brown and Souders, Properties of the Paraffin Hydrocarbons . . . , *Oil Gas J.*, May 26, 1932, p. 41.

[4] Brown, Souders, and Smith, Pressure-volume-temperature Relations . . . , several articles, *Ind. Eng. Chem.*, **24**, 513 (1932); Cope, Lewis, and Weber, *Ind. Eng. Chem.*, **23**, 887 (1931).

[5] Katz and Brown, Vapor Pressure and Vaporization of Petroleum Fractions, *Ind. Eng. Chem.*, **25**, 1373 (1933).

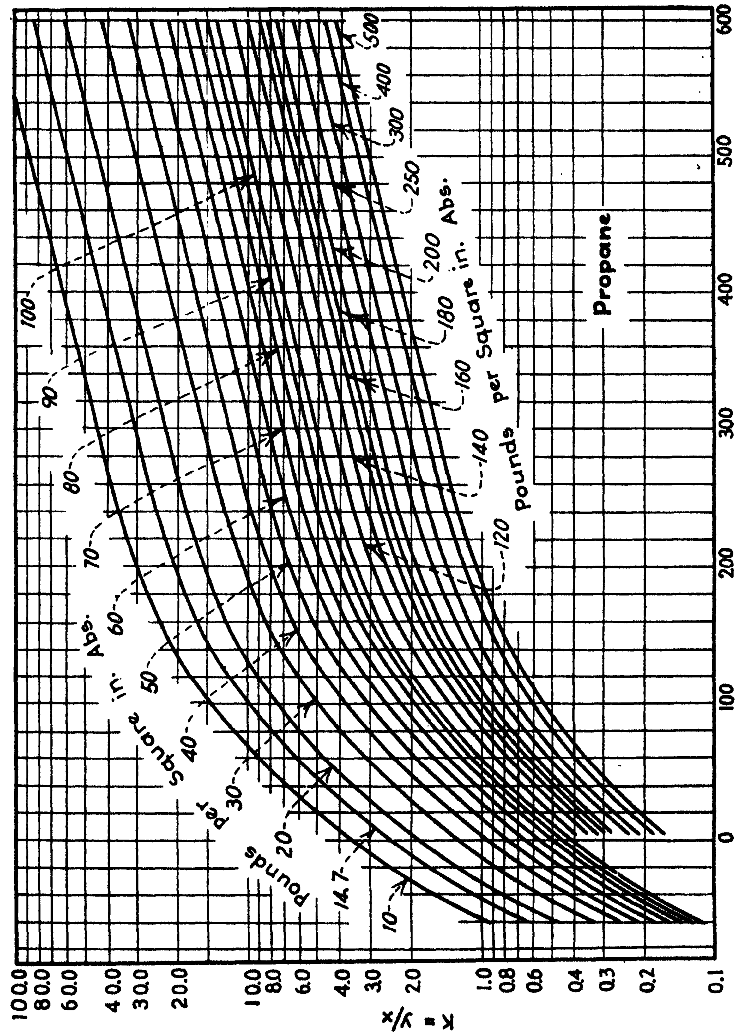

FIG. 73a.—Equilibrium constants for propane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

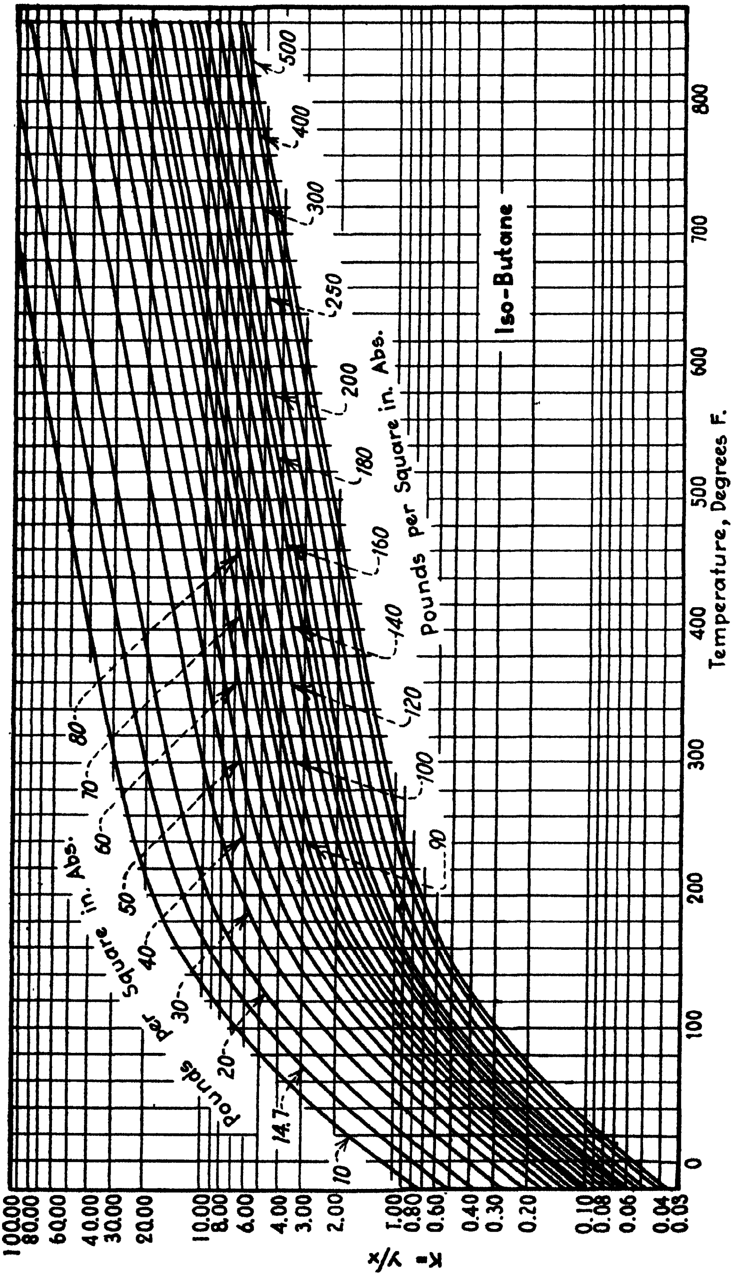

FIG. 73b.—Equilibrium constants for isobutane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

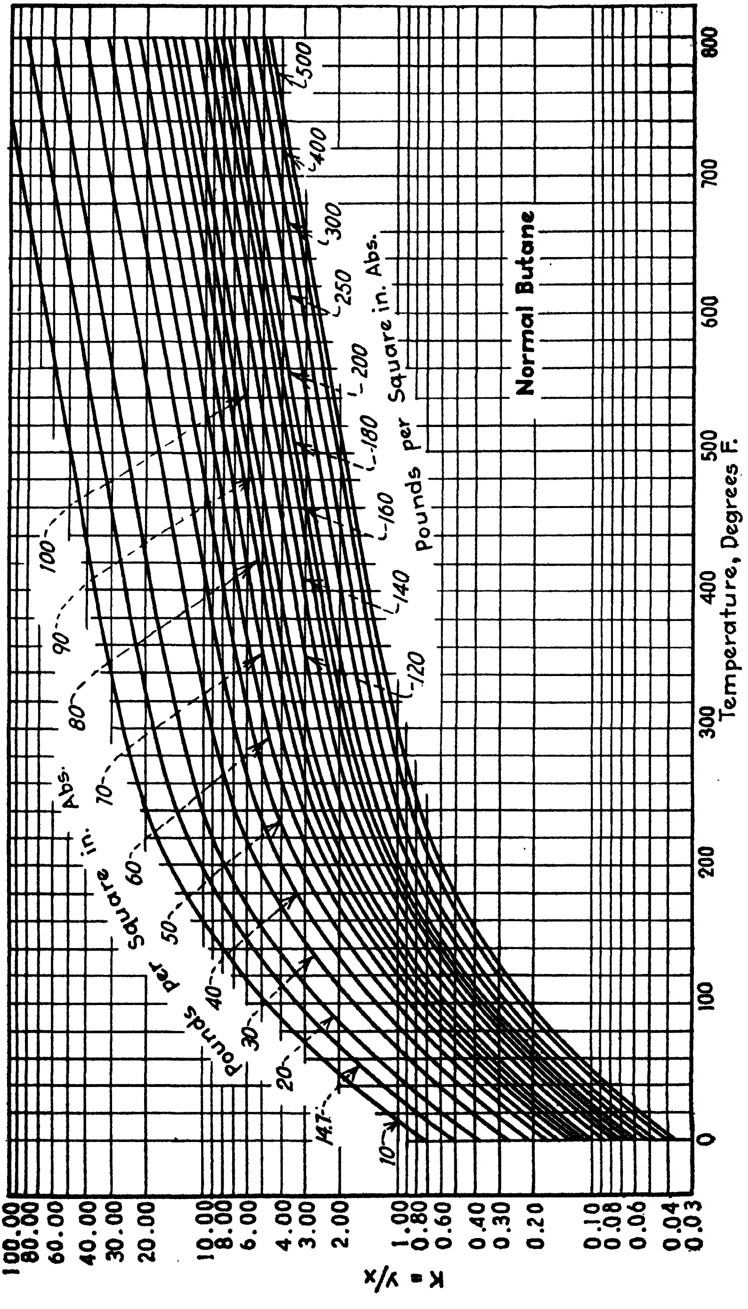

FIG. 73c.—Equilibrium constants for normal butane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

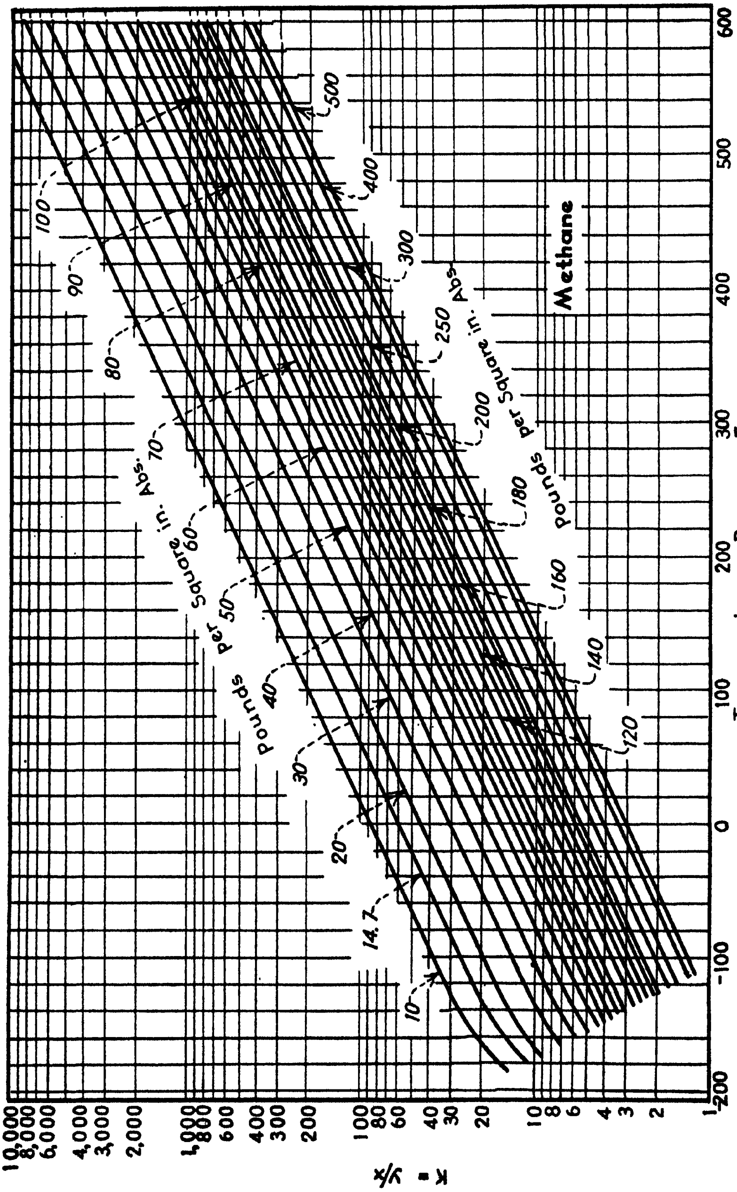

FIG. 74a.—Equilibrium constants for methane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

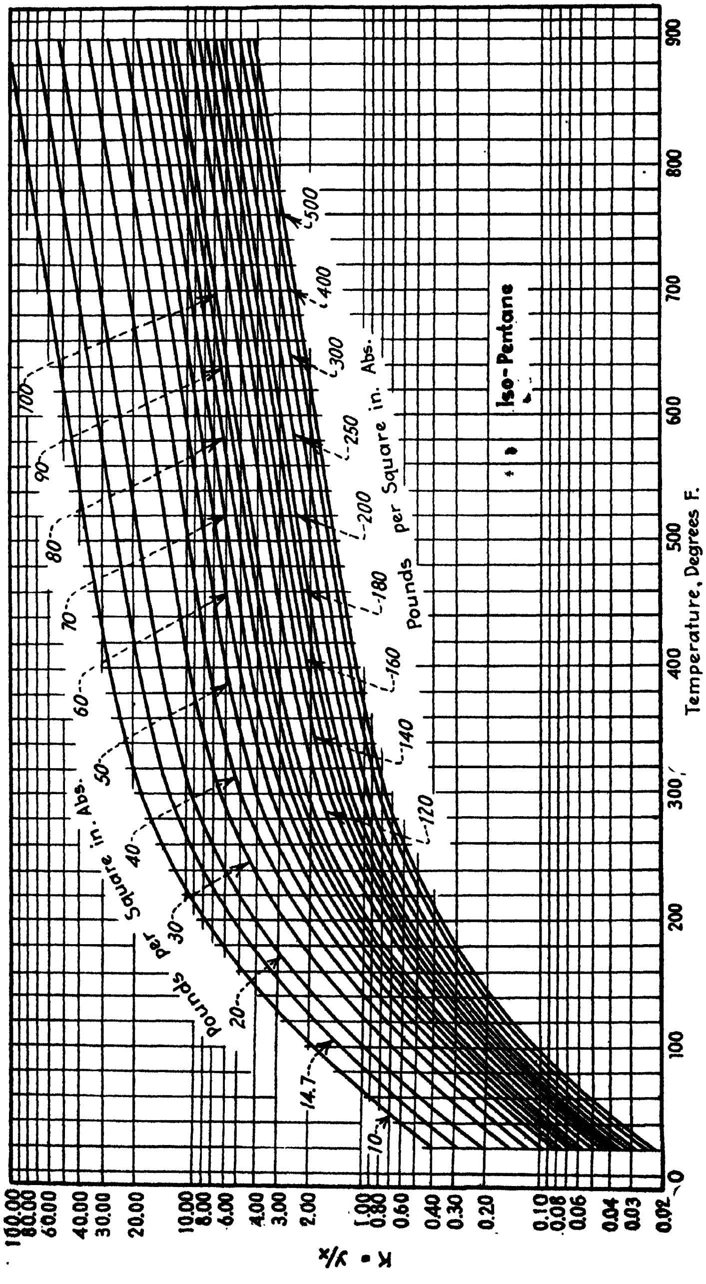

FIG. 74b.—Equilibrium constants for isopentane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

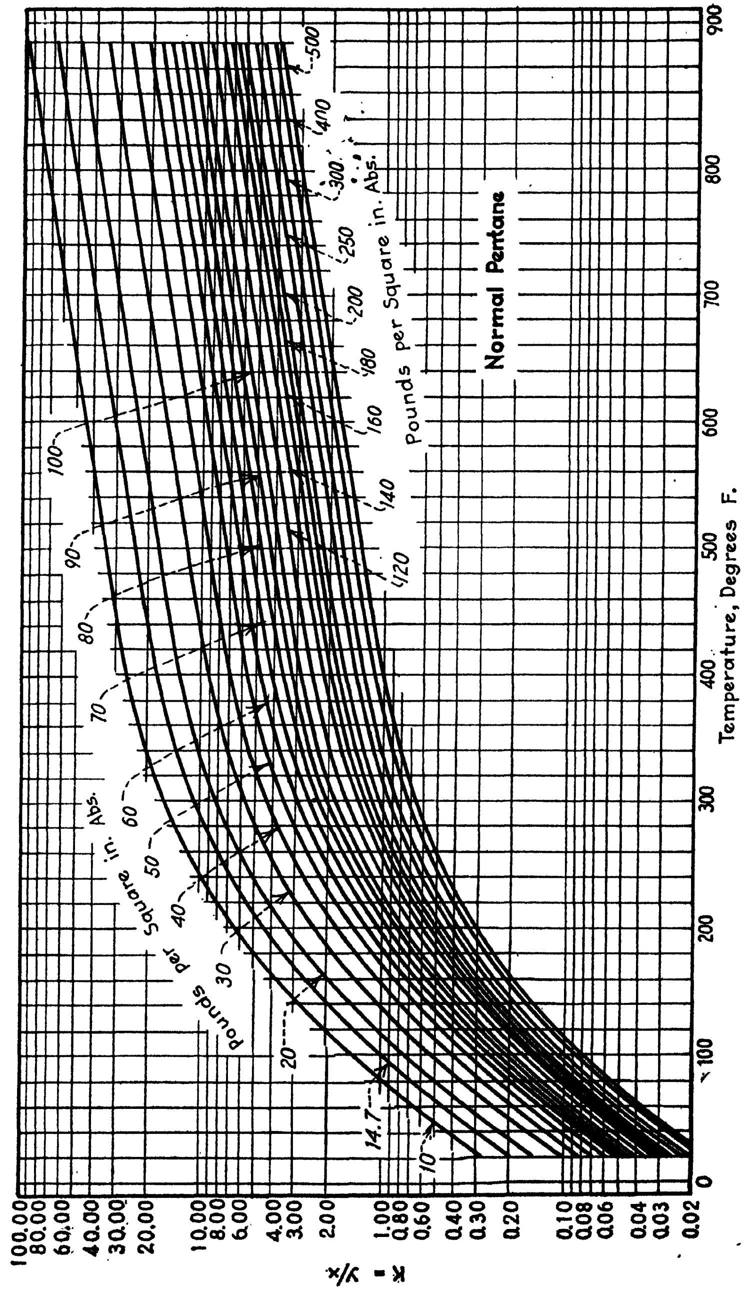

FIG. 74c.—Equilibrium constants for normal pentane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

Equilibrium Relations for Complex Mixtures.—Raoult's and Henry's laws [Eqs. (41 and (43)] may be applied to the solution of problems which involve complex mixtures in the same manner as in Examples 43 and 44 except that trial-and-error methods must be used. The percentage vaporized at a given temperature can be computed, and the composition of the residue liquid and vapor can also be determined.

Consider 100 mols of a liquid feed stock called X consisting of X_1, X_2, X_3, etc., mols of the different components designated by the subscripts 1, 2, 3, etc. By equilibrium vaporization of this mixture, by heating to a given temperature at a fixed pressure, V mols of gas is produced which contains V_1, V_2, V_3, etc., mols of the several components. A liquid residue, L mols, is left behind and it also consists of L_1, L_2, L_3, etc., mols of the several components which constitute the feed.

By a material balance:

Feed stock. . . . . $X = X_1 + X_2 + X_3 + \cdots$
Vapor. . . . . $V = V_1 + V_2 + V_3 + \cdots$
Residue liquid. . . . . . . $L = L_1 + L_2 + L_3 + \cdots$

The mol fraction of each component may be expressed as

$$\frac{X_1}{X}; \quad \frac{X_2}{X}; \quad \frac{V_2}{V}; \quad \frac{L_3}{L}; \text{ etc.}$$

Furthermore, for the total material or for any component, material balance equations of this nature may be written

$$X = L + V; \qquad X_1 = L_1 + V_1; \qquad \text{and} \qquad X_n = L_n + V_n$$

Henry's law applied to any component is

$$\frac{V_1}{V} = K_1\frac{L_1}{L}, \qquad \text{and} \qquad \frac{V_n}{V} = K_n\frac{L_n}{L}$$

Or

$$V_1 = K_1L_1\frac{V}{L}; \qquad V_3 = K_3L_3\frac{V}{L}, \text{ etc.}$$

Substituting $(X - V)$ for L, for each component,

$$V_1 = K_1(X_1 - V_1)\frac{V}{L}, \text{ etc.}$$

Solving for V_1 and simplifying

$$V_1 = \frac{K_1X_1}{\frac{L}{V} + K_1}, \text{ etc.}$$

Since the sum of the volumes or mols is the total mols of vapor,

$$\frac{K_1X_1}{\frac{L}{V} + K_1} + \frac{K_2X_2}{\frac{L}{V} + K_2} + \frac{K_3X_3}{\frac{L}{V} + K_3} \ldots, \text{ etc.} = V \qquad (44)$$

A similar statement assuming Raoult's law but stated for the liquid residue is as follows:

$$\frac{X_1\pi}{\pi + P_1\frac{V}{L}} + \frac{X_2\pi}{\pi + P_2\frac{V}{L}} + \frac{X_3\pi}{\pi + P_3\frac{V}{L}} \ldots = L \qquad (45)$$

In this equation π refers to the total pressure and P_1, P_2, etc., to the vapor-pressure of each component.

In solving these equations it is necessary to assume a value of L (or V), and by substituting this value, a value of L can be computed. If the computed value is not the same as the assumed value, other assumptions must be made until finally the assumption checks the computed value. By solving the equation for several temperatures, an equilibrium-flash-vaporization curve may be drawn.

A similar equation but for the mechanism of condensation is as follows:

$$\frac{K_1G_1}{\frac{C}{V} + K_1} + \frac{K_2G_2}{\frac{C}{V} + K_2} + \frac{K_3G_3}{\frac{C}{V} + K_3} + \cdots = V \qquad (46)$$

where G_1, G_2, G_3, etc. = mols of each component in original gas.
C_1, C_2, C_3, etc. = mols of each component in condensate.
V_1, V_2, V_3, etc. = mols of each component in final gas.

In solving an equation which contains several variables, there will be as many solutions as there are variables. Perhaps the most reliable method of selecting the true solution is to inspect the vapor-pressures or equilibrium constants of the components. The partition between liquid and vapor will occur at or near the component whose vapor-pressure is equal to the pressure of the system. The method is exact unless one of the equilibrium phases is much larger than the other.

Example 45. Equilibrium Vaporization of Complex Mixtures.—A wild gasoline contains 15 per cent of CH_4, 10 per cent of C_2H_6, 30 per cent of C_3H_8, 5 per cent of $i\ C_4H_{10}$, 10 per cent of C_4H_{10}, 15 per cent of C_5H_{12}, and 15 per cent of C_6H_{14} and heavier materials. Vaporization is conducted at 232 lb. per square inch absolute and at a temperature of 100°F. What is the composition of the residue gasoline and of the gas that is vaporized? Basis: 100 mols (or 100 volumes) of gas.

Since Eq. (45), which assumes Raoult's law, is the more complicated, this equation will be used. Note, however, that Raoult's law is not valid at these conditions and that more exact results would be obtained by using Eq. (44).

Inasmuch as the vapor-pressures of C_3H_8 and C_2H_6 are 194 and 750 lb. per square inch respectively, and the vaporization pressure is 232, the amount of vapor will be something larger than 25 per cent. Assume $L = 70$ (see Table 31, column 3).

For $L = 70$,

$$\frac{V}{L} = \frac{100 - 70}{70} = 0.429$$

Solving for L_3, as an example [Eq. (45)],

P_3 = vapor-pressure of C_3H_8 = 194 lb. per sq. in.

$$L_3 = \frac{X_3\pi}{\pi + P_3(V/L)} = \frac{30 \times 232}{232 + 194 \times 0.429} = 22.0$$

The values of L_1, L_2, L_4, etc., are computed in a tabulated form in Table 31.

TABLE 31

(1) Material	(2) Value of X's, mols	(3) Value of P's, lb. per sq. in.	(4) X's π	(5) P's $\frac{V}{L}$	(6) (5) + π	(7) (4) ÷ (6) L's, mols	(8) (2) − (6) V's, mols
CH_4......	15	4,100	3,480	1,755.0	1,987.0	1.75	13.25
C_2H_6......	10	750	2,320	321.0	553.0	4.2	5.8
C_3H_8......	30	194	6,950	83.1	315.1	22.0	8.0
iC_4H_{10}....	5	78	1,160	33.4	265.4	4.38	0.62
C_4H_{10}.....	10	56	2,320	24.0	256.0	9.06	0.94
C_5H_{12}.....	15	19	3,480	8.1	240.1	14.5	0.50
C_6H_{14} + ..	15	4	3,480	1.7	233.7	14.9	0.10
						70.79	29.21

Table 31 shows that the assumption of 30 mols vaporized was not exactly correct but the check was close (29.21). Another assumption and computation is not justified. About 29 per cent will be vaporized at 100°F.

The mol composition of the equilibrium vapor and liquid may be computed by dividing the mols of each component by the total mols

Component	Residue liquid	Vapor
CH_4	2.47	45.37
C_2H_6	5.93	19.85
C_3H_8	31.08	27.39
iC_4H_{10}	6.18	2.12
C_4H_{10}	12.80	3.22
C_5H_{12}	20.49	1.71
$C_6H_{14}+$	21.05	0.34
	100.0	100.0

Experimental Vaporization Curves.—When such complex materials as gasoline and petroleum fractions are dealt with, the application of the aforementioned equilibrium laws is cumbersome. Furthermore, the component analyses of these heavy oils cannot be easily obtained, and even if such analyses are available the vapor-pressure data for the compounds are not always available.

At present, the practical way to determine equilibrium relations is by means of experimental flash-vaporization curves (pages 65 and 88) and by empirical correlations of these curves.

Piromoov and Beiswenger[6] have presented a correlation of flash-vaporization curves. Twenty-two flash-vaporization curves were studied. The empirical correlations shown in Figs. 75 and 76 were derived by the author by the use of the foregoing[6] vaporization data and 42 other flash-vaporization curves.

The term slope, which is used on these two figures, refers to the increase in temperature required to cause an increase of 1 per cent in the quantity vaporized. The slope, on either the distillation or vaporization curve, is taken between the 10 and 70 per cent points. Of course, it may change along the entire distillation curve but the 10–70 slope is usually a good average for the entire curve. The slope is expressed as degrees per per cent distilled.

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[6] *Am. Pet. Inst. Bull.* 10, No. 2, Sec. II, p. 52, 1929.

For A.S.T.M. distillations of the lighter petroleum products, the computed flash curves are accurate within ±3 per cent throughout the middle of the vaporization curve. The "tails" which are present on the end of the curve introduce an error but the problem of predicting the curvature of the flash curve will be dealt with later. The correlation of data in Fig. 75 for A.S.T.M.

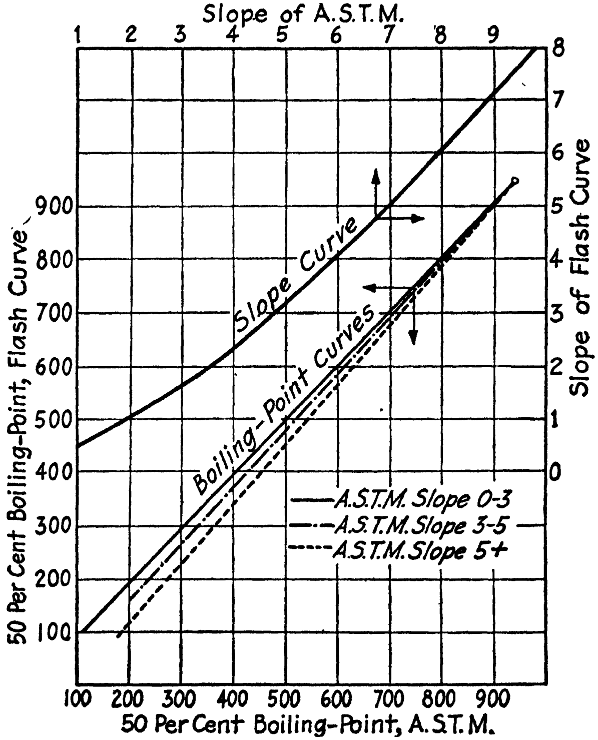

Fig. 75.—Correlation of flash curve and A.S.T.M. (or 10 per cent) distillation curve.

distillations is more exact than in Fig. 76. The superior correlation between nonfractionating (A.S.T.M.) distillations and flash curves may be explained by the semi-flash conditions which exist during the nonfractionating distillation. The A.S.T.M. distillation actually consists of an infinite number of successive flash vaporizations. The freak behavior of a stock due to an abnormal distribution of compounds or due to the presence of compounds or mixtures which do not behave in accordance with the common laws is at least partly eliminated in the A.S.T.M. distillation. In the true-boiling-point distillation these peculiarities are accentuated.

For relatively simple mixtures for which the component analysis is available, Eqs. (44) and (45) may be used. The equations are solved for several different temperatures to determine the amount of vaporization at each temperature under equilibrium conditions. The series of points constitutes the flash-vaporization curve.

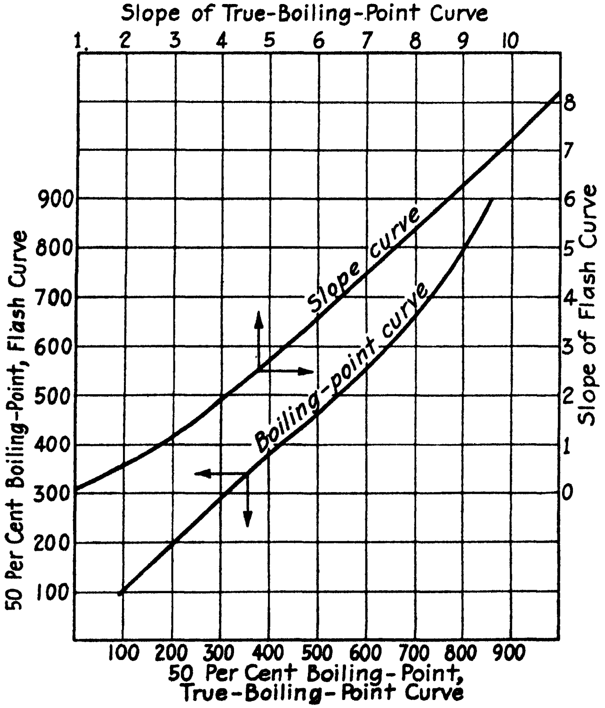

FIG. 76.—Correlation of flash curve and true-boiling-point distillation curve.

Curvature of Flash-vaporization Curves.—The foregoing correlation method results in a straight-line flash curve. If the distillation curve of the material is substantially a straight line, then the flash curve is also nearly straight. However, most materials have tails or pronounced curvatures at the ends of the distillation curve. If curvature exists, then the flash curve also exhibits a curvature but to a lesser degree. The departure from a straight line may be approximately computed from the curvature of the distillation curve. The deviation from the 10–70 slope that any particular section of the distillation curve may exhibit is directly proportional to the deviation of the actual flash curve from the straight-line flash curve. Thus

$$\frac{\text{Slope of dist. curve, 10–70\%}}{\text{Slope of flash curve, 10–70\%}} = \frac{\text{slope of dist. curve through short range}}{\text{slope of flash curve through short range}} \qquad (47)$$

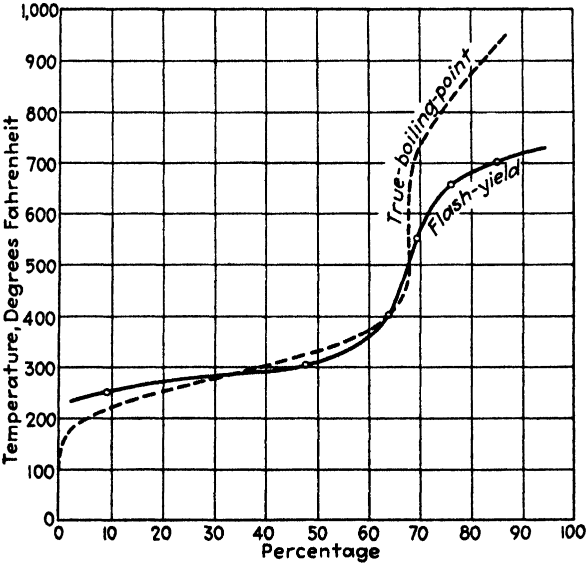

FIG. 77.—Vaporization curves of a Mid-Continent brightstock solution.

This method is accurate for those distillation curves that are substantially straight throughout the 10–70 per cent range but for curves whose slope changes throughout the entire distillation curve, the method is not entirely satisfactory. The difficulty probably lies with the inaccuracy of estimating a true average slope and not with the preceding relation.

The flash curves of freak stocks such as brightstock solution and some pressure distillates cannot be determined by these methods. At present the only way to obtain flash-vaporization data for such stocks is by laboratory experiments. Figure 77 indicates the type of flash-vaporization curve that is obtained with unusual stocks.

Example 46. Curvature of Flash-vaporization Curve.—The experimental flash-vaporization curve and the A.S.T.M. distillation of a pressure distillate are shown in Fig. 78. The computed straight-line flash curve is shown dotted, the triangular points are computed points, and the circle points are experimental ones.

$$\text{Slope of A.S.T.M., 10–70 per cent} = \frac{430 - 170}{60} = 4.34$$

$$\text{Slope of flash, 10–70 per cent (Fig. 75)} = 2.65$$

50 per cent B.P. on A.S.T.M. = 365°F.
50 per cent on flash (Fig. 75) = 335°F.

100 per cent point on linear flash curve,

$$335 + 2.65 \times 50 = 467°\text{F.}$$

As a check, at 0 per cent,

$$335 - 2.65 \times 50 = 203°\text{F.}$$

Computing Curvature:
Ratio of 10–70 per cent slopes

$$\frac{2.65}{4.34} = 0.609$$

Start at the 50 per cent boiling-point and work in both directions. As an example, the 60 per cent and 45 per cent points will be computed:

Slope of A.S.T.M. between 45 and 60 per cent = 3.46
Slope of flash between 45 and 60 per cent = $3.46 \times .609 = 2.11$
Temperature at 60 per cent on flash = $335 + 10 \times 2.11 = 365$°F.
Temperature at 45 per cent on flash = $335 - 5 \times 2.11 = 324$°F.

The other points were computed as shown in the following tabulation:

Range	Slope of A.S.T.M.	Computed slope of flash	Increment for range	Points on curve
45–60	3.46	2.11	15 × 2.11 = 31.7	324 and 356
60–75	3.06	1.86	28	356 and 384
75–90	3.6	2.2	33	384 and 417
30–45	4.2	2.56	38	286 and 324
15–30	5.45	3.32	50	236 and 286
5–15	7.7	4.7	10 × 4.7 = 47	191 and 236

Equilibrium-flash-vaporization curves may be converted to other pressures than atmospheric by means of Fig. 45 (page 127). Piromoov and Beiswenger[6] conclude that the effect of pressure is to lower or raise the boiling-point just as it does the boiling-points of the normal paraffin hydrocarbons. However, they suggest that the correction be made at the point where the two curves cross. They find that the curves cross at the same percentage point regardless of pressure and hence the intersection is the only point that can be accurately used in correcting the flash curve to another pressure.

Separation Obtained by Flash Vaporization.—Not many experiments have been conducted concerning the composition of the vapor and of the liquid which result by flash vaporization. Leslie and Good[7] have studied Cabin Creek Pennsylvania crude oil, and Fancher[8] has studied several other stocks. The distillate contains material that boils above the flash point, and the residue contains material that boils below the flash point. The results of these investigators[7,8] are reported in Table 32.

TABLE 32.—SEPARATION BY FLASH VAPORIZATION

Material	Reference	Material in distillate, boiling below flash temperature, per cent	Distillate, boiling below flash temperature, found in residuums, per cent
Cabin Creek crude..........	7	82.3	11.6
Mid-Continent crude........	8	80.8	8.9*
Ingelwood Calif. crude......	8	81.6	7.5*
Cabin Creek (successive flash)	7	80.65	16.4

* Approximate.

Fancher finds that for pressure distillates the items shown in Table 32 are not constants; *i.e.*, the higher the flash temperature the poorer the separation. As an example, Fancher's[8] data on shellstill pressure distillate are approximately as follows:

Flash Temperature	Material, in Distillate, Boiling below Flash Temperature
300	76
350	68.5
400	60
450	60

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[7] The Vaporization of Petroleum, *Ind. Eng. Chem.*, **19**, 453 (1927).

[8] The Vaporization of Petroleums and Pressure Distillates, *Petroleum Eng.*, March, 1931, p. 176.

Effect of Steam.—In many petroleum distillations, steam is admitted to the space in which vaporization occurs. The steam reduces the partial-pressure in the vapor by Dalton's law. The boiling-point of a material may be reduced in only two ways: the pressure may be reduced, or some inert gas such as steam may be introduced. In both cases, if the boiling-point is reduced the same number of degrees, the concentration of oil molecules in a unit volume of vapor is the same.

If O denotes the mols of oil vapor, S the mols of steam, p_o the partial-pressure of the oil vapor, p_s the partial-pressure of the steam, and π the total pressure,

$$\frac{O}{O + S} = \frac{p_o}{\pi}$$

and

$$\frac{S}{O + S} = \frac{p_s}{\pi}$$

Dividing,

$$\frac{S}{O} = \frac{p_s}{p_o}, \qquad \text{or} \qquad S = O\frac{p_s}{p_o}$$

but

$$p_s + p_o = \pi$$

and

$$S = O\frac{\pi - p_o}{p_o} = O\frac{p_s}{p_o} \tag{48}$$

The steam need not be bubbled through the oil although no harm results by so doing. The derivation of Eq. (41) shows that if the partial-pressure in the gas phase is reduced, the partial-vapor-pressure in the liquid must decrease. Thus the use of steam causes vaporization to proceed until the partial-vapor-pressure in the liquid is equal to the partial-pressure in the gas phase.

Gurwitsch[9] and others have reported that steam is more effective in reducing the boiling-point than Dalton's law indicates. Nevertheless, the error that is introduced by the use of Dalton's law in design work is probably not important.

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[9] GURWITSCH-MOORE, "Petroleum Technology," 2d ed., D. Van Nostrand Company, Inc., New York, 1924.

Example 47. Steam Required for Distillation.—A temperature of 370°F. is required to vaporize 65 per cent of the pressure distillate (Fig. 78) by flash vaporization. It is desired to reduce the temperature to 340°F. by means of steam. Vaporization takes place at atmospheric pressure.

Basis: 100 mols of oil vapor.

In order to reduce the boiling-point from 370 to 340°F., the vaporization must be conducted at 490 mm. pressure (Fig. 45, page 127). Enough steam to reduce the partial-pressure in the gas phase to 490 mm. will be used [see Eq. (48)].

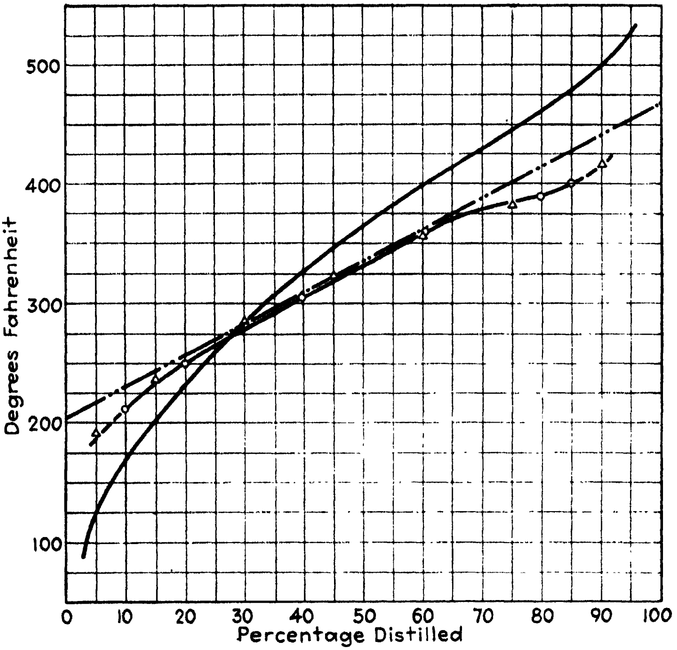

Fig. 78.—Vaporization curves of a pressure distillate.

$$\frac{S}{100} = \frac{(760 - 490)}{490}$$

$$S = 55 \text{ mols}$$

or

$$= 55 \times 18 = 990 \text{ lb.}$$

If the pressure in the tower were 10 lb. per square inch gage,

$$\frac{10}{14.7}760 + 760 = 1{,}277 \text{ mm.}$$

$$S = \frac{(1{,}277 - 490)}{490}100 = 158.5 \text{ mols or } 2{,}860 \text{ lb.}$$

APPLICATION OF FLASH-VAPORIZATION DATA

With the possible exception of heat-transfer data, there is no design fundamental of more importance and more widespread usefulness than equilibrium vaporization. The equilibrium relations between an oil and its vapor are necessary in the solution of almost all phases of design calculations. For complex mixtures no other relations than the empirical ones shown in Figs. 75 and 76 are available. By following an oil through a complete processing operation the following uses for flash-vaporization data appear:

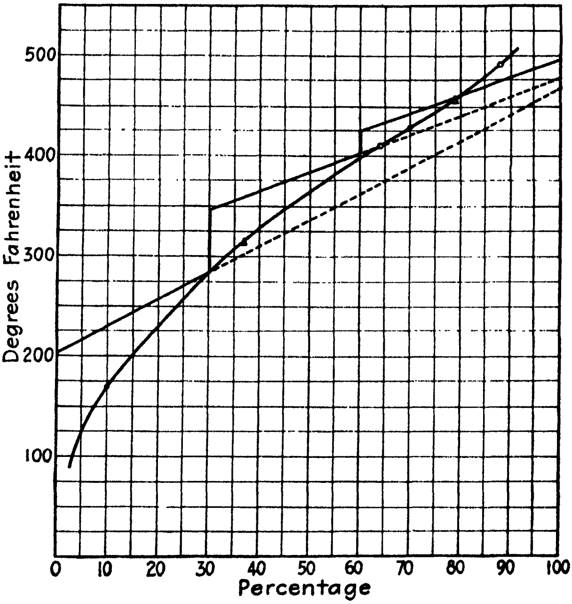

FIG. 79.—Successive flash vaporization.

1. Pipestill-outlet and tower-vaporizer temperatures.
2. Computation of the amount of vaporization in pipestill tubes.
3. Pressure-drop in pipestills (caused by vaporization).
4. Computation of tower plate-temperatures and the top temperature.
5. Heat-transfer rates in vapor condensers.
6. Design of condensers and partial condensers.

Indeed the complete usefulness of this kind of data has not yet been explored. Doubtless during the next few years it will be used in the computation of the number of plates required in heavy oil fractionators. The application of vaporization data to all of these problems cannot be illustrated here but many of them will be introduced in subsequent chapters.

Successive Flash Vaporization.—The effect of light vapors in aiding to vaporize heavier materials has aptly been referred to as the "carrying-effect of light ends."[6] In the case of successive flash vaporization the carrying-effect of the lighter materials is forcefully evident. A part of the vapor is removed in the first flash and hence the carrying-effect of this quantity of vapor is no longer available. Owing to the removal of the light vapor, the remaining liquid must be heated for several degrees before additional vaporization occurs. This effect is illustrated in Fig. 79. The same oil as that shown in Fig. 78 was used but it was vaporized by three successive flash vaporizations.

Example 48. Successive Flash Vaporization.

First flash (0 to 30 percent) (see example 46).

Second flash (30 to 60 per cent). To avoid confusion, the 70 per cent that remains should be redrawn as 100 per cent.

10–70 slope of dist. $= \frac{457 - 315}{60} = 2.37$
10–70 slope of flash curve = 1.3 (Fig. 75)*
50 per cent B.P. of dist. curve = 415°F.
50 per cent point of flash curve = 412°F. (Fig. 75)
100 per cent point $= 412 + 50 \times 1.3 = 477$°F.

Third flash (60 to 100 per cent).

10–70 slope of dist. $= \frac{492 - 410}{60} = 1.36$
10–70 slope of flash = 0.7
50 per cent point of dist. = 461°F.
50 per cent point of flash = 461°F.
100 per cent point of flash $= 461 + 50 \times 0.7 = 496$

The disadvantage of successive flashing is apparent. For example, to vaporize 80 per cent requires temperatures of approximately 415, 440, and 461°F. respectively by single, double, and triple flash.

* The use of the remaining part of the curve as an A.S.T.M. is not exact.

Pipestill-outlet Temperature.—If the flash temperature required to vaporize a given percentage of material is, say, 500°F., the pipestill-outlet temperature must be higher than this unless the entire vaporization takes place within the pipestill tubes.

Usually the pipestill outlet is under a pressure due to the friction losses in the transfer line, and the pressure suppresses vaporization. As the oil travels through the line, the pressure decreases and vaporization occurs by abstracting heat from the fluid as sensible heat. However, the vaporizer temperature at the outlet of the transfer line is a true flash temperature and may be computed as shown heretofore.

The pipestill-outlet temperature cannot be determined unless the amount of vaporization which has occurred in the pipestill is known. An example of the computation of the vaporization that occurs in a pipestill is given in Example 50.

Example 49. Calculation of Pipestill-outlet Temperature.—A pipestill is to be used to distill 65 per cent of the pressure distillate shown in Fig. 78. The tower pressure is 1,100 mm. and by experience with this oil it has been found that the vaporizer temperature of the tower must be reduced with steam to at least 325°F. in order to avoid discoloration. The gravity of the 65 per cent of gasoline is 58 A.P.I. and of the P.D. butts (or bottoms) 38 A.P.I.

A. How much steam is required?

B. What will the temperature at the outlet of the pipestill be if no vaporization occurs in the tubes?

C. What will this temperature be if half the vaporization occurs in the tubes?

Basis: 1,000 gal. of pressure distillate per hour.

A. A temperature of 370°F. is required to vaporize 65 per cent if no steam is used and the vaporization takes place at 760 mm. (Fig. 78). This temperature must be reduced by 45°F. (370 − 325). The intersection of the distillation and vaporization curves is at 270°F.

Since flash curves are parallel at different pressures, the flash curve in the presence of steam may be located by determining the partial-pressure required to reduce the temperature by 45°, *i.e.*, the 270 point is corrected to 225°F. From Fig. 45 (page 127) the partial-pressure is 360 mm. Molecular weight of gasoline is about 120 (Fig. 38).

$$\text{Mols gasoline} = \frac{1{,}000 \times 0.65 \times 6.216}{120} = 33.6$$

$$\text{Mols steam [Eq. (48)]} = \frac{1{,}100 - 360}{360} \times 33.6 = 69.2$$

$$\text{Lb. steam per hr.} = 69.2 \times 18 = 1{,}245$$

B. Pipestill-outlet temperature with no vaporization in tubes. This is a hypothetical case but it serves to illustrate the principle. Vaporization would take place at some temperature over 325°F., say at 375°F.

Latent heat at 375°F. = approx. 112 (Table 8).

Total latent heat = 1,000 × 0.65 × 6.216 × 112 = **452,000 B.t.u.**

Assume outlet temperature of 440 deg. F. and check. Use an average of the specific heats of liquid and of vapor, for gasoline.

$$\begin{array}{lll} \text{Gasoline:} & 1{,}000 \times 0.65 \times 6.216(440 - 325)\dfrac{0.68 + 0.53}{2} & = 281{,}000 \\ \text{Butts:} & 1{,}000 \times 0.35 \times 6.95(440 - 325)0.637 & = \underline{178{,}000} \\ & \text{Total heat from cooling} & = \mathbf{459{,}000\ B.t.u.} \end{array}$$

The total latent heat should equal the total sensible heat if the assumed temperature is correct. In this case the deviation of only 7,000 B.t.u. is sufficiently accurate. The outlet temperature will be about 439°F.

C. Pipestill with 50 per cent of vaporization occurring in the tubes. A.P.I. of material which vaporizes (32.5 to 65 per cent) is about 50.

Latent heat at about 355°F. = 116 B.t.u.
Total latent heat = 1,000 × 0.325 × 6.49 × 116 = **244,000 B.t.u.**
Assume pipestill outlet = 390°F.
Sensible heat of one-half gasoline

$$= 1{,}000 \times 0.325 \times 6.49(390 - 325)\frac{0.65 + 0.52}{2} = 80{,}100$$

Sensible heat of one-half gasoline (vapor)

$$= 1{,}000 \times 0.325 \times 6.0(390 - 325)0.523 = 66{,}200$$

$$\text{Sensible heat of butts} = 1{,}000 \times 0.35 \times 6.95(390 - 325)0.625 = \underline{98{,}800}$$

$$\text{Total sensible heat} = \mathbf{245{,}100}$$

This is also a sufficiently accurate check. The outlet temperature is about 390°F.

In solving this example the gravities, latent heats, etc., were not accurately computed because such accuracy is not justified.

The trial-and-error method used in solving parts *B* and *C* can be avoided by the use of sensible-heat quantities [Eqs. (3) and (4), page 108], instead of specific heats.

Pressure-drop in Pipestills.—The application of flash-vaporization data to the problem of computing the vaporization that occurs within pipestill tubes is complicated by the constantly changing pressure throughout the entire length of pipestill tubing. However, vaporization usually does not occur until the final tubes of the still are reached, because as soon as vaporization starts the friction loss and the pressure become so high that vaporization is suppressed. In fact a large part of the pressure-drop through a pipestill often occurs in the transfer line from the still to the fractionating tower. To shorten this line does little good because the vaporization is simply pushed back into the still. Likewise a larger transfer line decreases the pressure at the outlet of the still so that more vaporization occurs in the tubes. A trial-and-error solution is necessary in solving such problems.

Example 50. Approximation of Pressure-drop in Pipestill.—Two thousand six hundred and eighty barrels per day of the pressure distillate shown in Figs. 78 and 79 is to be heated in a pipestill to an outlet temperature of 400°F. Steam is used to reduce the vaporizer temperature to 300°F. when vaporizing 65 per cent of the pressure distillate. The pressure at the vaporizer section of the tower is 6 lb. per square inch. The transfer line is 50 ft. long (2 in. inside diameter). Straight-line flash-vaporization curves are used to simplify the illustration.

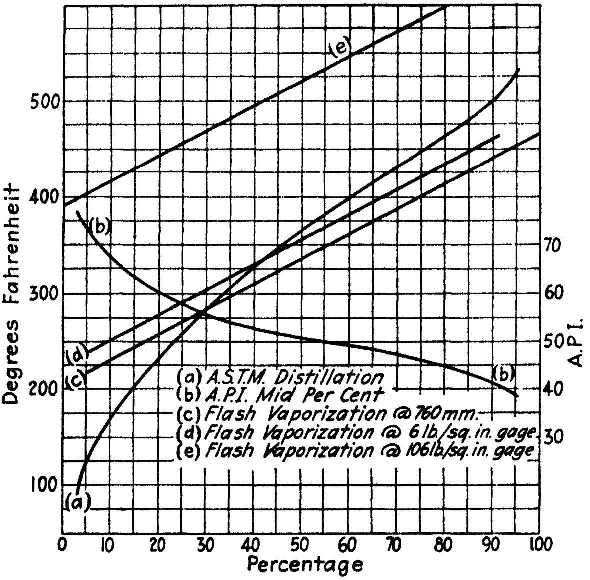

FIG. 80.—Vaporization data for Example 50.

The oil is heated from 180 to 250°F. in the convection section of the still. In convection section, 1,000 ft. of 2½-in. tubing. In radiant section, 1,330 ft. of 2-in. tubing.

What is the approximate pressure drop through the still?

Basis: 2,680 bbl. per day at 60°F. or 4,700 gal. per hour.

Loss in transfer line: Although 65 per cent is vaporized at the vaporizer section of the tower, a smaller amount is vaporized at the outlet of the transfer line because the partial-pressure effect of the steam is not available in the transfer line.

Pressure at end of line is 6 lb. gage or 1,070 mm. The flash-vaporization line at 1,070 mm. is shown in Fig. 80*d*. Assume temperature of oil in end of line is about 375°F.

Vaporization at outlet of line at 375° by Fig. 80*d* = 58 per cent. *Assume a pressure drop of* 100 *lb. in the transfer line. Check later.*

The vaporization curve at 106 lb. gage is shown in Fig. 80e. At the pipestill outlet (400°) the vaporization is about 4 per cent (neglect).

Velocity at inlet to transfer line:

Sp. gr. of pressure distillate at 400° = about 0.625 (Fig. 39).

$$\text{Volume of oil} = \frac{4{,}700}{7.5} \times \frac{1}{3{,}600} \times \frac{0.77}{0.625} = 0.2145 \text{ cu. ft. per sec.}$$

$$\text{Velocity} = \frac{0.2145}{3.14} \times 144 = 9.85 \text{ ft. per sec.}$$

Velocity at outlet transfer line (58 per cent vaporized):

$$\text{Volume of oil} = \frac{4{,}700 \times 0.42}{7.5 \times 3{,}600} \times \frac{0.8}{0.672} = 0.087$$

A.P.I. of vapor = 56; Mol. wt. = about 110.

$$\text{Volume of vapor} = \frac{4{,}700 \times 0.58 \times 6.28}{3{,}600 \times 110} \times 359\frac{835}{492} \times \frac{14.7}{20.7} = 18.6 \text{ cu. ft. per sec.}$$

$$\text{Outlet velocity} = \frac{18.687}{3.14} \times 144 = 855 \text{ ft. per sec.}$$

Since the pressure builds up approximately as the square of the velocity, the mean velocity will not be the arithmetic average.

Assume a mean velocity of about 330 ft. per second.

It would be more exact to consider the transfer line as two parts and compute the velocities and pressure-drops for each of the two parts by a trial-and-error solution.

The transfer line will contain at least two elbows.

$$L = 50 + \frac{3 \times 40}{12} = 60.0 \text{ ft.}$$

$$\text{Mean volume (assume)} = 18.687 \times \frac{330}{855} = 7.2$$

$$\text{Mean } s = \frac{4{,}700 \times 6.42}{7.2 \times 3{,}600} \times \frac{1}{62.4} = 0.01865$$

$$z = \text{approx. } 0.35 \text{ (for liquid see Fig. 49)}$$

$$\frac{Dus}{z} = \frac{2 \times 330 \times 0.01865}{0.35} = 35.2$$

$$f = 0.0048 \text{ (Fig. 47)}$$

$$\Delta P = \frac{0.323 \times 0.0048 \times 0.01865 \times (330)^2 \times 60}{2} = 94 \text{ lb. per sq. in.}$$

The assumed ΔP was 100 lb. per square inch and hence the foregoing solution is not correct. Another trial-and-error solution, as above, with an assumed pressure-drop of 97 lb. per square inch checks. The pressure-drop in the transfer line is about 97 lb.

Friction loss in radiant section:

$$\text{Sp. gr. at about } \frac{400 + 250}{2}\text{°F.} = 0.66$$

$$\text{Velocity of oil} = \frac{\frac{4{,}700}{7.5} \times \frac{0.77}{0.66} \times \frac{144}{3{,}600}}{3.1416} = 9.32 \text{ ft. per sec.}$$

$$\frac{Dus}{z} = \frac{2 \times 9.32 \times 0.66}{0.4} = 30.7 \qquad f = 0.0049$$

The equivalent length of a return bend is about 40 dia. If 75 tubes are used,

$$L = 1{,}330 + 75 \times 40 \times 2/12 = 1{,}830$$

$$\Delta P = \frac{0.323 \times 0.0049 \times 0.66 \times (9.32)^2 \times 1{,}830}{2} = 82.7 \text{ lb. per sq. in.}$$

Friction loss in convection section:

Area of $2\frac{1}{2}$-in. tubing = 4.91 sq. in.

$$\text{Velocity of oil} = \frac{\frac{4{,}700}{7.5} \times \frac{0.77}{0.705} \times \frac{144}{3{,}600}}{4.91} = 5.57 \text{ ft. per sec.}$$

$$\frac{Dus}{z} = \frac{2.5 \times 5.57 \times 0.705}{0.62} = 15.8 \qquad f = 0.0054$$

If 55 tubes are used,

$$L = 1{,}000 + 55 \times 40 \times \frac{2.5}{12} = 1{,}460 \text{ ft.}$$

$$\Delta P = \frac{0.323 \times 0.0054 \times 0.705 \times (5.57)^2 \times 1{,}460}{2.5} = 22.2 \text{ lb. per sq. in.}$$

Total pressure-drop,	Lb. per Sq. In.
At vaporizer	6
Through transfer line	97
Through radiant section	83
Through convection section	22
	208
10 per cent factor	22
Predicted pressure-drop	230

It must be remembered that extreme care must be used in selecting the proper physical constants in a problem of this kind. The results are only approximate but no other methods are available.

See Chap. XX (page 431) for computed and actual pressure-drops by the method used in this example.

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CHAPTER XV

COUNTERCURRENT OPERATIONS

Many of the unit processes of chemical engineering involve the transfer of a component from one material to another. Examples of such operations are fractionation, absorption, stripping, extraction, and drying. These operations are not always conducted as countercurrent ones but this manner of operation is usually advantageous.

The three general ways of conducting processes which depend upon equilibrium relations, are

1. *Single-contact or Batch Operation.*—In this method of operation the two materials are mixed or contacted with one another in a single operation. After equilibrium is established, the two materials are separated from each other and withdrawn from the system. Batch treatment of an oil with sulfuric acid is an example of a single-contact process.

2. *Countercurrent Multiple-contact Operation.*—This method of operation consists of a number of single-contact operations conducted in a countercurrent manner. The material being contacted is treated with contact agent that has been employed in previous contacting stages except in the final stage in which the material is contacted with fresh treating agent. As an example, in an absorption system a gas is contacted with an absorption liquid in a series of treatments as it ascends the absorption tower; the leanest gas is in contact with the lean (or pure) absorption liquid at the top of the tower, and the richest gas is in contact with the richest absorption liquid at the base of the tower (Fig. 88).

3. *Cocurrent Multiple-contact Operation.*—This method is similar to single-contact operation except that the material is repeatedly contacted, after separation, with fresh or pure contact agent. This operation is also used in the acid treatment of oils.

Any of these methods can be used for the treatment of a solid with a fluid, but most commercial operations involve the use of two fluids because fluids can be easily handled.

FRACTIONATION

The principles of fractionation have been developed mathematically by a study of two-component systems. Although these derivations are not directly applicable to the fractionation of petroleum oil mixtures, a complete understanding of fractionation cannot be gained without studying two-component systems. In the chemical industries these formulations have proved to be valuable and highly practical.

Fractionation may be broadly defined as any method by which a liquid or vapor mixture may be separated into individual components by vaporization or condensation. The components may be pure compounds or, if the original material is a complex mixture, the components may be products which are still mixtures but whose distillation range is limited by the fractionation process. In a more detailed way the various means of separation have been given special names. *Distillation* is usually considered to refer to a complete operation in which heating, vaporization, fractionation, condensation, and cooling are practiced. *Dephlegmation* is a particular kind of fractionation in which a vapor mixture is separated into components by partial condensation. In this operation the vapor is progressively cooled, and successively lower and lower boiling condensates are collected. The condensate is relatively rich in high-boiling components. At one time the term dephlegmator was used to designate any sort of fractionating-tower but today the meaning of the term is usually restricted to the use herein given. In a more restricted usage the term *fractionation* is used in referring to a countercurrent operation in which a vapor mixture is repeatedly contacted with liquids having nearly the same composition as the respective vapors. The liquids are at their boiling-points and hence a part of the vapor is condensed and part of the liquid is vaporized during each contact. By a series of contactings the vapor finally becomes rich in low-boiling components and the liquid becomes rich in high-boiling components. The terms *rectification* and *fractionation* are used synonymously.

Vapor-liquid fractionation may be practiced in a bubble-tower or in a packed column. Packed columns are not used extensively in the processing of petroleum and they will not be discussed in detail. The main disadvantage of the packed column is the channeling of the liquid that occurs as it flows down the tower. Excessive channeling may occur if the diameter of the tower is greater than 18 in. In a bubble column the liquid flows from plate to plate down the column and the vapor bubbles through the liquid on each plate. The plates above the feed point are called rectifying plates and all of them together are classified as the *rectifying section* of the column. The plates below the feed are called the *exhausting section*. The plates below the feed do not function as exhausting plates unless heat is added to the oil at the base of the column. Hence most petroleum oil columns do not have exhausting sections. The plates below the feed in petroleum columns are usually stripping plates. An exception is the natural gasoline stabilizer in which the stable gasoline in the base of the column is heated by steam. Occasionally an exhausting section is used in heavy oil systems (see Fig. 105, Chap. XVIII, which shows a reboiler system in a pressure distillate rerun unit).

Mechanism of Fractionation.—In computing the degree of fractionation that is accomplished in a particular equipment, the relation between the composition of the liquid and the vapor at equilibrium must be used. Either experimental equilibrium data must be available or the engineer must compute such data from known laws. Although Raoult's law is valid for only certain conditions, it is about the only general relationship by which equilibrium data can be computed.

Example 51. Equilibrium Relation by Raoult's Law.—[See Eqs. (41) and (42), page 244.] Compute the equilibrium relations of normal pentane and hexane.

$$y_1 = \frac{P_1}{\pi}x_1, \qquad \text{and} \qquad x_1 = \frac{\pi - P_2}{P_1 - P_2}$$

The equilibrium relation will be computed for atmospheric pressure. The vapor-pressure data were obtained from Fig. 5 (page 34). Complete data at a number of temperatures are presented in Table 33. The following computation illustrates how the points in Table 33 were obtained.
Equilibrium relation at 120°F.:

Vapor-pressure of C_5H_{12} at 120° = 1160 mm.
Vapor-pressure of C_6H_{14} at 120° = 396 mm.

$$x_1 \text{ for } C_5H_{12} = \frac{760 - 396}{1{,}160 - 396} = 0.477$$

$$y_1 \text{ for } C_5H_{12} = \frac{1{,}160}{760}0.477 = 0.73$$

TABLE 33.—EQUILIBRIUM DATA FOR PENTANE AND HEXANE

Temperature, °F.	Vapor-pressure		760 − P_2	$P_1 - P_2$	x_1 mol fraction	P_1x_1	y_1 mol fraction
	C_5H_{12}, P_1 mm.	C_6H_{14}, P_2 mm.					
97	760	238	522	522	1.0	760	1.0
100	800	255	504	545	0.925	740	0.975
105	895	280	480	615	0.78	698	0.92
110	960	325	435	635	0.685	657	0.865
120	1,160	396	364	764	0.477	554	0.73
130	1,350	478	282	872	0.323	436	0.575
135	1,460	530	230	930	0.248	359	0.476
140	1,600	580	180	1,020	0.176	282	0.371
145	1,750	638	122	1,112	0.109	191	0.252
150	1,900	700	60	1,200	0.050	95	0.125
154.4	2,010	740	20	1,270	0.0157	31.4	0.0414
156	2,150	760	0	1,300	0.0	0.0	0.0

Two common forms of equilibrium diagrams are shown in Figs. 81 and 82. As an example, the vapor from a liquid having a composition of 0.3 mol fraction of pentane contains 0.546 mol fraction of pentane. However, only a very small quantity of this composition of vapor can be produced, because the liquid becomes less rich in pentane as vapor is formed. If the heating is continued, the liquid becomes less and less rich in pentane and

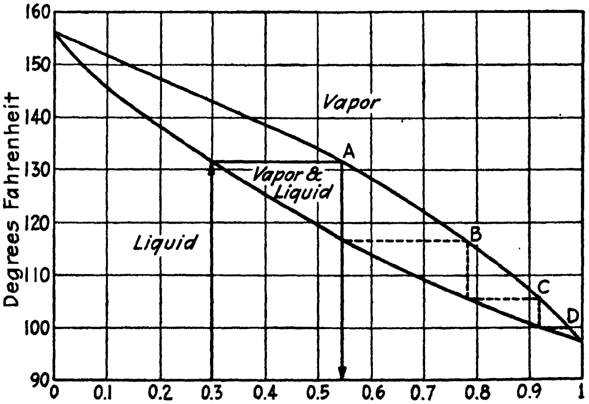

FIG. 81.—Phase diagram for pentane-hexane at atmospheric pressure.

finally after all the liquid is completely vaporized the composition of the total vapor is the same as that of the original liquid or 0.3 mol fraction.

As an illustration, the hypothetical case of the fractionation of an infinitely large quantity of liquid by a series of redistillations will be useful. Consider the series of stills shown in Fig. 83*a* and compare the compositions with the dotted lines on Fig. 81. An infinite amount of liquid containing 0.3 mol fraction of pentane is heated a fraction of a degree and a small amount of a vapor containing 0.546 mol fraction of pentane is evolved. This vapor is condensed by cooling it with a liquid which has the same composition as the vapor, and as the liquid is heated it evolves a vapor having a composition of $y = 0.782$. By repeating this operation several times, a vapor is produced at still *D* which is almost pure pentane. The heating coils in the stills are really unnecessary because the vapor within the coils is of the same composition as the liquid on the outside of the coils and hence the liquid and vapor can be mixed. The same change in composition will result and the exchange of heat will be much more effective. The bubble-tower shown in Fig. 83*b* is essentially the same as the

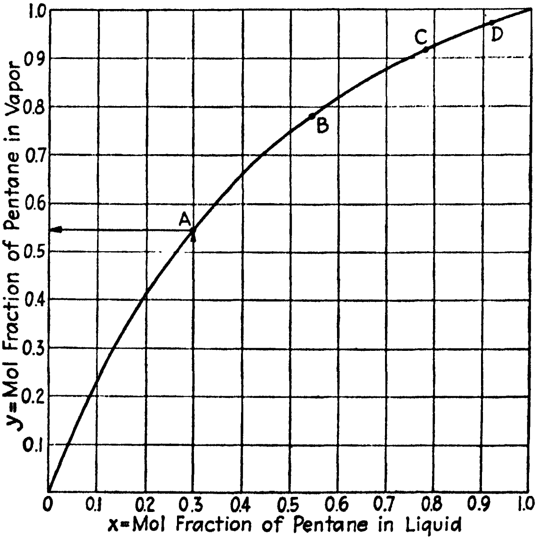

Fig. 82.—Equilibrium relation between pentane-hexane at atmospheric pressure. (See also Fig. 81.)

series of stills except that the liquid from each plate is allowed to flow continuously to the still or plate beneath. The compositions indicated in Fig. 83 are not practical ones because only a small quantity of purified vapor can be produced, but exactly the same principle is utilized in actual fractionating-towers. In actual towers a finite amount of vapor or product must be produced and hence the vapor is not so rich in pentane as indicated in Figs. 81 and 83. Thus more plates are required in actual towers because of the less rich vapor that is produced at each plate and because several bubble plates may be required to produce an equilibrium. The top plate must be continuously fed with a cooling liquid (reflux) or it would soon become dry. The vapor

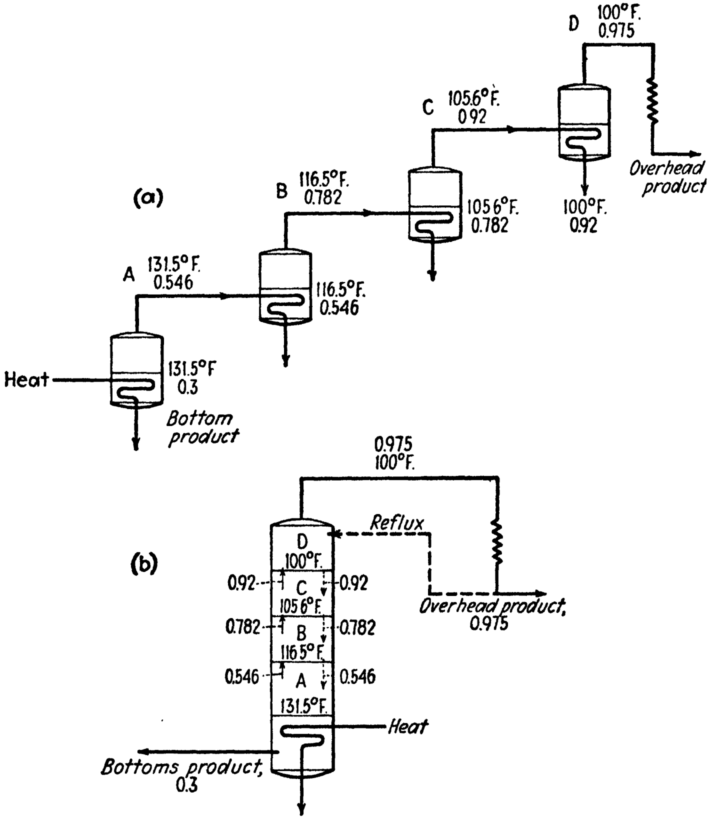

FIG. 83.—Fundamentals of fractionation. (See also Figs. 81 and 82.)

from the top plate is the final product, and hence the reflux must be rich in pentane or the vapor will be contaminated. Accordingly, the overhead product (0.975) is used as the reflux medium. The reflux flows down the column but it changes composition from plate to plate so that all of the material that is originally put into the top of the column as reflux is vaporized and returns to the product storage tank.

Theory of Fractionating Columns.—The derivation of mathematical formulas describing fractionation involves several assumptions. In dealing with two component systems these assumptions are reasonably accurate, but in dealing with complex materials they will introduce serious errors. The most important of these assumptions are (1) The molal latent heats of all materials are equal; (2) no reflux for cooling the overhead product from the feed-plate temperature is provided.

The molal latent heats of two compounds such as pentane and hexane are about the same. These two compounds are from the same chemical series and are adjacent members of the series. The molal latent heats of butane and heptane are not even approximately the same (see Table 34) and hence, for hydrocarbons which have widely differing boiling-points or which belong to different series, the assumption that the molal latent heat is a constant is inaccurate.

TABLE 34.—MOLAL LATENT HEAT

Compound	B.t.u. per lb.-mol	Compound	B.t.u. per lb.-mol
Ethane	6,300	Cyclohexane	12,900
Propane	8,000	Heptane	13,800
Butane	9,500	Cycloheptane	14,000
i-butane	9,150	Octane	14,500
Pentane	11,100	Nonane	15,500
2-methyl butane	11,400	Pentadecane	21,600
Hexane	12,300		

The assumption of equal molal latent heats greatly simplifies the calculations. If 1 mol of vapor (any composition) is condensed, the heat that is removed is just sufficient to vaporize a mol of liquid (at its boiling-point). Thus the number of mols of vapor that travel up the column is the same at any plate provided the feed is introduced as a liquid at its boiling-point. Likewise, the reflux or overflow from plate to plate is a constant amount in each section of the tower (see Envelope II, Fig. 84) because the reflux is equal to the mols of vapor minus the mols of product for the rectifying section and to mols of vapor plus mols of waste for the exhausting section.

The assumption that the temperature is the same in all parts of the column is obviously false. The temperature range is not large for combinations such as pentane-hexane but for petroleum mixtures the temperature at the top of the column may be several hundred degrees lower than at the feed plate.

Material Balances.—A number of envelopes inclosing parts of a fractionating-tower are shown in Fig. 84. According to the first law of thermodynamics, the weight or mols of material going into any one of these systems is exactly equal to the weight or mols leaving that system. The following symbols are used:

F = mols of liquid feed at its boiling-point.
P = mols of liquid product at its boiling-point.
B = mols of liquid residue-product.
R = mols of reflux, at its boiling-point, at any plate above the feed plate.
V = mols of vapor at any plate above the feed plate.
x = mol fraction of lower boiling component in liquid.
y = mol fraction of lower boiling component in vapor.

Subscripts:

p = product from top.
b = residue-product.
f = feed.
n = any plate in rectifying section.
$n + 1$ = plate above the nth plate.
$n - 1$ = plate below the nth plate.
t = top plate.
$t - 1$ = plate below the top plate.
m = any plate in the exhausting section.
s = still.

Envelope I encloses the entire tower system and shows the relation between the feed and the products.

$$F = B + P$$

And for the low-boiling component:

$$Fx_f = Bx_b + Px_p$$

Envelopes II and II′ show the relation between the vapor, reflux, and mols of overhead product:

$$V = P + R, \qquad \text{and} \qquad Vy_t = Px_p + Rx_p \tag{49}$$

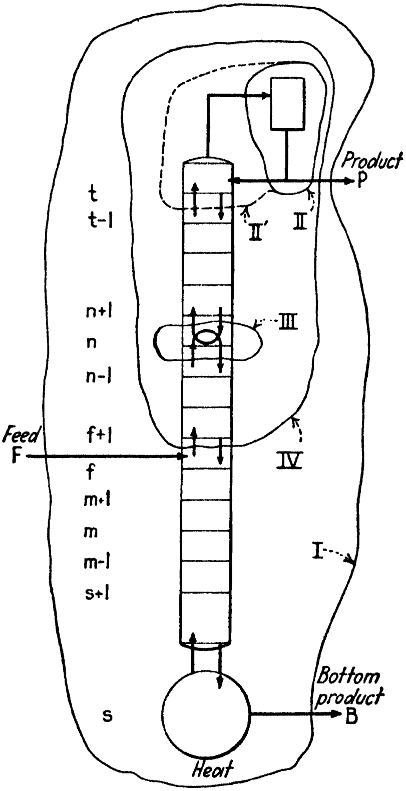

FIG. 84.—Continuous two-component fractionating system.

Similar equations for the plates below the feed are

$$V' = R' - B, \qquad \text{and} \qquad V'y_s = R'x_{s+1} - Bx_b$$

The change in composition from plate to plate is shown by Envelope III:

$$Vy_n + Rx_n = Vy_{n-1} + Rx_{n+1}$$
$$R(x_{n+1} - x_n) = V(y_n - y_{n-1})$$
$$\frac{R}{V} = \frac{y_n - y_{n-1}}{x_{n+1} - x_n} \tag{50}$$

also

$$y_{n-1} = \frac{R}{V}(x_n - x_{n+1}) + y_n$$

Minimum Vaporization and Reflux.—The minimum amount of vaporization that is necessary in order to separate a product having a composition x_p is an important quantity. With *minimum vaporization* or reflux, an infinite number of plates are required for the separation. Although this amount of vaporization cannot be used commercially, it is the limiting condition upon which practical vaporizations are based. The other extreme condition is the use of an *infinite* amount of *vaporization.* For infinite vaporization a minimum number of plates is required to effect a separation. The minimum vaporization may be computed as follows (Envelope IV):

$$Vy_f = Rx_{f+1} + Px_p$$

But at minimum vaporization an infinite number of plates are used and the change in composition from plate to plate is very small. Hence x_{f+1} is equal to x_f.

$$V_{\min}y_f = R_{\min}x_f + Px_p$$

But

$$R_{\min} = V_{\min} - P$$

$$V_{\min}y_f = (V_{\min} - P)x_f + Px_p$$

$$V_{\min} = \frac{P(x_p - x_f)}{y_f - x_f} \qquad (51)$$

or

$$R_{\min} = \frac{P(x_p - y_f)}{y_f - x_f} \qquad (52)$$

In practice, more reflux than the minimum is used. The relative values of x_f and y_f can be found by the equilibrium relation for the compounds that are being separated. The use of a basis of 1 lb.-mol of product P simplifies the computations.

Example 52. Number of Perfect Plates by Mathematical Method.—A mixture of pentane and hexane containing 0.6 mol fraction of pentane is to be fractionated at atmospheric pressure to produce a product containing 0.95 mol fraction of pentane. The feed is at its boiling-point. Use twice the minimum reflux.

How many theoretically perfect plates are required to get the separation? Basis: 1 mol of product [see Eq. (52)].

$$y_f = 0.82 \text{ (Fig. 82)}$$

$$R_{\min} = \frac{x_p - y_f}{y_f - x_f} = \frac{0.95 - 0.82}{0.82 - 0.60} = 0.59$$

Actual reflux:

$$R = 2 \times 0.59 = 1.18 \text{ mols}$$

$$V = 1.18 + 1 = 2.18 \text{ mols [See Eq. (49)]}$$

$$\frac{R}{V} = \frac{1.18}{2.18} = 0.541$$

Considering the top plate [see Eq. (50)]:

$$\frac{R}{V} = \frac{y_t - y_{t-1}}{x_p - x_t}$$

For this plate,

$$y_t = x_p.$$

Also x_t in equilibrium with y_t (0.95) is 0.86 (Fig. 82).

$$0.541 = \frac{0.95 - y_{t-1}}{0.95 - 0.86} \qquad y_{t-1} = 0.901$$

For the $t - 1$ plate,

$$\frac{R}{V} = \frac{y_{t-1} - y_{t-2}}{x_t - x_{t-1}} \qquad y_{t-1} = 0.901$$

$$0.541 = \frac{0.901 - y_{t-2}}{0.86 - 0.745} \qquad x_{t-1} = 0.745 \text{ (Fig. 82)} \quad y_{t-2} = 0.839$$

The liquid flowing from this plate has a composition of 0.625. Obviously only a part of another perfect plate is required to complete the rectifying section, because the feed composition is 0.6.

Graphical Method.—The graphical method of solving fractionation problems is usually shorter than the mathematical method used in Example 52. If infinite reflux is used, the composition of the vapor leaving the plate and the liquid arriving at the plate is the same. That is, $y_n = x_{n+1}$; $y_{n+1} = x_{n+2}$, etc. At each plate the composition of the vapor and that of the liquid are related to each other by the equilibrium relation shown in Fig. 82. The equilibrium relation is plotted in Fig. 85 and also a 45-deg. line whose equation is $x = y$. The 45-deg. line is the operating line for the condition of infinite reflux. The operating line relates the composition of the vapor leaving the plate and the composition of the liquid entering the plate. For conditions other than infinite reflux, the liquid composition x does not equal y and the operating line is less steep than a 45-deg. line. The equation of the operating line may be formulated as follows: At the top plate when producing 1 mol of product:

$$\frac{R}{V} = \frac{y_{t-1} - y_t}{x_t - x_p}$$

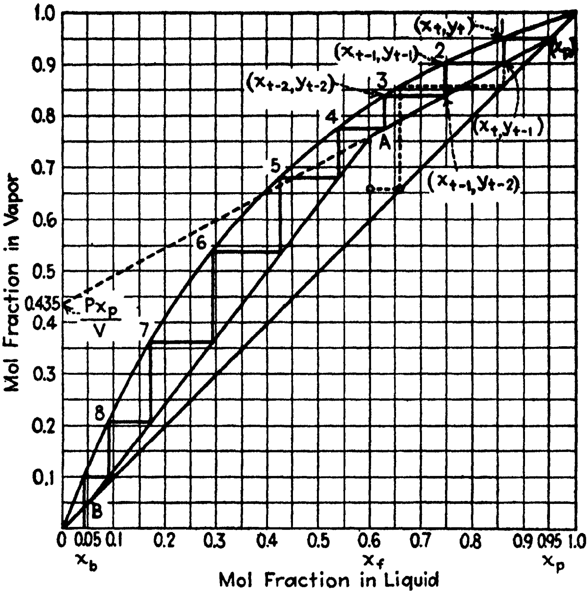

FIG. 85.—McCabe-Thiele diagram for pentane-hexane.

But $y_t = x_p$

$$\frac{R}{V} = \frac{y_{t-1} - x_p}{x_t - x_p}$$

$$y_{t-1} - x_p = \frac{R}{V}(x_t - x_p)$$

$$y_{t-1} = \frac{R}{V}(x_t - x_p) + \frac{V}{V}x_p$$

But

$$V = R + P$$

$$y_{t-1} = \frac{R(x_t - x_p) + (R + P)x_p}{V} = \frac{R}{V}x_t + \frac{P}{V}x_p \qquad (53)$$

This is an equation of a straight line having a slope of R/V and having an intercept on the y-axis of $(P/V)x_p$. Since the operating line extends from (x_p, y_p) to the intercept, the line can also be drawn without using the slope.

Example 53. Number of Plates by Graphical Method.—Example 52 will be repeated using the graphical method.

The y intercept of the operating line is

$$\frac{P}{V}x_p = \frac{1}{2.18} \times 0.95 = 0.435 \qquad \text{[see Eq. (53)]}$$

The operating line is drawn through the intercept $y = 0.435$, $x = 0$, and through the point x_p, y_t (0.95) (Fig. 85). The number of plates can then be ascertained by drawing horizontal and vertical lines as shown in Fig. 85. Each point on the equilibrium curve indicates one theoretical plate. Thus about 3⅓ perfect plates are required (see Example 52).

The dotted lines indicate the number of plates required at infinite reflux. The operating line for infinite reflux is the 45-deg. line. Only a little more than two plates are required if infinite reflux is used.

Exhausting Section.—The number of plates required in the exhausting section in order to separate a particular bottoms product can be formulated in exactly the same manner as for the rectifying section. However, the computation by graphical methods can be simplified by noting that the exhausting operating line passes through the point *A* (Fig. 85) and through point *B*. Hence the easiest way to handle the exhausting section is to determine and draw the rectifying operating line and then draw the exhausting line. The exhausting line *AB* shown in Fig. 85 is for the separation of a bottoms product having the composition $x_b = 0.05$.

Example 54. Graphical Method for Number of Plates If Feed Is at Center of Column.—Examples 52 and 53 will be continued for a column which is to produce a bottom product $x_b = 0.05$ as well as a top product $x_p = 0.95$.

The exhausting operating line is drawn as indicated above. The stepwise procedure is continued past the feed composition until the liquid has a composition of 0.05 or less (see Fig. 85). About nine perfect plates are required.

If the plate efficiency is 60 per cent,

$$\text{Actual plates} = \frac{8.8}{0.6} = 14.7$$

The Quantity of Reflux.—As mentioned previously, fractionating-towers must operate between two impractical extremes. In one of these the reflux is the minimum that can be used and an infinite number of plates is required, and in the other an infinite amount of reflux is used and a minimum number of plates is required.

The operation of practical columns falls between these two extremes. Several operating lines are shown in Fig. 86 for the system benzene-toluene. Line *PD* is for infinite reflux and lines *PC* and *CD* are for infinite plates. The compositions of the feed and products are $x_f = 0.3$, $x_p = 0.99$, and $x_b = 0.01$. The quantity of reflux for each of the operating lines is

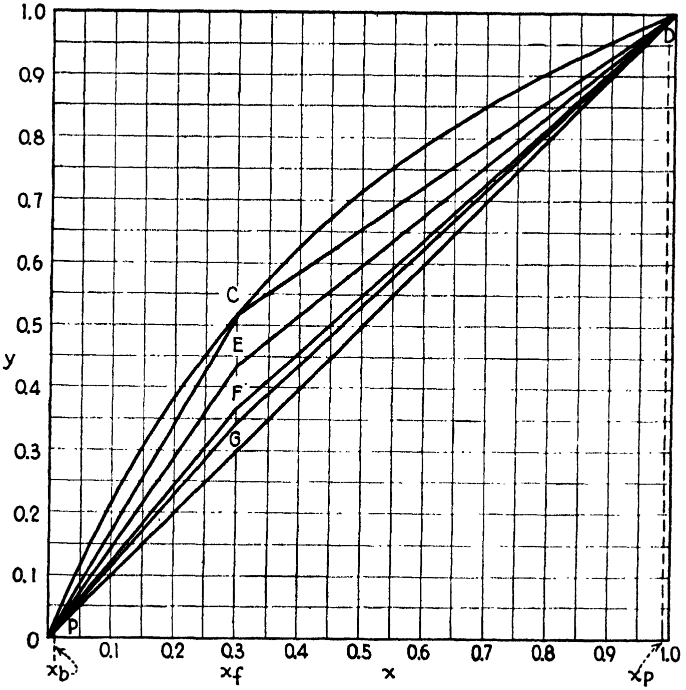

FIG. 86.—Fractionation diagram of benzene-toluene for several reflux ratios.

Operating Lines	Mols Reflux per Mol Product
PCD	2.125 (infinite plates)
PED	4.0
PFD	9.0
PGD	14.0
PD	Infinite (minimum plates)

From Fig. 86 it is obvious that a small increase in the reflux above 2.125 causes a great reduction in the number of plates that are required, and likewise the number of plates are hardly reduced at all if a reflux larger than 14 is used.

The rate of change of the composition of the liquid on the plates is shown graphically in Fig. 87. The plates are numbered from the bottom of the column. This figure clearly shows that the number of plates that is required increases rapidly as the reflux is decreased. In practice the engineer must decide whether it pays to purchase a large number of plates or to operate at a higher daily operating cost. The cost of reflux consists mainly of three items (1) heat to generate the vapor, (2) water with which to condense the reflux, and (3) cost for extra tower diameter.

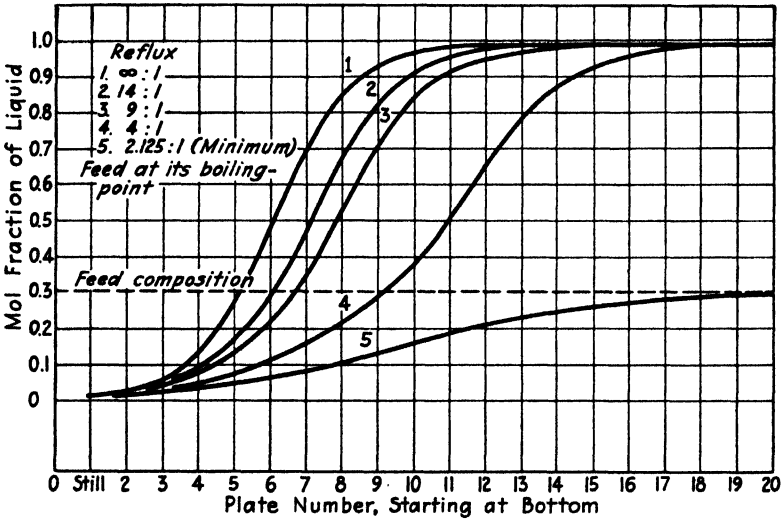

FIG. 87.—Benzene on plates for different reflux ratios. (See also Fig. 86.)

ABSORPTION

The process of absorbing part of a gas into a substantially nonvolatile liquid is in many respects similar to fractionation. Like fractionation, it depends upon the obtainment of equilibrium between a liquid and a gas. Hence it can also be practiced in a countercurrent manner in bubble-towers or packed columns. It differs from fractionation because the liquid and gas do not exchange places and only the component in which we are interested is transferred from one medium to the other.

In the petroleum industry, absorption processes are usually conducted in a bubble column, and hence the discussion that follows will be limited to this type of equipment. Envelope I (Fig. 88) gives the following material-balance equation:

$$G(y'_1 - y'_2) = L(x'_2 - x'_1)$$

$$\frac{L}{G} = \frac{y'_1 - y'_2}{x'_2 - x'_1}$$

where L = mols of pure absorbent liquid.
G = mols of pure inert gas.
x'_1 and x'_2 = mols of component per mol of L.
y'_1 and y'_2 = mols of component per mol of G.

Note that x' and y' are defined differently in the study of fractionation. Here, x' refers to the mols of component per mol of absorbent liquid, whereas in fractionation x referred to mol fraction or the mols of component per total mols of liquid and component. A pound basis as well as a mol basis can be used.

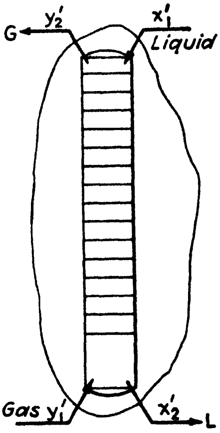

FIG. 88.—Absorption tower.

The ratio L/G corresponds to the ratio R/V that was used in fractionation. The ratio is a constant at all points in an absorbing column and is the slope of the operating line. The operating line has terminals at (x'_2, y'_1) and (x'_1, y'_2) and is shown in Fig. 89 as line AB. The transfer of the component from the gas to the liquid is a diffusion phenomena and hence the rate of transfer depends upon the difference in concentration of the component in the gas and in the liquid. The transfer of material occurs only when a difference in concentration exists and hence transfer stops when equilibrium is attained. The minimum amount of absorption liquid that can be used can be determined by noting that the outgoing gas is in equilibrium with the incoming absorbent. The operating line for this condition intersects the equilibrium line at y'_2. The equilibrium relation is shown in Fig. 89 as the line CD. The number of perfect plates is determined by the stepwise process as indicated in Fig. 89.

The computation of equilibrium data and the solution of an absorption problem are given in Example 55.

Example 55. Absorption of Pentane in Gas Oil.—Air from a solvent plant contains 2 per cent of *n*-pentane. The pentane concentration is to be reduced to 0.1 per cent by contacting the gas, at 80°F. and 147 lb. per square inch absolute pressure, with 6,950 lb. per hour of an absorption oil which contains 0.05 per cent by weight of pentane; 100,000 cu. ft. of the gas, measured at 60°F., is handled per hour. The molecular weight of the oil is 220. Raoult's law and Dalton's law are assumed to be valid at these conditions.

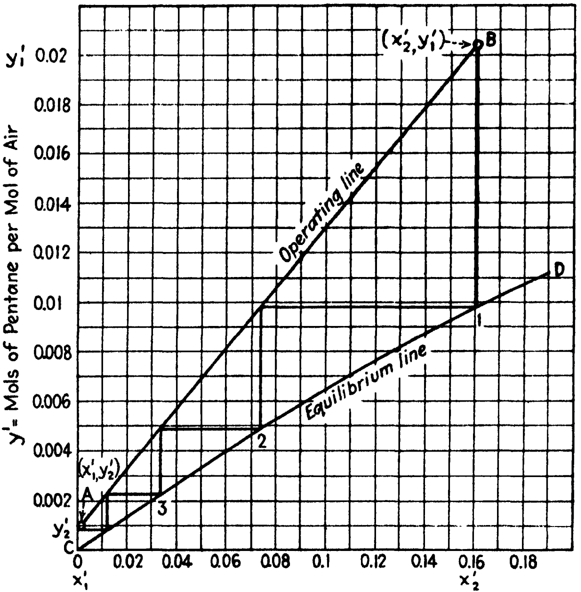

FIG. 89.—Absorption diagram.

Basis: 1 hr.

Construction of operating line:

Gas entering:

$$\text{Mols air} = \frac{100{,}000 \times 0.98}{379} = 259$$

$$\text{Mols pentane} = \frac{100{,}000 \times 0.02}{379} = 5.28$$

$$y'_1 = \frac{5.28}{259} = 0.0204$$

Gas leaving:

$$\text{Mols pentane} = 259\frac{0.1}{99.9} = 0.26$$

$$y'_2 = \frac{0.26}{259} = 0.001$$

Liquid entering:

$$\text{Mols oil} = \frac{6{,}950 \times 0.9995}{220} = 31.6$$

$$\text{Mols pentane} = \frac{6{,}950 \times 0.0005}{72} = 0.05$$

$$x'_1 = \frac{0.05}{31.6} = 0.00158$$

Liquid leaving:

$$\text{Mols pentane} = (5.28 - 0.26) + .05 = 5.07$$

$$x'_2 = \frac{5.07}{31.6} = 0.161$$

These points are plotted as line *AB* in Fig. 89.

Construction of equilibrium line [see Eq. (41), page 244].

$$y = \frac{P}{\pi}x \qquad y = \text{mol fraction in vapor}$$

$$x = \text{mol fraction in liquid}$$

But y' and x' are mols per mol of carrying agent,

$$y' = \frac{y}{1-y} \qquad \text{and} \qquad x' = \frac{x}{1-x}$$

The vapor-pressure of pentane at 80°F. is 532 mm. The relation between x' and y' can be computed as follows:

$$\text{where } x = 0.01$$

$$y = \frac{532}{7{,}600}0.01 = 0.0007$$

$$x' = \frac{0.01}{1 - 0.01} = 0.0101$$

$$y' = \frac{0.0007}{1 - 0.0007} = 0.0007$$

x	y	x'	y'
0	0	0	0
0.01	0.0007	0.0101	0.0007
0.02	0.0014	0.0204	0.0014
0.03	0.0021	0.031	0.0021
0.04	0.0028	0.0416	0.0028
0.05	0.0035	0.0525	0.00351
0.07	0.0049	0.0752	0.00492
0.09	0.0063	0.099	0.00635
0.10	0.0070	0.111	0.00705
0.15	0.0105	0.177	0.0106
0.20	0.0140	0.25	0.0142

The number of plates can be computed by the stepwise method. About 3.9 perfect plates are required.

STRIPPING

The process of stripping a component from a liquid by means of a gas may be considered as the reverse of absorption. In absorption the concentration in the gas is high enough to drive the component into the liquid, whereas in stripping the concentration in the liquid is high and the component is transferred from the liquid to the gas. The equilibrium line lies below the operating line (Fig. 90).

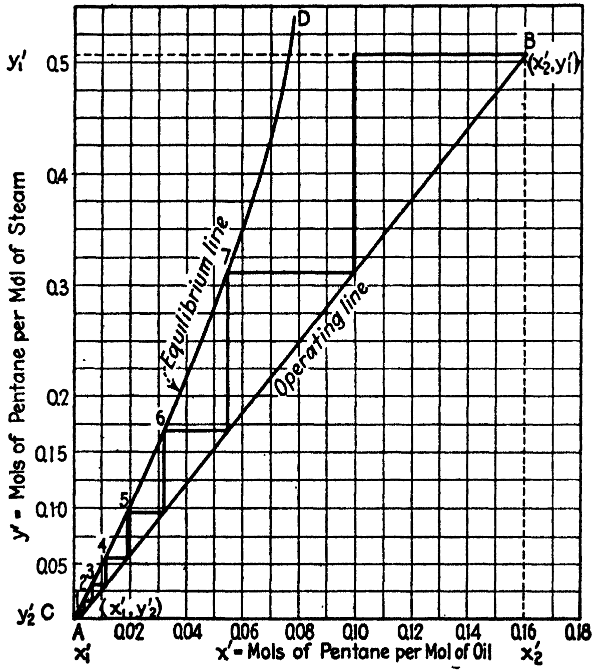

FIG. 90.—Stripping diagram.

Example 56. Stripping Hexane from Absorption Oil with Steam.—A rich absorption oil of the same composition as that produced in Example 55 but containing hexane is to be heated to 267°F. and contacted with 180 lb. per hour of steam. The tower operates at substantially 267°F. The pressure in the stripper is 1 lb. per square inch gage (812 mm.). The vapor-pressure of hexane at 267°F. is 3,800 mm.

Basis: 1 hr.

Construction of operating line:

$$x'_1 = 0.00158 \text{ (liquid leaving stripper)}$$
$$x'_2 = 0.161 \text{ (liquid entering stripper)}$$
$$y'_2 = 0 \text{ (pure steam)}$$
$$y'_1 = \frac{5.07}{\frac{180}{18}} = 0.507 \text{ (gas leaving stripper)}$$

These points are used to draw the line *AB* (Fig. 90).

Construction of equilibrium line: The equilibrium relation will be computed in a different way from that in Example 55 to illustrate another conception.

$$\text{partial-pressure} = p = Px$$
$$x = \frac{x'}{1 + x'}$$
$$\text{partial-pressure pentane} = p_p = 3{,}800\frac{x'}{1 + x'}$$
$$\text{partial-pressure steam} = p_s = 812 - 3{,}800\frac{x'}{1 + x'}$$
$$y' = \frac{p_p}{p_s} = \frac{3{,}800\frac{x'}{1 + x'}}{812 - 3{,}800\frac{x'}{1 + x'}}$$
$$y' = \frac{x'}{0.214 - 0.786x'}$$

This equation is plotted as line *CD* (Fig. 90). About 7½ perfect plates are required.

EXTRACTION

The process of extraction is used in petroleum refining in the new solvent treating processes for lubricating oils. The low-viscosity-index hydrocarbons and, to some extent, the coloring matter are removed from the oil by extraction with a solvent. Thus the operation is the extraction of a component from a liquid by means of the solvent action of another liquid.

Countercurrent processes involve two operations *viz.*, the obtainment of equilibrium and a separation of the contacted materials. The separation of the contacted materials in the operations of absorption and fractionation is relatively easy because one material is a vapor and the other a liquid, but in extraction both materials are liquids and the separation of these two liquids by settling is the major design difficulty.

The Distribution Law.—This law states that there is a constant ratio between the concentrations of a component that is distributed between two liquid phases. The distribution law is really a statement of Henry's law for two liquid phases.

$$\frac{C_1}{C_2} = K \tag{54}$$

where C_1 = concentration of solute in first liquid phase, per cent by weight.
C_2 = concentration of solute in second liquid phase, per cent by weight.
K = a constant that depends only on temperature.

If the solute is a mixture, the law holds for each material in the mixture.

A common method of estimating K is to get the ratio of the solubility of the solute in the two phases. However, it appears that such a method is not exact unless the solute is a very insoluble substance and unless the two liquids are mutually insoluble. Corrections must also be applied for dissociation and association and for changes in the mutual solubility of the two liquid phases because of the addition of the solute. The effect of dissociation or association on the distribution constant is

$$\left.\begin{array}{l}\text{1st liquid phase, dissociation occurring}\\ \text{2d liquid phase, no molecular change}\end{array}\right\}\frac{C_1(1-d)}{C_2} = K$$

$$\left.\begin{array}{l}\text{1st liquid phase, no molecular change}\\ \text{2d liquid phase, association occurring}\end{array}\right\}\frac{C_1}{\sqrt{C_2(1-a)}} = K$$

where d = dissociation constant, by independent methods.
a = association constant, by independent methods.

The effect of mutual solubility must be studied by the use of a ternary solubility diagram.

Equipment Design.—A countercurrent system for a liquid-liquid system is shown in Fig. 91. Although the diagram looks different from the tower systems shown for fractionation and absorption, it involves the same sequence of operations as those used in the liquid-gas systems. The operation can also be practiced in a packed tower or a tower with distributing plates at intervals of 3 or 4 ft. The tower extraction system has the advantage of utilizing gravity to transfer the materials from one stage to the next. It is also claimed that a packed tower of practical height is equivalent to six or seven stages of mixers and settlers.

If W represents the pounds of stock to be treated, S the pounds of pure solvent, x the pounds of component to be extracted per pound of stock, and y the pounds of component per pound of solvent (Fig. 91),

$$W(x_1 - x_2) = S(y_1 - y_2)$$

and

$$\frac{W}{S} = \frac{y_1 - y_2}{x_1 - x_2} \tag{55}$$

The subscript 1 refers to the incoming liquids and 2 to the outgoing liquids.

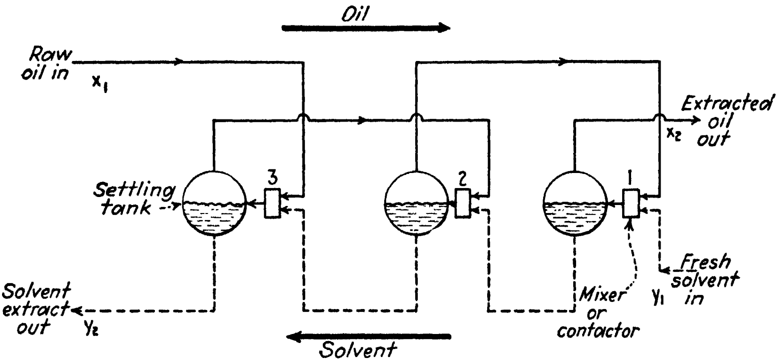

FIG. 91.—Diagram of solvent extraction system.

With conditions for which Eq. (54) is valid, the equilibrium relation in terms of x and y may be formulated as follows:

$$K = \frac{C_1}{C_2}$$

$$C_1 = \frac{x}{1 + x}; \qquad \text{and} \qquad C_2 = \frac{y}{1 + y}$$

$$\frac{y}{1 + y}K = \frac{x}{1 + x}$$

$$y = \frac{x}{K + xK - x} \tag{56}$$

These equations [Eqs. (55) and (56)] may be plotted exactly as in Fig. 90 for stripping operations, and the number of equilibrium contacts required for the given change in composition of the stock can be computed by the stepwise method. However, the minimum amount of solvent that can be used will be governed by the maximum solubility of the solute in the solvent, as well as the material balance of the system which states that the concentration in the stock must always be greater than in the solvent.

Stokes' law for the rate of settling of particles through fluids[1] is valid for the design of settlers, etc., but inasmuch as the particle size cannot be estimated without empirical tests, the theoretical relationship is of little value. However, it is interesting to note that horizontal settlers are more effective than vertical settlers because the velocity is lower.

In the practical application of extraction theory to the solvent treating of lubricating oils, difficulties arise because the solute is a very complex material, the oil and the solvent are usually not entirely insoluble in each other, and the solvents that are used are not completely preferential in their solvent action; *i.e.*, they dissolve some of the high-index hydrocarbons as well as the low-index hydrocarbons.

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[1] BADGER and McCABE, "Elements of Chemical Engineering," 1st ed. p. 535, McGraw-Hill Book Company, Inc., New York, 1931.

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CHAPTER XVI

CORROSION

All refineries suffer tremendous losses by corrosion. Those refiners that can escape sulfide and acid corrosion by processing selected oils still have the problems of soil corrosion, atmospheric oxidation, and high-temperature oxidation with which to contend. The loss by corrosion in 1928 amounted to about $135,000,000 for the entire petroleum industry and to $50,000,000 in the refinery branch alone. This is equivalent to a levy of about 1 ct. per gallon on each gallon of gasoline that is consumed. Although these figures seem staggering, a consideration of the average life of petroleum equipment makes the magnitude of the loss apparent at once.

Sulfide Corrosion.—Hydrogen sulfide is often found in natural gas or dissolved in crude oil, and in addition it may be formed by the decomposition of organic sulfur compounds at high temperatures. It rapidly attacks steel parts that are exposed to the gas. Equipment that suffers by this corrosion comprises storage tanks and gas lines, and pipestill tubes, evaporators, and fractionators at temperatures exceeding 400°F. The presence of moisture facilitates the action of hydrogen sulfide and the concentration of oxygen in the gaseous mixture is of great importance. Devine *et al.*[1] conclude

1. The presence of oxygen is necessary to cause serious corrosion at normal temperatures.
2. The ratio of oxygen to hydrogen sulfide largely governs the extent of corrosion. A ratio of 114 parts of oxygen per part of hydrogen sulfide causes maximum corrosion. This is equivalent to a sulfide concentration by volume of about 0.87 per cent.
3. Although a dilute sulfide gas is in general more corrosive than a concentrated gas, a minimum concentration of about 0.025 per cent is necessary to cause noticeable corrosion.
4. Corrosion proceeds proportionally with time. This indicates that sulfide scale is of a nonprotective character.

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[1] Oxygen Effect on Hydrogen Sulfide Gas Corrosion, *Oil Gas J.*, Apr. 7, 1932, p. 16.

In distillation equipment, sulfide corrosion becomes noticeable at 400° and rapid at 700°F. Thus sulfide corrosion is found to be most active in the hotter parts of distillation equipment such as in the furnace tubes, shellstills, vaporizers, fractionating-towers, and hot vapor lines, although certain high-sulfur crude oils have caused corrosion throughout the entire distillation equipment.

The corrosiveness of sulfur-bearing oils is not directly proportional to the sulfur content. Certain organic sulfur compounds decompose at high temperatures evolving hydrogen sulfide but others do not. Crude oils containing 2 per cent of sulfur and which cause little trouble by sulfide corrosion have been reported, but others containing less than 0.7 per cent have destroyed distillation equipment in less than six months. As a further example, the sulfur content of gasoline marketed in the United States has been limited to less than 0.1 per cent, but in Germany fuels have been sold that contained as much as 1.5 per cent of sulfur and no serious engine corrosion was reported. The corrosive properties of each oil are dependent on the kind of sulfur compounds that are present, and usually the corrosive action must be determined by experiment.

In general, all of the chromium steels are resistant to sulfide corrosion. However, the ternary chromium steels containing high percentages of chromium are so brittle that they cannot be easily handled or cleaned. Furthermore, they do not have so high a ductility at furnace temperatures as carbon steels and hence they may rupture during operation without bulging or swelling before failure. The danger attendant on such failures has led to modified alloys containing nickel, manganese, silicon, tungsten, and molybdenum, as well as chromium. The addition of small amounts of molybdenum to the chromium or chrome-nickel steels seems to be beneficial. The temper brittleness caused by cooling is greatly improved, the high-temperature strength (creep strength) is improved, and the corrosion resistance is improved to a small extent. Tungsten has been used for the same purposes but it is more expensive than molybdenum and is only about half as effective.

Neutralizing chemicals, particularly lime, are sometimes used to combat sulfide corrosion. Ammonia is not effective and caustic soda causes troublesome scaling or clogging of tubes and evaporator surfaces.

Acid Corrosion.—Hydrochloric acid is not present in crude oil, but it may be produced during distillation. It is probably produced by the hydrolysis of chloride salts, particularly magnesium chloride, which are present in the brine found in crude oils. Sulfuric acid is probably produced by the oxidation of hydrogen sulfide in the presence of moisture but only small amounts of sulfuric acid have been detected. These acids constitute the "acid" corrosion that occurs in vapor lines, condensers, coolers, run-down lines, and particularly at points in which water accumulates, such as in valves in horizontal lines.

The corrosive action of dilute hydrochloric acid at the temperatures encountered in distillation equipment cannot be satisfactorily withstood by any common materials. However, the copper-base alloys have been widely used for hydrochloric acid and brine corrosion. Admiralty-metal tubes are widely used for condensers and heat exchangers. The corrosion resistance of this material has been studied by Dr. S. Born and the author.[2] Ammonia is unsuitable as a neutralizer if admiralty metal is used, because it may destroy the metal faster than acid corrosion. The other neutralizers appear to produce protective films so that corrosion halts after an initial action. If scale-forming water is used, admiralty-metal tubes must be cleaned frequently, because corrosion occurs mainly beneath breaks or porous spots in the scale. The zinc in the brass is dissolved and is replaced by spongy copper.[3]

Oxidation.—Iron and steel oxidize or rust in the presence of air or moisture. At high temperatures such as those encountered in boilers and furnaces, oxidation or scaling occurs very rapidly. This type of corrosion is so common that it does not always receive the attention that it deserves. The chromium and chrome-nickel steels are excellent resistors to high-temperature oxidation and at the same time they retain their strength and toughness at elevated temperatures. For these reasons they

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[2] BORN and NELSON, Effect of Corrosive Agents on Admiralty Metal, *Nat. Petroleum News*, July, 19, 1933.

[3] PEW, A. E., Minimizing Corrosion in Condensers, *Oil Gas J.*, Apr. 16, 1931, p. 112.

are admirably suited for boiler and furnace parts that are exposed to high temperatures and to furnace gases. Figure 92 shows the relative scaling resistance of the common chromium steels.[4] These data were obtained by twelve intermittent heating and cooling cycles.

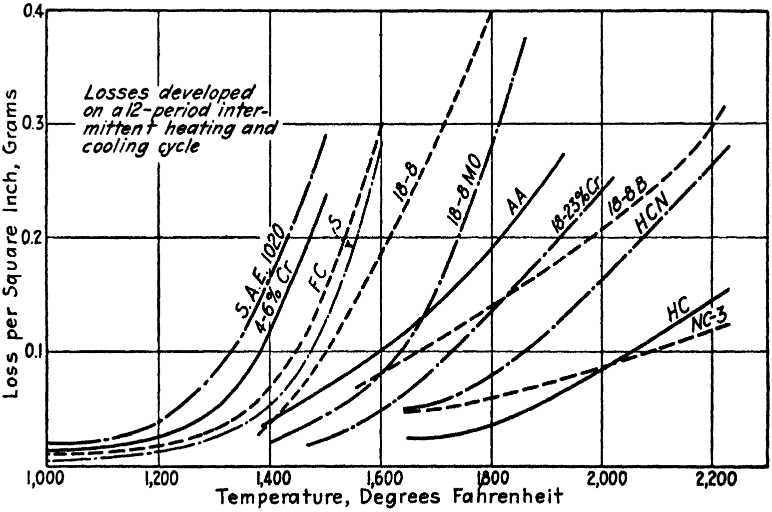

FIG. 92.—Oxidation of alloy steels at high temperatures. (*Republic Steel Company.*)

	Steel	Carbon	Chromium	Nickel	Silicon
Plain	1020	0.20			
Enduro	4-6	0.20 max.	4.0– 6.0	....	0.50 max.
Enduro	FC	0.12 max.	12.5–15.0	....	0.50 max.
Enduro	S	0.12 max.	12.5–15.0	....	0.50 max.
Enduro	18-8	0.16 max.	16.5–20.0	7.0–10.5	0.75 max.
Enduro*	18-8-Mo	0.16 max.	18.0–22.0	7.0–10.5	0.75 max.
Enduro	AA	0.10 max.	15.0–18.0	....	0.50 max.
Enduro	20-23	0.20 max.	18.0–23.0	....	0.50 max.
Enduro	18-8-B	0.18 max.	16.5–19.5	8.0–10.5	2.0–2.5
Enduro	HCN	0.20 max.	22.0–25.0	10.0–13.0	0.75 max.
Enduro	HC	0.20 max.	25.0–30.0	....	0.50 max.
Enduro	NC-3	0.20 max.	23.0–27.0	17.0–21.0	2.00 max.

* 2.0–4.0 Molybdenum.

Alloy steels containing a high percentage of special element are expensive and there has been a tendency to use the low-percentage steels, such as 4-6 chromium (or with 0.5 molybdenum or 1.0 tungsten), for parts of equipment that are not exposed

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[4] ANON, Alloy Steels . . . Refining Equipment, *Ref. Nat. Gaso. Mfr.*, April, 1933, p. 140.

to the most severe conditions. Pipestill tubes can be constructed of 4-6 chromium steel but supports that are not cooled must be constructed of high-percentage alloy steels.

Sulfuric Acid and Acid Sludge.—The universal materials for handling sulfuric acid are steel and lead. Ordinary mild steel withstands concentrated acid but lead must be used for dilute acid. Lead is such a ductile material that it presents many structural difficulties. For this reason, lead-lined rather than solid lead equipments, such as pipelines, agitators, and pumps, are gaining in favor. Recently some success has been attained in spraying steel with lead. A number of other materials including tin, zinc, aluminum, copper, brass, nickel silver, monel metal, and stainless steel are also being used. The coating[5] is applied by roughening the surface by a sand blast and spraying the surfacing metal from an oxyacetylene gun. Several coats must be applied.

Certain alloy cast irons such as Duriron (14.5 silicon) and the high-silica irons are useful for lines, valves, pumps, etc., for handling sulfuric acid and acid sludge. In fact, ordinary cast iron is used for many corrosive conditions because of its cheapness.

Neutralizing Chemicals.—Few materials are satisfactory resistors to "acid" corrosion and hence neutralizing chemicals such as ammonia, sodium hydroxide, sodium carbonate, and lime are widely used. In general, these chemicals are introduced into the vapor lines of distillation units. Ammonia is introduced as a gas, and the other materials as dilute solutions, although lime is preferably added as a slurry. Lime is often used in cracking plants by injecting it with the charge to the pipestill and it serves partly to reduce sulfide corrosion as well as acid corrosion. The other chemicals, particularly ammonia,[6] are not effective in combating sulfide corrosion.

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[5] RICE, H. B., Metal Spraying . . . , *Ref. Nat. Gaso. Mfr.*, April, 1933, p. 148.

[6] In cases where ammonia has been used in hot parts of the equipment such as pipestills, evaporators, or reaction chambers, the iron has been gradually attacked and given a thin film of nitrided steel which is very hard and somewhat resistant to corrosion. After ammonia is used for a while, the quantity of ammonia may be decreased somewhat, owing to nitriding of the surfaces.

The solutions are usually injected into the system by direct-acting pumps. A fine dispersion of the chemical in the oil is essential and hence the solutions are often mixed with a part of the oil by means of mixing columns before they are injected into the system. These columns consist of a pipe containing baffle plates. From 0.15 to 0.3 per cent by volume of caustic soda solution (about 10°Bé.) or 0.3 to 1.0 lb. of lime per barrel of charging-stock is usually sufficient, although the exact amount must be determined by plant experiments. Obviously, an excess of the neutralizer creates alkaline corrosion which may be more severe than the original acid corrosion, and hence the chemicals are not added in large enough quantities to neutralize the acid or sulfide materials completely. The corrosion can often be reduced to half by adding much less chemical than the amount required for complete neutralization.

Ammonia rapidly attacks admiralty metal and hence ammonia should not be used in a system having brass condenser tubes or parts. In some instances ammonia has been successfully used with admiralty-metal condensers but under careful supervision so that no large excess was ever present. Ammonium chloride gradually accumulates in the lines and condensers, and it must be "flushed out" with water or steam during cleaning periods. Caustic soda also causes deposits and these deposits are so difficult to remove that the use of caustic has been gradually abandoned. Caustic deposits are particularly troublesome within fractionating-towers so that, if acid corrosion occurs within a tower, ammonia has usually been adopted as the neutralizing agent. Caustic soda also causes caustic embrittlement of the steel shells of evaporators, towers, etc. Two and one-half to twenty lb. of anhydrous ammonia is used for 1,000 bbl. of crude oil, depending upon the amount of acid that is produced. Some refiners have reported a decrease of 97 per cent in the extent of acid corrosion by the use of ammonia.

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CHAPTER XVII

THEORY OF CRACKING

The thermal decomposition or cracking of oil was called to our attention by Silliman[1] in 1871 and, ever since commercial application in about 1910, the study of the theory of cracking has proved difficult. The complex composition of heavy oils has at times made the task seem almost unsurmountable. Even today, only a few of the hydrocarbons that boil above 200°F. have been isolated and studied. Hence the development of our great cracking facilities has been made mostly along other lines than fundamental theory.

Although data on cracking are not so complete as we desire, nevertheless they are complete enough to permit definite conclusions concerning almost any phase of cracking. The purpose of this chapter is to present and correlate, as completely as possible, the data that are available.

Mechanism of Cracking.—Cracking is a phenomenon by which large oil molecules are thermally decomposed into smaller lower boiling molecules; at the same time certain of these molecules, which are reactive, combine with each other to give even larger molecules than those in the original stock. The more stable molecules leave the system as cracked gasoline but the reactive ones polymerize, forming tar and even coke. Although gasoline is the common light product from cracking plants, all of the oils having boiling-ranges intermediate between fuel oil and gasoline are also produced. However, these intermediate materials are kept within the cracking system until they are decomposed and they normally do not appear as final products. These intermediate materials, called recycle stock, can be kept in the cracking system until they are decomposed, by recycling them in a continuous system or by operating a batch system under a high pressure. The production of intermediate stocks is illustrated by the following general chemical reactions:

[1] *Am. Chem. Soc. J.*, **2**, 18 (1871–1872).

Charge-stock.................................. $C_7H_{15}\cdot C_{15}H_{30}\cdot C_7H_{15}$
↓ *heavy gas oil*
Cracked stock.............................. $C_7H_{16} + C_{14}H_{28}:CH_2 + C_6H_{12}:CH_2$
↓ *gasoline* + *recycle stock* + *gasoline (antiknock)*
More cracking.............. $C_2H_6 + (C_4H_8:CH_2 + C_8H_{18} + C_6H_{12}:CH_2) + CH_2:CH\cdot CH_2\cdot CH:CH_2 + C_2H_4$
↓ *gas* + *gasoline* + *gum forming materials* + *gas*
Polymerization.......................... $C_2H_6 + (C_4H_8:CH_2 + C_8H_{18}) + C_{12}H_{22} + C_2H_4$
gas + *gasoline* + *tar or recycle* + *gas*

Although these exact reactions probably do not take place, they are representative of the over-all reaction that takes place during cracking.

Thus two general types of reactions take place: (1) primary reactions in which decomposition of large molecules into small molecules takes place and (2) secondary reactions by which active products polymerize to form heavy tarry materials. At the same time the products of polymerization may be again decomposed into smaller molecules. The nature of the primary reactions may be illustrated by the experimental work of Hurd and Spence[2] on the decomposition of *n*-butane at 600°C. (1112°F.). Their work indicates that the major part of the cracking occurs by these two reactions:

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_3 \rightarrow CH_4 + CH_3\cdot CH:CH_2$$

and

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_3 \rightarrow CH_3\cdot CH_3 + CH_2:CH_2$$

"At 600 degrees the first of these appears to proceed to the extent of about 55 per cent and the second to 40 per cent. Dehydrogenation reactions into butene or butadiene appear to represent less than 5 per cent of the total." The dehydrogenation reactions referred to are

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_3 \rightarrow H_2 + CH_3\cdot CH_2\cdot CH:CH_2$$

and

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_3 \rightarrow 2H_2 + CH_2:CH\cdot CH:CH_2$$

Their work also indicates that the tendency to dehydrogenate, leaving an olefin with the same number of carbon atoms as the original paraffin hydrocarbon, rapidly diminishes as the series is ascended. Thus the production of large amounts of hydrogen by cracking gas oil stocks, should not be expected.

The olefin hydrocarbons are not usually found in raw petroleum stocks and hence the decomposition of olefins should properly be considered as a secondary decomposition reaction. Both hydro-

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[2] *J. Am. Chem. Soc.*, **51**, 3353 (1929).

genation and dehydrogenation may occur during the decomposition of olefins. Diolefins, paraffins, polymers, new olefins, hydrogen, and probably many other materials are produced. As an example of diolefin and paraffin formation, pentene-1 reacts thus:

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \rightarrow CH_4 + CH_2{:}CH{\cdot}CH{:}CH_2$$

and

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + H_2 \rightarrow CH_4 + CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$$

The secondary reactions by which polymers are formed may be illustrated thus:

$$CH_2{:}CH_2 + CH_2{:}CH_2 \rightarrow CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 \text{ (dimer)}$$

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + CH_2{:}CH_2 \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 \text{ (trimer)}$$

or

$$RCH{:}CH_2 + R'CH{:}CH_2 \rightarrow \text{tars, oils, etc. (polymers)}$$

The data of Wheeler and Wood[3] on butene-1 illustrate the over-all results of all of the above types of reactions (see Table 35).

TABLE 35.—DECOMPOSITION OF BUTENE-1*

Temp., °C.	Calc. contact time, sec.	Per cent by weight of butene-1 heated			Gas analysis, per cent by volume of butene-1 heated						
		Total liquid	Distillate up to 170°	C	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	C_4H_8	C_4H_6
600	61.5	12.9	6.5	Nil	0.8	8.1	1.9	3.2	7.6	54.1	0.9
650	58.2	29.8	20.3	Nil	6.2	37.2	7.1	14.2	24.5	19.8	1.7
700	55.	35.8	23.6	Trace	11.9	62.1	10.6	22.3	19.6	2.1	1.4
750	52.5	39.6	22.4	Trace	17.3	78.5	9.7	31.4	5.6	1.3	0.2
800	50.	39.4	19.9	1.0	27.2	89.	7.6	30.2	2.0	1.0	
850	47.7	35.	16.2	4.7	50.5	95.7	6.1	20.6	....	1.0	
900	45.7	13.9	7.8	7.1	85.2	103.3	5.0	9.6	....	0.9	

* Wheeler and Wood.

In general, at higher temperatures the production of fixed gases, such as methane and hydrogen, increases (Table 35) and the polymerization reactions appear to decrease. How true these generalizations are for high-molecular-weight hydrocarbons

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[3] *J. Chem. Soc.*, 1819 (1930).

and particularly for naphthene hydrocarbons cannot be stated, but we expect that they are equally true.

The general reactions of the paraffin hydrocarbons may be summarized as follows:

Decomposition:

$$R\cdot CH_2\cdot CH_2\cdot CH_2\cdot R' \rightarrow R\cdot CH{:}CH_2 + CH_3\cdot R'$$
$$R\cdot CH_2\cdot CH_2\cdot CH_3 \rightarrow R\cdot CH{:}CH_2 + CH_4$$
$$R\cdot CH_2\cdot CH_3 \rightarrow R\cdot CH{:}CH_2 + H_2$$

Polymerization:

$$R\cdot CH{:}CH_2 + R'\cdot CH{:}CH_2 \rightarrow \text{tars, etc.}$$

Egloff and his associates Schaad, Lowry, Jr., Bollman, and Levinson have studied the technical literature thoroughly concerning the thermal reactions of the paraffin,[4] olefin,[5] and naphthene[6] hydrocarbons. Aromatic and naphthene hydrocarbons are produced by the thermal reactions of the olefins but the mechanisms of these reactions are not well understood. It appears that progressive dehydrogenation takes place until the resulting highly unsaturated straight-chain compounds connect to form ring compounds. The secondary reactions that are possible seem to be almost numberless so that a complete organization of the many reactions is difficult.

Properties of Cracked Materials.—The properties of the products that are produced by cracking depend greatly upon the extent of cracking that is practiced. Sachanen and Tilicheyev[7], have studied the mechanism of cracking by producing recycle stocks which had been cracked once, twice, and several times. In each cracking test the oil was cracked at 450°C. The fraction boiling between 200 and 350°C. was separated by distillation and subjected to another cracking operation at 450°C. The extent of cracking was not exactly the same for each recycle oil but the qualitative comparison (Table 36) is useful. Note the 30.6 A.P.I., 392°F. gasoline that was produced from the sixth recycle stock.

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[4] Paraffins, *J. Phys. Chem.*, **34**, 1617 (1930).

[5] Olefins, *J. Phys. Chem.*, **35**, 1825 (1931).

[6] Naphthenes, *J. Phys. Chem.*, **35**, 3489 (1931).

[7] *Oil Gas J.*, Dec. 19, 1929, p. 48.

TABLE 36.—CRACKING TESTS OF EMBA (RUSSIAN) GAS OIL*

No. of operation	Time, min. at 450°C.	Yield per cent by weight		A.P.I. gravities		
		Below 200°C. (392°F.)	Above 350°C. (672°F.)	Cracking-stock and recycle oils	Below 392°F.	Above 672°F.
1	42	28.7	10.5	30.8†	58.2	10.6
2	52	21.3	8.6	28.2	52.5	1.05‡
3	75	16.3	7.9	23.8	46.0	1.116‡
4	101	12.1	10.3	19.2	38.4	1.177‡
5	101	3.9	12.4	15.4	37.1	1.157‡
6	160	8.0	19.0	14.5	30.6	1.243‡

* See footnote 7, (p. 307).
† Emba gas oil (uncracked).
‡ Specific gravity.

Sydnor and Patterson[8] have studied a Mid-Continent gas oil, and cycle oils produced from it, in a similar manner. Their

TABLE 37.—EXPERIMENTS ON RECYCLING

Yields	Run 1 straight-run gas oil	Run 2 cycle gas oil from Run 1	Run 3 cycle gas oil from Run 2	Run 4 cycle gas oil from Run 3	Built-up yields	Yields on straight-run gas oil currently recycling
400°F. gasoline*	24.3	19.3	16.7	14.9	47.8	48.2
Cycle gas oil*	63.5	66.2	67.5	67.1	19.1	22.3
Fuel oil*	4.4	7.3	8.6	11.0	15.7	19.1
Gas†	5.5	4.2	4.5	5.5	11.7	12.7
Coke†	0.5	0.3	0.7	1.5	1.2	1.7
Total†	96.3	96.4	97.4	99.0	92.6	100.2
Operation:						
Conversion-per-pass	24.3	19.3	16.7	14.8	.....	21.3
Properties:						
Gas oil gravity	33.7	30.4	28.9	26.5	24.7‡	
Fuel oil gravity	10.0	12.0	9.0	8.5		
Fuel oil, furol vis. at 122°F	210.0	22.0	25.0	18.0		
Fuel oil, insoluble sediment, per cent	0.018	0.26	0.26	0.37		

* Per cent by volume.
† Per cent by weight.
‡ Cycle oil from Run 4.

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[8] *Ind. Eng. Chem.*, **22**, 1237 (1930).

experimental equipment simulated plant operations more accurately and they present more complete data than Sachanen and Tilicheyev.[7] They attempted to operate for the formation of a fuel oil of the same gravity in each cycle of cracking. They aimed to produce a 400°F. end-point gasoline and a 10 A.P.I. tar in each cycle. Their results are given in Table 37. Note that the viscosity of the 10 A.P.I. tars ranged from 210 for the first tar to 18 for the tar produced in the fourth crack. The insoluble sediment in the fuel oil increased from 0.018 to 0.37 for the same tars.

Egloff[9] reports the analysis of straight-run and cracked gasolines (from the same crude oil) as shown in Table 38. This table indicates that the percentage of paraffin (knockers) and of naphthene hydrocarbons is less in cracked gasolines than in straight-run gasolines but the percentage of unsaturated and of aromatic (antiknock) hydrocarbons is greater.

Cracked gasolines have higher octane-numbers than straight-run gasolines from the same parent stock. Gasolines from normal stocks usually have octane-numbers between 70 and 80 but if the stock is naphthene base, such as many Coastal, California, Texas, and Mexican stocks, the octane-number of the cracked gasolines may be between 80 and 90. Higher octane-numbers are obtained by operating at high temperatures and high pressures and the octane-number, when cracking is accomplished by vapor-phase processes (temperature 1050 to 1250°F.), may be as high as 100.

Recent work on the reforming of straight-run gasoline has added much to our knowledge of the factors that affect the octane-number. LeRoi and Ferguson[10] find that the smaller the yield of gasoline and the greater the loss by producing gas, the higher the octane-number. Their experimental work was conducted in a modified tank and tube equipment. They introduce the term degradation, which may be defined as the per cent decrease in the yield of total liquid products for an increase of one in the octane-number. General conclusions from their work are given in Table 39.

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[9] *Petroleum Eng.*, Midyear, 1930, p. 104.

[10] Developments in Naphtha Reforming Practice . . . , 3d Midyear Meeting, A.P.I., Tulsa, Okla., May, 1933.

TABLE 38.—CHEMICAL ANALYSES OF GASOLINE

Gasoline	Unsaturated hydrocarbons	Aromatic hydrocarbons	Naphthene hydrocarbons	Paraffin hydrocarbons
Pennsylvania, straight run	2.5	Trace	14.9	82.6
Pennsylvania, cracked	16.8	23.1	12.1	48.0
Mid-Continent, straight run	2.9	3.9	19.7	73.6
Mid-Continent, cracked	15.0	18.5	12.6	53.0
California, straight run	2.2	10.4	28.1	58.0
California, cracked	25.8	10.8	19.8	43.6
Smackover, cracked	16.8	23.1	12.1	48.0
Cushing, Okla., straight run	1.6	4.9	23.7	69.8
Cushing, Okla., cracked	10.9	19.8	18.0	51.3
Somerset, Ky., straight run	3.8	5.3	20.6	70.3
Somerset, Ky., cracked	12.5	14.9	11.8	60.8
Straight-run gasoline from Rumanian crudes as follows:				
Bustenari	3	13.3	29.0	54.7
Arbanasi	4	24.0	14.0	58.0
Ceptura	2	7.2	20.1	70.7
Arbanasi	....	15.7	21–23	61.3–63.3
Moreni	....	23.3	16.2	60.5
Rumanian cracked gasoline:				
After chemical treatment	9.7	28.9	17.4	44.0
Before treatment	19.0	23.5	14.6	42.9

More exact values are given in the original paper[10] and a comparison indicates that the degradation is not a constant but increases as the octane-number of the distillate is increased. Higher yields of a given octane-number product are obtained at higher pressures. By their tests, an increase of 10 per cent in the yield was obtained when the pressure was increased from

TABLE 39.—OCTANE-NUMBER AND YIELD

Stock	A.P.I.	Approximate degradation	Type of operation
Straight-run naphtha	51	0.37	Coil only or coil and soaker—once through
Cracked naphtha	45	0.68	Once through
Cracked naphtha	45	1.3	Currently recycling

250 to 800 lb. per square inch. Yields of total distillate are seldom more than 80 per cent, which means a gas loss of 20 per cent.

Example 57. Octane-number of Gasoline by Reforming.—A straight-run naphtha has an octane-number of 35. If it is cracked in a once-through cracking equipment for the production of 80 per cent of total distillate, what will be the octane-number of the distillate?

$$\text{Total change in percentage} = (100 - 80) = 20$$

Each decrease of 0.37 per cent causes an increase of one in the octane-number (Table 39).

$$\text{Octane-number of distillate} = \frac{20}{0.37} + 35 = 89$$

The octane-number of a 90 per cent yield would be lower:

$$\text{Octane-number} = \frac{(100 - 90)}{0.37} + 35 = 62$$

These experimenters[10] fail to report the exact operating conditions for each test, and hence the changes in octane-number which they report may be due, in part, to differences in the temperatures or operating conditions, as well as differences in the yield. In fact Egloff and Nelson[11] show no change in octane-number with different yields if the operating conditions are kept the same in each test. When Smackover fuel oil is cracked, the yield is increased from 39 to 63 per cent by cracking more and more completely, but the octane-number of the pressure distillate remained the same. Egloff's[11] tests are not comparable with those of LeRoi[10] because different equipments and conditions were used and particularly because Egloff reported the octane-number of the gasoline, and LeRoi reported the octane-number of the total product.

Albright[12] shows that an increase in temperature increases the octane-number of the gasoline, if other conditions are kept the same. The octane-number was increased from 69 to 72 by

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[11] Cracking Light and Heavy Oils, 3d Midyear Meeting, A.P.I., Tulsa, Okla., May, 1933.

[12] Influence of Temperature in Reforming Naphtha, *Ref. Nat. Gaso. Mfr.*, January, 1933, p. 2.

increasing the temperature in a commercial unit from 997 to 1010°F.

Reference 11 also constitutes a good résumé of the octane-number that may be expected when operating with various stocks and at different operating conditions. The data given in Table 40 were taken from this paper.[11] The Dubbs process was used.

TABLE 40.—YIELD AND OCTANE-NUMBER

Stock	Source	A.P.I.	Yield gaso.	Temp., °F.	Pressure, lb. per sq. in.	Octane-number	
						Stock	Gasoline
Gasoline	Pa.	64.6	76.7	1000	400	50	75
Gasoline	Joiner and E. Te.	58.7	84.4	950	500	56	75
Gasoline	Joiner and E. Te.	58.7	88.1	950	500	56	71
Gasoline	E. and W. Te.	61.3	85.8	995	450	59	73
Gasoline	M.C.	59.8	82.3	975	500	42	70
Gasoline	West Te.	58.1	87.4	950	750	61	78
Naphtha	Pa.	54.9	73.5	950	500	31	76
Naphtha	M.C.	53.5	75.5	1000	500	34	75
Naphtha	West Te.	51.5	80.4	950	750	52	78
Gas oil	Pa.	38.8	70.5	950	350	..	76
Gas oil	M.C.	35.3	65.2	965	350	..	80
Gas oil	Calif.	34.5	70.8	950	350	..	77
Gas oil	East Te.	32.0	60.5	950	350	..	75
Gas oil	Coastal	28.5	52.8	950	400	..	90
Gas oil	Calif.	26.1	55.6	950	350	..	79
Fuel oil	New Mex.	27.8	56.0	935	350	..	76
Fuel oil	Montana	27.3	60.2	950	300	..	81
Fuel oil	M.C.	25.3	51.2	915	250	..	72
Fuel oil	Ky.	23.4	55.1	900	265	..	76
Fuel oil	Calif. S. F. Spgs.	19.8	40.7	929	250	..	75
Fuel oil	Calif.	17.8	38.9	890	250	..	79
Fuel oil	Smackover, Ark.	17.9	48.8	935	200	..	80

Heat of Decomposition.—Little definite information can be given regarding the heat that is required for the cracking reaction. Theoretical methods of computing the heat of decomposition—and several of these are available—all fail because the data required to apply them are not usually available. Nevertheless, all of these methods indicate clearly that, if large amounts of gas are produced, the heat of decomposition is relatively high and, if a process could be operated so that no gas was produced, the cracking reaction would generate rather than require the addition of heat.[13] These methods also show that the heat of decomposition for heavy fuel oils is higher than for gas oil or naphtha stocks.

The magnitude of the heat of decomposition expressed as B.t.u. per pound of 437°F. gasoline that is produced is indicated in Table 41.

TABLE 41.—HEAT OF DECOMPOSITION

Reference	B.t.u. per lb. gasoline	Method of determination
[14]	900	Laboratory measurements
[15]	604	Heat-balance of commercial unit
[15]	630	Heat-balance of commercial unit
[15]	657	Heat-balance of commercial unit
The author (unpublished data)	615	Heat-balance of commercial unit
The author (unpublished data)	765	Heat-balance of commercial unit
The author (unpublished data)	637	Heat-balance of commercial unit
The author (unpublished data)	740	Heat-balance of commercial unit
The author (unpublished data)	752	Heat-balance of commercial unit
The author (unpublished data)	520	Heat-balance of commercial unit

The values are for normal stocks undergoing an amount of decomposition such as that which occurs in commercial practice.

Perhaps the most reliable method of computing the heat of decomposition is by means of the first law of thermodynamics as outlined in Examples 31 and 32 (Chap. XII). The heat of combustion is an accurate measure of the chemical energy content of a material. Hence the difference between the heat of combustion of the cracking-stock and the total heat of combustion of the products of cracking is the heat required for cracking. Heats of combustion are normally given at 60°F. and hence it is either necessary to convert all of these to the cracking temperature or to convert the computed heat of decomposition at 60°F.

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[13] Perhaps this accounts for the rise in temperature that sometimes occurs as an oil flows slowly through a soaking drum. This phenomenon has been frequently reported by plant operators.

[14] LESLIE and POTTHOFF, *Ind. Eng. Chem.*, **18**, 776 (1926).

[15] OBRAYACHIKOV and VELIKANOV, *Neftyanoe Khozyaistvo*, **17**, 370 (1929) and *C.A.*, **24**, 1206 (1930).

to the cracking temperature. Example 58 illustrates the application of this method.

Example 58. Computation of Heat of Decomposition.—One hundred pounds of a gas oil and recycle cracking-stock is cracked to produce 17.1 lb. of fixed gas, 57.5 lb. of pressure distillate, and 25.4 lb. of cracked tar. What is the heat of decomposition at 60°F. and at 900°F.?

Basis: 100 lb. cracking-stock. A negative sign means heat liberated.

Heats of combustion at 60°F.:

	B.t.u. per Lb.
Cracking-stock	19,370
Fixed gas	21,200
Pressure distillate	20,200
Cracked tar	18,100

These may be estimated by the data given in Chap. XI.

Energy available in stock:

Heat in cracking-stock 100(−19,370) = − 1,937,000 B.t.u.

Energy available in products:

Heat in gas...... 17.1(−21,200) = − 362,000
Heat in P.D..... 57.5(−20,200) = −1,160,000
Heat in tar...... 25.4(−18,100) = − 460,000

Subtracting.................... −1,982,000 − 1,982,000

Difference in energy........... Heat absorbed = + 45,000

Heat of decomposition B.t.u. per pound of gasoline at 60°F. $= \frac{45{,}000}{57.5} = 782$

Heat of decomposition at 900°F. (the sensible heat contents were computed from Figs. 33 and 34):

Cool stock from 900 to 60°F.... 100(−580) = − 58,000
Decomposition at 60°F........ = + 45,000
Heat gas to 900°.............. 17.1(655) = + 11,200
Heat P.D. to 900°............. 57.5(642) = + 36,900
Heat tar to 900°.............. 25.4(492) = + 12,650

+105,750 +105,750

Difference in energy........... Heat absorbed (adding) = + 47,750

$$\text{Heat of decomposition, B.t.u. per pound at 900} = \frac{47{,}750}{57.5} = 830$$

Although the method outlined in Example 58 is correct from the standpoint of theory, it is hardly satisfactory for practical work unless great care is used. Very small errors in the heats of combustion or in the yields of products that are assumed will introduce great errors in the computed heat of decomposition. However, many useful generalizations can be determined. As an example, Obrayachikov[16] has computed the following tabulation. The first column is the yield of gasoline in a single cracking operation (or the crack-per-pass) and the second column shows the heat required to produce a pound of gasoline.

Yield	Heat of Decomposition per Lb. Gasoline, B.t.u.
5	2,700
10	1,710
15	1,170
20	900
25	865
35	790

The results shown in this tabulation might be expected inasmuch as a large amount of energy is used to produce recycle stock when only a small amount of gasoline is produced, but relatively less heat is used to make recycle stock when the yield of gasoline is greater.

Yields by Cracking.—The estimation of the yields that may be expected when cracking a particular stock is always a troublesome problem. These may be obtained by laboratory cracking operations, but such yields are often worthless because the laboratory procedure does not duplicate plant operation. In the past the yields have been estimated by referring to scattered data from plant operations, but to the author's knowledge no comprehensive organization of these plant data has been made.

The over-all reaction of cracking involves the decomposition of a heavy oil into gas, low-boiling oils, and tar. In this operation the hydrogen in the stock is concentrated into the light products and hence the residue material becomes more and more deficient in hydrogen. Thus the larger the percentage of distillate produced, the higher will be the specific gravity of the residue that is left behind. The yield of gasoline is directly related to the difference in gravity of the stock and the gravity of the tar. Approximate yields by cracking are

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[16] *Ref. Nat. Gaso. Mfr.*, January, 1932, p. 34.

$$\text{Per cent 400 E.P. gasoline from gas oil or fuel oil} = 25 + 1.5(A_s - A_t) \quad (57)$$

$$\text{Per cent 400 E.P. gasoline by coking fuel oil} = 303 - 250s \quad (58)$$

$$\text{Per cent 400 E.P. gasoline by coking gas oil} = 331 - 300s \quad (59)$$

where A_s = A.P.I. of cracking-stock.
A_t = A.P.I. of cracked tar or residue.
s = specific gravity of cracking-stock.

For gas and unaccounted-for losses:

$$\text{Per cent gas and unaccounted-for loss} = 0.45(A_s - A_t) \quad (60)$$

In all, 77 sets of commercial data and 16 sets of laboratory data were used in determining these equations. Data from seven different commercial mixed-phase processes were used and little difference in the yields by each process were found. However, the gas and unaccounted-for losses were different for the several processes.

The accuracy of the equations may be judged from Fig. 93. The fact that gas oils and fuel oils give the same yields if they are degraded in gravity by the same amount is surprising. Equation (60) is not so accurate as the others. This equation is accurate to only about ±50 per cent. A more detailed study of the gas and unaccounted-for losses is given in Table 42.

TABLE 42.—GAS AND UNACCOUNTED-FOR LOSSES

Difference in sp. gr. of stock and tar	Per cent gas and unaccounted-for losses		
	Gas oil	Fuel oil	An average by Eq. (60)
0.05	7	4	4
0.10	9	6.5	7
0.15	11.7	10.0	11
0.20	15.5	12.0	14.2

Thus larger losses occur when gas oil is cracked than for fuel oil. This may be explained by the fact that gas oil must be heated to a higher temperature or for a longer time than fuel oil to produce the same yield of gasoline.

A comparison of the yield in the coking of gas oil and of fuel oil also reveals the more refractive nature of gas oil. For the same gravity of stock, the yield from fuel oil is greater than from gas oil. With reference to Eqs. (58) and (59), the yields when 0.9 specific gravity (25.8 A.P.I.) stocks are coked are

$$\text{Yield from fuel oil} = 303 - 250 \times 0.9 = 78 \text{ per cent}$$
$$\text{Yield from gas oil} = 331 - 300 \times 0.9 = 61 \text{ per cent}$$

This may be explained in the same way that the larger gas and unaccounted-for loss in cracking gas oil was explained.

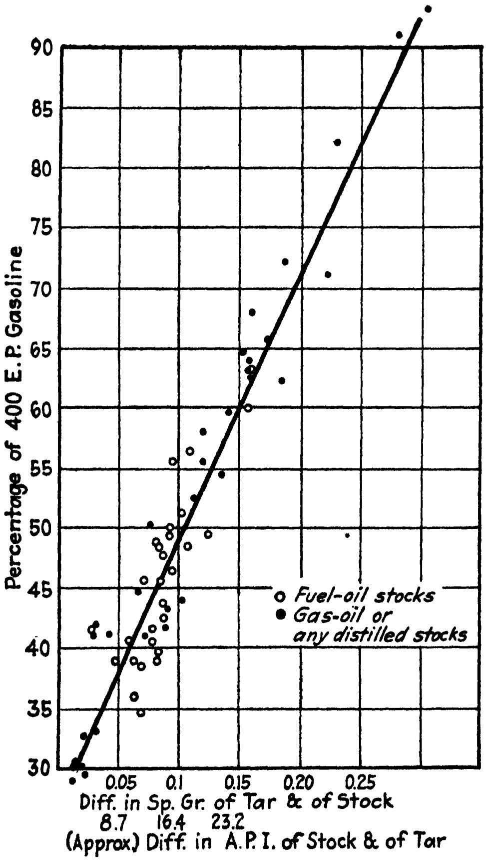

FIG. 93.—Yield of gasoline versus difference in gravity of stock and tar.

The yields that may be expected when various stocks are cracked for the production of a 10 A.P.I. tar are given in Table 43.

In applying the foregoing formulae it is necessary to rely upon experience in estimating what A.P.I. of the tar is possible. If the tar has too low a gravity it may be so viscous that it cannot be easily withdrawn from the cracking unit or it may not be marketable. Straight-run tars are viscous but cracked tars are much more fluid. When distillate stocks are cracked, tars having gravities from 3 to 7 A.P.I. are usually fluid enough to be marketable. The tars obtained by cracking all of a fuel oil are more viscous, and A.P.I. gravities of 6 to 9 are advisable. In some plants it is the practice to distill gas oil from fuel oil and leave a partially cracked straight-run tar behind. Thus the tar from many cracking plants consists of a mixture of straight-run and cracked tars. These mixed tars are even more viscous and gravities of 8 to 11 are necessary. Even these gravities cannot be obtained unless the tar is allowed to stand at 750 to 800° for 20 or 30 min. before it leaves the cracking plant (Fig. 148, page 477). In reforming operations, cracked tars having gravities of 3 to 5 A.P.I. are common.

TABLE 43.—YIELDS WHEN A 10 A.P.I. TAR IS PRODUCED

A.P.I. of stock	Kind of stock	Yield of 400 E.P. gasoline	Gas and loss
15	Fuel oil	32.5	2.25
20	Fuel oil or gas oil	40.0	4.5
25	Fuel oil or gas oil	47.5	6.75
30	Gas oil or fuel oil	55.0	9.0
35	Gas oil	62.5	11.25
40	Naphtha	70.0	13.5
45	Naphtha	77.5	15.75
50	Straight-run gasoline	85.0(?)	

In general, the yield of gasoline is increased by the following conditions:

1. A low crack-per-pass or a high recycle ratio.
2. A relatively low pressure (200 to 300 lb.).
3. A relatively low cracking temperature (860 to 900°F.).
4. The cracking of all of a black or residual stock rather than the production of a distilled cracking-stock and a residue of heavy tar. At the same time, a black stock tends to produce coke in the tubes.

These variables, doubtless, account for most of the variations that were found in deriving Eqs. (57), (58), (59), and (60) (see also Fig. 93).

Example 59. Yields by Cracking.—A 24 A.P.I. fuel oil is to be cracked to produce 400 end-point gasoline and an 8 A.P.I. tar. What approximate yields may be expected?

Yield gasoline = 25 + 1.5(24 − 8) = 49
Gas and loss = 0.45(24 − 8) = 7.2
Cracked tar = (by difference) = 43.8

These are ultimate yields. In determining the yield of pressure distillate, approximations must suffice. The loss during the rerunning of pressure distillate usually amounts to about 2 per cent, although the magnitude of the loss is determined by the character of the distillate. The bottoms obtained in the rerunning of the treated pressure distillate is often blended with the cracked tar. The viscosity of the tar is sometimes high, and the addition of even a small amount of pressure distillate butts serves to lower the viscosity a large amount.

If a 440 end-point distillate is produced, the approximate yields of raw stocks are

Yield of pressure distillate........ $49 \times {}^{440}\!/_{400} = 54$
Gas and loss.................... $7.2 - 54 \times 0.02 = 6.1$
Fuel oil, unblended (by difference)................ = 39.9

The approximate yields of gasoline when operating in other ways would be

When making a 10 A.P.I. tar.. 25 + 1.5(14) = 46 per cent
If coking................ 303 − 250 × 0.91 = 75 per cent

Rate of Cracking.—The rate at which cracking occurs is governed mainly by three factors: the temperature, the time, and the character of the cracking-stock. The yield in a given length of time increases rapidly with temperature; the yield at a fixed temperature increases with time up to a certain point and then it decreases; and the yield for a given length of time is greater for heavy stocks. The following tabulations, which were taken from

(Reference 17) Cracking time: 12 min.
Cracking temperature: 842°F.

Stock	Sp. gr.	Yield of 392°F. distillate, per cent by weight
Kerosene	.....	4.9
Solar oil	.....	18.6
Paraffin oil	0.833	26–30
Spindle oil	0.904	28.2
Three cylinder oils	0.931	29.5–30.5
Paraffin	.....	31.2

(Reference 18) Cracking time: 64 min.
Cracking temperature: 796°F.

Stock	Boiling-range, °F.	Sp. gr.	Yield of 392°F. distillate, per cent by weight
Kerosene	428–518	0.81	14.9
Gas oil	518–572	0.834	15.8
Solar oil	572–617	0.859	17.6
Engine oil	....	0.91	22.4

the work of Sachanen and Tilicheyev,[17,18] indicate the relation of the rate of cracking to the properties of the cracking-stock.

Thus the lighter the cracking-stock the longer the time required. In commercial practice the yield from light stocks is obtained not by using a long length of time but by using a higher temperature. As will be shown later, an increase in temperature is very effective in decreasing the time required.

Stocks that have already been cracked, such as recycle stock, also require a longer time. In general, stocks that require a relatively long time for a given yield are termed *refractory stocks.* Recycle stock, kerosene, naphtha, and gasoline are classed as refractory stocks.

Effect of Time.—In general, the longer the length of time the greater the yield. However, the yield decreases if the time is very long. This is illustrated by the data of Watermann and Perquin[19] (Fig. 94) for paraffin wax. As cracking starts, the primary decomposition reactions take place, but as the time is increased the concentration of reactive unsaturated materials increases and polymerization reactions begin to be important. These combination reactions use some of the material that has been formed by decomposition so that the yield of gasoline decreases. In Fig. 94 the curve of the cracking rate is nearly linear out to 30 per cent. This shows that only one factor, *viz.*, decomposition, is greatly affecting the yield. But at 30 per cent the effect of polymerization becomes marked and at 48 per cent the rate at which polymerization is taking place is more rapid than the rate of decomposition, and the yield becomes less. As the yield

[17] *Oil Gas J.*, June 23, 1927, p. 144.

[18] *J. Inst. Petroleum Tech.*, **14**, 761 (1928).

[19] *J. Inst. Petroleum Tech.*, **11**, 36 (1925).

becomes less, large amounts of tar are produced and coke may be formed. Hence commercial processes are never operated at times that are greater than the time at the maximum point in the time-yield curve.

Temperature affects the general shape of the time-yield curve. The maximum percentage point is lower for high cracking temperatures and also lower for stocks that have already been cracked. Thus at high temperatures the rate of polymerization is relatively faster than at low temperatures. The maximum points and times for several sets of data are shown in Table 44.

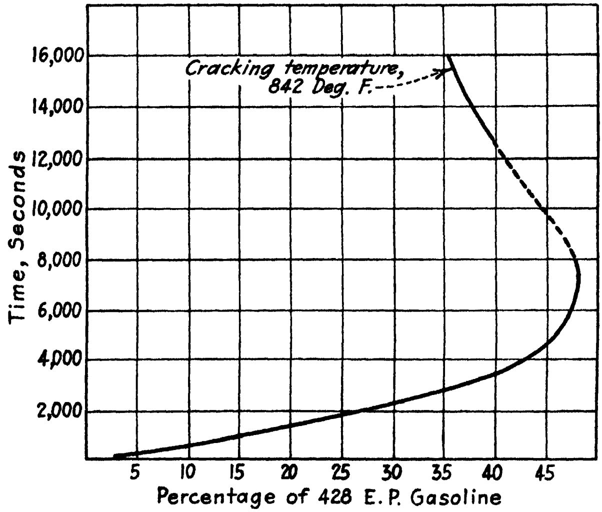

FIG. 94.—Yield of gasoline versus time at 842°F. (*Watermann and Perquin, J. Inst. Petroleum Tech.*)

The use of reaction chambers and soaking drums is to some extent being abandoned, except when coke is desired, because of the decreased yields at a long length of time. However, in some modern plants, the proper use of reaction chambers has resulted in both increased capacity and an increased yield. The maximum points are also the governing factor in determining the recycle ratio that is possible (Example 61, page 330).

A comparison of the rate of cracking at 900°F. is given in Fig. 95. No relation between the gravities of the stocks and the rate of cracking is apparent, but these data were reported by different investigators, each working with different equipments, and hence

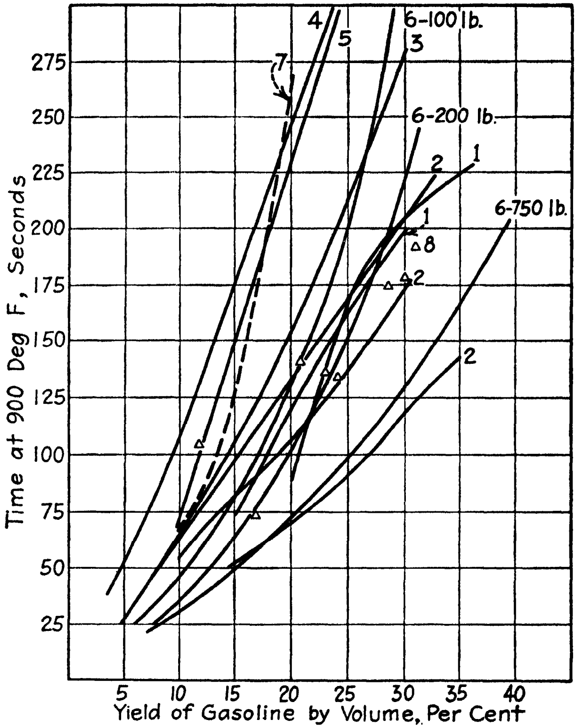

FIG. 95.—Yield of gasoline versus time at 900°F.

TABLE 44.—TIME FOR MAXIMUM YIELD OF GASOLINE

Temp., °F.	Max. yield in a single operation	Time, sec. at max. yield	Phase	Stock	Reference
700	Negative*	20,000+	Liquid	Recycle oil	14
800	40	14,000	Liquid	Gas oil	20
842	48†	7,500	Liquid	Paraffin wax	19
932	31	1,000	Vapor	Gas oil	21
1,076	26	30	Vapor	Gas oil	21
1,184	23	3	Vapor	Gas oil	21

* Yield decreases with time, probably owing to recycle stock.

† Either poor data or the stock, paraffin wax, caused the maximum point to be high.

[20] CROSS, "Handbook of Petroleum, Asphalt, and Natural Gas," *Bull.* 25, p. 287, 1928.

[21] GENIESSE and REUTER, *Ind. Eng. Chem.*, 24, 219 (1932)

perfect agreement should not be expected. The numbers on the curves refer to these experimenters.

Curve No.	Authors	Cracking temp., °F.	Cut point or E.P. of gasoline
1	Sachanen and Tilicheyev[22]	797	392
2	Sachanen and Tilicheyev[23]	752, 797, and 842	392
3	Cross, *Bull.* 25, p. 287[20]	800	437
4	Watermann and Perquin[19]	842	428
5	Leslie and Potthoff[14]	800	437
6	Keith, Ward, and Rubin,[24] average of all data	Range	400
7	Geniesse and Reuter,[21] average of all data	Range	437
Δ	Triangle points—plant data by author	900–915	437

The data of each experimentor were corrected to 900°F. for comparison. The correction for temperature was made either by the use of Fig. 97 or by data which the authors had determined for their particular stock. The data of Watermann and Perquin (curve 4) were for paraffin wax and perhaps this explains the longer time required. The relatively high data of Geniesse and Reuter (curve 7) were obtained by cracking in the vapor-phase. The data of Keith *et al.*, which are the most extensive data on liquid-phase cracking, are plotted as three curves for 100, 200, and 750 lb. pressure. The influence of pressure, as indicated by these curves, may not be significant inasmuch as the time of cracking must be determined by computing the volume of the stock at a high temperature and pressure. Thus the difference in time for the three pressures may be due, in part, to errors in the computation of the volume.

Little data are available concerning the rate of cracking in the vapor-phase. However, Geniesse and Reuter[21] have made an extensive study of the cracking of Lisbon 37.9 A.P.I. gas oil. Their work is too extensive to be treated in detail in this book, but

[22] *Oil Gas J.*, Dec. 19, 1929, p. 48.

[23] *Oil Gas J.*, June 23, 1929, p. 44.

[24] The Cracking of M. C. Virgin Gas Oil . . . Range of Temperature and Pressure, Refinery Division, *Proc. A.P.I.*, 1933.

an approximate summation of their results concerning the time required for cracking is

Per cent yield	Time required at these temperatures, sec.			
	1022°F.	1076°F.	1112°F.	1184°F.
10	8	2	1.2	
15	14	4	2.2	0.8
20	28	7	4.2	1.7

Recycle stocks require more time for a given yield than straight-run stocks. The following tabulation indicates the refractive nature of these stocks. The figures refer to the ratio of the yield from recycle stock to the yield from fresh stock, if the two are cracked under the same conditions of time, temperature, and pressure.

Once cracked	Twice cracked	Current recycling	Thrice cracked	Reference
0.6	0.318	....	0.175	7
0.79	.....	....	.....	7
0.795	0.69	....	.....	8
.....	.....	0.4–0.47	.....	14

Recycle stock, regardless of recycle ratio, will consist almost entirely of material that has been cracked once and twice. Hence the currently recycled stock will crack about half as readily as fresh stock.

Recycle Stock.—In commercial plants the ultimate yield of pressure distillate is not produced in a single cracking operation. Recycle stock and gas oil are charged to the cracking heater and a relatively small percentage yield from this large amount of mixed stock is a large yield when based on the original stock. As an example, assume that two parts of recycle and one part of fresh stock are cracked giving a yield, based on the mixture, of 20 per cent or $0.2 \times 3 = 0.6$ parts of distillate. Based on the one part of fresh stock, which is all that comes into the plant, the yield of pressure distillate is $0.6 \times 100 \div 1 = 60$ per cent.

Recycling is necessary because coke is deposited and a large gas loss occurs if high yields per pass are produced. The tarry material and the reactive materials that are produced during cracking seem to be the source of coke. If the yield is great, the maximum point shown in Fig. 94 is approached, and polymerization takes place with the formation of tar and coke. These products are always produced to some extent but in the recycling operation they are currently eliminated. The common arrangement is to cycle the cracked material that issues from the pipestill, through a fractionating system. In the fractionating system the tarry materials are eliminated into the pressure-still tar; the gas and pressure-still distillate pass overhead; and a heart-cut material consisting of fresh gas oil and recycle is withdrawn as a clean distillate which is continuously pumped into the pipestill. Thus the same quantity of recycle stock and of fresh gas oil or reduced crude oil is charged to the pipestill each hour, and constant quantities of recycle, gas, distillate, and cracked tar issue from the outlet of the still each hour.

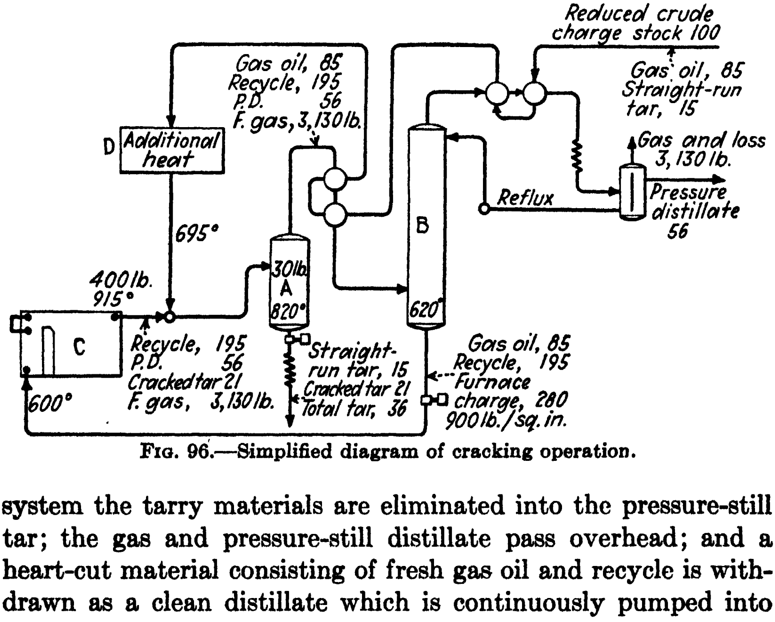

FIG. 96.—Simplified diagram of cracking operation.

The relative quantities handled at various points in a particular type of cracking system are illustrated in Fig. 96. The quantities in the figure are given in barrels and are based on a charge of 100 bbl. of a fuel oil charging-stock. The charging-stock consists of 85 bbl. of gas oil and 15 bbl. of straight-run tar. The charge is heated by exchangers and a heater, if necessary, and is then mixed with the hot cracked material which issues from the pipestill. In evaporator *A*, everything except the straight-run tar and the cracked tar is vaporized. In the fractionator *B*, the pressure distillate and gas are eliminated, and the gas oil and recycle stock are separated and returned to the pipestill.

The *recycle ratio* is defined as the barrels of recycle stock per barrel of fresh gas oil. The recycle ratio for this operation is 195/85 or 2.3, and the *crack-per-pass* is 56/280 or 20 per cent. The recycle ratio is sometimes used as the barrels of recycle divided by the plant charge (100 bbl. in this case). Such a definition of recycle ratio is not logical in the system illustrated because the entire 100 bbl. is not exposed to cracking conditions.

The general effect of increasing the crack- or conversion-per-pass is as follows:

1. Lower gasoline yield.
2. Higher octane-number.
3. An increased tendency to produce coke.
4. The production of more gas.
5. An increase in the volatility of the light-end of the gasoline.

In most respects it is an advantage to use a low crack-per-pass or a high recycle ratio, but the cost of the plant is much greater.

If the percentage of distillate that is produced per pass is high, coke will be deposited in the tubes and the entire operation may be prematurely terminated. Commercial operating-data show that the allowable crack-per-pass for liquid-phase processes is between 18 and 25 per cent and for vapor-phase processes 8 and 13 per cent. The crack-per-pass is definitely related to the maximum points shown in Table 44. The allowable crack-per-pass is about half of the maximum yield of gasoline that can be produced in a single cracking operation. Thus the allowable crack-per-pass for a liquid-phase process operating at 800°F. (Table 44) is about 40/2 or 20 per cent, and for a vapor-phase process operating at 1184°F. about 11 per cent. The reason for the relation between the crack-per-pass and the maximum yield is the fact that the fresh stock is cracked much more severely than the recycle stock. Both stocks are in the cracking zone for the same length of time, but the yield from the recycle stock is only about half as large as the yield from the gas oil. Thus the gas oil is being cracked at a yield that is close to the maximum point, but the recycle stock is being cracked for a yield that is less than the average crack-per-pass (Example 61). At very high cracks-per-pass the gas oil will be cracked for a time greater than that for the maximum yield, and coke will be formed.

Example 60. Material Balance and Crack-per-pass.—The stock and yields used in Example 59 will be used in the design of a cracking plant. The plant is to operate at a cracking temperature of 915°F. and at 400 lb. per square inch. At these conditions a substantially pure liquid-phase is present. Assume that 80 per cent of 27.5 A.P.I. gas oil can be distilled from the fuel oil. Make material balances to show the quantities of the stocks at all points. What recycle ratio and crack-per-pass should be used? Basis: 100 gal. of fuel oil charging-stock.

Ultimate yields (Example 59):

	Per Cent
Pressure distillate (440 E.P.)	54
Gas and loss	6.1
Fuel oil	39.9

MATERIAL BALANCE OF FUEL OIL CHARGING-STOCK

Material	Per cent or gal.	A.P.I.	Lb. per gal.	Total lb.
Fuel oil, charging-stock	100	24	7.58	758
Gas oil	80	27.5	7.41	593
St.-run tar	20	....	....	165

Lb. of st.-run tar 758 − 593 = 165

Lb. per gal. of tar $^{165}/_{20}$ = 8.25

The A.P.I. corresponding to 8.25 lb. per gal. is 11.3.

MATERIAL BALANCE OF PLANT TAR

Plant tar	Per cent or gal.	A.P.I.	Lb. per gal.	Total lb.
Total tar	39.9	8.0	8.45	337
St.-run tar	20	11.3	8.25	165
Cracked tar	19.9	....	....	172

$$\text{Lb. per gal. of cracked tar } \frac{172}{19.9} = 8.64$$

A.P.I. of cracked tar is about 4.8.

Recycle ratio:

When cracking at 915°F. the allowable crack-per-pass is about 34 divided by 2 (Table 44) or 17 per cent. In general, a little higher value than this is possible and hence 19 per cent will be used as the crack-per-pass. The total 54 gal. of distillate is 19 per cent of the charge to the furnace.

Furnace charge,

$$\frac{54}{0.19} = 284 \text{ gal.}$$

MATERIAL BALANCE OF FURNACE CHARGE

Material	Per cent or gal.	A.P.I.	Lb. per gal.	Total lb.
Gas oil	80	27.5	7.41	593
Recycle	204	15.0*	8.04	1,640
Furnace charge	284	....	....	2,233

* The A.P.I. of the recycle stock will be a little over half as much as the A.P.I. of the gas oil or about 15 A.P.I.

Lb. per gal. of furnace charge,

$$\frac{2{,}233}{284} = 7.86$$

A.P.I. is 18.4.

Recycle ratio,

$$204/80 = 2.55 \text{ parts recycle per part gas oil}$$

MATERIAL LEAVING PIPESTILL

Material	Per cent or gal.	A.P.I.	Lb. per gal.	Total lb.
Pressure distillate*	54	55	6.32	342
Recycle	204	15	8.04	1,640
Cracked tar	19.9	4.8	8.45	172
Fixed gas (by difference)	.....	....	....	79
Furnace charge	284.0	18.4	7.86	2,233

* Assume A.P.I. of distillate is 55.

Effect of Temperature.—The temperature at which cracking starts to take place is between 680 and 700°F. Leslie and Potthoff,[14] Geniesse and Reuter,[21] and Keith, Ward, and Rubin[24] have ventured to give definite statements regarding the rate at which the rate of cracking changes with temperature. Leslie finds that the rate of cracking doubles for each 22°F. rise in temperature when the cracking is at temperatures of 700 to 800°F. Geniesse finds that the rate doubles for an increase in temperature of 25 to 38° for cracking in the vapor-phase at temperatures of

842 to 1112°F. Keith reports a range of points for different temperatures (Fig. 97).

Other experimenters have presented data which can be analyzed for the effect of temperature and these data are compared in Fig. 97. Although the data are not consistent, it is possible to get an idea of the qualitative effect of temperature on the rate of cracking. One fact is obvious: the rise in cracking temperature that is required to double the yield increases as the cracking temperature is increased. Thus at 750°F. an increase of 22° doubles the yield, but at 1100°F. an increase of about 60° is necessary. The liquid-phase or mixed-phase points were obtained from the experimental data of Leslie,[14] Keith,[24] and Sachanen and Tilicheyev,[25] and the vapor-phase points are from the data of Geniesse,[21] and Osterstrom and Wagner.[26] It would seem that the amount of cracking that is conducted and the properties of the cracking-stock should affect the rate but no relationship of this kind could be determined from the data used in constructing Fig. 97. Several sets of Sachanen and Tilicheyev's data indicate

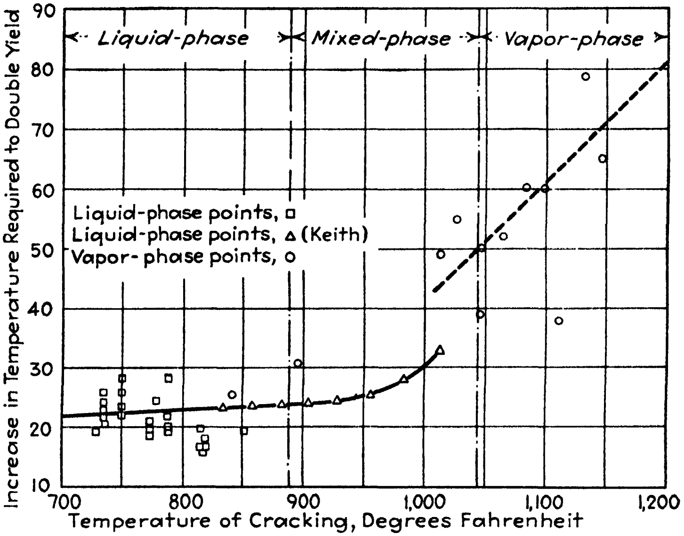

FIG. 97.—Number of degrees Fahrenheit required to double the yield of gasoline.

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[25] "The Chemistry and Technology of Cracking," Chemical Catalog Company, Inc., New York, 1932.

[26] *Ref. Nat. Gaso. Mfr.*, December, 1929, p. 59.

that the temperature rise for doubling the yield increases as the yield increases, but another set shows the opposite effect.

The data given in Fig. 97 can be conveniently used in the following equations:

Cracking at a constant length of time:

$$C_2 = C_0 2^{\left(\frac{T_2 - T_0}{x}\right)} \tag{61}$$

And for a constant yield,

$$V_2 = V_0 2^{\left(\frac{T_0 - T_2}{x}\right)} \quad \text{or} \quad = \frac{V_0}{2^{\left(\frac{T_2 - T_0}{x}\right)}} \tag{62}$$

where C_2 = yield for a given time at temperature T_2.
C_0 = yield for a given time at temperature T_0.
V_2 = time for a given yield at temperature T_2.
V_0 = time for a given yield at temperature T_0.
x = number of degrees required to double the yield (Fig. 97).

These equations apply only to the part of the time-yield curve (Fig. 95) that is substantially straight. If the maximum-yield point is approached, then the equations are of no significance. Doubtless this fact explains some of the disagreement of the points shown in Fig. 97. Equations (61) and (62) can be used to compute the time (or yield) at a new temperature if the time and yield are known at one temperature. Figure 95 provides data concerning the yield at 900°F.

Example 61. Cracking Yield and Time.—The cracking operation studied in Examples 59 and 60 will be continued. Cracking is to occur at about 915°F. How much time will be required to give the desired crack-per-pass of 19 per cent?

Basis: 284 bbl. of furnace charge.

Figure 95 shows that a time of approximately 125 sec. is required at 900°F. to give a yield of 19 per cent from an uncracked gas oil stock. But in this plant a mixture of gas oil and recycle will be cracked together, to give a yield of 19 per cent; 80 bbl. of gas oil and 204 bbl. of recycle will be cracked. The yield from the recycle in a given length of time will be half the yield from the gas oil.

Let x be the yield from the gas oil.

$$284(0.19) = 80x + 204\frac{x}{2}$$

$$x = 29.7 \text{ per cent}$$

Thus the yield from gas oil is 29.7 per cent, and from the recycle 14.85 per cent.

Time required to get 29.7 per cent from gas oil is about 200 sec. (Fig. 95).

Time at 915°: To double yield at 907.5°F. requires an increase in temperature of 24°F. (Fig. 97).

For a constant yield [see Eq. (62)],

$$V_2 = \frac{200}{2^{\left(\frac{915-900}{24}\right)}} = \frac{200}{1.542} = 129 \text{ sec. at } 915°\text{F.}$$

By a similar computation it is found that the gas oil will be cracked at the maximum-yield point (34 per cent) if the crack-per-pass is about 26 per cent.

The aforementioned method of computing the time (or yield) at different temperatures is satisfactory if the temperature is constant; but if the temperature changes, the method is not suitable. An equation of the rate of cracking, if the cracking temperature is not constant, can be derived as follows:

$$C = C_0 2^{\left(\frac{T-T_0}{x}\right)}$$

where C = yield during heating for time t, per cent.
C_0 = yield, per cent per sec. at T_0.
T = final temperature, °F.
T_0 = initial temperature, °F.
x = a constant, average number of degrees to double yield (Fig. 97).

If the heating takes place at a uniform rate,

$$T = T_0 + kt$$

where k = rate of heating, °F. per sec.
t = total time, sec.

$$C = \int_0^t dC = C_0 \int_0^t 2^{\left(\frac{kt+T_0-T_0}{x}\right)} dt = C_0 \int_0^t 2^{\left(\frac{kt}{x}\right)} dt$$

$$C = C_0 \left[\frac{1}{\ln 2} \cdot \frac{x}{k} \cdot 2^{\left(\frac{kt}{x}\right)} - \frac{1}{\ln 2} \cdot \frac{x}{k}\right]_0^t$$

$$C = 1.44 \frac{C_0 x}{k}\left(2^{\left(\frac{kt}{x}\right)} - 1\right) = 1.44 \frac{C_0 x}{k}\left(2^{\left(\frac{T-T_0}{x}\right)} - 1\right) \qquad (63)$$

Although cracking is said to occur at temperatures exceeding 680°F., there are other less vital changes that take place when oils are heated to lower temperatures. These changes are most noticeable with lubricating oils. Many untreated lubricating oil stocks are discolored if they are heated even to 300°F. in the presence of air. If they are heated to higher temperatures for a long time, the viscosity and the gravity are also lowered. In the author's laboratory a paraffin-base lubricating oil was redistilled three times for the purpose of separating the oil into well-fractionated products of short boiling-range. During these distillations the temperature in the main body of liquid never exceeded 620°F. and the pressure was kept at less than 10 mm. The oil was heated for a total time of 22 hr. at 300 to 620°F. The viscosity and gravity dropped as follows:

30°F. fractions boiling at these average atmospheric boiling-points	Viscosity at 100°F.		Sp. gr.	
	Before	After	Before	After
700	57	56	0.8484	0.8471
800	104	99	0.8636	0.8616
900	245	229	0.8742	0.8729
1000	415	350	0.8825	0.8794

Effect of Pressure.—The technical literature offers many conclusions as to the effect of pressure on the cracking reaction but most of these conclusions are based on experiments in which other variables, such as temperature or time, were not held constant. Such data are confusing because we cannot tell whether pressure or one of these other factors was the cause of the changes which occurred.

The most obvious effect of pressure is the fact that a high pressure suppresses vaporization and tends to produce a liquid-phase, whereas a low pressure allows a vapor-phase to be produced. Obviously, a gas oil which vaporizes completely at 880°F. (760 mm.) cannot be cracked at 880°F. at atmospheric pressure because it will be vaporized almost completely and will pass into the condenser without allowing time for cracking to occur. The products from such an operation are tar, gas oil, and a small amount of kerosene or gasoline. In order to distill only gasoline, the pressure must be sufficiently high to keep all materials, other than gasoline and gas, in the liquid-phase. These materials remain in the system until they are cracked into gasoline, recycle stock, or tar.

In a similar manner lubricating oils or heavy distillates can be the major products of decomposition if the pressure on the cracking system is less than atmospheric.[27] As indicated previously, the cracking reaction takes place as a series of decompositions in which the first product is lubricating oil. At high pressures the lubricating oil remains in the system and in turn is decomposed into gas oil, kerosene, and finally gasoline and gas. In other words, the decomposition continues until the decomposition products can vaporize at the temperature and pressure that are used in the cracking system. If the pressure is reduced to 30 to 100 mm., the lubricating oils that are produced during the decomposition reactions are vaporized and are automatically withdrawn from the system without decomposing into gasoline. The fact that decomposition is much more severe when gasoline is produced than when the action is stopped at intermediate stages of decomposition is illustrated by the following tabulation of yields. The tabulation shows the yields, when a 10 A.P.I. Mid-Continent straight-run tar is decomposed to produce coke by using different pressures in the equipment. In each run the products were gas, coke, and the major liquid product shown below.

Run No.	Total liquid product	Per cent total distillate
. . .	Gasoline, computed from Eq. (59)	53
1	Kerosene	63
2	Gas oil (35 A.P.I.)	65
3	Lubricating oil (600 vis. at 100°)	69
4	Heavy lubricating oil (93 vis. at 210°)	72

Thus, if a large molecule is decomposed into relatively small molecules such as those in gasoline, the yield is low; whereas if the decomposition is carried only to the production of molecules such as those found in lubricating oil, the yields are considerably larger. This process differs from cracking in that a complete decomposition to gasoline is not carried out, and the pressure is subatmospheric rather than above atmospheric pressure.

In addition to the aforementioned purely mechanical effects of pressure, the properties of gasolines produced at a high pressure are somewhat different from those produced at a low pressure.

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[27] NELSON and FANCHER, U.S. Pat. 1,990,664.

Sachanen and Tilicheyev[28] report that the amount of unsaturated hydrocarbons found in gasoline produced at moderate cracking conditions decreases by about half as the pressure is increased from 10 to 40 atm. But at the same time the percentage of naphthene hydrocarbons increases about 12 to 16 per cent. The increase in the percentage of naphthene hydrocarbons is even greater in the cracked kerosene fraction. They also find that the yield of gasoline is slightly less at high pressures. This may be explained by the decomposition of part of the gasoline into fixed gas by the prolonged time of cracking.[29] However, Keith, Ward, and Rubin,[24] and LeRoi and Ferguson[10] report just the opposite effect of pressure. Keith finds that the gas loss is three times as much at 100 lb. as at 1,000 lb. per square inch. Commercial practice also indicates that the gas loss is less at high pressures.

Most experimenters[10,24] find that the octane-number decreases as the pressure is increased, if the same amount of cracking is practiced.

The use of pressure in commercial processes is necessary from a physical standpoint. Mixtures of oil and vapor at cracking conditions tend to deposit coke. Apparently the liquid segregates and collects on the walls of the tubes and is cracked for a longer length of time than the main body of stock.

Liquid-phase and Vapor-phase Operation.—In general, three phase conditions are recognized in commercial processes. If the pressure is relatively low, so that a pure vapor-phase can be produced at the cracking temperature, the process may be classed as vapor-phase. Vapor-phase processes are not successful unless a vapor that is free from liquid is produced, because coke will be deposited in the tubes. At higher pressures and lower cracking temperatures a mixed-phase results and special precautions must be taken to avoid the formation of coke. Most modern commercial processes are classed as mixed-phase processes.

The ideal condition, from the standpoint of heating, would be either a pure liquid- or a pure vapor-phase. If a mixed-phase is

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[28] *Oil Gas J.*, Nov. 28, 1929, p. 46.

[29] The bomb equipment which Sachanen and Tilicheyev used promoted the cracking of gasoline by allowing part of it to condense and drip back into the cracking vessel. In some tests they kept the products of cracking in the cracking still until the test was completed.

heated, it is necessary to avoid segregation of the liquid from the vapor. This may be accomplished in two ways: (1) by maintaining such a high velocity that the liquid is scoured from the heating-walls or (2) by maintaining a pressure that is high enough to cause the density of the vapor to be about as large as the density of the liquid. Most of the hydrocarbons found in recycle stock and pressure distillate have critical pressures that are less than 400 lb. per square inch and hence these materials occupy a relatively small volume even though they are in the form of vapor. In other words, the density of the vapor that is produced at a pressure of 400 lb. is nearly as great as the density of the liquid, and hence little segregation occurs.

Volume Increase during Cracking.—Although both high- and low-molecular-weight hydrocarbons are produced during cracking, the major reaction is decomposition and the over-all result of the cracking reaction is the production of a less dense liquid. This decrease in density is of such a magnitude that it cannot be neglected. In simple distillation processes no chemical changes occur and the volume of material that enters the system is the same, except for losses, as the volume that leaves the system. In a cracking plant the volume of the total products, if measured as liquids, is greater than the volume that enters the system. Difficulty because of the increase in volume may be avoided by using a weight basis for the calculations but in some ways it is more convenient to retain the common liquid-volume basis and correct for the increase in volume.

Example 62. Increase in Volume during Cracking.—Example 60 provides data by which the volume increase can be computed. In this example the weight of fixed gas per 100 gal. of charging-stock was 79 lb. The density of cracked gas, if liquefied and measured at 60°F., would be approximately 3 lb. per gallon.

$$\text{The volume of fixed gas (liquid)} = {}^{79}\!/_{3} = 26.3 \text{ gal.}$$

The total liquid yield measured at 60° is

	Gal.
Pressure distillate	54
Fuel oil (cracked)	39.9
Fixed gas	26.3
	120.2

Thus the charge increased by 20.2 per cent in volume during cracking.

Although the gas cannot be liquefied at 60°F., nevertheless it may be dissolved in the other parts of the furnace stock at high pressures, and hence the volume as computed above becomes valuable for computing the volume of the cracking-stock while it is in the furnace tubes.

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PART IV

PLANT PROCESSING

CHAPTER XVIII

DISTILLATION PROCESSES

All petroleum distillation processes are fundamentally the same. The process engineer can make no headway in initiating new processes or in truly understanding the flow diagrams of processes until this fact is clearly understood. In the main, all distillation processes require the following essential units of equipment: (1) pipestills or other heaters, (2) fractionating towers, (3) steam stripping columns, (4) heat exchangers, (5) condensers and coolers, (6) pumps and connecting lines, and (7) storage and accumulator tanks. However, in adapting these units of equipment to the processing of a particular stock there are many factors that must be considered. Among the most important of these are

1. The boiling-range of the stock.
2. The stability of the stock with respect to heat.
3. The specifications of the products to be produced.

Boiling-range of Stock.—Some stocks boil at such a high temperature that they cannot be vaporized at atmospheric pressure without decomposing them, and other stocks must be kept under pressure or they will vaporize at room temperature. Raw natural gasoline contains relatively large amounts of gaseous hydrocarbons and is an example of a stock that must be distilled under pressure. These hydrocarbons must be removed if a stable low-vapor-pressure natural gasoline, which will perform suitably as a motor fuel, is to be produced. The gaseous hydrocarbons are most effectively removed by fractionation but the gaseous hydrocarbons are the overhead product from the column and they cannot be kept in the liquid state unless pressure is applied. Hence natural-gasoline stabilizers are operated at 125 to 300 lb. per square inch pressure and the reflux material consists of the volatile hydrocarbons ethane, propane, butane, etc. Of course, the top of the column could be kept at a low temperature by refrigeration but such methods have not proved practical. The temperature in.the reflux condensers is governed by the temperature of the cooling water. The pressure that is used is dependent on the vapor-pressure of the reflux material at the temperature that exists in the condenser.

With high-boiling stocks the opposite difficulty arises. Vigorous decomposition starts to take place at temperatures exceeding about 710°F. and for this reason many stocks such as reduced or topped crude oil, tars, and heavy crude oils cannot be distilled at atmospheric pressure. These stocks have such high boiling-ranges that they must be distilled in a vacuum or by the use of large amounts of steam. Some cannot be distilled unless both steam and vacuum are employed.

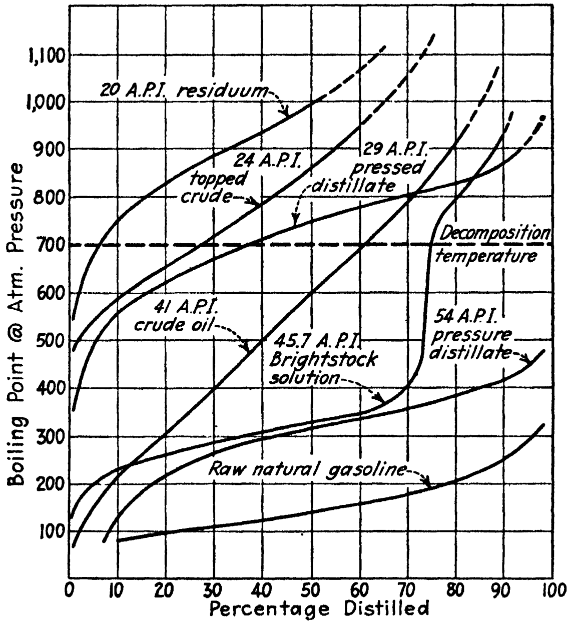

FIG. 98.—Distillation ranges of typical Mid-Continent stocks.

Between these two extremes are stocks such as crude oil, pressure distillate, pressed distillate, brightstock solution, and special naphtha stocks which can be distilled at atmospheric pressure but which may require the use of some steam. Figure 98 indicates the relative boiling-ranges of typical Mid-Continent stocks. In distilling crude oil for gasoline, kerosene, and a part of the gas oil, a pipestill-outlet temperature of about 740°F. may be required. Thus a small amount of steam is normally required to keep the temperature down to 710°F. This results in a vaporizer temperature in the tower of about 660°F. For other stocks, commonly used vaporizer and outlet temperatures are given in Table 45.

TABLE 45.—VAPORIZER TEMPERATURES

Stock	Products	Temperature		Pressure, lb. per sq. in. or mm.	Steam
		Vaporiser	Heater outlet		
1. Natural gasoline........	Gas	210	230	120–200	No
2. Pressure distillate.......	Gasoline	275	325	Atmospheric	Yes
3. Crude oil...............	Light oils	660	710	Atmospheric	Some
4. Pressed distillate........	Neutral oils	670	710	Atmospheric	Yes
5. Brightstock solution.....	Naphtha and neutral	670	710	Atmospheric	Yes
6. Reduced crude..........	Lub. oils	690	730	30–80 mm.	Yes
7. Fuel oil or tar..........	Asphalt residue	730	770	30–80 mm.	Yes
8. Fuel oil or tar..........	Distilled cracking-stock	775	850	Atmospheric	Yes

Thus modifications of the simple fractionating system are necessary for all except a few stocks. Some stocks require a pressure so that a low-boiling reflux material can be condensed, and others require a vacuum and steam.

Sensitive Stocks.—Although the boiling-range of a stock is an important factor, the sensitiveness of the stock to high temperatures must also be considered. All stocks start to decompose at about 680°F., yielding lower boiling products, but even lower temperatures may cause discoloration. In distilling crude oil a slight discoloration of the products is not important because most of the products receive chemical treatment before they are sold. Likewise, discoloration is not important in the distillation of a reduced crude for the production of a gas oil cracking-stock or for the production of asphalt. However, in distilling treated pressure distillate, pressed distillate, or brightstock solution, a discoloration during distillation cannot be allowed because the products are usually sold without further treatment. If treatment follows these distillations, then the cost of the treatment will be increased by the discoloration.

High temperatures also result in a loss of heavy lubricating oil stock. The yield of lubricating oils is often decreased by 10 to 15 per cent by the use of too high temperatures. A mild decomposition takes place in which light lubricating oil and gas oil are produced from the heavy stocks.

Treated pressure distillate is particularly sensitive to high temperatures. Redistillation should not be conducted at temperatures exceeding 375°F. and many refiners find that a maximum temperature of 275°F. is economical because of the reduction in treating costs.

In the manufacture of asphalt, most refiners limit the temperature to 770°F. Nevertheless, the temperature that may be used without ruining the ductility of the product is greatly dependent upon the characteristics of the stock and upon the manner of heating. One refiner has successfully used a temperature of 835°F. at the pipestill outlet but others have found that 770°F. was too high.

The engineer must bear in mind that some stocks are very different from others. The most satisfactory operating temperature can be determined only by experiments with the particular stock. A factor that cannot be neglected when considering temperature is the time that the oil is held at the high temperature. As mentioned above, some asphalt stocks may be heated to 835°F. without damage if the time at the elevated temperature is short. If the stock is held at this temperature for more than a few minutes, extensive cracking will occur and the operation will become a cracking process. Thus the temperature that can be attained without serious decomposition is dependent to some extent upon the time. Although a lubricating oil stock can be heated to 710 or even 740°F. in a low-absorption-rate pipestill heater, this same temperature, if maintained in a shellstill will cause serious losses in yield and a discoloration, the removal of which may necessitate a costly chemical treatment.

Flow Diagrams and Operating Conditions.—The remaining pages of the chapter are devoted to the common processing systems. The systems that are presented are not necessarily the best for all conditions. In fact, in some cases they are presented merely because they are novel or because they illustrate principles which would otherwise be neglected. The best performance cannot be obtained from a unit unless it is "tailor-made" for the particular stock and for the particular market and plant environment in which it must function.

The operating conditions are likewise of a general nature, although in most cases they are actual conditions which have been recorded in plant operation. The operating conditions will be different for each stock that is encountered. The evaluation curves that are shown with each process are discussed in Chap. VII.

A survey of the processing methods that are used in refineries appears to show that there are as many methods as there are refineries. Nevertheless, upon close inspection these many methods are found to be essentially the same and the major differences are in the arrangement and shape of the equipments rather than in the manner of operation. In most refineries the processing methods are the result of years of development and, although the processing methods may be modern, the equipment that is used may appear to be obsolete. This is often the result of the use of existing shellstills, towers, chambers, coolers, etc., from antiquated equipment. They appear obsolete but if they are properly utilized they may perform as satisfactorily as modern new equipment.

Topping or Reducing Crude Oil.—In many ways the initial break-up of crude oil into raw products is the most simple distillation process. Certainly it is the most widely known operation. In the past, shellstills, with or without fractionating towers, were commonly used. Today the shellstill is never installed but old shellstills are often utilized in conjunction with pipestills. Figure 99 shows a typical shellstill battery with a fractionating system. The operation is continuous. The oil, after passing through the exchangers under pump pressure, flows progressively through the shellstills by gravity or by means of steam jets. The system is needlessly complicated in the light of modern knowledge and it is included merely as an indication of the manner in which shellstills may be used.

A modern topping unit is shown in Fig. 100 and the evaluation curves of a typical Pennsylvanian crude oil are shown in Fig. 101. The oil is pumped continuously through the heat-exchange system at a pump pressure of 125 to 200 lb. per square inch, through the tubestill, and into the vaporizer section of the multiple-draw fractionating tower. At this point the temperature must be sufficiently high to cause vaporization of all of the products that are collected at points above the vaporizer and the temperature may be a little higher, so that about 20 per cent of the bottoms stock is also vaporized. The purpose of the additional vaporization is to provide better fractionation on the plates that are situated just above the vaporizer. Without excess vaporization, very little reflux will exist at these plates and no reflux will flow from the plate above the vaporizer into the vaporizer section. Reflux is circulated through the top of the column. The hot reflux material is drawn from the tower, cooled by a heat exchanger and a water cooler, and returned to the tower. It serves to cool and condense the vapors that arise from the vaporizer. The recirculating type of reflux shown in Fig. 100 is not the most common method of removing reflux heat but it is an excellent method for certain conditions. Various means of removing reflux heat are described on page 440. The plates above the vaporizer or feed-plate act as rectifying plates but the plates below the feed are steam stripping plates. Steam is admitted below or on the bottom tray, and the low-boiling

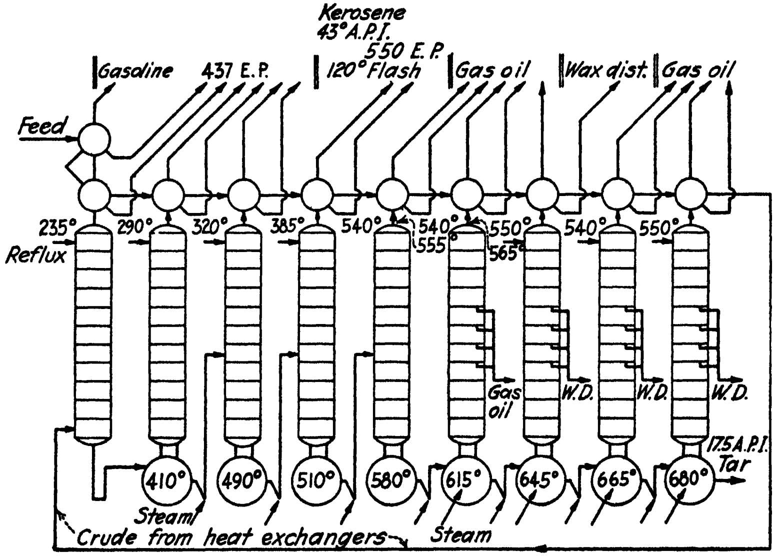

FIG. 99.—A continuous shellstill battery.

materials in the vaporizer residue are removed so that a high flash-point bottom-product is produced. The steam ascends the

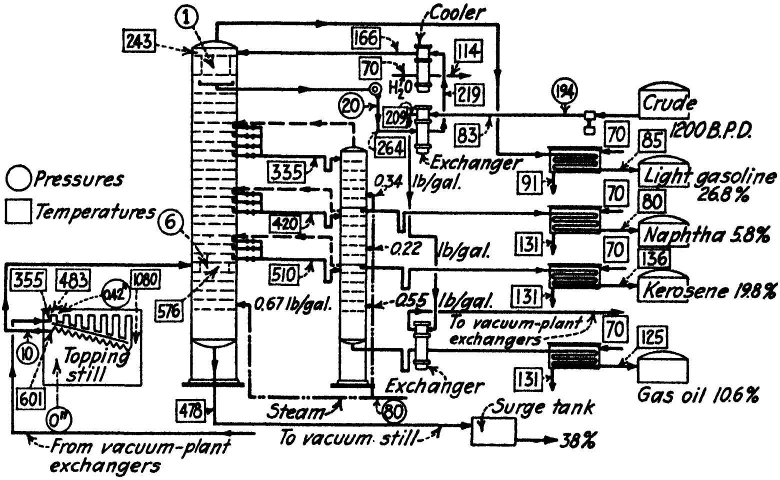

FIG. 100.—Continuous pipestill topping plant. (*A. J. Smith Engineering Company.*)

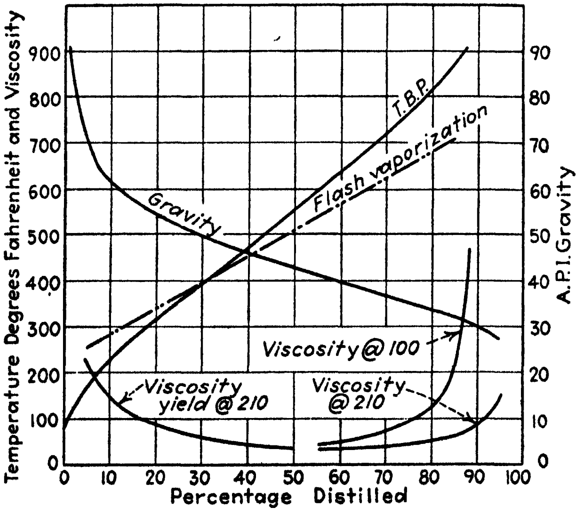

FIG. 101.—Typical paraffin-base crude oil. (Not the crude oil processed in Fig. 100.)

tower, and at the vaporizer it is effective in lowering the vaporizer temperature.

The system as shown in Fig. 100 is not limited to the production of five overhead products. As many as eight products have been withdrawn from a single tower. Furthermore, by the use of a large amount of steam, such heavy stocks as wax distillate and even cylinder stock may be vaporized from crude oil. However, the vaporizer temperature must be high (800 to 870°F.)[1] and such temperatures result in discoloration and losses by decomposition. The difficulties with dewaxing are also troublesome. Plants operating at atmospheric pressure for the manufacture of distilled cylinder stocks have never been entirely successful but many refiners distill wax distillate at atmospheric pressure.

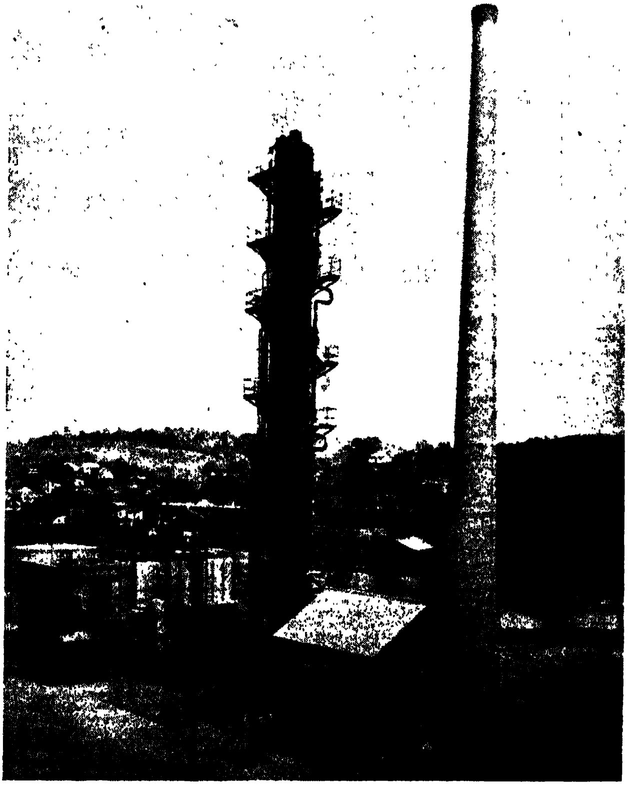

FIG. 102.—Modern topping plant. (*Arthur G. McKee and Company.*)

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[1] One plant operated at 870°F. distilling a 160 viscosity at 210 cylinder stock but the color was so poor and the loss of heavy stock was so great that the operation was discontinued.

Heat-exchange.—The number of heat exchangers that may be wisely utilized depends upon the quantities and temperatures of the several products. In general, a heat exchanger should pay for itself within a period of two years. In complete plants which conduct vacuum and cracking operations as well as the topping of crude oil, the crude oil may be advantageously heated by products from these other units because they are at a relatively high temperature. In conjunction with a vacuum plant, the crude oil may be pumped through the condenser exchangers in the topping plant, through the reflux and partial condensers of the vacuum plant, and finally back to the topping-plant pipestill. In this manner and in more elaborate heat exchanger systems, such as those which involve bottoms exchangers or exchangers in cracking plants, the temperature of the crude oil may be raised even to 500°F. Thus for certain low-boiling crude oils the topping pipestill may be eliminated entirely. In the same manner the enormous quantity of heat available in a cracking unit and at a high temperature level as well may be used to advantage. Although such an extensive use of heat-exchange appears to be advantageous, such systems are not without disadvantages. The dependency of several units upon one another is a serious complication. Thus if one unit must be shut down, the other unit or units must be shut down or operated in a crippled condition. Sometimes these plants are constructed with extra heating equipment so that any one of the plants can be operated independently, but these extra heaters cost almost as much as if they had been originally provided instead of exchangers. Exchangers may also be a source of great expense unless they are wisely chosen and the stocks are clean and noncorrosive.

As an example of the possibilities of heat-exchange, Fig. 103 shows an installation[2] in which gasoline, gas oil, and fuel oil are withdrawn from the system through a total of 10 heat exchangers. In addition, vapor is withdrawn from the tower at five points and allowed to flow back into the tower through five of these exchangers. Thus the reflux heat which is normally withdrawn at the relatively low temperature level that exists at the top of the tower is withdrawn at higher temperatures. In this system the crude oil is heated to about 450°F. before entering the pipestill. Although such a system is economical from the standpoint

[2] No Condensers Used in Topping Unit, *Oil Gas J.*, Dec. 18, 1930, p. 30.

of thermal efficiency, its real merit depends upon the cost of installing and repairing the complicated exchange system. Its value is doubtful when the low cost of heat in the refinery is considered. If a refinery management is certain that the system will be used for many years and that a long period of depreciation is certain, then a highly efficient system, such as the preceding, may be justified.

A unique part of the system is the use of only six bubble trays. The trays are separated by solid diagonal baffles. Reflux vapor is withdrawn below each of these baffles and passes once through its exchanger and back into the tower above the baffle plate. This amounts to a combination bubble-tray and partial-condenser system.

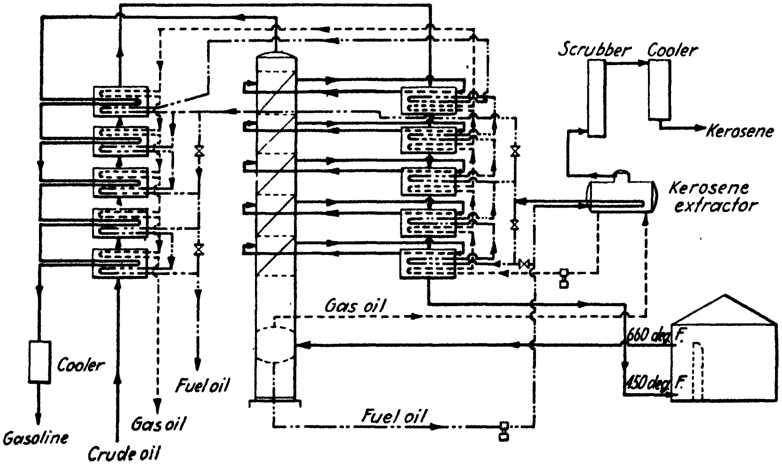

Fig. 103.—Topping system showing an extensive use of heat-exchange. (*Oil Gas J.*)

Pressure-still Distillate.—The raw distillate from cracking plants is a foul-smelling, dark-colored material that must be treated and redistilled before it is a satisfactory motor fuel. After acid treatment, the distillate is still a bright-yellow-colored material. Although part of the coloring material is high boiling and may be separated by distillation, some of it decomposes if a high temperature is used and causes discoloration of the distillate. Gumlike materials are also produced at high temperatures. These difficulties are apparently caused by the decomposition and hydrolysis of alkyl sulfates which are produced during acid treatment. The exact temperature below which discoloration and the formation of gum occur depends upon the chemical nature of the distillate, the manner in which the chemical treatment was conducted, and the way in which heat is applied. In the face of these many factors it is not surprising to find that little data are available regarding the exact temperature to be used in redistillation. This problem has been met by each refiner by conducting laboratory studies of the cracked distillate. Trusty[3] shows the effect of steam on the color of the finished distillates but unfortunately the maximum temperatures are not included in the paper. With this particular distillate, the effect of increasing the steam,[4] other conditions and operations being the same, was as follows:

Per Cent Steam in Overhead	Color
0	18
5	22
20	25

Refiners usually limit the temperature for redistillation to 325°F. although some plants have been operated at 375°F. The tendency has been to decrease the temperature because the treating operation is much simplified if the temperature is low. Several companies have installed vacuum systems[5] in which the temperature is limited to 275°F. The vacuum redistillation systems are usually of the two-stage type, in which part of the distillate is distilled at atmospheric pressure and the heavier part is vaporized in a second fractionator which operates at a reduced pressure. Laboratory tests indicate that discoloration may occur at even 150°F.

Many small refiners continue to redistill pressure distillate in shellstills but all newly erected plants are of the continuous pipestill and fractionator type of design, as shown in Fig. 104. The method of removing reflux heat, as shown in Fig. 104, is the most satisfactory and generally used method.

Debutanizers.—Pressure-still distillate is usually condensed and collected under pressure and part of the gas from the cracking

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[3] Acid Treatment of Cracked Distillates . . . , *Ref. Nat. Gaso. Mfr.*, August, 1932, p. 455.

[4] The sulfur content of the distillate when more steam was used was lower.

[5] NOLL, H. D., *Oil Gas J.*, Mar. 31, 1932, p. 66.

unit is absorbed by the pressure distillate. The pressure in the gas separator (15 lb. or higher) causes the gas to dissolve to such an extent that the pressure distillate usually has a vapor-pressure of 10 to 25 lb. per square inch. Burket[6] presents the analyses of pressure distillates that were collected at different pressures as shown in Table 46.

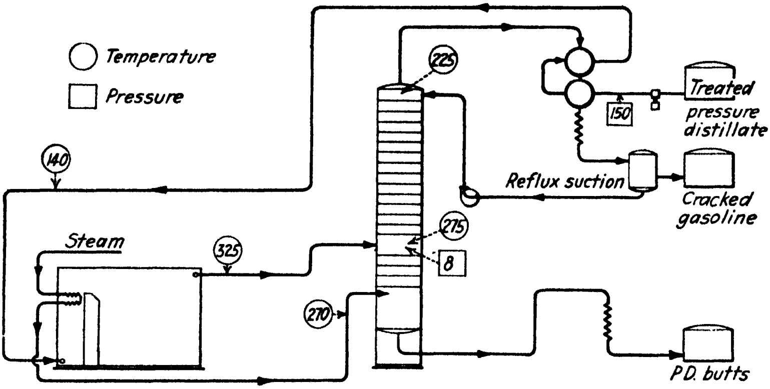

FIG. 104.—Pipestill pressure distillate rerun unit.

TABLE 46.—ANALYSES OF PRESSURE DISTILLATES*

	Volume percentage analyses of pressure distillates collected at pressures of, lb. per sq. in.			
	14.7	30	40	165
A.P.I.	52.6	58.2	55.3	61.3
Methane	.....	0.02	0.06	0.47
Ethane	0.33	0.24	0.69	2.22
Propane	3.4	1.63	3.22	5.67
Butanes	8.43	9.39	9.33	10.31
Pentanes	10.93	13.11	12.05	11.26
Hexanes and heavier	76.91	75.61	74.65	70.07

* The distillates were not from the same charging-stock.

All of these distillates contain appreciable quantities of propane and butane and will exert vapor-pressures that make them undesirable for blending purposes. In order to reduce the vapor-

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[6] P.D. Stabilization . . . , *Ref. Nat. Gaso. Mfr.*, March, 1931, p. 75.

pressure, many refiners are installing debutanizers or pressure-distillate stabilizers.

If low-vapor-pressure natural gasoline is used for blending or if an excess of naphtha blending stock is available, then the pressure distillate may not need to be stabilized. The pressure at which the distillate is collected from the cracking plant, as indicated above, is of great importance. Nevertheless, it is hardly practical to collect the distillate at pressures of less than 20 lb. per square inch because the gas cannot be easily handled at lower pressures. The fractionation of pressure distillate is conducted in a manner similar in all respects to the stabilization of raw natural gasoline (Fig. 107). However, pressure distillate contains less propane and butane than raw natural gasoline and hence the feed must be heated to a higher temperature. The raw pressure distillate is usually stabilized before acid treatment and the lowest boiling part of the distillate is sometimes collected from the stabilizer and incorporated into gasoline, without undergoing acid treatment.

Reboilers.—In fractionating two component feed-stocks, a part or sometimes all of the heat input is supplied at the bottom of the fractionator. The theories discussed in Chap. XV were based upon such a process system. In such systems the part of the column below the feed, *viz.*, the exhausting section, effects some separation. The lower part of most petroleum oil columns does not function as a fractionator but as a simple steam stripping section. At frequent intervals flow diagrams are proposed in which heat is supplied at the bottom of petroleum oil towers. Oil is circulated from the bottom of the tower, through a few tubes in the pipestill or other heating equipment; and back into one of the lower plates of the tower. Reboilers do increase the efficiency of fractionation but a satisfactory degree of separation can usually be obtained more cheaply by the use of a stripping section. The use of two coils in a pipestill is a difficult problem. The exact heat input in each coil can hardly be determined except by experiments with the pipestill during operation. This has often caused reboiler installations to perform poorly with the result that reboiling has never been widely used.

Figure 105 indicates a reboiler arrangement as used in redistilling pressure distillate and Fig. 106 shows the analyses of the feed and distillate. Reboilers heated by steam are used in stabilizer towers for natural gasoline, pressure distillate, butane-propane mixtures, and some solvents. In these cases the bottom product must be well fractionated, whereas in most of the

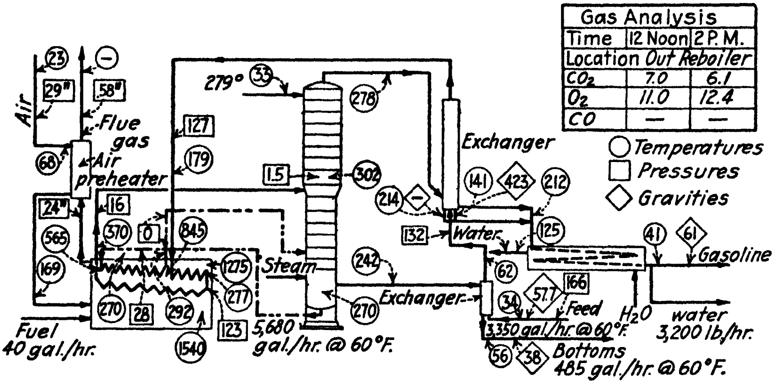

Fig. 105.—Pressure distillate rerun unit with reboiler arrangement. (See Fig. 106.) (*E. B. Badger and Sons Company.*)

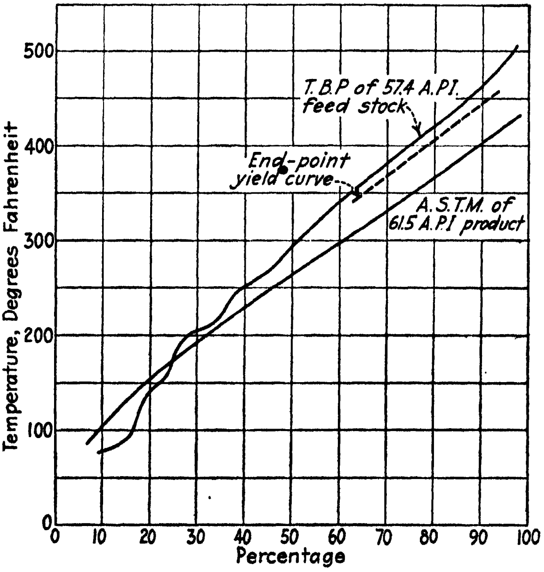

Fig. 106.—Evaluation curves of pressure distillate (see Fig. 105).

processes that have been discussed heretofore the fractionation of the overhead product was most important. Fractionators for the production of special cuts, such as solvents, are frequently operated with reboilers or with fired shells at the bottom of the towers.

Natural-gasoline Stabilizer.—The natural-gasoline stabilizer or fractionator is one of the best examples that the industry offers of the application of the fundamentals of distillation, as discussed

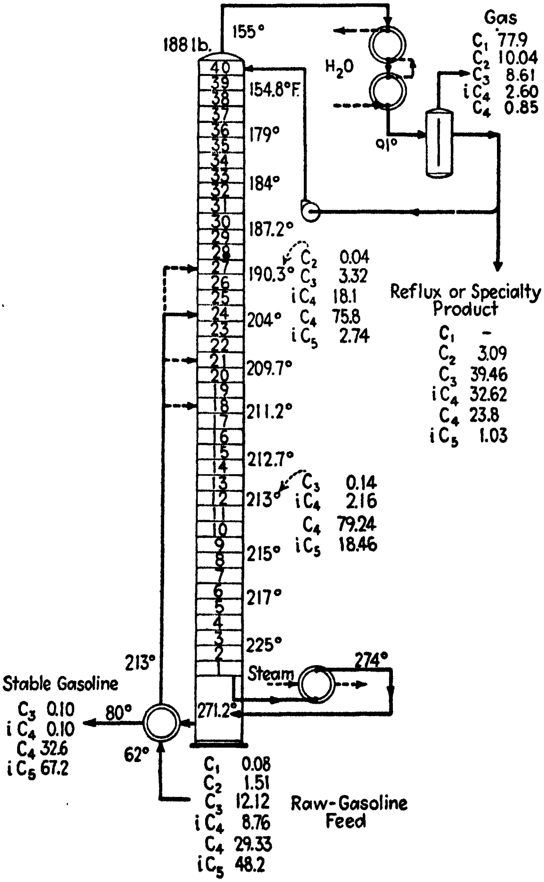

FIG. 107.—Natural-gasoline stabilizer. (*Burdick, Oil Gas J.*)

for two component systems in Chap. XV. Nevertheless, the feed to a stabilizer always consists of at least six components so that the application of the equations for two component systems is difficult. Heat is supplied at the bottom of the tower by a steam reboiler and, if the feed is heated by heat-exchange with the stabilized gasoline, no additional preheating of the stock may be necessary. An effective separation of butane from the lighter hydrocarbons is necessary and hence a large number of trays are used in the tower. Even though many trays are used, a high reflux ratio is necessary. In a few refineries a side-stream product or a part of the reflux is collected and subsequently separated into commercial butane, bottle gas (largely propane), etc. A typical stabilizer diagram is shown in Fig. 107.[7] The diagram shows more plates than are normally used.

Naphthas and Specialty Products.—The manufacture of narrow boiling-range solvents is one of the most exacting operations that is carried out in the refinery. The boiling-range must be narrow and the product must be well fractionated, but in addition the color must be excellent and stable with regard to light. No gum is tolerated and the sulfur must be low. These requirements necessitate a thorough treating operation as well as careful fractionation. Most refiners do not manufacture solvents and those that do are often secretive about the exact methods they use.

In small refineries in which the shipments of solvents may not exceed a tank car per month, a common method of processing is to withdraw a small quantity of roughly cut material from the main distillation process and rerun this cut in a shellstill and tower, using a large quantity of reflux and conducting the distillation very slowly. In large refineries which specialize in the production of solvents, this method is unsuitable.

A product that is withdrawn from the side of a multiple-draw column can never be well fractionated. It will always contain some low-boiling material because the vapor that passes the draw-plate always contains the lighter products of the process. The end-point can be regulated to some extent by the use of many plates and large amounts of reflux, but a satisfactory initial boiling-point cannot be obtained by these methods. The regulation of the initial boiling-point is usually obtained by the use of a steam stripper. However, these common methods are ordinarily not satisfactory for the manufacture of solvents, and it is usually necessary to withdraw a partly fractionated material from the main tower and redistill this material under controlled conditions. Figure 108 indicates a flexible system that can be used in redistilling solvents. The auxiliary tower (enlarged in Fig. 108)

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[7] Burdick, G., *Oil Gas J.*, Apr. 9, 1931, p. 26.

is a rectifying and exhausting system having a reboiler that may be heated with high-pressure steam or by circulation of hot fuel oil from the main distillation unit. The system may be operated in many ways. The charge-stock may be drawn from any part of the main tower, the solvent may be either an overhead or a bottoms product, and in some cases it might even be advisable to collect it as a side-draw product from the auxiliary tower, although a side-draw connection is not shown in Fig. 108.

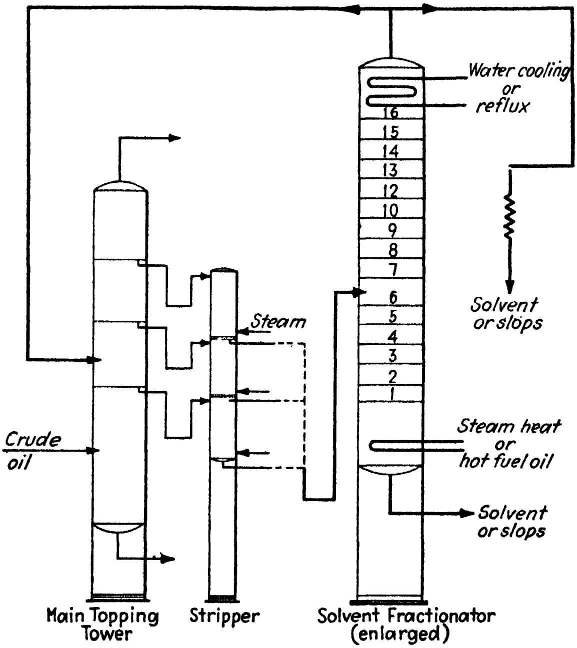

FIG. 108.—Diagram of solvent fractionator.

Pressed Distillate and Brightstock Solution.—The redistillation of pressed distillate in the manufacture of neutral oils must be conducted under vacuum or with the use of large amounts of steam. In other respects the equipment and method of operation are similar to those used in topping crude oil. Discoloration will result in a high treating cost and hence the pipestill must be built with a large amount of radiant surface and for high oil velocities. Figure 109 shows a typical steam-atmospheric pressed distillate rerun plant and Fig. 110 the evaluation curves of the stock.

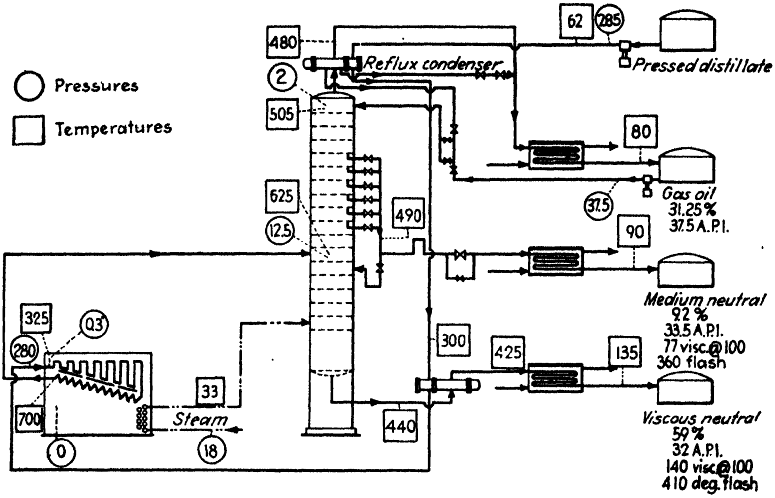

FIG. 109.—Diagram of a steam-atmospheric pressed distillate rerun plant. (A stripper for the side product is usually used.) (*A. J. Smith Engineering Company.*)

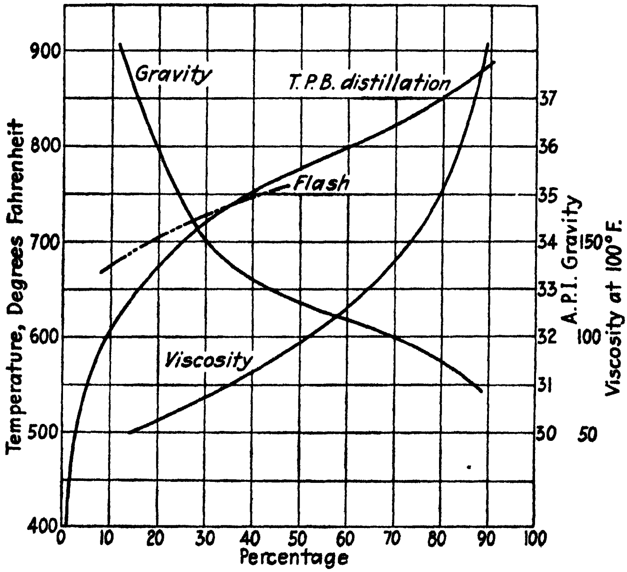

FIG. 110.—Evaluation curves of a pressed distillate.

The same equipment may be used to redistill brightstock solution but, of course, a different quantity of material will be processed. The use of a single pipestill and fractionator system for several distillation operations is becoming a more and more common practice. By careful design a unit can be built that can be

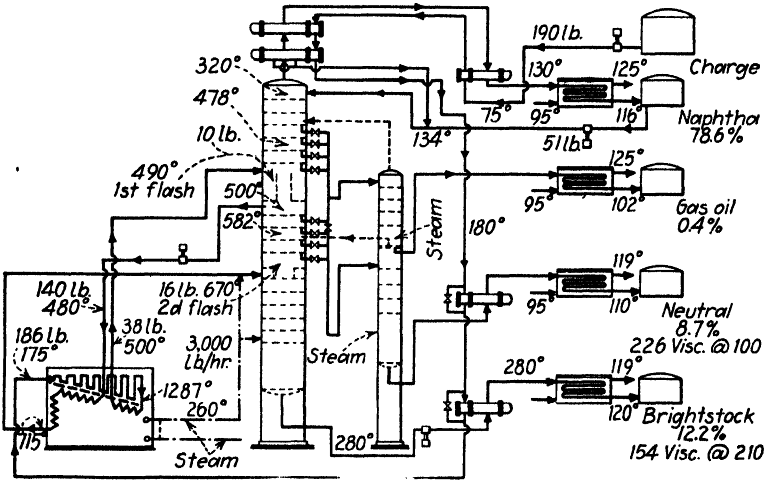

Fig. 111.—Diagram of two-flash solution rerun unit. (*A. J. Smith Engineering Company.*)

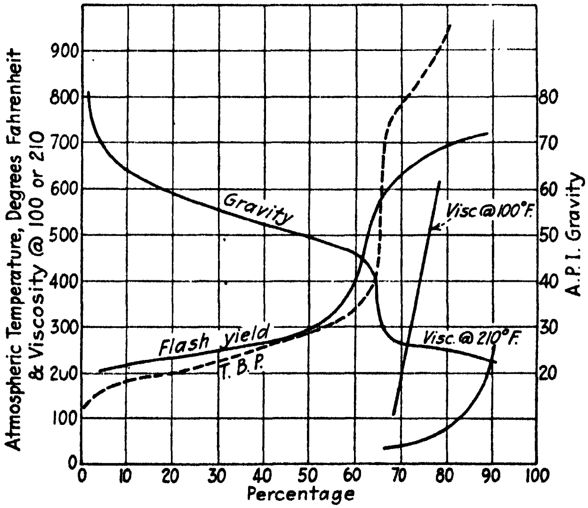

Fig. 112.—Evaluation curves of brightstock solution.

operated on either pressed distillate or brightstock solution. The unit is operated for several weeks on one of the stocks while the other stock is being accumulated in storage tanks. One small Pennsylvanian refiner is storing brightstock solution for about three weeks out of a month and processing it during the fourth week in the topping plant. It is reported that only 1 hr. is required to switch from the crude oil charging-stock to brightstock solution as the charging-stock.

Brightstock solution, like pressed distillate, must be distilled with as little discoloration as possible. Several two-flash systems have been built. In the first flash, the naphtha is removed. The residue is then further heated in a part of the pipestill, and gas oil and a neutral oil are vaporized in the second flash. The two-flash system holds no important advantages over the single-flash system but as an illustration the two-flash method of operation is shown in Fig. 111. Evaluation curves are shown in Fig. 112. The steam required in a pipestill rerun system is often less than one-fifth the amount required by shellstill redistillation.

Steam Required for Stripping.—The amount of steam that is required for stripping side-draw and bottoms products cannot be a definite quantity. It will depend upon the flash-point that is required in the stripped product and upon the degree of fractionation that is obtained in the main tower. For ordinary conditions the following quantities of steam are recommended:

Material	Lb. Steam per Gal. Oil
Naphtha	0.1–0.2
Kerosene	0.2–0.3
Gas oil	0.3–0.6
Fuel oil	0.4–0.8
Pressure-distillate bottoms	0.6–1.0

If products of particularly high flash-point are required, then much larger quantities may be necessary. As an example, in a topping plant a 180°F. flash-point kerosene required 0.4 lb. of steam per gallon and a 280°F. flash-point gas oil required 2.25 lb. of steam per gallon.

Vacuum Distillation.—Vacuum distillation may be employed for the redistillation of pressure distillate, pressed distillate, or brightstock solution. It may be used for distilling topped crude oils for the production of wax distillate and cylinder stock or it may be used to reduce a tar stock to asphalt or pitch. Vacuum systems have been used to produce gas oil (cracking-stock) from heavy tars.

The advantages of vacuum distillation for distilling asphalt bearing crude oils is obvious, because the asphalt in such stocks makes the cost of acid treatment almost prohibitive. In the case of paraffin-base oils the advantages are not so obvious. The advantage with such oils lies in the larger recovery of the valuable heavy stocks which in the case of residual steam operation are partly decomposed into lower boiling, less viscous oils.

Although the wax distillate and cylinder stocks from vacuum units are usually dewaxed without difficulty, some refiners have found that an intermediate heavy wax distillate cut must be produced to the amount of 3 to 6 per cent if the wax distillate and cylinder stock are to have good dewaxing characteristics.

Because of the high boiling-points of lubricating oil stocks the use of vacuum alone is not usually sufficient. Process steam must also be used and sometimes in such quantities as 1 lb. of steam for each gallon of reduced crude oil that is processed. Of course, the exact amount of steam to be used is dependent upon the boiling-range of the stock and the quantity vaporized. Many plants have operated with process steam not exceeding 0.3 lb. per gallon. The dry process of vacuum distillation which utilizes no steam has many theoretical advantages. Most important among these are the much smaller tower and condensing equipment required. Nevertheless, the absolute pressure that is required for the dry processing of most petroleum oils amounts to less than 1 mm. and such a vacuum cannot be produced at a reasonable cost in large-scale vacuum equipment.

The common method of maintaining a vacuum is by the use of a barometric condenser and steam jets. The steam and uncondensed gases pass into the barometric condenser. As the steam condenses, it shrinks greatly in volume, and a vacuum is produced. The fixed gases cannot be condensed and they must be ejected from the system by steam jets. By the use of a barometric condenser and steam jets, the lowest economical pressure that can be produced at the barometric is about 16 mm. and large amounts of steam and cooling water are required. Even this pressure cannot be obtained if the cooling water is above about 70°.

To obtain lower pressures than 16 mm. or to obtain 16 mm. with normal cooling water, a thermocompresser or booster-

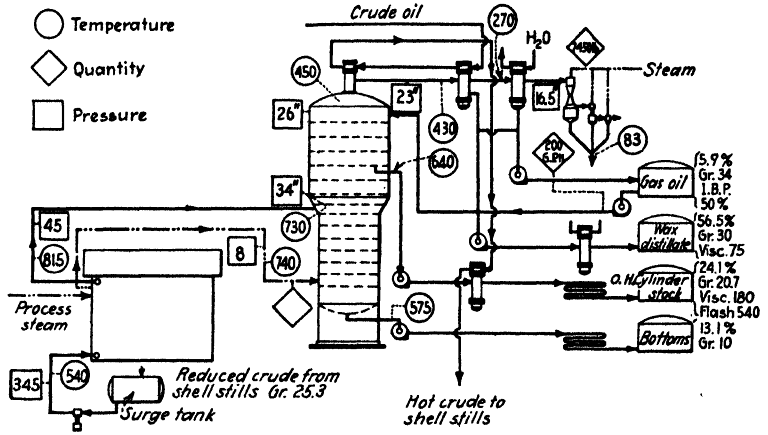

FIG. 113.—Vacuum distillation plant using a booster-ejector. (*A. J. Smith Engineering Company.*)

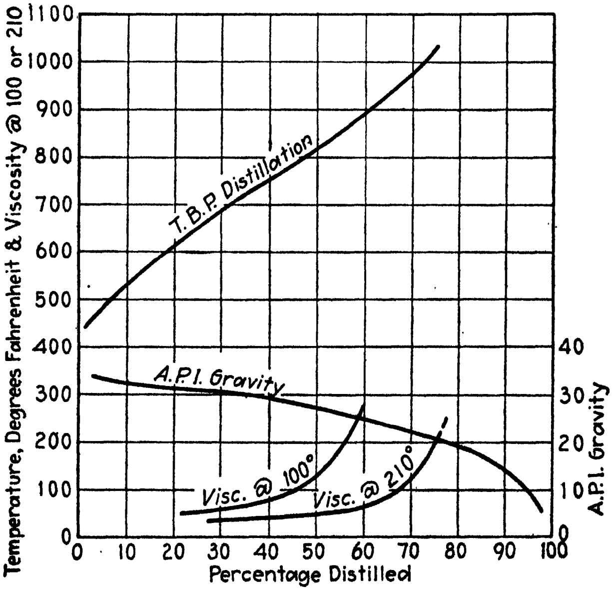

FIG. 114.—Evaluation curves for reduced crude oil charged to the plant shown in FIG. 113.

ejector must be used. By the use of a barometric condenser, three stages of steam jets, and a booster-ejector, the low pressure of 8 mm. can be obtained (at the booster) if the water is cold. However, the steam consumption of a booster-ejector is very high and they are not widely used. The booster-ejector is nothing more than a large steam jet that is used to compress not only the fixed gases but also the process steam. Thus the booster-ejector is used before the barometric condenser, whereas the regular steam jets are used to remove gas from the barometric condenser (Fig. 113).

The pressure-drop that occurs between the barometric condenser and the vaporizer section of the tower is of great importance. The effective pressure at the vaporizer is the purpose of creating a vacuum and hence the vacuum must not be lost by excessive friction loss through the vapor line, condensers, and tower plates. As an example, the following tabulation shows the pounds of process steam required at different effective vaporizer pressures. The table was computed for the processing of 1,500 bbl. per day of an average Mid-Continent reduced crude oil. The first column shows the pressure at the vaporizer; the second and third show the consumption of process steam at vaporizer temperatures of 680 and 700°F.; and the fourth column shows the approximate vaporizer temperature that is required if no process steam is used.

Operating pressure at vaporizer, mm. of mercury	Lb. of steam required per hr.		Temperature at vaporizer if no steam is used
	680°F.	700°F.	
760	54,000	38,200	980
100	6,480	4,420	810
50	2,880	1,850	765
40	2,160	1,340	752
30	1,440	822	740
25	1,080	565	728
20	720	308	720
18	575	206	712
16	432	103	703

Thus the avoidance of a few millimeters of pressure-drop, from the barometric to the vaporizer, is worth many pounds of process steam. The saving in the quantity of steam is important but the reduction in tower size and the quantity of cooling water that is required are also worthy of note. From the tabulation it would appear that pressures of 25 to 30 mm. would be economical, but such is not always the case. In addition to the process steam as shown in the tabulation, steam is required to operate the steam jets, and water is required to operate the barometric condenser. The steam requirement for the steam jets increases rapidly as the pressure is reduced so that the most economical vaporizer pressure often exceeds 30 mm.

In an effort to obtain a minimum pressure-drop, many novel arrangements and designs of vacuum towers and condensing equipment have been developed. The plates are designed for as low a liquid head above the slots of the caps as possible and sometimes the customary bubble caps are discarded entirely for baffle or splash types of plates. In some installations the vapor line has been eliminated by doing the condensing in the top of the tower. In this arrangement the barometric and jet equipment is situated along the side of the vacuum tower (Fig. 115). The processing of a reduced crude oil in a vacuum unit for the production of distilled cylinder stock is illustrated in Figs. 113 and 114. In this plant a reflux condenser is placed in the top of the tower and the partial condensers for gas oil and wax distillate are outside the tower but not at a great distance. One of the difficulties with the arrangement shown in Fig. 113 is the weight of the large condensers. They are so heavy for a large installation that they cannot be supported by the tower. This necessitates independent structural supports and an elaborate expansion joint between the tower and condensers. Vacuum steam strippers are sometimes used on vacuum systems.

Fractionation is more effective at low temperatures or in a vacuum than at high temperatures. Fractionation is more effective because there is a larger difference between the vapor-pressures of the components at low pressures than at high pressures. This is illustrated by the tabulation shown on page 363 for propane and pentane. Thus the relative tendency for propane to leave the liquid when at −50°F. is about four times as great as when the mixture is distilled at +50°F. Perhaps this accounts in part for the relatively small number of plates that are used in vacuum towers.

Asphalt Plants.—The distillation of tarry residues in a vacuum, for the manufacture of asphalt, differs little in principle from the

VAPOR-PRESSURES, mm.

	−50°F.	0°F.	50°F.
Propane	630	1,913	4,395
Pentane	12	70	350
Ratio $\frac{\text{V.P. propane}}{\text{V.P. pentane}}$	52.5	27.3	12.5

unit just described. The operation is simplified by the following factors:

1. Elaborate fractionation is not necessary. In the case of lubricating oil distillation, entrainment may discolor the products and increase the treating costs, and poor fractionation may result in trouble with dewaxing of both the wax distillate and the cylinder stock. Fewer plates are required in asphalt towers. Vacuum asphalt towers often have so few plates in them that they are referred to as flash jugs.

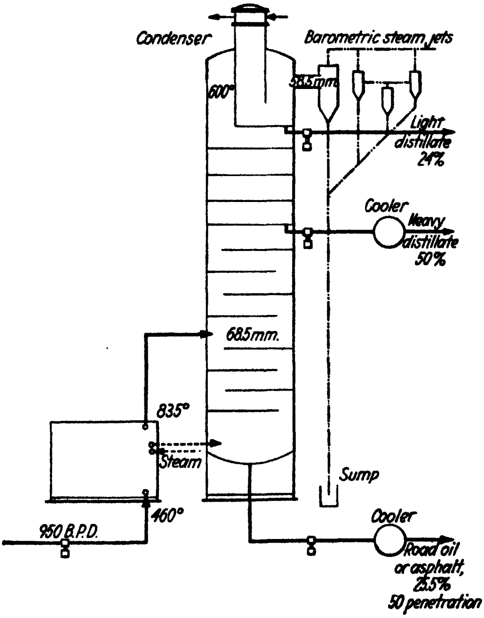

FIG. 115.—Vacuum flash system for asphalt manufacture.

2. Higher vaporizer temperatures can be maintained without damage to the properties of the asphalt. Whereas the vaporizer temperature in lubricating oil towers is limited to a maximum of about 710°F., asphalt stocks are often heated to 790°F. without damage.

3. Only one product need be taken overhead. This eliminates the extra plates that are required for a side-draw cut or the partial condensers for two overhead cuts (Fig. 113). If two overhead cuts are taken, the separation is not difficult because both cuts are gas oils and they need not be well fractionated.
4. Tar stocks are usually available at a high temperature. A small heater is usually required but in some cases a sufficient amount of vaporization occurs by simply reducing the pressure without the addition of heat.

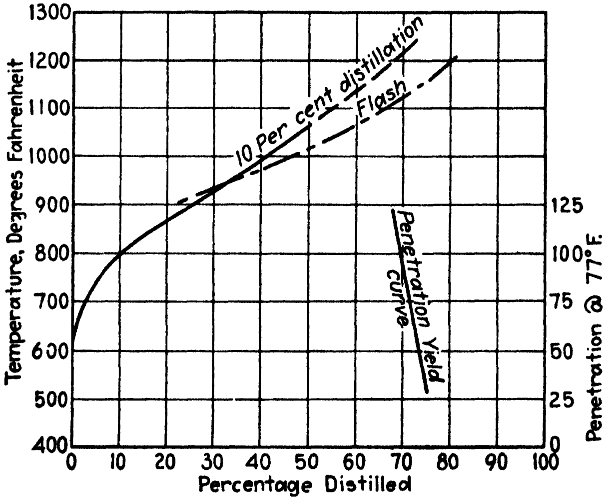

FIG. 116.—Charge-stock for unit shown in Fig. 115.

A typical diagram, showing operating conditions, is shown in Fig. 115. Evaluation curves are shown in Fig. 116.

CONTROL INSTRUMENTS

The full usefulness of refinery equipment can be attained only by the use of control instruments. Certain of these are a necessity but others may or may not be necessary depending upon the type of operation that is being conducted. An attempt to discuss the different control instruments in detail would be futile (1) because there are many satisfactory instruments for each purpose, and (2) because radical improvements are made each year.

Figure 117 indicates the location of the various control instruments that may be used in a topping plant. Many of these are optional but all of the controls shown are commonly used.

Among the most important are (1) top temperature controller, (2) recording pyrometer at vaporizer and inlet and outlet of pipestill, (3) pressure at inlet and outlet of pipestill, at charge pump, and in tower, and (4) temperatures on side-draw plates. Control instruments are extensively used in natural-gasoline plants. Figure 118 illustrates the use of instruments in such a plant.

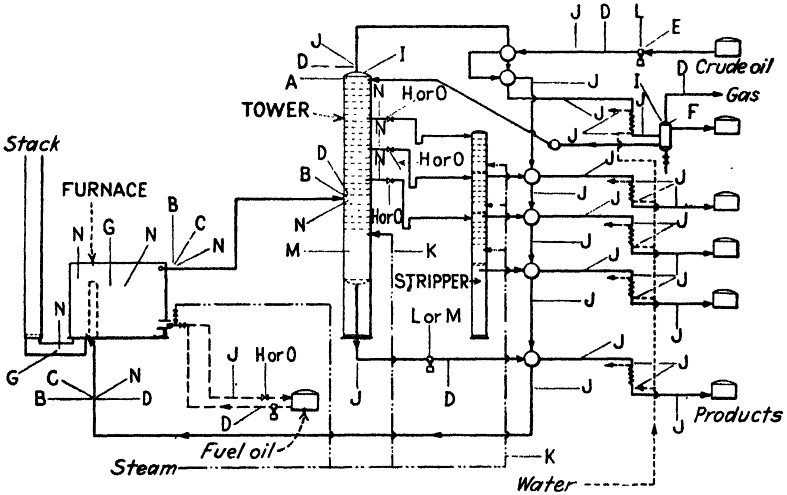

Fig. 117.—Instruments that may be used in a topping plant. The letters refer to the following instruments: *A*, temperature recorder controller; *B*, recording pyrometer; *C*, recording pressure gage; *D*, indicating pressure gage; *E*, rate-of-flow controller; *F*, pressure regulator; *G*, draft gage; *H*, hand-control valve; *I*, safety valve; *M*, liquid-level control.

Optional instruments: *J*, industrial thermometers or thermocouple wells; *K*, flow meter; *L*, stroke regulator and counter; *N*, indicating thermocouples or connections for them; *O*, by-pass adjustment valves or proportional draw-off devices.

In the control of a continuously operating system, certain variables must be fixed or the control of others is almost impossible. Of prime importance are (1) the rate of feed, (2) the temperature of feed, and (3) the top temperature of the tower. With these variables fixed, the control of the others is well within the capability of a competent operator. Even an expert operator is almost helpless if these three variables are not fixed. A plant can be operated with these controls alone but the operation will be even more efficient if other controls are utilized. The rate of feed is commonly controlled by manual operation with the help of stroke regulators and stroke counters. The effect of a variable feed rate can be minimized by the use of proportional draw-off weirs.[8] The temperature of the feed normally gives little trouble and several types of satisfactory top temperature controllers for towers are available.

The principle of trend-analyzing has been one of the notable improvements in instrument design. A trend-analyzing instrument is so constructed that it will begin to stop the actuating mechanism before the condition (temperature, pressure, or rate of flow) has been brought back to the desired condition. In this way the tendency to overcontrol or "hunt" has been corrected. Such instruments apply a large correction if the condition is far from the control-point and a small correction (or none at all) if the condition is nearly at the control-point. This principle has been applied to many types of instruments although not always under the name of trend-analyzer.

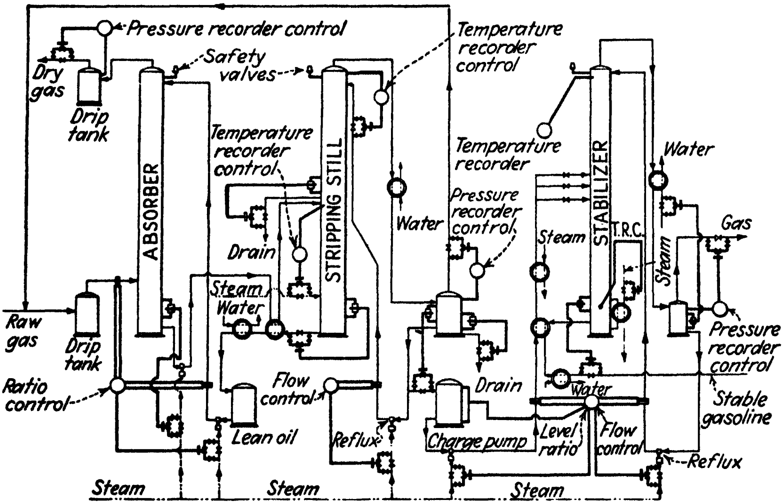

FIG. 118.—An extensive control system for a natural-gasoline plant.

Centralized Control.—The central control room has become an integral part of the modern petroleum distillation unit. The grouping of recording and controlling instruments facilitates the work of the operator and concentrates the responsibility for the operation of the plant. Although the first cost of centralized

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[8] CHILLAS and WEIR, *Ind. Eng. Chem.*, **22**, 206 (1930).

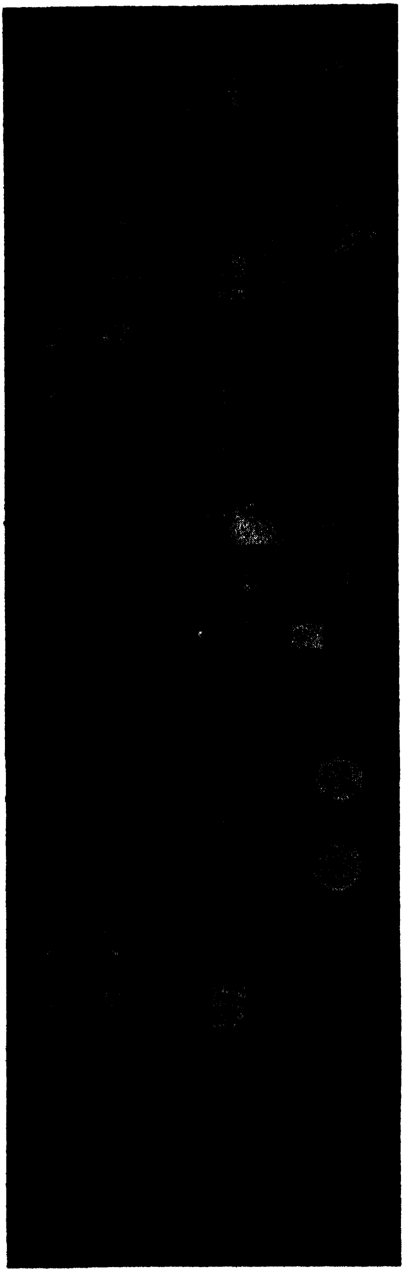

Fig. 119.—An elaborate instrument board used in controlling three pipestill distillation units. (*A. J. Smith Engineering Company.*)

and automatic control is high, it reduces the number of operators required to man the plant and provides an appreciable saving in operating cost. In dealing with emergency shut-downs, such as those arising from explosions and fires, the facility afforded by centralized control is of vital importance.

On the other hand, enthusiasm for the very real advantages of centralized control should not be allowed to obscure its limitations. Control instruments are expensive and the lines between the control room and the equipment are costly. For this reason the less important measurements should be taken at the equipment, and indicating instruments should be given preference over recording instruments except where a record of the operating conditions is of definite service. A large number of instruments in the control room divides the attention of the operator, and hence careful thought should be given to the selection of the data which are to be presented for the attention of the control-room operator. Figure 119 shows a single control board for three distillation units.

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CHAPTER XIX

EXCHANGERS, COOLERS, CONDENSERS, AND STEAM HEATERS

The operation, maintenance, and design of heating equipment form an important part of the duties of the refinery engineer. Although most tubular equipment is designed and installed by manufacturing companies, under contract, the refinery engineer can hardly operate this equipment wisely or apply existing equipment to new uses without a clear understanding of the principles underlying their design.

The ultimate source of heat in the refinery is the steam boiler and the petroleum shell or pipestill. Indirectly, heat is obtained or saved from the various petroleum products by cooling them with the raw charging-stock. These products, at a high temperature, are passed through tubular equipments called heat exchangers, vapor heat exchangers, vapor condensers, or tubular coolers. If the two materials that exchange heat are liquids, the equipment is referred to as a heat exchanger. If the hot material is a vapor and it is cooled without much condensation, the equipment is called a vapor heat exchanger. If the vapor is condensed, the equipment is called a condenser, and the equipment subsequently used to cool the condensate is usually referred to as a cooler or after-cooler. These cooling and condensing operations may be conducted in so-called coil-in-box equipments although many refiners have discarded the coil-in-box arrangement except for particular services.

The large amount of water that is contained in coil-in-box equipment may be an advantage. Thus, if the water supply should fail, the run-down house will not be filled with uncondensed vapors with the attendant danger of a serious fire. In large refineries the water supply is unfailing and tubular equipment can be used with safety. In smaller refineries the danger has been largely eliminated by the use of oil as the cooling medium in at least part of the condensing system. During the last few years the design of tubular equipment has been so improved that they can be built as cheaply or even more cheaply than coil-in-box arrangements. Owing to higher velocities and the relative ease of cleaning, the heat transfer rates in tubular equipment are usually more than twice as great as in coil-in-box equipment.

If the cooling water is very hard or dirty or severe corrosive conditions exist, tubular equipment is usually not satisfactory. The scale that is produced is such a resistance to the flow of heat that the transfer rate in the tubular equipment may be scarcely larger than in coil-in-box equipment. Hence the advantages of tubular equipment are lost and the cost of the installation mounts. The scale can be cleaned from the tubular equipment but the scale may be deposited again so quickly, often after a few hours, that little is accomplished by the cleaning. Some refiners have found it necessary to return to the use of coil-in-box condensers and coolers. However, in many cases the apparent failure of tubular equipment to perform properly may be attributed to carelessness on the part of the refiner. Tubular equipment must be periodically cleaned or blown with steam, and those refiners that have followed this practice have usually found that the use of tubular equipment is economical.

The foregoing items are standard equipment. In addition, the jet type of condenser has been finding some application. The barometric jet-type condenser is now universally used in vacuum distillation to condense steam and at the same time create part of the vacuum. In this type of condenser, the vapor and cooling medium are intimately mixed by high-pressure jets, and heat is exchanged by pure mixing or conduction. Theoretically, heat transfer by mixing is 100 per cent perfect and is the cheapest means of transferring heat. For ordinary condensation, jets have not been used extensively, perhaps because of the tendency of water to form emulsions with oil. The Fleming jet condenser (patented) is an example of the jet-type condenser and almost all manufacturers build barometric condensers.

The use of air-cooled condensers and partial condensers for the separation of products that have different boiling-ranges has been discarded almost entirely in American practice. An exception is the use of partial condensers for the separation of wax distillate and gas oil in modern vacuum plants. In this case, the separation of wax distillate and gas oil is purposely not exact. Furthermore, partial condensers can easily be placed near the tower, and the more quickly the large volume of the vapor can be eliminated the less is the pressure-drop in the vapor line.

HEAT EXCHANGERS

Heat exchangers are built in a multitude of structural types. The primary aim in all of these designs is to obtain a high transfer rate without exceeding the allowable pressure-drop. Sometimes the pressure-drop is not important, as in pumping a charging-stock through a number of exchangers into a pipestill or in withdrawing hot liquids from a high-pressure process. However, very often the only pressure that is available with which to force the material through the exchangers and coolers is the static head of the fluid above the storage tank. Of course, pumps can be installed, but other factors such as the cost of power and the expense of upkeep, which are involved with all moving equipment, prohibit the use of pumps in many circumstances. In the rest of the chapter it will become apparent that an exchanger for a specific service can be built in a large number of ways. The liquid velocity may be varied on both sides of the heating surface, and various structural differences such as the type of shell-baffles, routing of the liquids, and other features, all have a definite effect on the over-all transfer rate and the pressure-drop. Some arrangements are less expensive than others and it behooves the designer to find, or at least approach, the most economical combination of these factors.

Number of Passes.—In order to obtain a high velocity, it is usually necessary to arrange the flow of liquid through the tubes so that the fluid passes through one section of tubes and then returns through another section of tubes. As many as 16 sections or passes have been used. The same effect is produced on the outside of the tubes by means of baffles. In the past, exchangers have been built with as many as six liquid passes outside the tubes and even more passes within the tubes. Today, most manufacturers agree that two or at the most four passes of the liquid through the shell (shell-side of exchanger) are desirable and that multiple-passes of more than six on the tube-side are undesirable. If more passes are used, the conditions of true countercurrent flow cannot be attained and the mean temperature difference and total heat transferred may be decreased even though much higher shell and tube velocities are maintained. Occasionally, conditions are encountered in which an actual crossing of the temperatures of the two liquids tends to occur. As exceptions, multiple tube-passes are perhaps an advantage if several exchangers are used in series and in the case of vapor condensers.

In an attempt to obtain true countercurrent flow, some refiners require single-pass exchangers for all services. In this extreme, the cost of several small shells, as against the cost of fewer large shells with several passes, is great, and particularly so if only a small amount of heat is transferred. In the case of vapor condensers, the mean temperature difference may be sacrificed to advantage by the use of higher shell velocities and multiple tube-passes. From an operating standpoint the single-pass exchanger has many advantages and theoretically is the ideal arrangement. Some of these advantages are:

1. Cleaning is facilitated because one unit at a time can be removed from the system and cleaned without markedly interrupting continuous operation or changing the operating conditions.
2. For the same reason the repair of leaky tubes is facilitated.
3. Small tube bundles can be more easily removed and more easily flushed or cleaned.
4. Large multiple-pass units are bulky and cannot be easily installed and removed. In the case of vacuum partial condensers, the weight of the several units of condenser often amounts to over 50 tons. This great bulk at a height of 40 ft. or more is indeed awkward.

Countercurrent Flow.—One of the troublesome difficulties in heater design is to compute or estimate the average temperature difference that exists in multiple-pass exchangers. The most simple manner of approach is to compute the logarithmic mean temperature difference and apply correction factors. If a change of state occurs on either side of the exchanger, this method is not satisfactory and a more detailed method as explained under the heading of condensers should be used. As an approximation, fractions of the logarithmic mean temperature difference are suggested as shown in Table 47.

If an extremely large temperature difference exists between the two fluids throughout the entire exchanger, the foregoing factors will be somewhat higher and vice versa. A uniformly large temperature difference is essentially equivalent to the use of a large number of units of exchangers. The deviation from the logarithmic mean temperature difference is dependent on the temperature differences as well as the number of passes. For more exact calculations the paper by Nagle[1] should be consulted.

TABLE 47.—CORRECTION FOR MEAN TEMPERATURE DIFFERENCE IN MULTIPASS EXCHANGERS

No. of exchangers	Passes through the shell	No. of passes through the tubes			
		1	2	4	6
1	1	0.98	0.65	0.80	0.84
1	2	....	0.95	0.75	0.80
2	1	0.99	0.77	0.85	0.86
2	2	....	0.96	0.92	0.89
3	1	1.0	0.87	0.90	0.90
3	2	....	0.97	0.95	0.94
4	1	1.0	0.95	0.97	0.97
4	2	....	0.98	0.96	0.95

Selection of Material through Tubes.—If one liquid is more viscous than the other, it should preferably be sent through the shell where turbulence can be obtained by the use of baffles. For the same friction loss, the over-all transfer rate is increased more than by sending the material through the tubes.

If the volume of one liquid is much smaller than the volume of the other, the material should be sent through the shell and again by the use of close-spaced baffles a greater transfer of heat can be obtained with a minimum pressure loss. This is particularly true for the orifice-type baffles that will be discussed later. Very small tubes or a large number of passes would be required if the small volume were sent through the tubes, but both of these methods of increasing the rate of heat transfer are not considered as good practice.

The tubes of an exchanger can be easily built to withstand high pressures and hence, if possible, fluids under high pressure are

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[1] Mean Temperature Differences in Multipass Exchangers, *Ind. Eng. Chem.*, **25**, 604 (1933).

routed through the tubes. Shells are normally constructed of cast iron and to build steel shells greatly increases the cost.

If coke or sediment may be deposited, the fluid should be sent through the tubes because the tubes can be easily cleaned. Further, if the fluid is corrosive, special corrosion-resistant tubes can be obtained at a cost far below the cost of corrosion-resistant shells.

Obviously, materials which must occupy a large volume, such as gases or condensing vapor, should be routed through the shell so that structurally the passage can be large enough to avoid high velocities and prohibitive pressure-drops.

Water, used as the final cooling agent, is usually passed through the tubes because scale will be deposited and the tubes can be more easily cleaned.

Baffle Arrangements.—Baffles are widely used to increase the turbulence and film transfer rate on the outside of the tubes. With the more widespread use of exchangers that have only a few passes on the tube-side, the baffle arrangements have become somewhat standardized. With multiple-passes on the shell-side, the number of possible baffle arrangements becomes so large that they cannot be discussed, but for exchangers having only one or two passes on the shell-side the following standard baffle types are generally recognized:

1. *Cross Flow. Alternate Circular Ports and Annular Spaces (Fig.* 120*a). Half-moon or Cut-out (Fig.* 120*b).*—This type of baffle imparts a zig-zag flow back and forth across the tubes. Obviously, dead-spaces cannot be avoided (Fig. 120*a* and *b*) but pressure-drops are comparatively low with this type of baffle. In general, this type is valuable for viscous fluids if only a small pressure-drop is permissible.

2. *Orifice (Fig.* 120*c).*—This type is built as oversize holes or ports through the baffle sheet. The tubes fit loosely in the holes and the fluid is thus forced to scour the tube wall. Thus far, this type has proved to be one of the most effective means of increasing the film coefficient on the shell-side but it has the disadvantage of causing a comparatively large pressure-drop. This type is particularly suited for use with light liquids under ordinary pressure heads.

3. *Spiral Flow (Fig.* 120*d).*—This type imparts a spiral flow to the fluid so that it crosses the tubes besides traveling longi-

tudinally. The baffles are either continuous spirals or separate baffle plates, so placed that the liquid is directed into circular flow. The fluid suffers a friction loss by scouring the shell, and the turbulence created at the shell surface is not effective in causing heat transfer. In other words, the liquid tends to by-pass in the space nearest the shell and thus fail to transfer heat. The tube bundles must be easily removed and hence the baffles must not fit the tubes closely. In this type a large amount of liquid fails to move spirally because of by-passing. This is not altogether a disadvantage because the baffle thus acts partly as an orifice baffle.

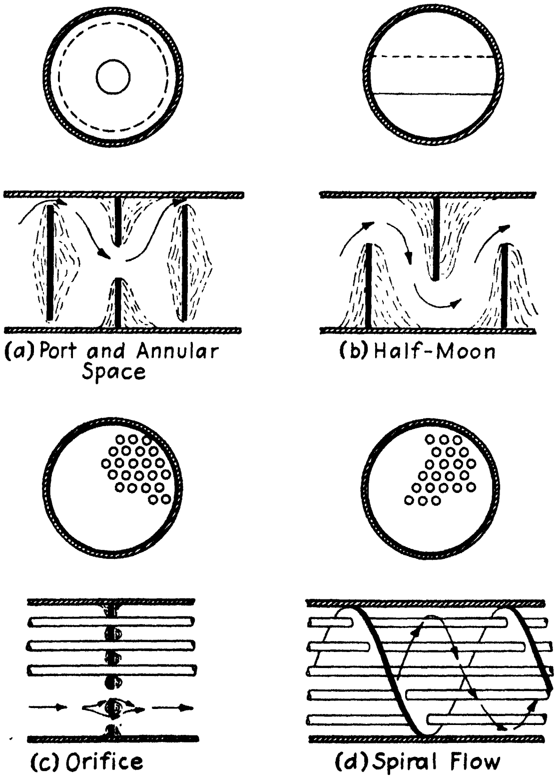

FIG. 120.—Types of baffles for the shell side of small exchangers.

Impingement baffles are placed at points which may be eroded by the velocity of the fluid. Usually these baffles are used only at the fluid entrance point, but at any point where the fluid suddenly changes direction impingement plates are recommended. Tubes in vapor condensers have been entirely severed by erosion in a few months of operation.

The closer the baffles are spaced, the greater the turbulence and heat transfer. The pressure-drop increases at close spacings but not in proportion to the increased transfer rate. However, spacings of less than 6 in. are seldom used because of the difficulty encountered in cleaning the outside of the tubes. Exchangers in use today have spacings of 3 to 18 in.

Longitudinal baffles are sometimes used but their use is usually limited to vapor exchangers and condensers. In long small-diameter exchangers the longitudinal baffle provides too much area for by-passing and efficiency is sacrificed thereby.

If severe corrosion takes place on the shell-side or if the fluid contains large amounts of suspended matter, baffles may be a liability rather than an advantage. Removal of the baffles decreases the transfer rate but a large amount of dirt in the stock may decrease the rate more than the removal of baffles. With no baffles the probability of plugging the shell-side is greatly decreased.

Tubes and Tube Spacing.—Tubes of ½ to 1½ in. outside diameter are used. In the past, ½- and ⅝-in.-diameter tubes were extensively used but they often became plugged and the outside could not be easily cleaned. Hence the use of ¾- and 1-in. tubes is now almost standard practice. For tubes above 1 in. in diameter, thicknesses of 10 to 16 B.w.g. are common and for smaller sizes the thickness ranges from 12 to 18 B.w.g. Owing to the more vigorous cleaning methods that are now employed, the thicker tubes are more in demand.

The tubes are usually spaced at ¼ to ⅜ in. clear space from adjacent tubes and in an equilateral-triangle arrangement. Exchangers built with closer tube spacing are not accessible for cleaning. Later in the chapter the importance of frequent tube cleaning will be discussed. For severe fouling conditions, a square pitch arrangement with wide spacing is suggested, although for regular service the diamond or equilateral-triangle arrangement is the standard. A diamond pitch allows the tubes to be brushed on six sides.

Tubes are usually constructed of about 0.15 carbon steel, but in processing high-sulfur or salt-bearing crude oils, steel is rapidly destroyed by corrosion. For sulfur corrosion, stainless steel or 18-8 chrome-nickel tubes may be used. For acid corrosion, admiralty metal, a 70-29 brass containing 1 per cent of tin, is recommended. Admiralty metal is slowly destroyed by dilute hydrochloric and sulfuric acid but most of the neutralizers used for these acids do not act rapidly on admiralty metal. Ammonia is the only one of the neutralizing agents that attacks admiralty metal rapidly. The mechanical properties of this alloy are impaired by temperatures above 500°F., although under favorable conditions admiralty metal has been used at tube wall temperatures of 600°F. The list of conditions as shown in the table on page 378 are recommended.

Table 48.—Standard Condenser Tube Data

O. D. of tube, in.	No. gage, B.w.g.	Weight per lin. ft., lb.	Thickness, in.	I. D., in.	Surface outside, sq. ft.		Surface inside per lin. ft., sq. ft.	Inside sectional area per tube, sq. in.	Velocity for 1 gal. per min., ft. per sec.
					Per lin. ft.	Per lin. in.			
⅝	14	0.520	0.083	0.459	0.16362	0.01364	0.1205	0.165	1.98
	16	0.421	0.065	0.495	0.16362	0.01364	0.1299	0.193	1.633
	18	0.326	0.049	0.527	0.16362	0.01364	0.1382	0.218	1.472
	20	0.238	0.035	0.555	0.16362	0.01364	0.1455	0.242	1.328
¾	14	0.64	0.083	0.584	0.19365	0.01637	0.1530	0.268	1.20
	16	0.514	0.065	0.620	0.19365	0.01637	0.1627	0.302	1.069
	18	0.396	0.049	0.652	0.19365	0.01637	0.1706	0.334	0.9617
1	12	1.12	0.109	0.782	0.26180	0.02179	0.205	0.479	0.67
	14	0.88	0.083	0.834	0.26180	0.02179	0.2183	0.5463	0.586
	16	0.700	0.065	0.870	0.26180	0.02179	0.2279	0.595	0.540
	18	0.540	0.049	0.902	0.26180	0.02179	0.2360	0.638	0.503
1¼	10	1.73	0.134	0.982	0.32708	0.02725	0.258	0.757	0.424
	12	1.44	0.109	1.032	0.32708	0.02725	0.271	0.838	0.385
	14	1.12	0.083	1.084	0.32708	0.02725	0.284	0.923	0.347
	16	0.890	0.065	1.120	0.32708	0.02725	0.2935	0.985	0.3262
	18	0.680	0.049	1.152	0.32708	0.02725	0.3020	1.045	0.3075
1½	10	2.110	0.134	1.232	0.3925	0.03275	0.3237	1.195	0.2688
	12	1.75	0.109	1.282	0.3925	0.03275	0.3382	1.292	0.2488
	14	1.36	0.083	1.334	0.3925	0.03275	0.3500	1.400	0.2298

In certain localities brackish cooling water cannot be avoided and for such a service the tube sheets and if possible the shells should be constructed of the same material as the tubes, in order to avoid localized electrolytic corrosion.

Material	Highest working tube temperature, °F.	Max. temperature difference between adjacent tubes, °F.
Admiralty	450	145
Steel	500	130
Steel	800	95

Shells and Heads.—Most petroleum oil exchangers are of the floating-head type. As shown in Fig. 121, the tubes are free to expand and contract longitudinally by pushing the floating head back and forth within the shell. However, the head and tubes are not altogether free from stresses because the tubes that contain the hottest fluid expand more than the others. For this reason a number of floating heads in a single shell are sometimes employed. If the temperature difference between the two fluids is great or, in other words, a rapid rate of heat transfer occurs, two floating heads are advisable. This difficulty is sometimes avoided by the use of several small units of exchanger rather than one large exchanger with several floating heads. As an example, the hot vapors from a cracking plant evaporator are never cooled with crude oil or water at normal temperatures. The crude oil must be heated by other means to approximately 300°F. before sending it through the vapor condensers. Such condensers are usually built in several units. Too cold a medium (see tabulation above) may produce stresses and cause the tubes to fail.

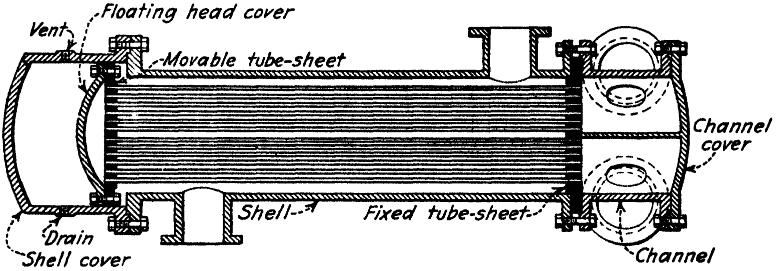

FIG. 121.—Double pass through tubes, floating-head-type exchanger. No baffles are shown on the outside of the tubes.

Tubes lighter than 12 B.w.g. tend to fail because the joint between them and the tube-sheet fails.

Cast-iron shells and heads should not be used at temperatures above 400°F. and pressures above 150 lb. per square inch. Below these maximum conditions, cast iron is to be preferred not alone because of cost but also because cast iron resists corrosion. Most active corrosion occurs during condensation of the vapor and little action occurs after the material is completely condensed. At higher temperatures and pressures, cast, forged, or welded steel shells are used. Cast steel is not an entirely homogeneous material and sometimes the manufacturer must make several of these large and expensive castings before a satisfactory shell or head is obtained. Forged-steel shells are expensive but when properly manufactured they can be used safely up to 1,000 lb. per square inch and at a temperature of 700°F. Recently the art of welding has been so improved that shells and particularly heads are now manufactured by machining and welding heavy plate steel. This method seems to be among the best for very high-temperature high-pressure equipment and the cost is about equal to that of forged-steel construction.

FILM TRANSFER RATES

The film rates that are presented in this chapter are based primarily on the equations given in Chap. XIII. However, the equations are for clean surfaces that in some cases had been polished, and hence the values of the film rates had to be decreased in order to represent commercial conditions. The magnitude of the correction was estimated by a study of observed transfer rates in new clean commercial equipment. In some cases approximations were necessary because of inadequate data and in others it was necessary to simplify the cumbersome equations so that the film rates could be presented in a usable form.

The over-all rates that are obtained by the film rates given herein are far too high for most commercial equipment, and the *fouling factors* that are given in Fig. 125 *must be used.* Unfortunately, plant men have made no determined effort to catalogue fouling factors. This lack of information has led many engineers to attempt to correlate transfer rates without isolating a factor to care for the surface condition, and these efforts have been without success. When the transfer rates and fouling factors that are

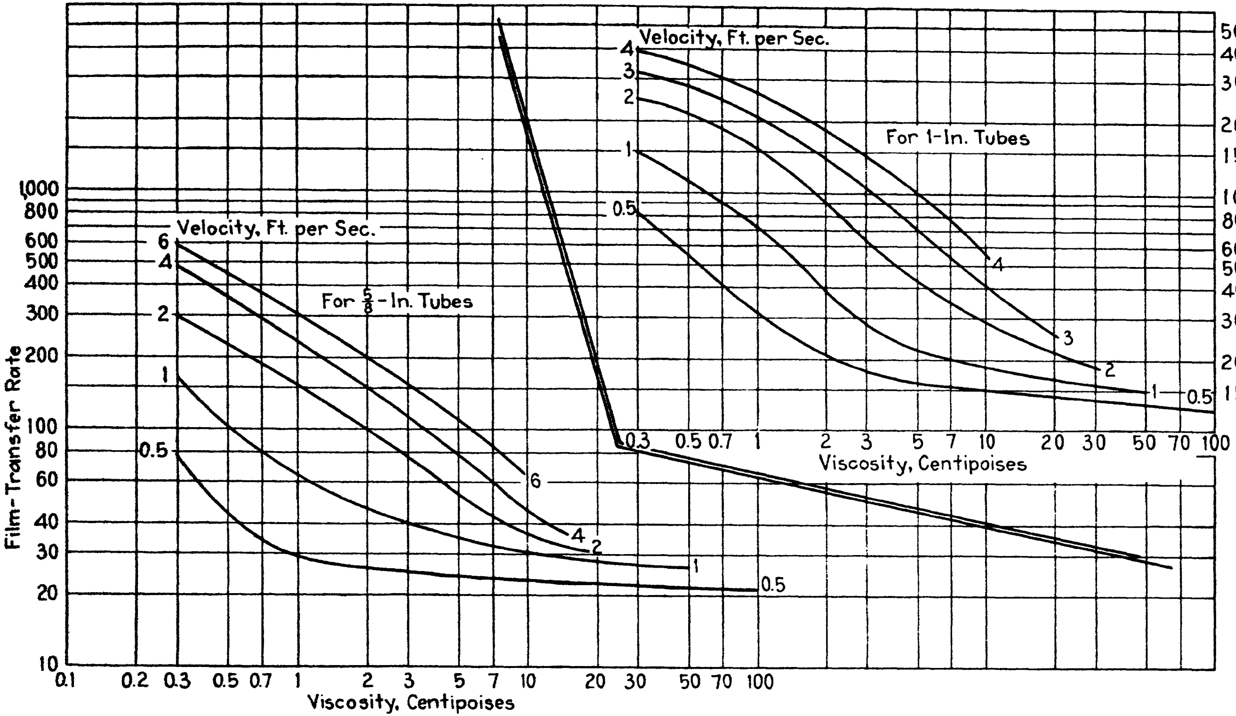

Fig. 122.—Approximate film transfer rates for oils inside of 5/8- and 1-in. tubing. A fouling factor must be applied to these rates.

given in this chapter are used, the computed rates check reasonably well with commercial exchanger data. However, the method of evaluating fouling factors and dirtiness resistances, as given in the chapter, is by no means a finished correlation.

In order to get the high rates given in Chap. XIII, it is usually necessary to clean all scale from the surface, remove the dirt and grease that always accumulate during handling, and in some cases the surface must be polished or cleaned with chemical solutions.

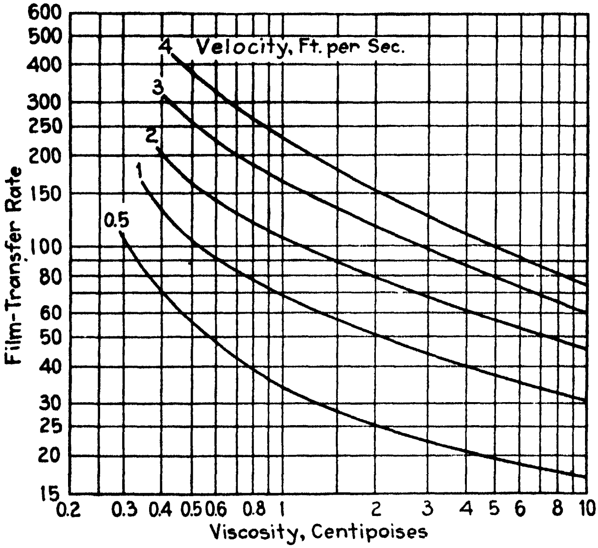

FIG. 123.—Approximate film transfer rates for oils on the outside of tubes in tubular-type equipment. These rates will vary with different types of shell baffles. Fouling factors must be used with these rates.

Liquid Film Coefficients.—Figure 122 shows the film coefficients for oils flowing in ⅝- and 1-in. tubing. No correction for turbulence at the ends of the tubes need be applied. The size of tube has little effect if the viscosity is low, but if the viscosity is high the size of tube is very important. If large film temperature differences exist (see page 216), the viscosity at the mean film temperature should be used; otherwise the viscosity at the main body temperature of the fluid may be used without introducing serious errors.

Figure 123 shows the magnitude of film coefficients for oils flowing on the outside of tubes. Owing to the many types of baffles and many possible arrangements, these shell-side rates cannot be exact for all exchangers. The velocity referred to in Fig. 123 is the mean resultant velocity of the fluid through the shell and baffles and between tubes.

The velocity through the tubes and through the shell is dependent upon the pressure-drop that can be permitted. However, there is a relation between the velocity through the shell and the velocity through the tubes because of the structural design of an exchanger. If the same quantity of fluid is handled on each side of the surface and the exchanger has the same number of passes through the tubes and through the shell, the velocity through the tubes is about equal to the velocity through the shell. However, if the baffles are closely spaced (6 to 8 in.), the shell velocity may be as much as 70 per cent larger than the tube velocity. Furthermore, if the quantity of one of the fluids is much greater than the quantity of the other, then additional corrections must be made. As an example, if four volumes of fluid is passed through the tubes and one volume through the shell, the shell velocity will be only about one-fourth as large as the tube velocity.

When exchangers that have an unequal number of passes through the shell and through the tubes are considered, the ratio of the two velocities becomes very complicated and no definite rules can be given.

TABLE 49.—TRANSFER RATES FOR WATER

Velocity	Rate		Notes
	Inside	Outside	
. . .	. . .	50	Natural convection, pipe coil (small equipment)
. . .	. . .	110	Natural convection, ribbed sections (small equipment)
0.5	180	170	Natural convection (commercial), small temperature difference
1.0	230	200	Natural convection outside coils (commercial conditions)
2.0	350	280	Forced circulation
4.0	560	400	Forced circulation
6.0	660	500	Forced circulation

Table 49 summarizes the water film coefficients for coolers and condensers operating at normal water temperatures and oil temperatures.

Condensing Petroleum Vapors.—Many factors are involved in the film condensation coefficient. These are mathematically related in Eqs. (39) and (40) (page 226). For exact calculations these equations should be consulted but for most commercial work, the rates given in Table 50 are satisfactory.

TABLE 50.—FILM COEFFICIENTS, CONDENSING

Material	B.t.u. per hr. per °F. (diff.) per sq. ft.	
	No steam	With steam, but steam not condensing in same temperature-range as vapor
Gasoline	180–220	130–160
Kerosene	150–190	100–120
Gas oil	130–180	60– 70
Wax distillate	110–160	50– 60

If steam condenses with the vapor, Eq. (40) should be used. The variation in the coefficients found in Table 50 is due mainly to the temperature difference across the film. If the temperature difference is large the rate is low, and if it is small the rate is high. This is due to the accumulation of a thick film of liquid at high rates of condensation. In parts of the condenser in which no vapor remains and liquid stands about the tubes, the transfer rate is very low and probably does not amount to more than 30 to 50.

Pure steam condenses at a rate of about 2,500 but in the presence of liquids and small amounts of vapor, as in a distillate condenser, the rate probably does not exceed 400.

Cooling Vapors without Condensation.—Scattered data on commercial vapor coolers indicate that the film rates are a little lower but nearly the same as those given in Eq. (32) (page 221). The film rates for cooling vapors, by Eq. (32), are shown in Fig. 124. The mass velocity which is used as one axis in this figure can be most easily computed by multiplying the linear velocity, in feet per second, by the density expressed as pounds per cubic foot. It may be visualized as the pounds of material that passes a square foot of free cross section per second.

FOULING FACTORS

Most of the difficulties that arise in heat exchanger design and operation are due to an inadequate knowledge of the fouling of the surfaces of the equipment. Except under special conditions the effect of these fouling resistances can never be exactly known. If the stocks are exceptionally clean, if the equipment is periodically cleaned, or if the condition may be carefully studied in the plant for several months, then it is possible to foretell with fair accuracy the magnitude of the fouling factor.

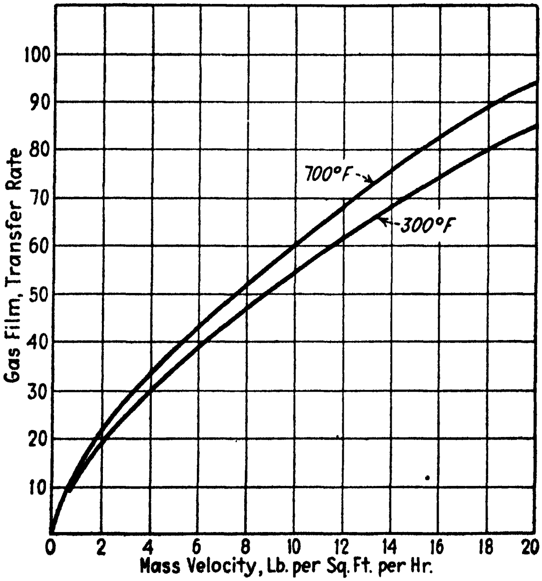

FIG. 124.—Film transfer rates for cooling or heating gases and vapors on the outside of tubes. A fouling factor must be applied.

In order thoroughly to understand fouling, it is necessary to compute film temperatures, wall temperatures, etc. These may be computed by means of the following equation:

$$\Delta T : \Delta T_1 : \Delta T_2 : \Delta T_f : \text{etc.} = \frac{1}{H} : \frac{1}{h_1} : \frac{1}{h_2} : R_f : \text{etc.} \qquad (64)$$

Difficulties arise in applying the equation because the film transfer rates are not usually known until the temperature differences are computed. This necessitates a cut-and-try solution to determine the film rates and the temperature differences at the same time.

The great lowering of clean film rates by fouling has often led plant engineers to believe that something must be wrong with the film rates that have been published. As an example, two exchangers operate under such conditions that the over-all rates computed by the film coefficients, are 125 and 25. If both exchangers become fouled by the same amount, *i.e.*, a fouling resistance of, say, 0.02, the over-all rates drop to 36 and 17 respectively. The decrease in transfer rate is so large in the first exchanger and so little in the second that naturally the plant engineer felt that something must be wrong. This serves to illustrate the great importance of fouling factors.

The resistance due to fouling is often so small that the position of the decimal point may become confusing. Hence the use of the term fouling factor has become common. The *fouling factor* is obtained by multiplying the fouling resistance by 1,000. Thus, if the fouling resistance is 0.005, the fouling factor is 5.

Classification of Fouling Conditions.—Although there are many individual conditions of fouling, all of them can be generally classified as follows:

1. *Hard Deposits.*—Examples of this type of fouling are water scale, corrosion scales, rust, and hard coke. In general, the thickness and resistance of these deposits increase with time and nearly directly proportional to time. They cannot be effectively removed by blowing with steam or by flushing with hot water but some of them can be removed by the use of chemicals. The chemical solution may be pumped through the equipment but sometimes the tube bundle is removed and dipped into a vat which contains the chemical.[2] The usual manner of removing hard deposits is by the use of cleaning tools and brushes. The resistance offered by hard, dense deposits is directly related to the conductivity of the material composing the scale.

The rate at which fouling occurred in a particular naphtha condenser, cooled with water, is given by Samans.[3] The decrease in rate and the corresponding fouling factors are given in Table 51.

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[2] ANON, Cleaning Refinery and Gasoline Equipment, *Ref. Nat. Gaso. Mfr.*, August, 1933, p. 340.

[3] A.S.M.E. Section Meeting, May, 1933.

TABLE 51.—FOULING OF A NAPHTHA CONDENSER

Days	Not cleaned		Blown with steam, and blown daily after 18th day	
	Transfer rate	Fouling factor	Transfer rate	Fouling factor
1	50	0	50	0
2	44	2.7		
4	40	5.0		
6	37.5	6.7		
10	33	10.3		
14	29.4	14.1		
20	....	....	34	9.4
30	....	....	32.4	11.0
50	....	....	30.0	13.5

In another naphtha condenser (water cooled) the following data were recorded:

Days after Cleaning	Transfer Rate
2	39
4	33.2
7 and 8	28.7

2. *Porous Deposits.*—These deposits often consist of essentially the same materials that compose the hard deposits. In addition, coke or carbon may be deposited from fluids such as topping-still bottoms, asphalt or tar from vacuum plants, or cracking-still bottoms. Scale-forming mud and dirt may be deposited from water or from crude oil. Frequently the scales caused by corrosion are porous but not loose enough to be removed by blowing with steam. These deposits may be more serious than hard scales because the fluid that is contained in the porous material usually has a lower conductivity than the hard skeleton of the scale, and thus the over-all conductivity is low.

Sieder[4] presents data showing the rate at which one type of porous deposit was accumulated. An evaporator was operated with steam on the outside of the tube bundle, and a mixture of oil and water containing lint, in the tubes. The lint was deposited at a rate directly proportional to time. At 13 hr. the fouling

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[4] *Oil Gas J.*, May 10, 1934, p. 104.

factor was about 2, and if the deposit continued to grow at the same rate it would have caused a factor of 20 in about five and one-half days. However, it is not to be inferred that porous scales are deposited at a rate directly proportional to time. The deposit described by Sieder might dislodge itself after attaining a greater thickness and hence might properly be classed as a loose deposit. Both the hard and the porous deposits can be removed to some extent by the use of bent-tube sections. These sections consist of a bank of condenser tubes (usually in an open box) which are bowed slightly during manufacture so that, as heating and cooling occurs, they bend and cause the scale to loosen.

3. *Loose Deposits.*—Examples of this type of deposit are silt, mud, soot, powdered coke, leaves, or vegetable fiber. Many of these can be removed by swabs or brushes, and some can be effectively removed by blowing with steam or air or by flushing with hot water. The resistance caused by these deposits is not greatly dependent on the material composing the deposits but rather upon the liquid that is trapped within them. As far as decreasing the rate of transfer is concerned, loose deposits may be more effective than other types. Hard scales, and sometimes porous deposits, are usually so tightly fastened to the surface that they are affected little by a high velocity, but many loose deposits can be almost completely removed by maintaining a velocity of over 4 ft. per second.

The effect of blowing with steam, even for a fairly tight scale, is illustrated in Table 51. The condenser showed a better rate at 50 days, when blown with steam, than it did at 14 days if no blowing was practiced.

Commercial Fouling Factors.—The magnitude of commercial factors can be best approached by means of a chart.[5] Figure 125 shows factors that were obtained in commercial equipment. The lines in the figure are merely boundaries of the several conditions of fouling. It would be more convenient to draw average curves for each condition but to draw such a definite relation would be misleading. The desire of every engineer is to have definite fouling factors so that the responsibility can thus be lifted from his shoulders. This would be a restful solution to this troublesome problem but such a solution will probably never be possible.

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[5] NELSON, W. L., Fouling Factors in Heat Transfer Equipment, *Ref. Nat. Gaso. Mfr.*, August, 1934, p. 292.

Each condition of fouling is a new condition and can be met only by the judgment of the designer.

The fouling factors given in Fig. 125 are for one surface only. That is, two factors must be obtained and the sum of the two is the total fouling factor. It is difficult to isolate the fouling factor for each side of the surface, but to isolate the factors does allow the application of judgment in a sound manner. The fouling factor may be estimated as follows:

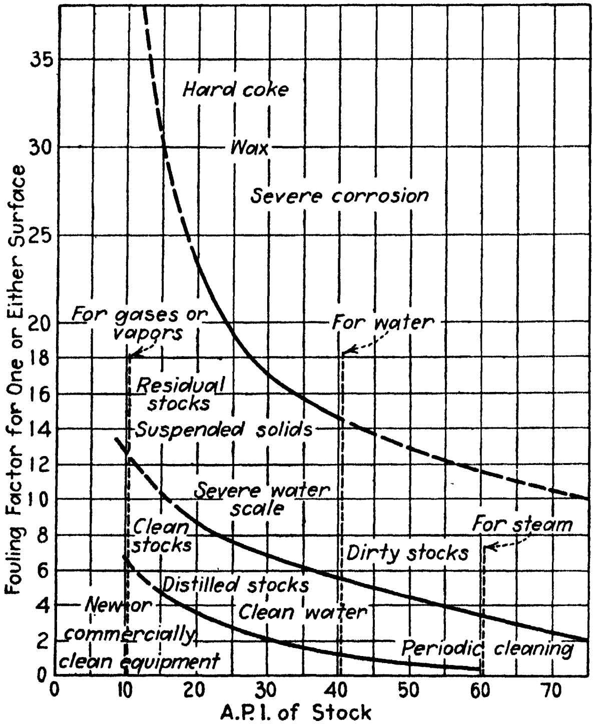

FIG. 125.—Approximate fouling factors for commercial oil equipment. This chart shows the individual factors for each side of a surface and hence, in the usual case, two factors must be added together to get the total fouling factor.

An exchanger is to cool a clean wax distillate (480 to 280°F.) in the tubes (3.7 ft. per second) by means of crude oil. The crude is heated (160 to 230°F.) on the outside of the tubes (1.8 ft. per second). The exchanger will be blown with steam once a week. The factor for the tube-side will be about 3 because the stock is clean and the velocity is fairly high. The factor for the shell-side will be about 4 because the velocity is high and the crude oil does not contain a large amount of dirt. Both of these factors are lower than normal because of periodic cleaning with steam. The total factor will be about 7. If the exchanger were not blown with steam, the factor might be 10 or 11. If the wax distillate were cooled with water, a wax film would be produced and the total factor might be 25 or even higher.

Example 63. Transfer Rate for Exchanger.—Kerosene is to be cooled from 400 to 300°F. by means of 35 A.P.I. crude oil. The crude oil rises in temperature from 270 to 285°F. The exchanger has $\frac{5}{8}$-in. tubes. The crude oil is relatively clean so that little dirt settles from it and the exchanger will be blown with steam each month. The conditions are as follows:

Place	Material	Viscosity, centipoises	Ave. temperature, °F.	Velocity	No. passes
Shell..............	Crude oil	0.6	280	1.5	2
Tubes.............	Kerosene	0.3	340	3.2	4

The film transfer rates (Figs. 122 and 123) are 390 for the kerosene and 117 for the crude oil. The fouling factors will be about as follows:

Shell (crude) factor of......................	3.0 (Fig. 125)
Tubes (kerosene) factor of..................	2.0
Total fouling factor......................	5.0

$$\text{Over-all transfer rate} = H = \frac{1}{\frac{1}{117} + \frac{1}{390} + 0.005} = 62$$

Without periodic cleaning, the rate might be

$$H = \frac{1}{\frac{1}{117} + \frac{1}{390} + 0.009} = 49.8$$

At a duty of 550,000 B.t.u. per hour, the surface is

log mean temperature difference = 63° (Fig. 67)

For one exchanger with passes as above,

Actual mean temperature difference = 63 × 0.75 = 47.3°

$$\text{Surface} = \frac{550{,}000}{62 \times 47.3} = 187.5 \text{ sq. ft., with 10 per cent factor} = 206 \text{ sq. ft.}$$

Example 64. Transfer Rate in a Steam Heater.—A tank of fuel oil, 13 A.P.I. 60 viscosity at 210°F., is to be heated from 60 to 110°F. by means of a steam coil. The oil has a pour-point below 60°F. The oil stands in the tank and circulates only by natural convection. Exhaust steam is used and it leaves the coil at atmospheric pressure but not cooled below 212°F.

The problem is complicated by the fact that the velocity of the oil must be estimated and because the operation is not continuous. The oil is at 60° at the beginning, and ends after a length of time which depends upon the amount of surface used, at 110°F.

Average temperature of oil is approximately

$$\frac{60 + 110}{2} = 85\text{°F.}$$

Approximate film temperature,

$$\frac{0.95 \times (212 - 85)}{2} + 85 = 148\text{°F.}$$

Viscosity of fuel oil at 148°F. (Fig. 49) = 25 centipoises

Velocity at heating surface (estimate) is probably less than 0.3 ft. per second (Table 49). Film transfer rate (Fig. 123 extrapolated) is about 12.

The oil is relatively clean or it could not be used as a fuel oil and hence the approximate fouling factors (Fig. 125) are

Steam	1.5
Fuel oil	7.0
Total	8.5

$$H = \frac{1}{\frac{1}{2{,}500} + \frac{1}{12} + 0.0085} = 10.8$$

If the heater is to heat the oil in 1 hr. and the duty is 200,000 B.t.u., the surface is

$$\begin{aligned} \text{Larger difference} &= 212 - 60 = 152 \\ \text{Smaller difference} &= 212 - 110 = 102 \\ \text{log mean temperature difference} &= 125 \end{aligned}$$

$$A = \frac{200{,}000}{10.8 \times 125} = 148 \text{ sq. ft.}$$

With a 40 per cent factor to allow more rapid heating, the surface is 207 sq. ft.

FRICTION LOSSES IN EXCHANGERS

The friction loss through an exchanger is often the governing factor in exchanger design. However, because of the large number of possible arrangements, particularly on the shell-side, the formulation of exact equations is impossible. The loss in pressure on the tube-side can be computed with fair accuracy by the general formulations given in Chap. X but the losses caused by enlargements, contractions, and turns must be included in the calculations.

Short and Stack[6] have studied the pressure losses on the shell-side of a small commercial type of exchanger. Half-moon-type baffles were used. They found that the friction factors could be correlated by Reynolds' criterion (Fig. 47, p. 161) but that the curve was a little lower than that given for copper pipe. However, it is necessary to use a special average velocity and an equivalent diameter. They suggest that u_x, the average velocity, be computed as follows:

$$(u_x)^2 = \frac{(N - 1)Au_1^2}{B} + u_2^2$$

where N = number of baffles.
A = distance between baffles.
B = horizontal length of flow.
u_1 = velocity perpendicular to tubes (ft. per sec.).
u_2 = velocity parallel to tubes (ft. per sec.).

The equivalent diameter D' can be computed by the following empirical formula:

$$D' = \frac{d_t D_s}{N}$$

d_t = O.D. of tubes, in.
D_s = I.D. of shell, in.

By the use of these equations and approximate friction factors from Fig. 47, the friction loss can be computed as follows:

$$\Delta p = \frac{f \rho L u_x^2}{24 g D'} \tag{65}$$

where Δp = lb. per sq. in.
f = friction factor (Fig. 47).
ρ = density of liquid, lb. per cu. ft.
L = length of passage measured along tubes, in.
g = gravity constant, ft. per sec.^{2}

This equation applies to only the one arrangement of baffles, etc., as used in the experiments, but doubtless it can be used with fair accuracy for other arrangements. The foregoing formula does

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[6] *Oil Gas J.*, May 10, 1934, p. 115.

not account for the leakage of oil through the tube holes in the baffle.

The friction losses for liquids flowing on the outside of tubes through a single unit of exchanger may be estimated from the following:

Liquids	Lb. per Sq. In. per Ft. of Direct Travel
Light oils: gasoline, kerosene, and hot gas oil	0.04–0.8
Crude oil, gas oil, light lubes, and hot lubes	0.1 –1.1
Viscous stocks	0.3 –1.6

The range is caused by the different velocities that are used. The low values are for 1 ft. per second and the high for 8 ft. per second.

The pressure-drop through a vapor condenser is often the governing factor in design and especially so for condensers for vacuum systems. The Ross Heater and Manufacturing Company suggest the following formula:[7]

$$\Delta p = \frac{Lu^2}{ks}$$

where Δp = pressure-drop, lb. per sq. in.
L = length of vapor travel, ft.
u = average velocity, ft. per sec.
s = specific volume, ft.^{3} per lb.

The constant k probably has a value of 9,000 to 13,000 depending upon the particular design.

TUBULAR VAPOR COOLERS AND CONDENSERS

Tubular equipment are frequently used to cool superheated vapors and to condense them by exchange with the charging-stock. On one side of the exchanger, usually the tube-side, the rates of heat transfer found in the preceding discussion are valid. On the other or shell-side of the exchanger, a new set of conditions arise. Vapor cooling is a straightforward problem but the condensation of complex vapor mixtures in the presence of steam is indeed a complicated problem.

Structural Design.—Fundamentally the structural design of condensers differs little from the design of simple liquid-to-liquid heat exchangers. However, ample space must be provided on the outside of the tubes so that prohibitive vapor velocities and

[7] Heat Exchangers, *Bull.* 350, 1931.

friction losses will not occur. This problem becomes of prime importance in the design of vacuum condensers. In such designs, the friction loss must not exceed a few millimeters and often the condenser is designed primarily with regard to friction losses. Oil vapors are the highest temperature materials commonly handled in the refinery. In order to avoid unequal expansions, condensers are usually built in several units so that the temperature difference across each unit of exchanger is not large. A temperature difference of 75°F. is considered safe. If the vapor is at a very high temperature, the cooling stock must be heated by other exchangers before it is passed through the vapor condensers. In other words, a large temperature differential between the two stocks cannot be permitted. The vapor is usually admitted to the top of the condenser so that the condensate, which might entrain, is carried toward the liquid line. At the same time the condensate drips or flows over the remaining tubes.

Most manufacturers have developed so-called drip-type condensers embodying the foregoing principles. The advantages claimed for the drip-type condenser are

1. Low pressure-drops.
2. Less entrainment.
3. The condensate leaves at the same temperature as the remaining uncondensed vapor and hence little or no reheating or revaporization of the light-ends occurs.
4. Ideal countercurrent flow is more nearly approached.

Erosion by droplets of liquid and by high vapor velocities requires thicker tubes than those used in exchangers.

Film Conditions during Condensation.—The film conditions are different in all parts of a condenser. For convenience the following zones may be adopted:

1. Cooling oil-vapor, steam, or both.
2. Condensing vapor, cooling vapor, and cooling the condensate.
3. Condensing steam and cooling oil.
4. Cooling oil and water.

These zones all tend to overlap. As an example, condensation starts soon after cooling of the superheated vapors begins; the cooling of vapor, steam, and condensate occurs throughout the condensation of the vapors; and, finally, the last vapor is not condensed until the steam is condensed. However, for design purposes it is necessary to adopt these zones and assign transfer rates to each of them if dependable rates are to be attained. It is apparent that each of the zones has a different mean temperature difference and that under certain conditions the temperature of the cooling medium may tend to be even higher than the temperature of the heating medium on the other side of the tube.

The total heat to be removed is usually computed as heat required (1) to cool vapor and steam, (2) to condense the vapor, (3) to condense steam, and (4) to cool oil and water. These items need not be computed at the actual conditions existing in the condenser because, as mentioned in the chapter on heat and material balances, the total quantity of heat that is removed between the fixed inlet and outlet conditions is a constant, regardless of the intermediate conditions.

However, when the mean temperature difference is computed, the actual temperatures throughout the equipment must be used. In the condensation zone, the temperature may be computed with accuracy by means of the equilibrium condensation curve of the oil vapor, corrected for the total pressure within the condenser and for the partial-pressure effect of the steam. Such a method need not be tedious because the designer soon becomes facile at drawing condensation curves and can often accurately estimate the condensation range without computations. For example, steam condenses in an atmospheric light oil condenser between 205 and 185°F. unless an abnormally large quantity of steam is used. In special problems, such as the design of vacuum condensers or condensers handling large quantities of steam, the labor in drawing the curves, etc., is justified because more simple methods are not dependable.

The vapor usually condenses almost entirely between the inlet temperature and the steam-condensation temperature, but if the vapor is superheated an additional simple cooling zone must be recognized. Even in the cooling zone a small quantity of vapor is condensed because of the wide boiling-range of all petroleum products. In the so-called vapor-condensation zone a cooling of both vapor and liquid-condensate takes place as well as condensation and hence most experimenters have found it necessary to use a combined condensing, vapor-cooling, and condensate-cooling coefficient for the vapor-condensation range. The coefficients given in this chapter are combination coefficients of this kind. The steam-condensation temperature is usually not a constant and its condensation range may be computed by correcting the condensation temperature, at the total pressure, for the partial-pressure effect of the remaining vapors. In the special case in which a very high-boiling vapor is condensed with steam, two distinct zones of condensation may appear and the steam will condense at nearly a constant temperature. Except in special cases the steam may be assumed to condense at a constant temperature of about 195°F. The pressure-drop in ordinary condensers may be neglected in drawing the condensing curves, but in vacuum condensers the pressure-drop becomes of great importance. The following examples will prove valuable in clarifying the computation methods:

Example 65. Transfer Rate for a Pressure Distillate Condenser.—A pressure distillate condenser is to be designed for the following materials:

	Lb. per Hr.
P. D. and reflux (57 A.P.I.)	63,000
Cracked gas (wet)	2,000
Steam	6,000

The materials are available at 305°F. and the vapor is not superheated. The water is available at 72° and it will be heated to 120°F. Pressure at the top of the tower = 10 lb. per sq. in.

Duty of Condenser.

Basis: 1 hr.

Assume cooling to 180°F. condenses all vapor and steam. Assume steam condenses at 195°F. These assumptions can be approximately computed by the methods used in Example 66.

Zone 1: Cooling vapor and steam. No such zone.
Zone 2: Condense vapor between 305 and 195.
Cool steam and vapor to 195.
Cool condensate to 195.

		B.t.u. per Hr.
Cool vapor or condensate	$63{,}000(305 - 195)\frac{0.60 + 0.46^{*}}{2}$	= 3,670,000
Cool gas (Fig. 34)	$2{,}000(305 - 195) \times 0.65^{\dagger}$	= 143,000
Cool steam	$6{,}000(305 - 195) \times 0.5$	= 330,000
Condense vapor (Table 8)	$63{,}000 \times 130$	= 8,200,000
		12,343,000

* Average liquid and vapor specific heat.

† Approximate specific heat.

Zone 3: Condense steam at 195.
Latent heat of steam = 981

$$6{,}000 \times 981 = 5{,}890{,}000 \text{ B.t.u. per hr.}$$

Zone 4: Cool oil, water, and gas.

B.t.u. per Hr.
$63{,}000(195 - 180) \times 0.56 = 529{,}000$
$6{,}000(195 - 180) \times 1.0 = 90{,}000$
$2{,}000(195 - 180) \times 0.6 = 18{,}000$

637,000

The percentage of heat that is absorbed in each zone and the rise in water temperature in each zone, for countercurrent flow, are

Zone	B.t.u.	Per cent	Rise in water temperature (total 48°)
1			
2	12,343,000	65.4	31
3	5,890,000	31.2	15
4	637,000	3.4	2
Total................	18,870,000	100.0	48

The temperatures in the zones are shown in Fig. 126.

Computation of Transfer Rate.—Assume a water velocity of 2 ft. per second in the tubes. This corresponds to a water film rate of 350.

The surface required for each zone can be computed separately and added together, thus:

Zone	Duty	Mean temp. diff.	h_o	h_w	R_f*	H	A	Notes
1. Cooling vapor....	....	...	...	...	.....	..	.....	No such zone
2. Condensing vapor	12,343,000	143	150	350	0.006	64	1,350	Table 50
3. Condensing steam	5,890,000	113	400	350	0.007	81	643	Page 383
4. Cooling liquid....	637,000	114	45	350	0.009	29	192	Page 383
Total...........	18,870,000	...	...	...	.....	..	2,185	

* See Fig. 125. A water factor of 5, and different factors for each of the other conditions.

As a comparison, the over-all transfer rate which corresponds to the four zones is

$$H = \frac{18{,}870{,}000}{2{,}185 \times 144} = 60.0$$

In vacuum condensers the foregoing method (Example 65) becomes more involved. Approximations of the steam-condensing temperature, etc., cannot be relied upon. In most modern vacuum plants a large quantity of steam is used to reduce the vaporization temperature of the oil. This steam passes through the partial condensers and is finally condensed in a barometric condenser. Thus the pressure in the barometric condenser and in the partial condenser is dependent upon the vapor-pressure that is exerted by the cooling water. With cold water and several steam jets, the barometric condenser can be operated at 8 mm. pressure and hence the partial condenser operates at pressures of 10 or 12 mm. or above, depending upon the processing plan. Sometimes these partial condensers are built in several units so that different products, such as gas oil and wax distillate, may be collected from the different units. A poor separation is permissible in this case because wax distillate can be more easily filter-pressed if it contains some gas oil.

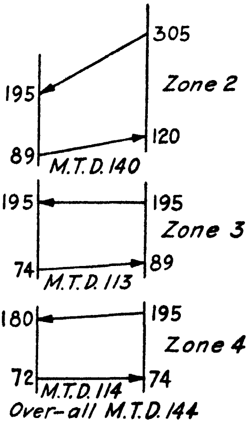

FIG. 126.—Temperature conditions for Example 65.

If the condensation is conducted in several units or steps, with the condensate removed separately from each partial condenser, each unit may be handled as a separate condenser. For example, if wax distillate and gas oil are separated in a partial condenser, the vapors of wax distillate and gas oil are cooled in the first unit and condensation occurs along the equilibrium condensation curve of these mixed vapors. The wax distillate is withdrawn from this unit, and the remaining gas oil vapor is condensed according to the equilibrium condensation curve of the gas oil vapor alone (Figs. 127 and 128).

The condensing coefficients are lowered greatly by vacuum. The exact values are not known but it is customary practice to decrease the atmospheric condensation coefficients by half.

Example 66. Design of Vacuum Surface Condenser.—A large vacuum condenser is to handle the following materials per hour:

106,000 lb. of wax distillate and reflux, 31 A.P.I.
12,000 lb. of gas oil, 33 A.P.I.
1,400 lb. of steam

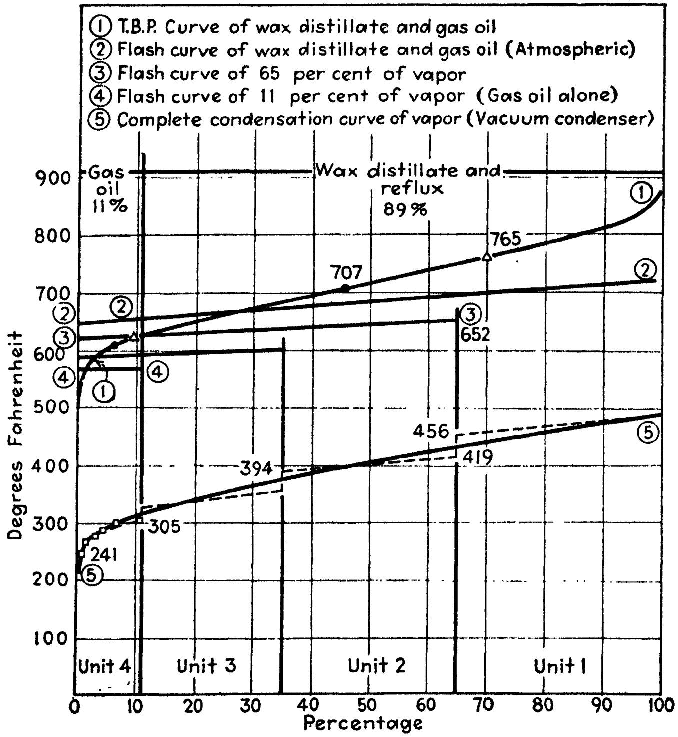

Fig. 127.—Condensation temperatures in vacuum condenser. Refer to Example 66.

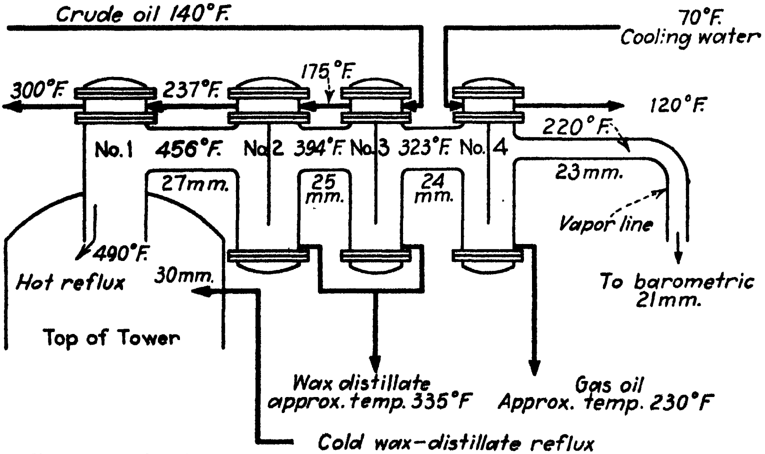

Fig. 128.—Condenser arrangement for Example 66. (See also Fig. 127.)

The wax distillate and gas oil are to be separated by partial condensation in four units of condenser. Three of these are for wax distillate and one for gas oil. The first of the three wax distillate condensers supplies hot reflux to the tower but cold reflux is also used.

The following pressures are assumed for purposes of calculation. In an actual design, the accuracy of the assumed pressures should be checked after the tentative design is completed.

	Mm. of Mercury
Pressure at barometric	21
Loss in vapor line	2
Loss in Unit 4	1
Loss in Unit 3	1
Loss in Unit 2	2
Loss in Unit 1	3
Pressure at top of tower	30
Temperature at top of tower	490°F.

The approximate condensation and true-boiling-point distillation curves of the products are shown in Fig. 127 and a diagram of the system is shown in Fig. 128.

Condensation Curves under Vacuum. *Partial Condenser* 1 (*hot reflux condenser*).—The conditions are such that equilibrium condensation (page 241) occurs in all four of the condensers. The condensation curves are computed by means of Fig. 76.

70 per cent point of T.B.P. curve	765°F.
10 per cent point of T.B.P. curve	620°F.
Slope of T.B.P. curve	$^{145}/_{60}$ = 2.42° per per cent.
Corresponding slope of flash curve	0.8 (Fig. 76)
50 per cent point on T.B.P. curve	718°F.
Corresponding 50 per cent point on flash curve	684°F.

100 per cent point on flash curve = 684 + 0.8(100 − 50) = 724°F.

The curve is drawn through the 50 and 100 per cent points.

The data given in curves 1 and 2 (Fig. 127) apply to condensation at atmospheric pressure and hence curve 5 for vacuum conditions must be computed.

The total pressure at the inlet to Condenser 1 is 30 mm. but at the end it is (30 − 3) or 27 mm. Furthermore, steam is present and it further reduces the partial-pressure of the oil vapor and decreases the temperature of condensation.

$$\begin{array}{llr}
\text{Mols W.D.} & = \dfrac{106{,}000}{320} = & 331.0 \\
\text{Mols gas oil} & = \dfrac{12{,}000}{242} = & 49.6 \\
\text{Mols vapor} & = & \overline{381.0} \\
\text{Mols steam} & = \dfrac{1{,}400}{18} = & 78.0 \\
\text{Total mols} & = & \overline{459.0}
\end{array}$$

$$\text{Partial-pressure} = 30 \times {}^{381}/_{459} = 24.9 \text{ mm.}$$

The atmospheric initial-condensation temperature (724°F.) corrected to 24.9 mm. (Fig. 45, page 127) gives a temperature of 492°F.

Temperature at the Outlet of Unit 1.

About 122 mols of hot reflux are condensed in Unit 1 so that at the outlet the partial-pressure is

$$27 \times \frac{381 - 122}{459 - 122} = 20.8 \text{ mm.}$$

Correcting 696°F. to 20.8 mm. gives an outlet temperature of 456°F. These temperatures are shown on Figs. 127 and 128.

Partial Condenser Unit 2.—The atmospheric condensation curve for the remaining 65 per cent of vapor is computed in a manner similar to the method used for Unit 1. This curve is shown as 3 (Fig. 127). As the condensate is removed from Unit 1, the vapor must be cooled in Unit 2 before condensation starts. Note curve 5 (Fig. 127) and particularly the two points at 65 per cent. In practice, no sharp break in the temperature is noted because pure countercurrent flow is not attained and perfect equilibrium condensation does not occur.

Furthermore, it would appear in Fig. 127 that the hot reflux boils between exactly 753 and 890°F. Actually, the wax distillate and the hot reflux have different boiling-ranges but much the same composition because of the very poor separation obtained by partial condensation.

70 per cent B.P. of 65 per cent of remaining vapor	707°F.
10 per cent B.P. of 65 per cent of remaining vapor	607°F.
Slope of distillation curve	1.67.
Slope of vaporization curve	0.35
50 per cent on distillation curve	677°F.
50 per cent on vaporization curve	635°F.
100 per cent point on vaporization curve	652°F.

Note curve 3 (Fig. 127).

Partial-pressure at inlet to Unit 2 is the same as for the outlet of Unit 1 or 20.8 mm. Correcting 652 to 20.8 mm. gives 419°F.

About 130 mols are condensed in Unit 2 so that the partial-pressure at the outlet of 2 is

$$25 \times {}^{129}\!/_{207} = 15.5 \text{ mm.}$$

Correcting 635° to 15.5 mm. gives 394°F. Partial condenser Unit 3 was computed in a similar manner.

Partial Condenser Unit 4.—By the time Unit 4 is reached, the amount of noncondensible gases (steam) has become relatively so large that a more detailed analysis is necessary. The following tabulation was computed (curve 4, Fig. 127) by using the same general principles that were used in studying Units 1 and 2.

The pressure-drop is very small (1 mm.) and hence a constant pressure of 23.5 mm. was used throughout the entire unit. Likewise the flash curve 4 is so flat that a temperature of 563° was used to represent the entire curve.

Per cent vapor remaining	Mols not condensed (approx.)	Partial-pressure	Condensation points
11.0	50	8.6	305
7.5	33	6.5	296
5.0	22	4.8	283
3.5	16	3.8	274
1.5	11	2.7	264
1.0	6	1.4	241

The sharply curving tail on the front of the condensation curve shows that all of the vapor can never be completely condensed until the steam is condensed. Refiners find that the water leg of the barometric condenser always contains oil and wax stocks, and traps or skimming devices must be installed.

Thermal Duties of the Units. *Unit* 1 (47,000 *Lb. Condensed*).—Condensing zone throughout

		B.t.u. per Hr.
Cool vapor........	$71{,}000(490 - 456) \times 0.56$	= 1,350,000
Cool steam........	$1{,}400(490 - 456) \times 0.5$	= 238,000
Cool.......	$47{,}000(490 - 456)\left(\frac{0.68 + 0.55}{2}\right)$	= 983,000
Condense..........	$47{,}000 \times 101$ (Table 8)	= 4,750,000
		7,321,000

For the other units the duties are about as follows

Condenser unit	Lb. condensed	Temperature range	Approx. duties, B.t.u. per hr.
1	47,000	490–456	7,321,000
2	39,000	456–394	7,213,000
3	20,000	394–323	4,058,000
4	12,000	323–220	2,856,000
Total................	......	....	21,448,000

Transfer Rates, Surfaces, and Temperature Differences.—Crude oil is heated from 140 to 300°F. in the first three units, and water is heated from 70 to 120°F. in the fourth unit. The crude oil velocity is 3 ft. per second, and the water 2 ft. per second. The temperature ranges are shown in Fig. 129. One-inch tubes are used throughout.

The transfer rates are considered as two items, one pure condensing and the other cooling of vapors. Table 52 shows the completed calculations.

Note that the logarithmic mean temperature difference gives confusing results if it is used for the three units together. Its use in this manner shows an over-all rate of heat transfer (11.4) which is lower than the transfer rates in any of the three units.

TABLE 52.—COMPUTATIONS FOR SURFACES IN EXAMPLE 66

Unit No.	Duty	Mean temp. diff. (logarithmic)	Mass velocity† (approx.)	h_o	h_{tubes}	R_f	H	A
1. Condensing	5,733,000	204	...	23‡	160	0.013	15.9	1,760
Vapor cooling*	1,588,000	204	1.0	11	160	0.013	9.0	865
Over-all	7,321,000	204	...	...	...	.....	13.6	2,625
2. Condensing	5,730,000	219	...	25‡	130	0.013	16.5	1,580
Vapor cooling*	1,483,000	219	0.8	10	130	0.013	9.0	752
Over-all	7,213,000	219	...	...	...	.....	14.1	2,332
3. Condensing	3,136,000	196	...	27‡	85	0.012	16.2	990
Vapor cooling*	922,000	196	0.5	7	85	0.012	6.1	770
Over-all	4,058,000	196	...	...	...	.....	11.8	1,760
1, 2, and 3, over-all	18,592,000	243	...	...	...	.....	11.4	6,717
4. Condensing	2,135,000	187	...	28‡	400	0.011	20.2	565
Vapor cooling*	721,000	187	0.2	3	400	0.011	2.9	1,330
Over-all	2,856,000	187	...	...	...	.....	8.0	1,895

* Some liquid cooling also included.

† Dependent on velocity on shell-side.

‡ Condensing coefficients are halved for vacuum service.

COIL-IN-BOX CONDENSERS AND COOLERS

In the past, these equipments have been standard and even today they are used extensively for final cooling before storage. Heat transfer rates are low in this type of equipment owing (1) to the low velocities that must be used and the low natural-convection rate and (2) to the gradual accumulation of pipe scale and fouled surfaces on the water side. Special cast-iron condenser sections with ribbed outside surfaces, such as the Stirling section of the American Radiator Company, are sometimes used. The main advantage of this condenser section is the large vapor space afforded and the compact arrangement that is possible. To allow for the rapid decrease in vapor volume, coil-in-box condenser coils are usually built as a series of large-diameter pipes connected in parallel to a header, and smaller pipe sizes are used on each of the parallel branches in the liquid cooling zone. For simple cooling, the coils are usually connected in series throughout the entire cooler. The usual inlet vapor velocity is approximately 50 ft. per second and the outlet liquid velocity is between 0.5 and 2.0 ft. per second. The higher liquid velocity is used for light materials such as gasoline and the 0.5 velocity for cold tar, wax distillate, etc. In best practice the coils are built in pairs with about 15 in. between pairs to facilitate cleaning and repairs. Using flanged pipe facilitates the removal of pipe but the coils are not so compact. The Griscom Russell Company manufactures a "bent-tube" section for coil-in-box service or for cooling by means of water sprays in a cooling tower. These sections consist of two headers with a large number of small tubes between them. The tubes are bowed slightly during manufacture so that by expansion and contraction the accumulation of scale, etc., on the outside of the tubes will be dislodged. For certain scales, the bent-tube section functions properly but for others the tubes must be cleaned by the usual hand methods.

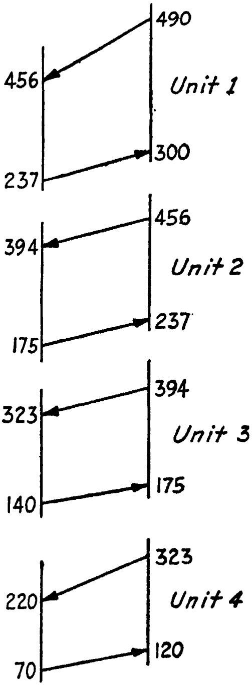

Fig. 129.—Temperatures for Example 66.

Coils of standard or extra-heavy steel pipe with double-extra-heavy malleable fittings are used for normal conditions. For hard water, many refiners require the use of genuine wrought-iron pipe. Best practice for long service requires the use of Classes B and C flanged cast-iron pipe with Class D fittings.

The transfer rate inside normal-size pipe cannot be given as for tubular equipments because fouling factors are not available.

Owing to the many variables in the design and use of coil-in-box equipment and particularly the wide range of velocity and surface conditions, the rates are not so consistent as for tubular equipment. For natural convection on the outside of pipe coils, the film rates given in Table 49 are suggested but they must be used with large fouling factors.

Over-all Transfer Rates for Estimating Purposes.—Although the use of over-all rates is not recommended, at times the engineer has reason to make very approximate estimations of surfaces, etc.

TABLE 53.—APPROXIMATE OVER-ALL RATES OF HEAT TRANSFER

Duty	Authority number					Ave.
	1	2	3	4	5	
Coil-in-box equipment:						
Vapor cooling	..	.....	7	..	..	7
Condensing and cooling naphtha	15	20	11	18	32	19
Cooling naphtha	..	.....	..	18	20	19
Cooling kerosene and gas oil	15	15–18	..	16	17	16
Cooling wax distillate	..	.....	..	12	14	13
Cooling lubes	..	.....	..	14	11	12
Cooling tars, bottoms, etc	12	13	..	10	7	10
Condensing kerosene	..	.....	23	..	26	24
Condensing gas oil	..	.....	27	24	23	25
Condensing fuel oil and lubes	..	.....	36	..	18	27
Tubular equipment:						
Condensing naphtha:						
Water	52	39	55	48	62	51
Oil	26	25	..	37	27	29
Condensing kerosene:						
Water	..	.....	65	31	48	48
Oil	..	.....	..	25	24	24
Cooling naphtha:						
Water	..	.....	..	47	54	50
Oil	..	.....	..	..	20	20
Cooling kerosene and gas oil:						
Water	40	45	..	28	36	37
Oil	20	.....	..	28	18	22
Cooling wax distillate:						
Water	25	25	..	14	32	24
Oil	..	.....	..	27	16	22
Cooling fuel oils and lubes:						
Water	..	.....	..	..	19	19
Oil	..	.....	..	12	9	10

Table 53 is a tabulation of over-all rates which were obtained from various authorities in refinery positions and with engineering companies. The discrepancies in the values indicate clearly the difficulties involved in attempting to use over-all rates and why the use of over-all rates is being abandoned.

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CHAPTER XX

TUBESTILL HEATERS

When pipestills or tubestills were first built, the important part that radiation plays in any furnace type of heater was not appreciated and the first stills were nearly pure convection types of stills (Fig. 130*f*). In such stills the tubes nearest to the flame absorb heat at a very high rate and the tubes nearest the stack absorb very little heat. Such an arrangement was unsatisfactory because coke was deposited in the tubes that were heated by radiation and the final tubes absorbed so little heat that the efficiency was low. By costly experience it was found that, when the offending radiant tubes (hot ones) were removed, the other tubes began to overheat and the removal of tubes in the radiant section only aggravated the condition. When designers finally realized that a large proportion of the pipestill surface should be in the radiant section, the pipestill was developed into the useful type of heating equipment that it now is.

Advantages of the pipestill over shellstill equipment are

1. They are unquestionably best suited for continuous operation. From the standpoint of operation, a continuous process is usually the most economical because the operating conditions such as temperature, pressure, and rate of flow can be easily controlled and studied. Continuous operation was also an important factor in the development of such obviously useful operations and equipment as flash vaporization, heat-exchange, multiple-draw fractionating towers, exact control instruments, etc. Without continuous heating, these operations could never have been developed into the position of importance that they now occupy.

2. The pipestill adapts itself to any sort of a heating operation because the rate of heating can be easily controlled. The rate of heat input can be controlled by adjusting the relative proportion of radiant and convection surface, by the use of a recirculating quantity of flue gas, by preheating the air, by changing the fuel

or character of the flame, and last, by varying the velocity within the tubes.

3. The average rate of heat transfer can be increased without overheating the oil stock. This permits the thermal efficiency of the pipestill to be relatively high. Thus far, economic conditions have limited the economic thermal efficiency to about 75 per cent but many stills have been built that operate at an efficiency of 85 per cent.

In a shellstill, local overheating occurs near the bottom of the still. Oil is decomposed, which causes a loss of yield, and the bottom plates are frequently weakened so that they must be replaced.

4. Pipestill operation is flexible. A still designed to operate at 75 per cent efficiency can, at a low capacity, operate at 80 per cent efficiency and at a high capacity at about 70 per cent efficiency. The capacity can often range between 50 and 200 per cent of the rated capacity without causing serious deleterious effects. During the development of pipestills, the redistillation operations that are necessary for such stocks as pressure distillate, kerosene, special naphthas, brightstock solution, pressed distillate, and "slops" were conducted in shellstills. Perhaps this was due, at least in part, to the existence of shellstills in the plant. At any rate, refiners are now installing pipestill units for any or all of these rerunning operations. In some small plants the raw stocks are allowed to accumulate for several weeks and then are redistilled in a pipestill unit in a few days of operation. Thus a single pipestill unit may be used to process several stocks.

5. Pipestill heaters greatly reduce the danger of fire. Although fires are perhaps more frequent with pipestills than with shellstills, the fires are not of such a dangerous nature. In normal-size pipestills the quantity of oil that is present in the still at any time amounts to only about 60 bbl. and most of this may be discharged into a sump and extinguished with steam. At the same time the furnace interior and header boxes can be filled with steam so that little oil burns. Several hundred barrels of oil may be present in a shellstill when a fire occurs and the possibility of an explosion or the escape of flaming oil into the refinery yard and drains is indeed serious.

6. The compact nature of a pipestill distillation equipment should not be overlooked. A pipestill unit for processing

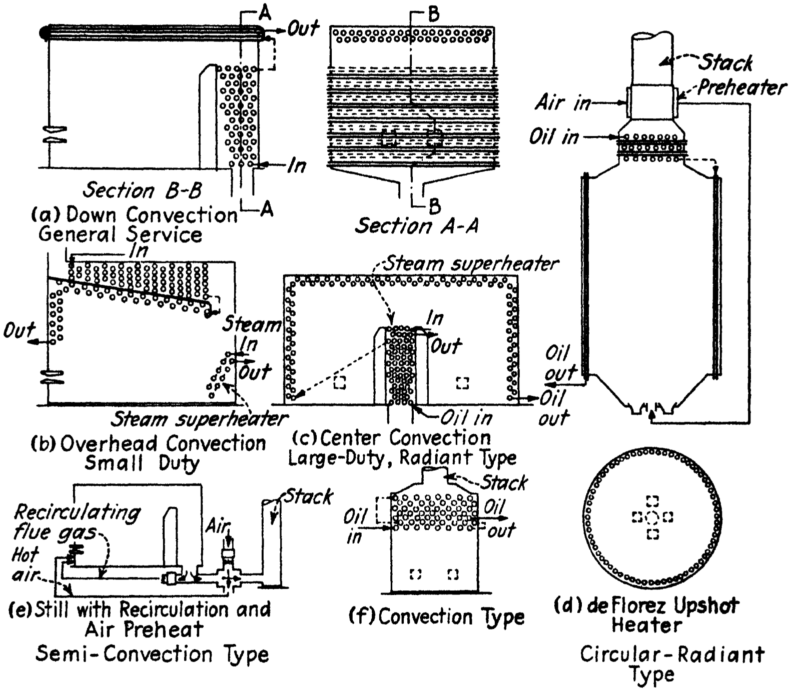
10,000 bbl. per day can be installed within a 50 by 50 yd. area. Such a unit will replace a battery of at least 12 shellstills. However, the saving in space and personnel is not the main advantage of a compact unit. The operation can be more easily supervised, the stillman will give more attention to details if distances are not great, and records can be taken with ease. The entire operating data may be recorded in a single control room and the responsibility for operation may thus be placed on one man.

Indirectly, the pipestill is largely responsible for the development of modern vacuum distillation plants. The modern vacuum processes could not have been developed without the combined advantages of controlled heating and flash vaporization.

Types of Stills.—All modern pipestills are built with two distinct heating sections: a radiant section and a convection section. Figure 130 indicates diagrammatically the flow in several types of heaters.

The type shown in Fig. 130*a* has been for many years the standard design. The still is usually less expensive than the other types but it is being displaced by the other types because the radiant roof tubes above the partition wall tend to become overheated. Furthermore, a large percentage of radiant-absorption surface cannot be provided unless the still is very wide and such a design proves to be expensive. In this type, usually about 40 per cent of the heat is absorbed in the radiant section and 30 per cent in the convection section. Figure 130*b* shows a type that is particularly adapted to processing small amounts of oil. The radiant and convection sections are separated by metal partition plates, with insulating material between them. This partition rests on the tubes, thereby eliminating an expensive suspended refractory arch. The distribution of radiation is poor but this causes no difficulty in the heating of normal stocks.

The center-convection-type radiant heater that is shown in Fig. 130*c* provides a large percentage of radiant surface and is adapted to the processing of large quantities. The distribution of radiation in the furnace box is excellent but not so good as in the cylindrical heater shown in Fig. 130*d*. In the center-convection still, enough radiant surface can be provided, without undue expense, to absorb 65 per cent of the total heat liberation as radiant heat. The radiant-absorption rate in this type of still can be reduced by using a large amount of radiant surface until it compares with the rates that are obtained in flue-gas recirculation furnaces. The heater shown in Fig. 130*d*, from a theoretical standpoint, is an ideal heater but it is expensive. A tall superstructure is necessary for the removal of tubes. At the same time the vertical position of the still makes it act partly as a stack and hence only a short stack is necessary. This type is particularly suited for vapor-phase cracking although it is equally successful in ordinary processing. In the case of vapor-phase cracking, the cost of such a still is justified because, to the author's knowledge, no petroleum oil heating problem is more delicate than the heating of petroleum vapor at decomposition temperatures. In this type, as high as 70 per cent of the heat liberation may be absorbed in the radiant section.



(*a*) Down Convection General Service

(*b*) Overhead Convection Small Duty

(*c*) Center Convection Large-Duty, Radiant Type

(*d*) deFlorez Upshot Heater Circular-Radiant Type

(*e*) Still with Recirculation and Air Preheat Semi-Convection Type

(*f*) Convection Type

FIG. 130.—General types of pipestill construction.

The principles of flue-gas recirculation and air preheating as indicated in Fig. 130*e* may be applied, with modifications, to any of the foregoing types. A portion of the flue gas is circulated back into the radiant section by a fan. Here the flue gas is reheated by the flame causing a lower flame temperature and a milder radiation rate, and at the same time the high gas velocity increases the rate in the convection section. The greater the ratio of recirculating flue gas to the flue gas entering the stack, the more the heat-duty is transferred from the radiant to the convection section. Recirculation allows a precise regulation of the absorption rate, and until the development of radiant-type stills the recirculating type was used for nearly all cracking processes or delicate heating operations because of the low radiant rates.

FIG. 131.—Overhead-convection still (header-boxes open). (*A. J. Smith Engineering Company.*)

Preheating the air that is used in combustion has just the reverse effect. It tends to increase the absorption rate in the radiant section and to increase the flame temperature. To be most effective, the air should be heated by only the gases that are passing to the stack. To store too much heat in the air, as by cooling the entire recirculating stream of gases, would defeat the purpose of flue-gas recirculation. Nevertheless, air preheat provides a means of cooling the stack gases and thereby increase the efficiency of the still.

The efficiency of a process can be increased in only two ways. The loss through the walls and in the stack gas from the furnace can be decreased or heat can be saved from the products of the process. The use of air-cooled walls, aside from the preservation of brickwork, has often been referred to as an economy. Unless the loss through the walls is decreased, no economy is effected.

The heat that is absorbed by heat exchangers is often credited as a direct saving in heat. Such is not always the case because the efficiency of the still decreases as the temperature of the charge-stock is increased by exchangers. As an example, consider a pipestill distillation unit which operates with no exchangers and at a stack gas temperature of 350°F. The stack loss is only about 8.4 per cent (Fig. 57). If the charge-stock is then heated by exchangers to 300°F., the stack temperature will be about 550°F. and the stack loss 14 per cent. In such a case, the saving of heat by raising the temperature of the charge-stock from 100 to 300° must more than compensate for the decrease in the efficiency of the still. The exchangers do save heat, but they cannot be accredited with saving the amount of heat that is represented by the rise in temperature from 100 to 300°. A study of the economics of the complete unit, including both the pipestill and the exchangers, is the only way to determine the amount of heat that is actually saved.

RADIATION

The problem of evaluating the percentage of radiant absorption that will occur in a particular pipestill, and the distribution of this radiation throughout the furnace cavity, has always been difficult. However, in the last nine years, owing primarily to the efforts of Professor Wohlenberg[1,2,3] of Yale and Professor Hottel[4,5,6,7] of the Massachusetts Institute of Technology, a

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[1] WOHLENBERG and MORROW, Radiation in the Pulverized Fuel Furnace, *Trans. A.S.M.E.*, **47**, 127 (1925).

[2] WOHLENBERG and LINDSETH, The Influence of Radiation on Boiler Surface and a Simplified Method for Its Calculation, *Trans. A.S.M.E.*, **48**, 849 (1926).

[3] WOHLENBERG, W. J., *Mech. Eng.*, **52**, 853 and 915 (1930).

[4] HOTTEL, H. C., Heat Transfer by Radiation from Non-Luminous Flames, *Ind. Eng. Chem.*, 19, 888 (1927).

[5] HOTTEL, H. C., Radiant Heat Transmission, *Mech. Eng.*, **52**, 699 (1930).

[6] HASLAM and HOTTEL, Combustion and Heat Transfer, *Trans. A.S.M.E.*, **50**, *Fuel Steam Power Division*, p. 9 (1928).

[7] HOTTEL, H. C., Radiant Heat Transmission between Surfaces Sepa-

comprehensive theoretical background has been developed. By this background the existing empirical data can be explained with gratifying success and theoretical treatments are so sound that plant data can be checked closely if the data are sufficiently extensive. Still more recently work by Wilson, Lobo, and Hottel[8] has placed at our command a correlation of a number of plant experiments on radiation.

Physical Nature of Radiation.—Radiation may be considered as an outlet for the chemical energy that is set free during combustion reactions. The heat energy that is liberated during combustion is confined in such a small space at the start of combustion that either a very high temperature is attained or heat must be dissipated to the surroundings by radiation, convection, or conduction. No doubt heat is initially used in heating the reactant materials to the flame temperature by conduction. However, if all of the heat were utilized in this manner, the theoretical flame temperature would be attained and experience teaches that this temperature is never reached in ordinary combustion reactions.

The two gaseous materials that are most active in producing radiation are carbon dioxide and water vapor. Most of the radiation from nonluminous flames has wave lengths corresponding to the wave lengths that are emitted by these two molecules. Radiation from luminous flames differs from nonluminous because finely dispersed carbon or solid particles are present in the flame. These particles absorb heat by conduction and convection, and are even more effective than gaseous molecules in radiating energy. The difference in the actual flame temperature and the theoretical flame temperature is a direct comparison of the radiant properties of a fuel.

Radiant-absorption Rate.—Radiation between solid surfaces is dependent upon the fourth power of the temperature difference and upon a constant, the value of which is dependent on the kind of material and the condition of the surface. Radiation from a flame, as in pipestill or boiler furnaces, is governed by the same laws

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rated by Non-absorbing Media, *Trans. A.S.M.E.*, **53**, *Fuel Steam Power Division*, p. 265 (1931).

[8] Heat Transmission in Radiant Sections of Tube Stills, *Ind. Eng. Chem.*, **24**, 486 (1932).

except that the size of the flame and the conditions within the flame are so difficult to evaluate that empirical relationships have been adopted. The most important factors that affect radiation from flames are (1) percentage of total heat that is absorbed as radiant heat, (2) ratio of air to fuel, (3) arrangement and spacing of absorbing surface, and (4) kind of fuel.

Regarding the first of these, let us consider a flame burning within a furnace whose walls consist entirely of absorbing surface. Rays of radiation proceed in all directions from the flame and, with the exception of the small amount of heat that is used in heating the intervening gas, all the heat from the flame is absorbed by the cool surface. In this case, a *large percentage* of the heat is transferred by radiation, although the rate of heat absorption per square foot of surface is low. If all the absorbing surface, except a single tube, is removed from such a furnace, the radiation strikes the refractory walls and is reflected or reradiated about the furnace interior so that the single tube receives a relatively larger amount of radiation per unit of surface. Although the single tube absorbs heat at a high rate, it absorbs a relatively small percentage of the total heat liberation.

The ratio of air to fuel is important mainly because it affects the flame temperature. The larger the quantity of air (or products of combustion) that must be heated in the flame, the lower will be the resultant flame temperature. Thus large quantities of excess air reduce the radiant absorption. For the same reason the recirculation of flue gas reduces the flame temperature, but air preheat increases it. Obviously the higher the flame temperature, the greater the emission of radiation. The arrangement of the cooling surfaces also affects the rate of radiant absorption. The closer the surface is to the flame, the greater the amount of radiation that falls upon it. Thus corners and ends of furnaces receive less radiation than other surfaces.

These factors have been related by Wilson, Lobo, and Hottel[8] by the following equation:

$$R = \frac{1}{1 + \frac{G\sqrt{\frac{Q}{aA}}}{4{,}200}} \tag{66}$$

where R = fraction of heat liberation (above 60°F.) that is absorbed by the cold surfaces in the combustion chamber.

G = air-fuel ratio, lb. of air per lb. of fuel. For flue-gas recirculation: lb. of air and recirculated gases per lb. of fuel.

Q = total net heating value of fuel plus any heat (above 60°F.) added otherwise, B.t.u. per hr.

A = area of plane replacing tubes, sq. ft. (projected area).

a = a factor by which A is multiplied to obtain the effective cool surface. Usually 0.98 (Fig. 132).

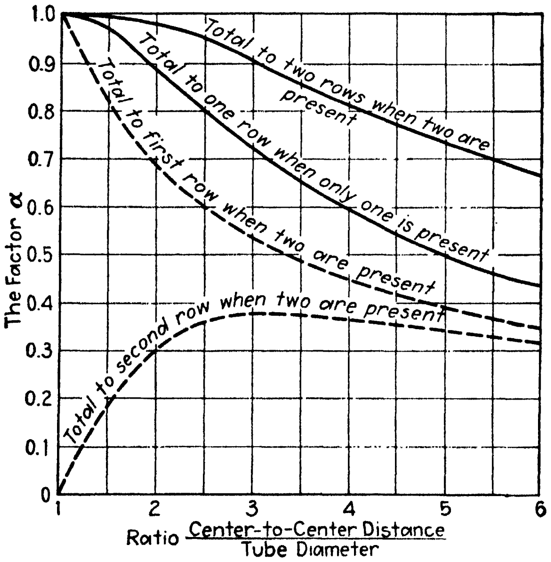

Fig. 132.—Distribution of radiation with regard to arrangement of tubes. (*Hottel, Mechanical Engineering.*)

This equation applies to any conventional box-type furnace with radiant tubes any number of rows deep, with or without air preheat, with or without flue-gas recirculation, and with any percentage of excess air. The factor a may be obtained from Fig. 132,[9] but for normal tube arrangements, such as two rows of tubes spaced at a center to center of about twice the tube diameter, the value of a is 0.98. The relative absorption rates in the

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[9] Hottel, H. C., *Mech. Eng.*, **52**, 699 (1930).

first three rows of tubes, when only three are present, is approximately 7:3:1 so that the third row is of little value.

A study of this equation for the effect of the type of fuel is useful. Table 54 is based on the fuel analyses and data given in Chap. XI. The radiant-absorption factors and rates of absorption per square foot of projected area are computed for 30 per cent excess air when 50,000 B.t.u. are liberated for each square foot of projected tube surface. Thus the common refinery fuels do not give largely different rates of radiation. However, gas flames give a slightly milder rate of heating.

TABLE 54.—COMPARISON OF RADIATION PROPERTIES OF REFINERY FUELS

Fuel	Heating value		Lb. flue gas per lb. fuel	Fraction absorbed by radiant section	B.t.u. absorbed per sq. ft. (proj.)
	Gross	Net			
1. Pure methane	1,009	909	23.5	0.443	22,100
2. Dry natural gas	1,160	1,051	23.2	0.445	22,200
3. Wet cracked gas	2,058	1,893	22.0	0.462	23,200
4. Wet natural gas	1,360	1,239	21.0	0.482	24,100
5. 24.4 A.P.I. Ky. topped crude	19,358	18,168	19.7	0.485	24,250
6. 9.2 A.P.I. cracked tar (M.C.)	18,274	17,324	18.8	0.497	24,850
7. 7.6 A.P.I. resid. fuel oil (Calif.)	17,970	17,075	18.4	0.502	25,100
8. Bituminous coal (Mo.)	13,533	13,098	13.6	0.578	28,900*

* Of questionable value because Eq. (66) is not for solid fuels.

The effect of the percentage of excess air is indicated in Fig. 133. The radiation rates for the two extreme fuels, *i.e.*, dry natural gas and heavy fuel oil, are shown for 0, 25, 50, and 100 per cent excess air. Other fuels can be represented by lines between these two extremes. Table 54 will be useful in judging the approximate position of these lines. This chart may be used directly in the design of simple furnaces but it should not be used for furnaces using air preheat or flue-gas recirculation. With proper burners and experienced fireman, it is possible to fire with less than 25 per cent excess air. In the past, many furnaces have been operated with 100 or even 200 per cent excess air because the still was originally designed with too little radiant surface with the result that the absorption rate was too high.

If a low rate of absorption is not necessary, but gas is available and must be burned, a mixture of oil and gas may be fired together. The luminosity or radiating power of such flames appears to be almost as good as for pure oil flames. Hence for such mixed flames the curves in Fig. 133 for oil flames may be used. The radiating power of these mixed flames may be explained by considering the carbon particles in an oil flame as radiators. These particles also exist in the mixed flame. The heat generated in burning the gas heats the carbon particles by conduction and they in turn radiate heat to the surroundings.

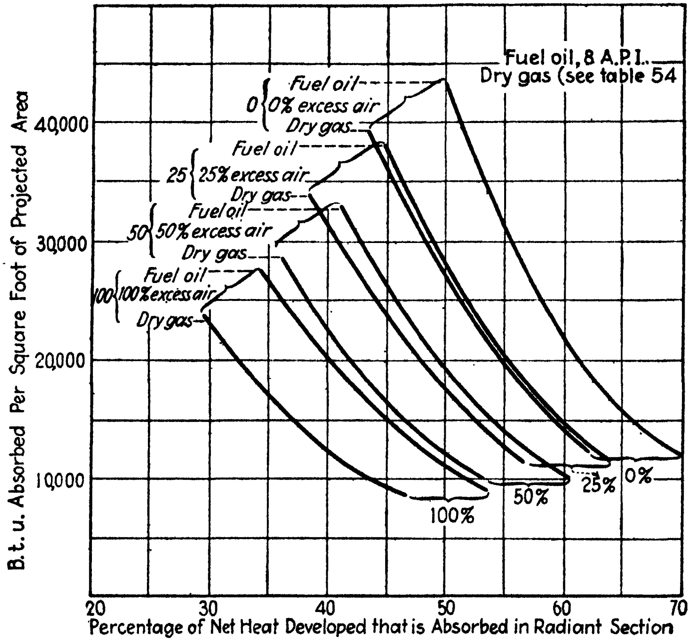

FIG. 133.—Rate of radiant absorption in simple stills with no recirculation or air preheat.

Various types of elaborate burner systems for the production of more radiation and a better distribution of heat in the combustion chamber have been suggested. Some of these consist of a furnace floor of small gas jets and, although they perform well, they are expensive. A successful artificial-radiation device is the muffle burner of the Alcorn Combustion Company. In this burner the gas fuel is fired through a long muffle which may extend along the entire length of the floor of the still. The muffle becomes hot and acts as a radiator, and the flame which issues from the end of the muffle also contributes to the radiation.

Example 67. Rate of Absorption in the Radiant Section.—A pipestill uses 500 lb. per hour of an oil fuel (net heating value 17,500). The radiant section has 156 sq. ft. of projected area and the tubes (4 in., outside diameter) are spaced at a center-to-center distance of 8 in. There are two rows of tubes in the radiant section. The ratio of air to fuel is 17.9 (30 per cent excess air). What percentage of the heat liberation is absorbed in the radiant section and how many B.t.u. are absorbed per hour through each square foot of projected tube area?

$$Q = 500 \times 17{,}500 = \text{heat liberation} = 8{,}750{,}000$$
$$a = 0.98 \text{ (Fig. 132)}$$
$$R = \frac{1}{1 + \dfrac{17.9\sqrt{8{,}750{,}000/0.98 \times 156}}{4{,}200}} = \frac{1}{1 + \dfrac{17.9 \times 240}{4{,}200}} = \frac{1}{2.02} = 0.495$$

Heat absorbed in radiant section $= 8{,}750{,}000 \times 0.495 = 4{,}330{,}000$

B.t.u. absorbed per sq. ft. of projected area $= \dfrac{4{,}330{,}000}{156} = 27{,}700$ per hr.

The results may be checked by the use of Fig. 133. Reading up from 49.5 on the base to the 30 per cent excess air line for an oil fuel, the rate of absorption is estimated as 27,000 B.t.u.

Commercial Radiant Rates.—The radiation rates that should be used in pipestills cannot be given as definite figures because of the many factors which appear in commercial operation. Among these are the wide variety of stocks, the variation in the liquid velocity, and the different temperatures that are used for the different stocks. However, Table 55 presents rates that have been used in commercial plants. Doubtless many stills deviate from the recommendations in the table.

Distribution of Radiant Heat.—In designing the details of a pipestill or in designing a still for a special service, a knowledge of the distribution of radiation in different parts of the radiant section is important. Usually only two rows of radiant tubes are used in the radiant section. If three tubes are used, the third row receives only about 12 per cent as much heat as the first row and hence a third row is of little value. Several stills have been built with only one row of tubes.

The first rows of tubes in the convection section also absorb heat by radiation from the flame as well as heat by convection. The radiation into the convection section, if the tubes are not screened by superheater tubes or by brickwork, is about as follows: first row, 100 per cent; second row, 56 per cent; third row, 19 per cent; fourth row, 4 per cent; and fifth row, 1.5 per cent.

TABLE 55.—RADIATION RATES

Service	Radiant absorption rate, B.t.u. per sq. ft. projected area	Radiation factor (25 per cent excess air). No preheat or recirculation	Usual oil velocity, ft. per sec. at 60°F.	Radiant absorption rate, B.t.u. per sq. ft. outside surface*
Topping crude oil	31,000	0.48	3	9860
Reduced crude, vacuum	25,500	0.51	4	8110
Cracking (outlet in convection)	25,500	0.51	5	8110
Rerunning pressure distillate	25,500	0.51	4	8110
Cracking (outlet in radiant)	17,000–10,000	0.57–0.66	6	5410–3800
Rerunning lubricating oils:				
a. Light oils (pressed dist.)	20,000	0.55	5	6370
b. Heavy oils (bright-stock sol.)	17,000	0.57	7	5410

* Rate on projected area divided by 3.1416.

The first convection tubes must withstand a more severe rate of heat absorption than any other tubes in the still. Not only do these tubes absorb more heat by convection than any other tubes in the convection section but they also receive heat by radiation. Often the first row of convection tubes absorbs 18,000 B.t.u. per square foot of outside surface (11,000 B.t.u. by radiation and 7,000 by convection). This is a rate far higher than those suggested in Table 55. For this reason the first rows of the convection section are often designed with the same diameter as the radiant tubes or, in other words, for a high oil velocity. Steam superheater tubes are often placed between the radiant and convection sections to protect the first convection tubes. In a superheater the high rate of absorption is desirable if the superheater is constructed of an alloy steel that can withstand high temperature oxidation.

The rate of radiant absorption varies at different parts of the radiant section. In ordinary stills the exact distribution of radiation is not important but for (1) heating sensitive stocks such as treated lubricating oils, (2) heating to very high temperatures as in cracking stills, and (3) heating two different stocks in separate coils in the same radiant section, the rate of heat absorption in the different parts of the furnace box becomes very important. Data on several stills have been reported that indicate radiation rates that varied by 400 per cent in different parts of the radiant section. Although the fundamental theories of radiation are well understood, the constants by which these theories can be applied to furnaces heated by a flame are not available. The following method yields approximate data on the variation of radiant absorption.[10]

Radiation proceeds in all directions from point sources within the flame. It proceeds in straight lines and either strikes a cold tube surface and is absorbed, or strikes a refractory wall. Upon striking a wall, the radiation first heats the wall but after the wall reaches a temperature higher than that of the tubes the wall itself begins to radiate. At the high temperature existing in pipestill walls, the walls act as reflectors so that radiation falling upon the wall is reflected in such a way that the angle of reflection equals the angle of incidence. Each time the radiation is reflected it becomes less intense, owing, first, to the heat lost through the walls by conduction and, second, because the intervening gas is heated. The intensity of reflected radiation, with the heat liberated considered as unity, is somewhat as follows: initial radiation, 0.75; once reflected, 0.68; twice reflected, 0.61; and thrice reflected, 0.54. The way in which this information can be used is shown in Example 68.

Example 68. Distribution of Radiation in Radiant Section.—A scale drawing of the inside of a commercial furnace is shown in Fig. 134. The distribution of radiation can be determined graphically by selecting a source of radiation in about the center of the flame and dividing the total radiation into equal parts. Thirty-five equal units or rays of radiation are used in this example. Only 9 rays are shown in Fig. 134 because, if 35 are shown, such a maze of lines results that the drawing is not intelligible.

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[10] Although the method is termed as approximate, it has been checked against four different sets of plant data on three stills, and the computed results are dependable.

The 35 lines or rays were completed as for the 9 shown in Fig. 134. Nine rays of initial radiation fall upon the first coil; eight rays of once-reflected radiation; three rays of twice-reflected radiation; and three of thrice-reflected radiation. The total radiation (comparative units only) that is absorbed by the first coil is

Initial	$9 \times 0.75 =$	6.0
Once reflected	$8 \times 0.68 =$	5.44
Twice reflected	$3 \times 0.61 =$	1.83
Thrice reflected	$3 \times 0.54 =$	1.62
Total radiation to first coil	=	14.89

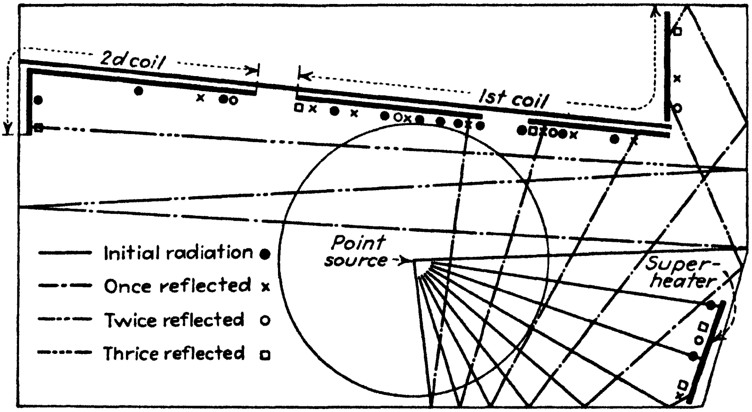

FIG. 134.—Distribution of radiation in radiant section. Refer to Example 68.

There were 88 sq. ft. in the first coil so that the relative radiation per square foot is

$$\frac{14.89}{88} = 0.1695$$

The average relative rate per square foot for all of the radiant surface was 0.126 (see tabulation, p. 421) and the actual average absorption rate was 11,000 B.t.u. per square foot of projected area per hour. Hence the rate in the first coil is

$$\frac{0.1695}{0.126} \times 11{,}000 = 14{,}800 \text{ B.t.u.}$$

The same computations for each of the three coils are shown in the following tabulation:

	Relative heat units absorbed by		
	First coil	Second coil	Superheater
Initial radiation (No. rays × 0.75)........	6	2.25	1.5
Once reflected (No. rays × 0.68)..........	5.44	1.36	0.68
Twice reflected (No. rays × 0.61).........	1.83	0.61	0.61
Thrice reflected (No. rays × 0.54)........	1.62	0	1.08
Total heat units for each coil...........	14.89	4.22	3.87
Surface in each coil (sq. ft.)..............	88.0	71.0	23.0
Relative abs. rate, heat units per sq. ft....	0.1695	0.0595	0.168

$$\text{Ave. relative abs. rate} = \frac{14.89 + 4.22 + 3.78}{88 + 71 + 23} = 0.126$$

$$\text{Actual ave. absorption rate} = 11{,}000 \text{ B.t.u. per sq. ft.}$$

Actual rates:

First coil........................ $11{,}000 \times \frac{0.1695}{0.126} = 14{,}800$

Second coil...................... $11{,}000 \times \frac{0.0595}{0.126} = 5{,}100$

Superheater..................... $11{,}000 \times \frac{0.168}{0.126} = 14{,}750$

The accuracy of the method can be improved by repeating the foregoing computations for several planes and for several point sources of radiation.

CONVECTION

The rate of heat absorption in the convection section can be approached with more assurance than for the radiant section. The only troublesome points are (1) the combination of radiation and convection heating which occurs through the first rows of the convection section and (2) the radiation from the hot gas and the walls of the convection section. The first difficulty is often handled by counting these tubes twice; *i.e.*, the first two rows are counted as radiant tubes and they are also counted as convection tubes. The second difficulty is discussed later.

The empirical equation by Monrad[11] is the only comprehensive

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[11] Heat Transmission in Convection Sections of Pipestills, *Ind. Eng. Chem.*, **24**, 505 (1932).

formulation of convection transfer rates. For pipestills he suggests

$$h_c = \frac{1.6G^{0.667}T^{0.3}}{D^{0.33}} \qquad (67)$$

where h_c = pure convection film transfer rate for flue gas flowing at right angles to staggered tubes (no radiation).
G = mass velocity of gas at minimum cross section (lb. per sec. per sq. ft.).
T = average gas temperature, °F.
D = tube diameter, in.

Equation (67) applies to any conventional arrangement of the convection section. However, the coefficient h_c is the pure convection coefficient and it does not include radiation from the flame, from the hot gas, or from the walls. Monrad[11] has made a study of these factors. The first of these is designated as h_{rg} or the coefficient of heat transfer from the gas by radiation. As an approximation, the value of the gas radiation coefficient may be found by the following relation:

$$h_{rg} = 0.0025T - 0.5$$

where T is the average temperature in degree Fahrenheit of the flue gas. More exact methods of computing this factor are given in the aforementioned reference.[11]

The second factor, the wall effect, ranges in magnitude between 6 and 15 per cent of the sum of the pure convection and the radiation coefficients.

$$\text{Per cent wall effect} = \frac{h_{rb} \times A_w \times 100}{(h_c + h_{rg} + h_{rb})A_t}$$

where h_{rb} = radiation coefficient from walls = $0.00688p(T/100)^3$.
p = emissivity of wall surface, usually about 0.95.
T = absolute temperature, °F., of tube.
h_c = pure convection coefficient (Eq .67).
h_{rg} = gas radiation coefficient.

Subscripts w and t refer to the wall and tube respectively. The complete coefficient of heat transfer in the convection section may be computed from the preceding items as follows:

$$h = \left(\frac{100 + \text{per cent wall effect}}{100}\right) \times (h_c + h_{rg}) \qquad (68)$$

In addition, the first convection tubes receive radiation directly from the furnace but this additional heat may be better considered as a part of the radiant section.

A tabulation of approximate total transfer coefficients is given in Table 56.

TABLE 56.—APPROXIMATE CONVECTION COEFFICIENTS

Velocity, ft. per sec.	Temperature, °F.	Size of tube (O.D.), in.		
		2	4	6
10	800	4.6	5.4	5.9
10	1400	6.1	6.9	7.4
15	800	5.6	6.6	7.4
15	1400	7.0	8.0	8.7

The area through which heat is transferred may be considered as the outside area of the tubes because the gas film coefficient controls. The resistances that are due to the oil film and the metal wall are so small that they are usually negligible. The gas velocity seldom exceeds 15 ft. per second in stills that are dependent on a stack for draft. A stack draft of 0.6 in. of water will cause a velocity of about 15 ft. per second. At low capacities the velocity may be only 10 but in recirculation stills the velocity may exceed 25 ft. per second.

Air preheaters are of many designs. Little data on the transfer rates are available. However, the rates are low because two gas films are present and because little radiation occurs. The rate probably ranges between 2 and 4 depending upon the velocity.

Pipestill Losses.—The heat losses in pipestills, when based on the net heating value, consist mainly of two items: (1) the sensible heat content of the stack gases above 60°F. and (2) the losses through the furnace walls, header boxes, roof, floor, etc. Pipestills are usually fired with 25 per cent or more of excess air and hence carbon monoxide is seldom reported in the flue gas, and no loss occurs by incomplete combustion of the fuel. No loss due to the heat contained in the cinder or combustible in the cinder is necessary unless coal is fired.

The brickwork of pipestills and boilers is not usually air-tight. The following tabulation shows the flue-gas analysis at two points in a commercial still.

Flue gas	Radiant section	Breeching
Carbon dioxide	13.5	7.6
Oxygen	0.7	9.4
Carbon monoxide	0.3	0.0

Air leaked into the still in the radiant and convection sections and lowered the percentage of carbon dioxide. In this still, radiation occurred at a low percentage of excess air but the stack loss was for a high percentage of excess air.

The stack loss may be rapidly computed by referring to Figs. 57 and 58 (Chap. XI), but the method outlined in Example 33 (page 200) should be used for exact computations. In making a detailed heat-balance, the steam that is required to atomize the oil is easily forgotten (page 188).

Actual plant data on the losses through walls, headers, roof, etc., of a pipestill will be discussed. The temperatures[12] on the outside of the furnace were as follows:

Surfaces	Average surface temp., °F.	Air temp., °F.
Refractory walls, etc.:		
Shady end	140	70
Sunny end (slight breeze)	158	72
Shady side (between headers)	132	69
Sunny side (between headers, breezes)	183	72
Steel walkways and supports	105	69 and 72
Surface of suspended roof tile	323	173
Header boxes, etc.:		
Shady side	230	69
Sunny side (breezes)	261	72

The walls were constructed with 13½ in. of refractory brick, 4½ in. of insulation brick, an average sealed air space of 1 in., and a covering of cement board ¼ in. thick. Inasmuch as the temperatures were higher on the sides exposed to the sun, and

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[12] These temperatures were obtained by pressing a thermometer against the surface by means of a piece of dry loose asbestos. Such temperatures are low, but in this case a correction was determined by measuring known temperatures by the same method.

the air temperature is not appreciably raised by the sun, the most dependable surface temperatures are those of the shady walls.

From the foregoing data and the natural-convection rates as given by Eq. (33), the following losses were computed (Table 57):

TABLE 57.—LOSSES FROM PIPESTILL WALLS

Surfaces	Wall temp.	Air temp.	Surface, sq. ft.	ΔT	h_g	Loss, B.t.u. per hr.
Refractory walls....	136	69	1,632	67	1.92	210,000
Header boxes, etc...	230	69	640	161	2.43	250,000
Roof..............	323	173	1,020	250	2.96	755,000
Exposed steel.......	105	69	80*	36	1.71	5,000
Floor*.............	...	...	......	...	....	180,000*
Total............	...	...	......	...	....	1,400,000

* Estimated.

At the time of this test, the still was developing 26,500,000 B.t.u. per hour so that the radiation losses were approximately

$$\frac{1,400,000}{26,500,000} \times 100 = 5.3 \text{ per cent}$$

This is a reasonable loss for stills operating in dry weather with a normal movement of air. For carefully built stills the loss from the radiant section may be considered as 3 per cent and from the convection section 2 per cent.

Example 69. Design of Pipestill.—Thirty thousand pounds of oil per hour is to be heated from 300 to 700°F., vaporizing about 66 per cent of the oil. About 10,000,000 B.t.u. per hour is required for this service. A radiant-absorption rate of 20,000 B.t.u. per hour per square foot of projected area is advisable. An efficiency of 75 per cent is satisfactory. The fuel oil has a net heating value of 17,600 B.t.u. per pound and produces 14.7 lb. of flue gas if burned with no excess air. Twenty-five per cent of excess air will be used in the design calculations.

The pounds of air (no excess) per pound of fuel is $14.7 - 1 = 13.7$.

Tables 23 and 54 indicate that this fuel will have radiant properties between a heavy oil fuel and natural gas.

Figure 133 shows that the percentage of the total heat liberation that will be absorbed in the radiant section will be about 53.5.

If wall losses of 3 and 2 per cent are adopted for the radiant and convection sections, the heat-balance can be set up as follows:

	Per cent	B.t.u.
Efficiency (given)	75	10,000,000
Heat in fuel (heat liberation)	100	13,330,000
Radiant section loss	3	400,000
Convection section loss	2	260,000
Stack loss (25–3–2)	20	2,670,000
Radiant absorption	53.5	7,140,000
Convection absorption (75–53.5)	21.5	2,860,000
Total	100.0	13,330,000

Radiant section:

$$\text{Radiant surface} = \frac{7{,}140{,}000}{20{,}000} = 357 \text{ sq. ft. (projected)}$$

If 3- by 4-in. tubes are used, the length of the effective radiant tubing is

$$\frac{357}{0.33} = 1{,}070 \text{ ft.}$$

Convection section: The temperature of the stack gas is 810°F. (Fig. 57). The temperature of the gas as it enters the convection section can be obtained from the same figure. The heat that remains in the gas as it leaves the radiant section is

$$100 - 53.5 - 3 = 43.5 \text{ per cent}$$

At 43.5 per cent (Fig. 57) the temperature is 1700°F. (This high temperature indicates that more excess air should be used unless some decomposition can be tolerated.)

The temperature of the oil as it enters the convection section is 300°F. and the temperature at which it leaves can be computed as follows:

$$2{,}860{,}000 = 30{,}000\ (t - 300)\ 0.6$$
$$t = 460°\text{F.}$$

The logarithmic mean temperature difference between the flue gas and the oil is

$$\frac{(1{,}700 - 460) - (810 - 300)}{\log_e \dfrac{1{,}700 - 4{,}600}{810 - 300}} = 825$$

The transfer rate can be estimated from Table 56. At a velocity of 12 ft. per second and an average temperature of 1250°F. the transfer rate for 3 × 4 tubes is about 6.95.

$$\text{Convection surface} = \frac{2{,}860{,}000}{6.95 \times 825} = 500 \text{ sq. ft. outside surface}$$

$$\text{Length of tubing} = 477 \text{ ft.}$$

The total effective length for radiant and convection sections is 1,070 plus 477 or 1,547 ft.

Recirculation and Air Preheat.—Many claims have been made for the recirculation type of pipestill. In part these claims are justified, but often they lead to misconceptions. The important advantages of the recirculation still are (1) the rate of radiant absorption can be controlled by adjusting the quantity of flue gas that is recirculated and (2) a low rate of radiant absorption can be obtained without building an excessively large radiant section. If the duty of an ordinary still is increased to above its rated capacity, the rate of absorption in the radiant section increases greatly and all out of proportion to the increase in the duty. In the recirculation still the rate of absorption can be kept low by increasing the circulation of flue gas. In both types of stills the efficiency may decrease slightly but the efficiency of pipestill heaters is not of major importance to the refiner. The most real concern of the refiner is to avoid deposits of coke with resulting costly shut-downs, and to avoid discoloration of finished stocks by localized overheating. The absorption rate can be regulated in ordinary stills by using different quantities of excess air, but a great loss in the efficiency occurs if the absorption rate is lowered by even a few thousand B.t.u.

In general, recirculation stills require less surface than simple stills of the same efficiency.[13] However, the saving in the cost of surface must pay for the recirculation equipment, the gas-tight construction of the still, and the increased operating cost. Thus the initial cost is usually greater for the recirculating still, as well as the operating cost, so that the adoption of a recirculating still rests entirely with the advantage that it affords as a means of controlling the rate of radiant heat absorption. In the past, the design of pipestills for low radiant-absorption rates was not well understood and the recirculation still was widely used. Today the industry is reverting to the use of simple radiant-type stills that are designed for a specific service.

Table 58[13] indicates the effect of flue-gas recirculation. Still 1 was designed for no recirculation, an efficiency of 75 per cent, and a radiation factor of 0.5. Stills 2 and 3 are the same still as

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[13] NELSON, W. L., Modern Pipestill Heater Design, Recirculation, *Petroleum Eng.*, June, 1933, p. 23.

TABLE 58.—COMPARISON OF RECIRCULATION AND SIMPLE STILLS

Absorption 10,000,000 B.t.u. per hr.
4- by 5-in. tubes.
15 ft. per sec. flue-gas velocity in the simple stills.

Stills 1, 2, and 3, radiant surface, 266 sq. ft. proj.
convection surface, 540 sq. ft. (O.D.)
Stills 4, 5, and 6, radiant surface, 119 sq. ft. proj.
convection surface, 570 sq. ft. (O.D.)

Still no.	Recirculation	Duty ÷ 10^6		Convection section				Radiant section			Eff.	Length of tubing	Length of tubing for simple still*
		On fuel	On Q or on heat developed	In, °F.	Out, °F.	Mean temp. diff. °F.	h	Factor on Q	Per cent of heat in fuel	Absorption rate			
1	0 − 1	13.3	13.3	1680	810	810	7.6	0.5	50	25,000	75	1,055	1,055
2	0.5 − 1	13.3	14.7	1630	810	800	9.5	0.40	44	22,100	75	1,055	1,105
3	1 − 1	13.1	15.4	1540	780	750	12.0	0.325	38	19,000	76	1,055	1,204
4	0 − 1	13.3	13.3	2100	810	975	8.4	0.40	40	44,700	75	720	720
5	0.5 − 1	13.3	14.7	1930	810	915	10.8	0.311	34	38,500	75	720	746
6	1 − 1	13.3	15.8	1700	810	845	12.3	0.24	29	32,500	75	720	802

* Non-recirculation stills designed for the same radiant absorption rate as the corresponding recirculation stills.

No. 1 except that flue gas was recirculated. The comparison is hardly fair because a recirculation still should be built with more convection surface. Hence stills 4, 5, and 6 are compared in the same manner except that the nonrecirculation still 4 was designed for a radiant factor of 0.4. All of the stills were designed for an absorption of 10,000,000 B.t.u. per hour, the use of 25 per cent excess air, and heating a crude oil stock from 300 to 700°F. The last column in Table 58 shows the surface required to get the same radiant factor as with recirculation but without recirculation of flue gas.

Examination of Table 58 shows essentially no difference between simple and recirculation stills except the rate of absorption in the radiant section. Recirculation stills usually appear to more advantage than shown in the table because the convection section can be arranged for higher gas velocities than those used in computing Table 58.

The effect of recirculation on the rate of radiant absorption is shown graphically in Fig. 135. In studying recirculation stills the exact definition of the radiation factor R [Eq. (66)] must be kept clearly in mind. This factor is the fraction of the total heat, developed in the flame, that is absorbed in the radiant section. Thus, in simple stills, R is the fraction of the heat contained in the fuel, whereas in circulation stills or air preheat stills it is the fraction of the total heat liberated in the flame; this total may consist of the sum of the heat in the fuel, the heat in the recirculated gases (above 60°F.), and the heat in the air (above 60°F.).

Air preheat increases the flame temperature and the rate of radiant absorption so that it tends to defeat the advantage of flue-gas recirculation. Higher efficiencies can be obtained by air preheat but the same efficiency can be obtained at about the same expense by building a larger convection section in the still. However, the burners can be more exactly adjusted if the primary air is under a slight pressure as in a preheat system.

Pressure-drop.—The pressure-drop through a pipestill is usually of little importance provided the designer has an approximate idea of its magnitude. An amply large pump should be selected, because of these factors: (1) the still will, at times, be operated at capacities far above the rated capacity; (2) coke, etc., will accumulate in the tubes and cause the pressure-drop to rise as the still remains on stream for a long period of time; and (3) the steam pressure will be low at times and a larger steam cylinder will be necessary to maintain even the rated pressure.

For an outline of a method that may be used in estimating the pressure-drop, Example 50 may be consulted. The tabulation shown on page 431 indicates the accuracy of the method outlined in the example.

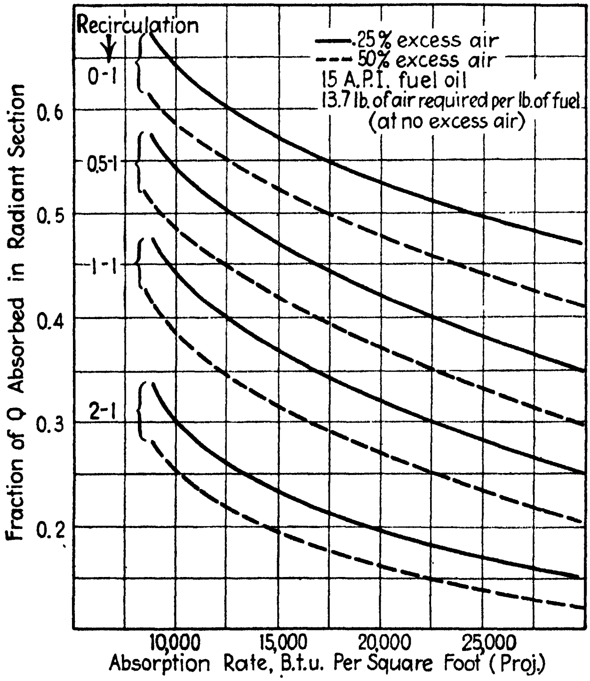

FIG. 135.—Radiant-absorption rate when recirculating flue gas.

Tube Design.—The temperature difference that always exists when heat is delivered through a series of resistances becomes of great importance in the selection of pipestill tubes. Nearly all of the radiation that falls upon a tube must be absorbed, regardless of the transfer rate on the inside of the tube. The transfer of heat through the oil film is a conduction phenomenon and hence a difference in temperature must exist between the main body of oil and the tube wall. Thus the temperature in the film and tube is higher than in the fluid.

Solid coke may be deposited because of the high temperature in the oil film. As coke is deposited, the temperature in the tube rises and it continues to rise as coke is deposited until finally the tube attains the temperature of the furnace or it bursts. For normal thicknesses of coke, the amount of heat absorption is not decreased greatly. Partridge and White[14] find that a normal thickness of boiler scale does not decrease the rate of radiant heat absorption by more than about 3 per cent. In general, coke deposits act in the same manner.

Material	Pressure-drop, lb. per sq. in.	
	Actual	Computed
Crude oil	198	192
Reduced crude oil	124	115
Brightstock solution	197	209
Treated cylinder stock	85	103
Distilled cracking-stock	605	563
Distilled cracking-stock	394	362
Distilled cracking-stock	238	275

Pipestill tubes often receive radiation at the rate of about 5500 B.t.u. per sq. ft. per hr. of outside surface or a rate of about 9500 B.t.u. per square foot of inside surface. The velocity of the oil is usually such that the film transfer rate is about 200 B.t.u. per sq. ft. per hr. per deg. of temperature difference. Obviously the temperature difference through the oil film, if the tube is clean, is

$$\frac{9{,}500}{200} = \frac{\dfrac{\cancel{\text{B.t.u.}}}{\cancel{\text{Hr.}} \times \cancel{\text{Ft.}^2}}}{\dfrac{\cancel{\text{B.t.u.}}}{\cancel{\text{Hr.}} \times \cancel{\text{Ft.}^2} \times {}^\circ\text{F.}}} = 47.5^\circ\text{F.}$$

If the oil temperature is 900°, the temperature at the inside of the wall is (900 + 47.5) or 947.5°F. If the wall is ½ in. thick, the temperature drop in the wall will be

$$^\circ \text{ drop in wall}^{15} = \frac{9{,}500}{25} \times \frac{0.5}{12} = 15.8$$

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[14] The Effect of Boiler Scale, *Ind. Eng. Chem.*, **21**, 839 (1929).

[15] Conductivity of steel is about 25 B.t.u.

and the outside of the metal tube is at (900 + 47.5 + 15.8) or 963.3°.

If a coke deposit (conductivity about 0.5) ⅛ in. thick is produced, the tube temperature is increased by

$$\frac{9{,}500}{0.5} \times \frac{0.125}{12} = 198^\circ\text{F}.$$

and the outside tube temperature is

$$900 + 47.5 + 198 + 15.8 = 1161.3^\circ\text{F}.$$

These temperatures are shown in Fig. 136.

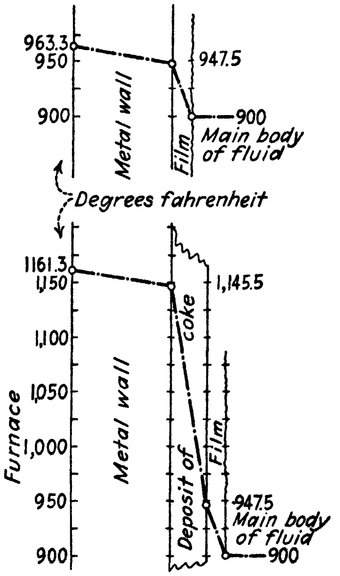

FIG. 136.—Effect of coke on wall temperature.

A temperature of 1160° (red heat) is too high for a carbon steel tube because the strength drops to about 1,000 lb. per square inch (creep strength) and the tube will fail. However, if the pressure is very low so that the coke can be deposited to thicknesses greater than ⅛ in., the tube wall temperature continues to rise with increase in coke thickness and eventually the tube will attain the temperature of the furnace. At this stage the furnace must be fired harder, the temperature in the tube increases proportionally, the pressure-drop increases rapidly, and eventually the tubes become plugged or they fail.

The rate of coke deposition is not greatly dependent on the amount of coke already deposited but the rate can be retarded by increasing the velocity or the transfer rate through the oil film. The rate of depositing coke is directly dependent on the thickness of the oil film because the thicker the film the greater the volume of oil (in the film) that is exposed to the high temperature. Thus the rate of coke deposition will be related to the transfer rate and the temperature in the film. Figure 137 shows the relative rate of coking for different film transfer rates and for common rates of total heat absorption. They are based on a rate of unity for a transfer rate of 300 and an absorption rate of 10,000. These conditions are commonly found in cracking plants. The data are only approximate because the velocity and the film transfer rate cannot be accurately computed. Only two factors were accounted for in computing Fig. 137: one, the temperature in the film and the way that it affects the rate of cracking, and the other, the thickness of the film.

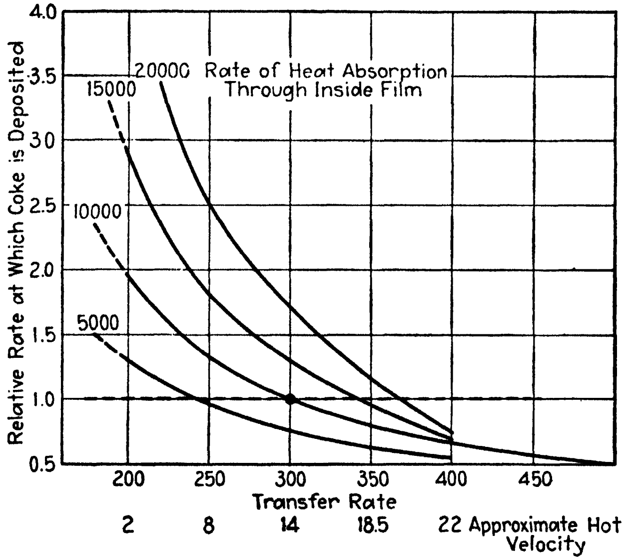

FIG. 137.—Approximate relative rate of coke formation.

Figure 137 clearly shows why a hot velocity of about 13 ft. per second is now commonly used in cracking plants. A higher velocity greatly increases the pressure-drop and aids little in decreasing the formation of coke. Absorption rates of 10,000 to 13,000, through the inside surface of the tube, are widely used. In topping plants the temperature in the main body of oil is much lower and hence Fig. 137 does not apply.

Materials for High Temperatures.—The common method of measuring the strength of metals at high temperatures is by long-time heating tests. Short-time tests are unsuccessful because in a furnace the metal stretches or creeps as time progresses and will fail under a load that appears to be safe by short-time tests. The effect of time on the strength of cast carbon steel is shown in Fig. 139.[16] The creep strength or creep limit may be defined as the load (pounds per square inch) that a material can withstand

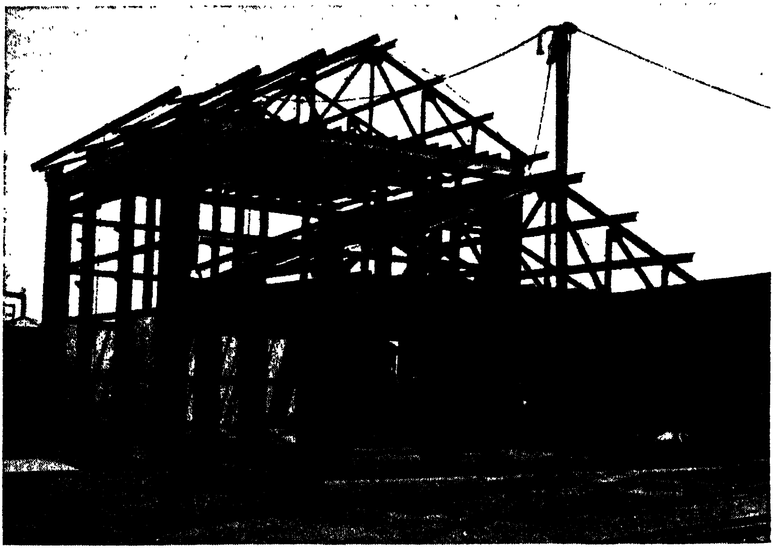

Fig. 138.—Steel structure of pipestill. (*A. J. Smith Engineering Company.*)

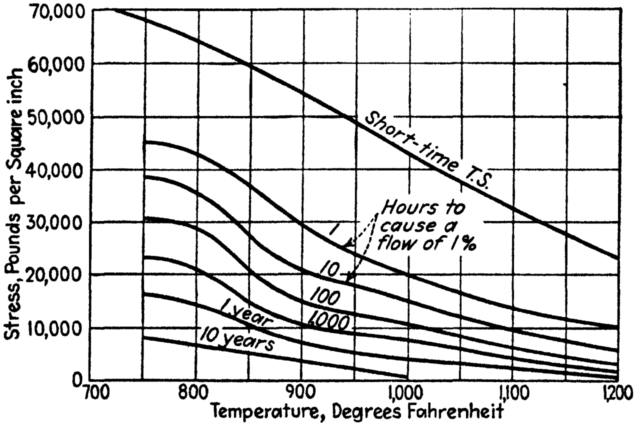

Fig. 139.—Rate of flow of cast carbon steel at elevated temperatures. (*Kanter and Spring, American Society for Testing Materials.*)

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[16] Strauss, Jerome, *Trans. Am. Soc. Steel Treating*, **16**, 191 (1929).

at a high temperature without exceeding a given rate of stretch. Creep strengths are frequently given as the pounds per square inch that will not cause an elongation of more than 1 per cent in 10,000 hr. A time of 100,000 hr. has also been used in many tests. Table 59 shows the creep strength of several common alloy steels.

TABLE 59.—STRENGTH OF STEEL AT HIGH TEMPERATURES

Material	Creep strength, lb. per sq. in., for a 1 per cent elongation in 10,000 hr. at, °F.							
	800	900	1000	1100	1200	1400	1600	1800
Low carbon steel (0.08)	11,000	6,000	3,000	825				
Mild carbon steel (0.2)	14,000	10,000	3,700	1,300	550			
4–6% Cr	15,000	7,500	4,000	2,200	1,000			
4–6% Cr (1%W)	19,000	10,000	5,200	3,000	1,400			
4–6% Cr (0.5%Mo)	23,000	13,000	7,500	4,000	1,700			
0.5% Mo	......	......	......	4,000	1,650			
18–8 chrome nickel	......	24,000	18,000	11,200	6,500	1,800		
Calite B	......	......	......	......	.....	8,800	3,200	2,800

Tubes for cracking stills (2 in., inside diameter) usually have walls that are 0.5 in. thick. Such a tube, if used at a pressure of 1,000 lb. per square inch, must have a strength of about 3,000 lb. per square inch at the temperature that the tube will attain in service. Regular mild carbon steel (0.2 per cent carbon) has a creep strength (1 per cent in 417 days) of 3,000 lb. at about 1030°F. In heating an oil at 900°F., the maximum thickness of the coke deposit can be estimated as follows:

°F.

Total allowable temp. drop.............(1030–900) = 130

Drop through film..................33°F. approx.

Drop through tube.................16°F. approx.

49......... = 49 (see page 212)

Drop through coke scale........................... 81

Using an absorption rate of 10,000 B.t.u. per hour based on inside surface and a conductivity (coke) of 0.5,

$$\left.\begin{array}{c}\text{Thickness of coke}\\ \text{inches}\end{array}\right\} = \frac{kA\Delta T}{Q} \times 12 = \frac{0.5 \times 81 \times 12}{10,000} = 0.0485$$

This is a thickness of about 3/64 in. It is not to be inferred that the tube will fail immediately after a deposit of 3/64 in. is produced. The material will stand this condition for a short time but it will begin to soften and will soon fail. No real gain in the length of operating time is possible by using the tube in this condition and the danger of fire increases.

Many alloy steels (Table 59) retain their strength at an elevated temperature and hence they are being widely used as tube materials. Several of these alloys were studied, as above, to determine the relative thickness of coke deposit that can be tolerated with each of the alloys. The coke is deposited at a rate nearly proportional to time and hence the coke thickness, barring plugging of the tube or the production of an excessive pressure-drop, that can be allowed is a measure of the time that the tube can be used before it must be cleaned. Table 60 presents this information.

TABLE 60.—ALLOWABLE THICKNESS OF COKE FOR SEVERAL TUBE MATERIALS

Material	Temp. for a creep strength of 3,000 lb. (1 per cent in 10,000), an oil pressure of 1,000 lb.	Temp. drop through coke, °F.	Allowable thickness of coke deposit, in.	Relative length of service before cleaning
Carbon steel	1030	81	0.0485	1.0
4–6 chromium	1060	111	0.0666	1.38
0.5 molybdenum	1110	161	0.0965	2.0
4–6 chrome, 0.5 molybdenum	1150	201	0.1205	2.5
18–8 chrome nickel	1300	351	0.210*	4.5*
Calite B	1620	671	0.403*	8.3*

* True unless the pump pressure becomes prohibitive.

The last two materials in Table 60 cannot be used as long as shown in the table because the pump pressure will increase.

Furthermore, the furnace temperature near the tube seldom exceeds 1400°F. and hence the thick deposits indicated in the table would necessitate that the furnace be fired harder. It appears that the 0.5 molybdenum tubes would be worth the small additional cost of the alloy material. Most alloy steels are also resistant to corrosion and high temperature oxidation.

Egloff and Morrell[17] present the following comparison of return fitting plugs when used in Dubbs cracking stills:

Material	Life before replacement, Months
Chrome plated iron	4
Steel	4½–5
Nickel chrome iron	5
Aluminum bronze	1–12
Forged chrome iron	Over 18
Cast chrome iron	Over 17
Forged steel	24

Although forged steel will last for a long time, it is not so satisfactory as some other materials because the plugs cannot be easily removed.

Shellstills and Heated Chambers.—The heating of oil in shells or chambers is limited by the amount of heat that can be conducted from the heated surface by means of the boiling oil. In commercial stills the maximum transfer rate is about 6 B.t.u. per sq. ft. per °F. temperature difference per hr., and most stills operate at a transfer rate of about 4. However, if forced circulation is used or internal flues, the rate of transfer may be increased to as much as 12. The temperature difference is the difference between the oil temperature and the gas temperature. Thus the total heat transmission per square foot per hour amounts to about 4000 B.t.u. for an oil at 400°F. to as low as 2000 B.t.u. for an oil at 800°F.

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[17] Safety and Costs Chief Factors in Considering Alloy Steel for Cracking Equipment, *Ref. Nat. Gaso. Mfr.*, April, 1931, p. 77.

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CHAPTER XXI

FRACTIONATING TOWERS

In the practical design of petroleum fractionating towers, the principles outlined for two component systems are of only general value. These principles operate just as surely in the complex-mixture column as in two-component columns, but means of rigorously applying these principles have not been devised. To complicate the application of these principles further, petroleum columns are usually operated as multiple-draw columns; *i.e.*, several products may be withdrawn from the plates intermediate between the top plate and the feed plate. Needless to say, fractionation is not effective at these plates because a part of the vapor that passes these plates is the overhead or lightest column product and hence the products that are withdrawn from the intermediate plates must contain some of this low-boiling material. Customarily, the products that are drawn from the side of the tower are separately stripped with steam, in auxiliary stripping columns or stripping sections.

Heat and Material Balances.—Inasmuch as equilibrium methods of determining the reflux are not available, the reflux is universally computed by means of a heat-balance. The vapor-liquid feed enters the tower at a high temperature and the products are withdrawn at lower temperatures. Hence heat must be removed and it is referred to as reflux heat. The reflux heat does not consist of sensible heat alone because the products that are withdrawn as liquids must be condensed. For a particular operation, the reflux heat is an exact[1] quantity of heat, but the heat may be removed in many ways, *i.e.*, by hot, cold, or circulating reflux.

The most satisfactory temperature datum appears to be the vaporizer temperature because this temperature can be accurately

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[1] It actually differs slightly because of small differences in the top temperature (Example 71).

estimated and is the temperature about which the entire design of tower and pipestill hinges. By using this datum plane, the heat-balance consists simply of the sensible heat that is required to (1) cool each product from the vaporizer temperature to its withdrawal temperature and (2) condense the products which are withdrawn as liquids. The reflux that is computed by a heat-balance is the minimum amount by which the process can function. Just enough cooling (by reflux) is provided, to cool and condense the products, and hence no reflux flows into the vaporizer section of the tower.[2] At each side-draw plate the internal reflux is depleted by the amount of side-draw product which is withdrawn. The depletion of the reflux as it flows down the column is illustrated in Fig. 140. The dotted lines refer to another manner of withdrawing reflux heat (page 441).

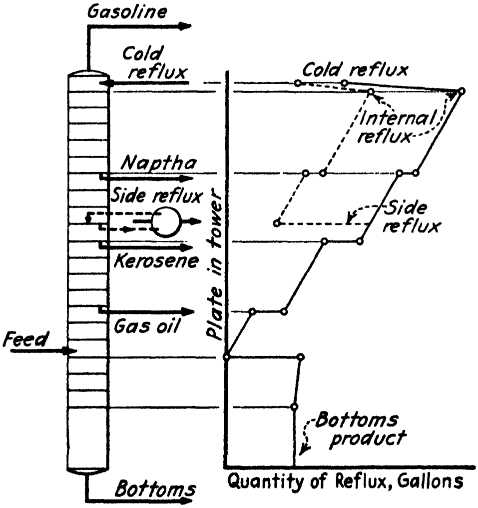

FIG. 140.—Relative amount of reflux or overflow liquid at each tray of a bubble-tower.

Types of Reflux.—The ways of withdrawing reflux heat or the types of reflux are illustrated in Fig. 141. With any of these types, regardless of the volume of liquid reflux, the same quantity of heat is removed. *Cold reflux* may be defined as reflux that is

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[2] It is always possible to vaporize some of the bottom-product by using a higher vaporizer temperature. This causes some reflux to penetrate to the vaporizer section.

supplied at any temperature below the equilibrium boiling-point of the top product or, more simply, below the temperature of the top of the tower. Each pound of this reflux can remove a quantity of heat, equal to the sum of its latent heat and the sensible heat required to raise its temperature, from the storage-tank temperature to the temperature at the top of the tower. A constant quantity of reflux is recirculated from the product storage tank into the top of the tower. It is vaporized and condensed, and returns in like quantity to the product storage tank. This recirculating quantity often amounts to three times the quantity of overhead product.

Hot reflux is reflux that is admitted to the tower at the same temperature as that maintained at the top of the tower. Obviously, the reflux or overflow from plate to plate in the tower is essentially hot reflux because it is always substantially at its boiling-point. For convenience, the overflow reflux or reflux in the tower is referred to as *internal reflux*. Both hot and internal reflux are capable of removing only the latent heat, because no difference in temperature is involved. Sometimes five volumes of hot reflux are required per volume of product.

Circulating reflux differs from the foregoing because it is not vaporized. It is able to remove only the sensible heat quantity that is represented by its change in temperature as it circulates. This reflux is withdrawn from the tower as a liquid at a high temperature and is returned to the tower after having been cooled. This type of reflux may be conveniently used to remove heat at points below the top of the tower (side reflux). If used in this manner, it tends to decrease the volume of vapor that the tower must handle. This is illustrated in Fig. 140 by the dotted lines.

Obviously, hot reflux is subject to fluctuations in the quantity and properties of the feed to the plant or to the quantity of cooling agent used, so that it is not entirely satisfactory. In certain cases, when this type is advisable, such as in vacuum-tower systems, the major part of the reflux heat may be removed by hot reflux, and cold reflux may be used to remove the rest of the reflux heat. Cold reflux has the advantage of affording an absolute control by means of the reflux pump. Circulating reflux can be controlled in the same manner, but the cost of pumping large quantities of liquid is excessive and larger heat exchangers are necessary. Regarding the heat that can be saved by heat-exchange, the three systems are comparable although higher transfer rates can usually be obtained in condensers than in liquid-to-liquid exchangers.

The fact that the quantity of internal reflux that flows from the top plate of the tower is always the same amount, regardless of the type of external reflux that is used, is always confusing. Vapor arises from the plate below the top and is condensed by the reflux on the top plate. If cold reflux is used, it will take about 2 lb. of vapor to heat and vaporize 1 lb. of cold reflux.

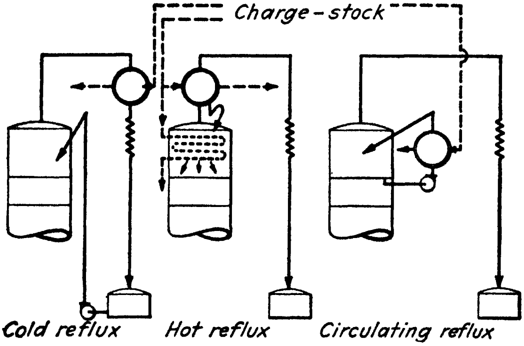

FIG. 141.—Methods of removing reflux heat.

Thus 2 lb. of internal reflux flow from the top plate for each pound of cold reflux that is admitted to the top of the tower. Similarly, a pound of vapor may deliver enough heat, as it condenses, to heat more than 2 lb. of circulating reflux. In this case, the amount of internal reflux is less than the amount of circulating reflux. When hot reflux is used, the amount of reflux is about the same as the amount of internal reflux.

Example 70. Quantity of Reflux.—A tower fractionating system is such that 2,000,000 B.t.u. per hour of reflux heat must be removed. Example 34 illustrates the method of determining the reflux heat. How many pounds and gallons of (1) hot, (2) cold, and (3) circulating reflux are required? Basis: 1 hr.

The overhead product is assumed to be a 58 A.P.I. gasoline (6.22 lb. per gallon). The temperature at the top of the tower is 300°F.

1. *Hot Reflux.*—The latent heat of the gasoline is about 123 (Table 8).

Lb. of hot reflux............ $\frac{2{,}000{,}000}{123} = 16{,}250$ lb. per hr.

Gal. hot reflux.............. $\frac{16{,}250}{6.22} = 2{,}615$ gal. per hr.

2. *Cold Reflux.*—Assume storage tank at 100°F.

Lb. cold reflux......... $\frac{2{,}000{,}000}{123 + (300 - 100)0.575} = 8{,}400$ (Fig. 33)

Gal. cold reflux............... $\frac{8{,}400}{6.22} = 1{,}350$

3. *Circulating Reflux.*—Assume the reflux is cooled from 300 to 200°F.

Lb. circulating reflux........... $\frac{2{,}000{,}000}{(300 - 200)0.605} = 33{,}100$

Gal. circulating reflux.......... $\frac{33{,}100}{6.22} = 5{,}310$

Tower Temperatures.—In making a heat-balance, the temperatures at which the various products are withdrawn from the tower must be determined. These are usually assumed but the sagacity of these assumptions vitally affects the entire tower design. Hence these temperatures must be as nearly correct as possible. In dealing with a standard design—if there is such a design—the temperatures can be estimated with fair accuracy, but in most cases some factor such as a freak stock, excessive steam quantities, or abnormal pressures connives to introduce great errors into the estimation of these temperatures. The points in Fig. 142 were obtained from commercial operating data and they show the wide range of tower temperatures that are possible in even the simplest sort of a tower system. Nevertheless, this figure may be used to approximate tower temperatures if great accuracy is not required. Note that this figure is for crude oil topping towers operating with less than 0.6 lb. of steam per gallon of feed-stock.

Although the following method of determining tower temperatures is open to many criticisms, it does take into account the several variables mentioned above and yields results which are in close agreement with plant data. Table 61 is a tabulation of computed and actual side-draw and top temperatures.

Tower temperatures are dependent upon equilibrium vaporization phenomena. The temperature at the top of the tower must be just high enough to cause complete vaporization of the overhead product. A lower temperature will condense a part of the desired overhead product and incorporate it in the first side-draw product, and a higher temperature will cause the inclusion of high-boiling materials which are not desired in the overhead product. If the top of the tower is at atmospheric pressure and no steam is used, the equilibrium vaporization curve of the overhead product will give the top temperature directly. The 100 per cent point on the vaporization curve (see gasoline, Fig. 143) is the lowest temperature at which the overhead product can be a vapor, and this is the top temperature for the simple conditions of a tower operating at a pressure of 760 mm. with no steam. Such a simple case is seldom found and for normal conditions the top temperature at 760 mm. must be corrected

TABLE 61.—TOWER TEMPERATURES

Plant unit No.	Material	Actual temp., °F.	Computed temp., °F.	Per cent error
Plate temperatures:				
1. Crude, S. Am.	Kerosene	375	367	−2.1
2. Crude, Seminole	Kerosene	374	376	+0.5
3. Crude, Ranger	Kerosene	392	392	
4. Crude, Pa	Naphtha	335	335	
4. Crude, Pa	Kerosene	420	417	−0.7
1. Crude, S. Am.	Gas oil	474	473	−0.2
2. Crude, Seminole	Gas oil	469	474	+1.1
3. Crude, Ranger	Gas oil	497	470	+5.4
4. Crude, Pa	Gas oil	510	519	+1.8
5. Brightstock sol	Gas oil	450	455	+1.1
8. Cracking, M.C.	Recycle	555	562	+1.3
1. Crude, S. Am	Wax distillate	600	600	
2. Crude, Seminole	Wax distillate	591	630	+6.6
3. Crude, Ranger	Wax distillate	599	605	+1.0
5. Brightstock sol	Neutral oil	500	520	+4.0
6. Vacuum, 31 mm	Cylinder stock	635	625	−1.6
Top temperatures:				
1. Crude, S. Am	Gasoline	252	268	+6.35
3. Crude, Ranger	Gasoline	256	268	+4.7
4. Crude, Pa	Light gasoline	243	250	+2.9
5. Brightstock sol	Naphtha	308	319	+3.6
6. Vacuum, 28.5 mm	Gas oil and wax dist.	450	452	+0.4
7. Brightstock sol	Naphtha	308	312	+1.3
8. Cracking, 15 lb. gage	Pressure dist.	390	402	+3.1
9. Crude, Pa	Gasoline	244	253	+3.7
10. Crude, Pa	Gasoline	286	287	+0.3

for the tower pressure and for the partial-pressure effect of steam. Example 71 shows how these corrections can be made.

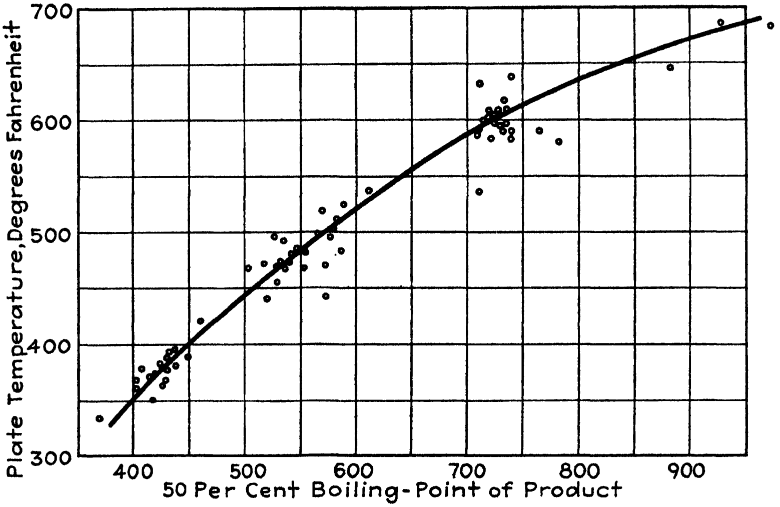

Fig. 142.—Approximate side-draw plate temperatures for topping towers.

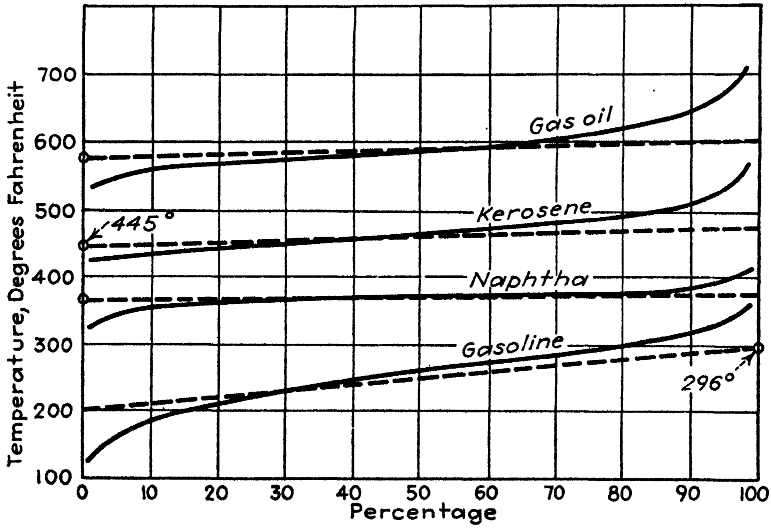

Fig. 143.—A.S.T.M. distillation and flash-vaporization curves of products used in Examples 71 and 72.

Example 71. Calculation of Top Temperature.—See Fig. 63 (page 202) and Example 34. The top temperatures for hot, cold, and circulating reflux will be computed. This system was actually operated with hot reflux and with circulating reflux, and hence a comparison with the actual temperatures is possible. Tower pressure 780 mm. at the top.

A. Hot Reflux.—See the quantities, etc. (Example 34).

Mols reflux:

$$
\begin{array}{lll}
\text{Reflux heat} & = 1{,}836{,}200 \text{ B.t.u. (Example 34)} & \\
\text{L.H. at 286} & = \text{about 127 (Table 8)} & \\
\text{Lb. reflux} & = \dfrac{1{,}836{,}200}{127} & = 14{,}400 \\
\text{Mols reflux} & = \dfrac{1{,}836{,}200}{127 \times 110} & = 131.5 \\
\text{Mols gasoline} & = \dfrac{3{,}415}{110} & = \underline{31} \\
\text{Mols vapor} & = & \ 162.5 \\
\text{Mols steam} & = {}^{567}\!/_{18} & = \underline{31.5} \\
\text{Total mols at top of tower} & & = 194.0
\end{array}
$$

According to Dalton's law, the partial-pressure in the gas phase is

$$\frac{162.5}{194} \times 780 = 652 \text{ mm.}$$

The initial condensation temperature for the gasoline (100 per cent point on equilibrium vaporization curve) is 296°F. (Fig. 143).

The temperature of 296 corrected to 652 mm. is 287°F.

The *actual* top temperature when using hot reflux was 286°F.

B. Circulating Reflux.—When circulating reflux was used, the top temperature was 244°F. The reflux circulated between 264 and 166°F. The circulating reflux does not vaporize and hence only the gasoline vapor and the steam need be considered.

Mols gasoline	31
Mols steam	31.5
Total mols	62.5

$$\text{Partial-pressure} = \frac{31}{62.5} \times 780 = 387 \text{ mm.}$$

Correcting 296 to 387 mm. pressure gives 253°F.

The *actual* top temperature was 244°F.

C. Cold Reflux.—With a lower top temperature (approximately 280°F.) more reflux heat will be required. The heat-balance given in Example 34 is correct except that the sensible heat of the gasoline and of the steam will be different.

Corrections to heat-balance given in Example 34 for a top temperature of 280°F.

		B.t.u.
Gasoline	$3415\ (286 - 280)\ 0.485 =$	9,900
Steam	$567\ (286 - 280)\ 0.5 =$	1,700
	Correction $=$	11,600

$$\text{Reflux heat} = 1{,}836{,}200 + 11{,}600 = 1{,}847{,}800 \text{ B.t.u.}$$

If the cold reflux is available at 80°F.,

$$\text{Lb. cold reflux} = \frac{1{,}847{,}800}{127 + (280 - 80)0.58} = 7{,}600$$

Mols cold reflux $= \frac{7{,}600}{110} =$	69
Mols gasoline	31
Mols vapor	100
Mols steam	31.5
Total mols	131.5

$$\text{Partial-pressure} = \frac{100}{131.5} \times 780 = 592 \text{ mm.}$$

The equilibrium temperature of 296° corrected to 592 mm., gives 279°F.

The method of calculating side-draw temperatures is much the same as the calculation of the top temperature except that complications arise because of the presence of the low-boiling materials which pass the draw-plate. Furthermore, the equilibrium condensation curve, and particularly the point on this curve which denotes complete condensation, is the basis for computing these temperatures. Flash vaporization and quench condensation are identical phenomena under equilibrium conditions, and hence the 0 per cent point on the flash-vaporization curve is the final condensation-point. At this temperature the side-draw product can be completely condensed at 760 mm. pressure if no lighter products or steam are present at the plate.

In practice, steam and the vapor of lighter products are usually present and hence the effect of these vapors on the final condensation temperature must be estimated. The lighter vapors which pass the plate exhibit a wide range of composition. These light vapors extend from materials boiling at almost the same temperature as the side-draw product to materials which are substantially fixed gases. Those vapor materials that are far above their boiling-point behave as fixed gases and lower the condensation-point by Dalton's law of partial-pressures just as steam does, but those vapor materials that are at or near their boiling-point are not effective in reducing the partial-pressure. Arbitrarily, the vapors of materials that will be condensed at the second or higher draw-plate above the plate under consideration may be considered to act as fixed gases. Also, the vapors that constitute the material which is withdrawn from the draw-plate above the one under consideration are assumed to have no effect at all on the partial-pressure. Thus in a tower producing gasoline, kerosene, and gas oil, at the gas oil draw-plate the gasoline vapor would be considered as a fixed gas, whereas kerosene vapor would be assumed to have no effect on the condensation point. This arbitrary classification of vapors appears to be accurate unless the quantity of one of the products is very large or very small. In such a case, the designer can only rely upon judgment. Example 72 illustrates these factors.

Example 72. Calculation of Side Temperatures.—This example is a continuation of Examples 34 and 71. The temperature (420°F.) of the kerosene plate (Fig. 63) will be computed (Envelope II, Fig. 63).

The quantity of reflux heat and reflux (or vapor reflux) that is present on the kerosene plate must be determined. This is computed by making a heat-balance up to the kerosene plate.

Heat-balance to kerosene plate (Example 34):

Cool gaso. vapor	3,415(576 − 420)0.595	=	316,000
Cool naph. vapor	754(576 − 420)0.59	=	69,500
Cool kero. vapor	2,765(576 − 420)0.58	=	250,000
Cool gasoil vapor	1,530(576 − 510)0.592	=	59,800
Cool reduced crude liquid	5,610(576 − 510)0.722	=	268,000
			963,300
Cool steam	567(535 − 420)0.5	=	44,000
Condense gas oil	1,535 × 96	=	147,000
Condense kero	2,765 × 106	=	294,000
Reflux heat at kerosene plate			1,448,300

$$\text{Mols internal reflux} \ldots\ldots \frac{1{,}448{,}300}{178 \times 106} = 77$$

The internal reflux contains the kerosene and hence the kerosene need not be added as a material whose partial-pressure must be reduced.

Mols of material which act as fixed gases:

Steam	31.5
Gasoline	31.0
Naphtha (no effect one way or other)	....
	62.5
Total mols of vapor	77.0 + 62.5 = 139.5

Assume a tower pressure of 950 mm.

$$\text{Partial-pressure at kero. plate} = \frac{77.0}{139.5} \times 950 = 523 \text{ mm.}$$

The atmospheric complete condensation point is 445°F. (Fig. 143). Correcting this temperature to 523 mm. gives 417°F. The *actual* temperature was 420°F.

The gas oil plate temperature can be computed in a similar manner except that kerosene is considered as an inert material and the gasoline and naphtha both act as fixed gases.

In applying the foregoing method to the design of a fractionating tower, the lowest draw-plate temperature should be computed first. The temperature on the lowest plate is assumed and after the heat balance is computed the assumption can be checked. If it is not correct, then a second assumption must be made. Each draw-plate temperature, progressing upward in the tower, is computed by such a trial-and-error method until all of the plate temperatures and the top temperature have been computed.

COLUMN DESIGN

The design and construction of petroleum oil columns are governed largely by empirical methods. So many variables may affect the performance of a fractionating column that engineers have not been able to study all of them carefully.

Even the thickness of the tower shell and plates is estimated by a consideration of the corrosion that may occur rather than on a consideration of the pressure. The thickness normally ranges from ¼ in. for columns less than 3 ft. in diameter to more than ½ in. for columns exceeding 5 ft. in diameter. For very high-pressure columns or chambers the thickness is computed and it may be as great as 4 in. for a column that is to operate at 1,000 lb. per square inch and at a high temperature.

Plate Design.—In the past, columns containing only baffle plates were widely used but such towers have been rapidly replaced by the more effective bubble-plate type of tower. However, the baffle-type tower is sometimes used for the following special services.

1. Fractionating very high-temperature vapor which tends to deposit coke.
2. Contacting hot vapor and cold oil for the purpose of pure heat-exchange or when the effectiveness of the separation or fractionation is not important.
3. For certain vacuum fractionation systems in which only an extremely small pressure-drop is permissible.
4. Fractionating materials which contain suspended matter, such as lime or coke.

Another type of column which is occasionally used is the packed column. However, packed columns should not be used in diameters exceeding about 20 in. because the liquid tends to channel and drain down the walls rather than through the packing. Packed columns are occasionally used as steam stripping columns if the quantity to be stripped is very small, but they are not used to a great extent in the oil industry.

Nearly all modern columns are modifications of the bubble-tower type of column. The vapor that travels up the column bubbles through a bath of reflux liquid that is contained on each plate. Figure 144 illustrates the general features of a bubble plate. The plates are most often constructed of plate steel. Steel plates are welded to the shell of the tower but cast-iron trays must be sealed into the tower shell by means of packing. Cast iron is more resistant to corrosion than steel but the major corrosive action takes place at the liquid-vapor contact line and hence the superior resistance of the cast-iron plate is of little value. Cast-iron bubble caps are used almost exclusively although pressed alloy-steel caps are sometimes used in vacuum towers. Steel caps can be more closely spaced, thus allowing a larger area for the vapor as it passes through the caps. Many caps are of the removable type; *i.e.*, the vapor uptake and cap proper can be assembled on the plate. Usually a single bolt is used to fasten the cap, and the cap is sealed to the plate by a gasket. The fastening of caps to the plate by means of bolts is not an entirely satisfactory arrangement. The bolts become rusted and many of the caps cannot be removed without breaking them. A more satisfactory arrangement is shown in Fig. 144. Here the vapor uptake-port is rolled into the plate and the cap which sets over the uptake is held down by a bar. In other arrangements the heavy bell of the cap rests by its own weight over the uptake. Removable caps and a manhole above each plate are considered as best practice.

The exact design of the bubble cap is probably of little importance except from the standpoint of cost. The shape of the slots appears to have little or no effect.[3] The same shape of bubble is produced regardless of the shape of the slot. At low velocities,[3] flat disk-shaped bubbles are produced and at high velocities a channeling appears to occur and a continuous elongated bubble space extends through the liquid. Contrary to common belief, Kallam[3] reports that more effective contacting occurs at low velocities than at high velocities.

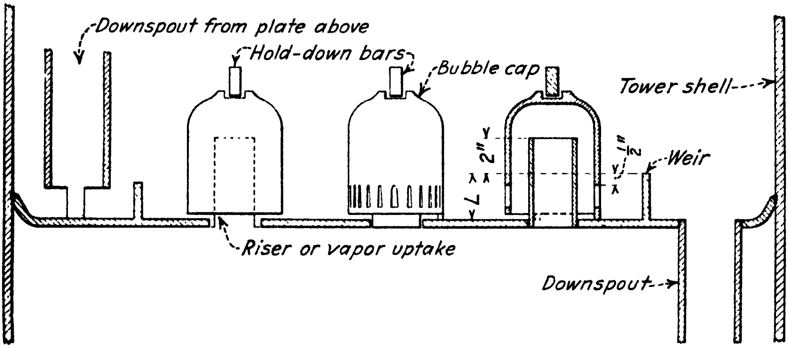

Fig. 144.—Features of a bubble plate.

Table 62 is a tabulation of the dimensions and areas of several bubble caps.

In addition to round or bell-shaped bubble caps, the so-called tunnel type trays and caps are used by many companies. These trays consist of liquid troughs several feet in length, or even across the entire tray, and vapor uptakes of the same length. A curved elongated cap or tunnel lies over the uptake causing the vapors to bubble through the trough of liquid. The trays function satisfactorily although spouting of the liquid has been reported. Perhaps the difficulty was as much due to faulty leveling of the plates or placement of the tunnels as to errors in the theory of this type of plate.

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[3] **Kallam, F. L.**, Notes on Absorber Design No. 1, *Petroleum Eng.*, April, 1934, p. 33.

Many designs of the so-called sieve-type plates have been proposed from time to time although they have never been adopted as standard tray designs. In these plates, small apertures are provided and both the liquid and the vapor pass through the same opening. Obviously, such plates cannot be operated at a high capacity because the liquid fails to drain through the plate. However, these plates operate with very low pressure-drops and hence they may become of importance in vacuum fractionation.

TABLE 62.—COMPARISON OF BUBBLE CAPS

Manufacturer	O.D., in.	Chimney or vapor uptake per cap, sq. ft.	Slots, area per cap, sq. ft.	$\frac{\text{Slot area}}{\text{Column area}}$	Material
A............	4	0.0204	0.0372	0.144	C.I.
A............	3	0.0232	0.0165	0.183	Steel
B............	5	......	0.0356	0.115	C.I.
C............	6½	......	0.0496	0.145	C.I.
D............	4½	0.0204	0.0348	0.112	C.I.
E............	4	0.0208	0.0396	0.150	C.I.
F............	3 × 10*	0.1001	0.0921	0.161	C.I.

* Rectangular cap.

The design of the *downpipes* or *downspouts* which carry the overflow liquid from one tray to the next has not received the attention that it deserves. Many towers fail to perform properly simply because the downspouts are inadequate. The liquid that flows through the downpipe is in the form of a froth. The weir or edge of the downspout (Fig. 144) may be the limiting factor or the cross-sectional area of the downpipe may cause liquid to accumulate. Either of these two factors will materially decrease the capacity of the fractionating tower.

Kallam[3] has made a study of the construction of downpipes. Several downspout arrangements were installed in the same tower. At an oil-to-gas ratio of 30 gal. of oil per thousand cubic feet of gas, the plates performed as shown in Table 63. A study of the fall-distance and the interference of several streams of oil flowing into the same downspout is also discussed.[3]

Table 63 indicates that two factors are involved in the performance of the downspout, one the area and the other the perimeter. However, the perimeter must be placed so that the liquid can overflow easily as well as be sufficiently long. The weir on plate 2 is effective along its entire length but the weirs on the other plates are not completely effective.

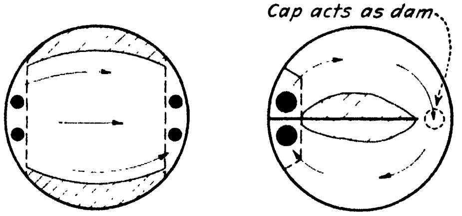
TABLE 63.—PERFORMANCE OF DOWNSPOUTS

Plate No.	Arrangement*	Downspout area, sq. in.	Downspout periphery, in.	Approximate† effective downspout periphery, in.	Allowable vapor velocity, ft. per min.
1		1.48	4.32	3.0	31.5
2		7.33	6.5	6.5	38.5
3		1.85	6.5	5.0	34.0
4		7.33	13.8	6.5	37.5
5		5.15	13.8	5.5	34.0

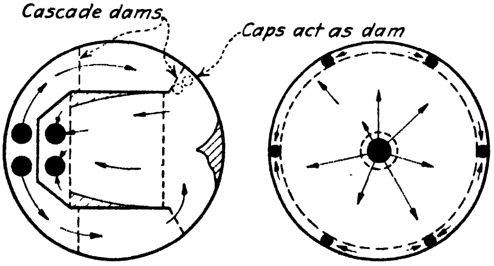
* Plate area 0.338 sq. ft.
† Estimated.

At the present time the downspout periphery or perimeter is usually estimated by the weir formulae given in Chap. X, but an ample length of weir and an ample downspout area should be provided. The liquid velocity in the downpipe (based on no froth) usually should not exceed 4 in. per second. In many designs a velocity of 2 in. per second will not incur a large expense and the use of a low velocity gives better results.

The overflow weir or dam is usually designed so that it will hold a liquid level (no froth) of 0.5 to 1.5 in. above the top of the slots. Actually, the liquid flows across the tray as a froth and the level is higher than 0.5 in. The liquid may tend to short-cut across the plate and cause some of the caps to be ineffective. This tendency can be corrected to some extent by means of another weir or dam which is used to distribute the liquid as it flows from the downspout into the tray (Fig. 144). For large plates, over 5 ft. diameter, special baffles must be used to direct the flow of the liquid so that all of the caps are effective. Common baffle arrangements are shown in Fig. 145. The parts of the plate that the liquid tends to by-pass are shown as shaded areas. The passage for the liquid must not be greatly constricted at any point or the liquid level on part of the plate may become so great that vapor will fail to bubble through some of the caps. The caps that are marked on *b* and *c* (Fig. 145) may act as dams to the flow of liquid. In experiments with the type of plate shown as *b* (Fig. 145), the liquid level was 1 in. higher on the upstream side when the air velocity was 0.5 ft. per second and the water rate exceeded 40 gal. per minute. The removal of the cap at the end of the baffle greatly improved the level gradient. Likewise in plate *d* (Fig. 145) the caps nearest the center often fail to function because of a high liquid level. In large towers it is sometimes necessary to arrange the plate as a series of cascades, each deck of caps being separated by dams so that the level on each deck will be independent of the level on the deck before it. In this manner, the submergence at each part of the plate can be kept about the same. Plate *c* (Fig. 145) indicates four cascade decks.



(a) Small Diameter (b) Medium Diameter



(c) Large Diameter (d) Very large Diameter

FIG. 145.—Typical arrangements of bubble trays.

The velocity of the vapor through the slots in the caps is also of importance in column design. A high slot velocity promotes agitation and is thought to aid in the attainment of equilibrium. However, an excessive slot velocity causes liquid droplets to be thrown to the plate above unless the plates are far apart, and Kallam[3] finds that mixing may not be effective at high velocities because the gas tends to channel through the liquid. Most petroleum oil columns are designed for slot velocities of 9 to 14 ft. per second.

A high velocity also increases the pressure-drop that occurs across the plate. In atmospheric towers the pressure-drop is not of great importance, but in vacuum towers the pressure-drop from the vaporizer to the top of the tower, and even to the ejector equipment, must be kept at a minimum. In towers operating at atmospheric pressure, the average pressure-drop per plate is about as follows:

Top Tower Velocity, Ft. per Sec.	Lb. per Sq. In. per Plate
1	0.05
2	0.12
3	0.18
4	0.25

The pressure-drop increases as the amount of liquid that flows across the plate is increased. These figures are for normal rates of liquid flow. The pressure-drop through pressed-steel caps, when installed in vacuum towers operating at about 40 mm. pressure, ranges from about 0.7 mm. per plate at a superficial vapor velocity of 7 ft. per second to about 1.2 mm. per plate at a velocity of 13 ft. per second. The submergence of the slots in the liquid was 1/16 in.

Kallam[4] reports that absorption towers, operating at a superficial gas velocity of 1.1 ft. per second, give pressure-drops as follows:

Oil-to-gas ratio, gal. per 1,000 cu. ft.	Pressure-drop per plate, lb. per sq. in.	
	16 plate column	Single plate
10	0.04	0.02
30	0.06	0.08
50	0.08	0.14

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[4] Notes on Absorber Design No. 2, *Petroleum Eng.*, June, 1934, p. 29.

As an aid in computing liquid quantities and the general conditions within the tower, the following data will prove useful. The properties of the various liquids in a tower approach a constant value if compared at the temperature in the tower. However, if a large amount of steam is used or if the processing is conducted in a vacuum, the constants are not exact. These data were compiled by using actual plant temperatures.

Specific gravity	0.684 (42.7 lb. per cu. ft.)
Surface tension	15.5 dynes per sq. cm.
Viscosity:	
Gas oil—470°F	0.45 centipoises
Kerosene—375°F	0.27 centipoises
Naphtha—335°F	0.23 centipoises

Plate Spacing and Entrainment.—The obtainment of equilibrium on a bubble plate is governed by two opposing factors. One of these, the intimacy of vapor-liquid contact, tends to produce equilibrium but, if the contacting or bubbling is too violent, liquid particles will be carried from one plate to the next by the vapor and will tend to destroy the separation that has been obtained. Thus agitation produces equilibrium but at the same time entrainment occurs and partly destroys the equilibrium.

Two kinds of entrainment can occur. One is a distinct splashing, spraying, or spouting of liquid particles. The particles are thrown upward by the velocity which they attain at the slot of the cap and they will fall back into the liquid if they expend their energy content before they reach the next plate. The liquid particles are relatively large and a relatively high velocity is necessary to cause them to be thrown to a height of 18 in. This kind of entrainment can be eliminated almost entirely by placing the trays far apart.

The other kind of entrainment might be referred to as "carrying." Very small particles of liquid do not fall through the vapor as fast as the vapor rises and they are carried by the vapor stream to the plate above. At a given velocity, all particles smaller than a certain size will be carried by the vapor to the plate above and the larger particles will fall slowly back to the parent plate. At ordinary vapor velocities, the size of the particle that can be carried from plate to plate by the vapor appears to be between 0.1 and 0.2 mm. in diameter.

Thus the velocity is limited by two factors: It should be high so that intimate contact will result and yet it must not be so high that undue entrainment will occur. Chillas and Weir[5] report that entrainment is negligible at a velocity of 2 ft. per second but that it amounts to 7 and 20.5 per cent at 4 ft. and 5.5 ft. per second. In commercial columns, having trays spaced at 22 in., the entrainment[6] is approximately as follows:

Material	Pressure	Linear velocity, ft. per sec.	Per cent entrainment
Gasoline	Atmospheric	1.4	0.25
Gasoline	Atmospheric	3.0	0.8
Gas oil	20 mm.	10.0	1.8
Air-water	Atmospheric	0.3	0.04
Air-water	Atmospheric	2.2	0.7

Souders and Brown[7] have derived the theoretical suspending velocity and they show the effect of tray spacing on entrainment. Equation (69) (page 462) for the allowable vapor velocity in columns is based on a consideration of entrainment. For a water-air system operating at the velocity normally maintained in petroleum towers, the entrainment at a spacing of 22 in. is less than 4 per cent of the entrainment at 12 in.

The use of baffles or other devices to remove entrainment naturally permits the use of higher velocities. However, the cost of these devices and the difficulties with corrosion have been deterrents to their use. A separating device, termed the Centrifix,[8] appears to be effective in removing entrainment. This device has been used to clean the vapor from a tubestill before it enters the fractionating tower. Steel wool has been used for the same purpose but it becomes plugged with coke and corrosion scale. When used in this manner, the Centrifix is effective in

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[5] *Ind. Eng. Chem.*, **22**, 206 (1930).

[6] Analysis of commercial plates by the author.

[7] Fractionating Columns—Entrainment and Capacity, *Ref. Nat. Gaso. Mfr.*, January, 1934, p. 32.

[8] ANON., Prevention of Entrainment in Tube Still Processing, *Ref. Nat. Gaso. Mfr.*, February, 1934, p. 70.

improving the color of the product that is withdrawn above the vaporizer and in reducing the amount of acid that is required to treat the product. The performance of the Centrifix separator is indicated in Table 64.[8]

TABLE 64.—REMOVAL OF ENTRAINMENT FROM VAPOR

Crude	Hivis product				
	Per cent of crude	Vis. at 210°	O.D. color without Centrifix	O.D. color with Centrifix	Color reduced to these per cents of original color
Reagan	6	140	5,800	1,550	27.0
East Texas	6	140	11,900	1,650	13.8
Little Panhandle	5	125	13,400	4,000	30.0
Barbers Hill	8	145	3,600	1,500	42.0

The Optical Density color scale referred to in Table 64 was developed by the Atlantic Refining Company. By this scale, the color number is directly proportional to the depth of color. The relation between the O.D. color and the N.P.A. color is

$$\text{N.P.A.} = 1.081\ (\text{O.D. color})^{0.32}$$

A 9-in. layer of steel wool[8] is able to reduce the color to about one-twentieth of the color when no wool is used. Chillas and Weir[9] have also studied the effect of a special baffle, similar to venetian blinds, on entrainment.

Kallam[4] presents about the only published information concerning tray spacing. He finds that the capacity of an absorber was more than doubled by increasing the tray spacing from 7 to 14 in., and at the same time half as many trays gave almost as good a separation. The trays in petroleum oil columns are usually spaced at 18 to 24 in. and for vacuum service they are sometimes spaced at 36 in. There are two reasons for this spacing: (1) The entrainment is low and (2) space is available for the installation of manholes above each tray and for the steel bracing that is necessary in large-diameter towers. In

[9] *Ind. Eng. Chem.*, **22**, 206 (1930).

several instances, refiners have found that the removal of every other tray in a closely spaced column (10 in.) has resulted in better fractionation. The spacing of the trays is involved in the velocity equation [Eq. (69), page 462]. By using Eq. (69), the cost of building and operating a crude oil topping tower is found to be lower at a spacing of about 25 in. than at any other spacing.

The centrifuge contactor[10] developed by Podbielniak promises radical improvements in our methods of conducting fractionation and other countercurrent processes. In a bubble-tower the separation of liquid and vapor between each plate is effected by means of gravity, whereas in the centrifuge contactor the separation is facilitated by means of centrifugal force. One arrangement of the equipment consists of a spiral plate having a space between turns of only about ⅛ in. A connection for withdrawing the fractionated vapor and another for introducing reflux liquid are situated at the center of the spiral; and the mixture of vapor from the still is introduced at the outside of the spiral. The spiral revolves at a high speed and by centrifugal force causes the liquid to travel as a thin film along the entire length of the spiral plate from the center to the outside. The vapor travels in the opposite direction through the spiral, by the difference in pressure between the outside and the inside of the spiral. It is claimed that a vapor velocity of 40 to 80 ft. per second can be maintained because of the elimination of entrainment, and more than 50 theoretical plate equivalents can be obtained in a practical commercial equipment.

Plate Efficiency.—In general, plate efficiency is the ratio of the performance of an actual plate to the performance of some ideal plate. Plate efficiency may be defined as the ratio of the amount of a given component that is absorbed by the liquid upon the plate to the amount that would be absorbed were equilibrium actually attained.

A thermal definition has also been used. Plate efficiency may be defined as the heat actually removed from the vapor passing through the plate divided by the heat that would be removed if equilibrium were attained. At equilibrium the temperature of the vapor above a plate and of the liquid on the

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[10] Podbielniak Industrial Research and Engineering Laboratories, Chicago.

plate are equal, whereas on an actual plate the temperature of the vapor is higher than the temperature of the liquid.

The "ideal plate" tacitly assumed in fractionation equations is one in which all the vapor from the plate below comes in contact with liquid of constant composition from the plate above and is in equilibrium with the liquid overflowing to the plate below. That is, the ideal plate assumes a single perfect equilibrium contact per plate. However, plates in an actual column usually involve a number of successive contacts per plate. The liquid changes composition progressively as it flows across the plate, so that the vapor flowing through each successive row of caps approaches equilibrium with a liquid of different composition. Even if equilibrium were attained at each contact, the composition of the average vapor leaving the plate would be considerably different from the composition of the vapor that is in equilibrium with the liquid that overflows from the plate. It has been shown[11] that the successive contact plate, upon which equilibrium is attained at each contact, produces a greater change in the composition of the vapor passing through it (*i.e.*, it is more efficient under ideal conditions) than is the usual ideal plate which involves a single equilibrium contact. This phenomenon probably accounts for some of the high plate efficiencies (greater than 100 per cent) that have been reported in the literature.

In general, plate efficiency may be regarded as the resultant of two distinct and opposing effects. One of these is the approach to equilibrium between liquid and vapor, while the other, the entrainment of liquid by the vapor, tends to destroy the equilibrium that has been attained. Plate efficiency is an exceedingly complex factor. It varies with the mechanical details of plate and column, with vapor velocity and density, and with the properties of the oil. The plate efficiency is different not only for various fractionating towers but also from plate to plate in a single column.

The plate efficiency probably ranges from 45 to 70 per cent for petroleum oil columns. Authorities on natural-gasoline plant design use 55 to 65 per cent for absorber-column plates operating at a low pressure (30 to 50 lb. gage). The efficiency for high-

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[11] BREWSTER, O. C., *Oil Gas J.*, Apr. 3, 1930, p. 41.

pressure (400 to 600 lb.) absorber plates is said to be 45 to 55 per cent. However, Brown and others[12] report plate efficiencies of 100 to 108 per cent in the analysis of the performance of a commercial natural-gasoline stabilizer.

DIAMETER OF FRACTIONATOR

The function of a bubble column is to establish a series of equilibrium contacts between vapor and liquid. In so doing, an intimate contact is necessary but too high a velocity results in entrainment. Thus two opposing factors develop as the velocity is increased. The separation of petroleum products probably requires only a few perfect equilibrium contacts and hence entrainment is the factor that is most closely related to the allowable tower velocity.

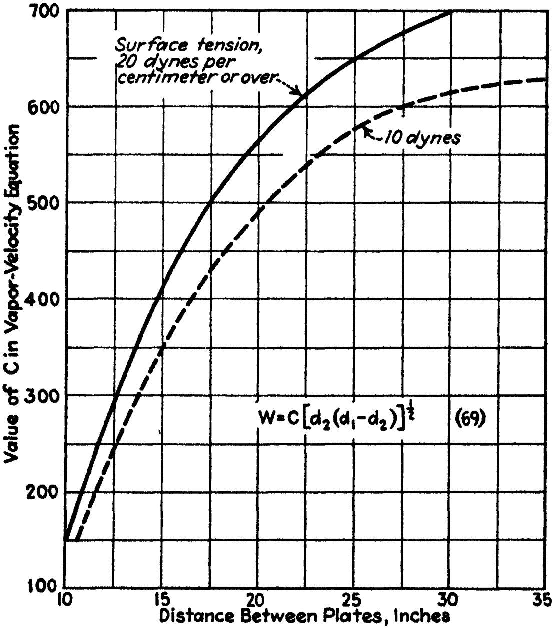

Fig. 146.—Effect of tray spacing on vapor velocity. (*Dr. G. G. Brown and Ind. Eng. Chem.*)

Entrainment is governed by several factors. Some of these are (1) velocity of vapor, (2) density of vapor, (3) density of

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[12] Brown, Souders, Nyland, and Hesler, Design of Fractionating Columns, *Ref. Nat. Gaso. Mfg.*, May, 1935, p. 227.

liquid, and (4) the structural design of the plate. These factors are related to one another, as shown in the following equation.[7]

$$W = C\sqrt{d_2(d_1 - d_2)} \tag{69}$$

where W = mass velocity, lb. per sq. ft. per hr.
d_1 = density of liquid, lb. per cu. ft. (at tower temperature).
d_2 = density of vapor, lb. per cu. ft. (at tower conditions).
C = a constant (Fig. 146).

The value of the constant C is dependent on the tray spacing, the properties of the material, and the construction of the plate. Values of C are given in Fig. 146. The foregoing equation and Fig. 146 were published by Souders and Brown.[7] In order to use Fig. 146 it is necessary to estimate the surface tension. Table 65 is a tabulation of surface tension measurements.

TABLE 65.—SURFACE TENSION OF OILS

Material	Operation	Temperature, °F.	Surface tension, dynes per cm.	Reference
146 vis. at 210 oil	....	500	16.4	13
146 vis. at 210 oil	....	600	12.5*	13
230 vis. at 210 oil	....	500	17.0	13
230 vis. at 210 oil	....	600	14.4	13
1,000 vis. at 210 oil	....	500	18.0	13
1,000 vis. at 210 oil	....	600	15.1	13
Pressure distillate	Rerun	...	13.0	7
Gas oil, 50 mm	Vacuum overhead	...	23.0	7
Natural gasoline	Stabiliser	...	9.0	7
Gas oil, 10 mm	Vacuum (lab.)	...	25.0	7
Pressure distillate	Rerun	...	19.0	7
Gasoline	Topping	...	19.0	7
Pressure distillate	Cracking	...	14.0	7
Gas oil, 20 mm	Vacuum (lab.)	...	24.0	7
Gas oil, 33 mm	Vacuum	...	24.0	7
Benzol	....	178	21.3	Int. Crit. Tables
Normal octane	....	140	17.9	Int. Crit. Tables
2-5 dimethyl hexane	....	230	11.5	Int. Crit. Tables
Decane	....	320	10.7	Int. Crit. Tables
$C_{60}H_{122}$	....	376	19.8	Int. Crit. Tables
$C_{26}H_{54}$	....	316	19.9	Int. Crit. Tables

* Extrapolated.

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[13] WINCHESTER and REBER, Variation of Surface Tension of Lubricating Oils with Temperature, *Ind. Eng. Chem.*, **21**, 1093 (1929).

The velocity is usually greatest at the top of the column and hence the surface tension at the tower temperature of the overhead product should be used in determining the value of the constant C.

The linear velocity is such a complex variable that it cannot be given with accuracy. It is dependent on the pressure, the temperature, the amount of steam that is used, the kind of material, the tray spacing, the structural details of the plate, and the degree of separation that is required. However, for estimating purposes, Table 66 will be useful.

TABLE 66.—SUPERFICIAL VELOCITIES IN TOWERS

Operation	Pressure, lb. per sq. in. abs. or mm.	Tray spacing, in.	Superficial tower velocity, ft. per sec.
Topping	17 lb.	22	2–2.5
Cracking	40 lb.	22	1.2–1.7
Pressure dist. rerun	20 lb.	22	2.2–3.0*
Solution rerun	25 lb.	22	2.2–2.7
Pressed dist. rerun	25 lb.	22	2.2–3.0*
Pressed dist. rerun	60 mm.	24	6–9
Vacuum	30 mm.	30	9–12
Vacuum	90 mm.	24	5–8
Stabilizer	160 lb.	18	1.7–2.2
Nat. gaso. absorber	50 lb.	14	0.8–1.2
Nat. gaso. absorber	400 lb.	18	0.4–0.7

* Greatly dependent on quantity of steam.

Example 73. Diameter of Topping Tower.—See Examples 34, 71, and 72. The quantities and conditions will be taken from these examples.

Density of vapor at top of column (the reflux in the column is always hot reflux):

Lb. of gasoline	3,415	(Example 34)
Lb. internal or hot reflux	14,400	(Example 71)
Lb. steam	567	(Example 72)
Total lb. per hr	18,382	
Total mols material	194	(Example 71)

At a pressure of 780 mm. and a temperature of 286°F., the approximate volume at the top of the tower is

$$\text{Approx. vol.} \ldots 194 \times 379 \times \frac{286 + 460}{520} \times \frac{760}{780} = 102{,}000 \text{ cu. ft. per hr.}$$

$$\text{Density} \ldots d_2 = \frac{\text{lb.}}{\text{cu. ft.}} = \frac{18{,}382}{102{,}000} = 0.18$$

Assume density of liquid, d_1 is 42.7 lb. per cubic foot (page 456).

By Eq. (69)

$$W = C\sqrt{d_2(d_1 - d_2)}$$

$$d_2(d_1 - d_2) = 0.18(42.7 - 0.18) = 7.64$$

C at a tray spacing of 22 in. and a surface tension of 17 is 570 (Fig. 146). Mass velocity, $W = 1{,}580$:

$$\text{Sq. ft. area} = \frac{18{,}382}{1{,}580} = 11.6$$

$$(\text{Diameter})^2 = \frac{11.6}{0.785} = 14.8$$

$$\text{Diameter} = 3.85 \text{ ft.}$$

This corresponds to a linear velocity of $\frac{102{,}000}{11.6 \times 3{,}600}$ or 2.44 ft. per second.

The actual tower (Example 34 and 71) was 4 ft. 6 in. in diameter (a factor of safety of about 35 per cent) but it may never have worked at its full capacity.

Example 74. Diameter of Vacuum Tower.—See Example 66 (page 397). Trays at 30 in. Pressure at top, 30 mm. Top tower temperature, 490°F.

Material	Lb.	Mols
Wax distillate and reflux........	106,000	331.0
Gas oil........................	12,000	49.6
Steam.........................	1,400	78.0
Total.........................	119,400	459.0

Approx. vol....$459 \times 379 \times \frac{760}{30} \times \frac{490 + 460}{520} = 8{,}050{,}000$ cu. ft. per hr.

Density of vapor............................$\frac{119{,}400}{8{,}050{,}000} = 0.0148 = d_2$

Assume $d_1 = 50$ lb. per cu. ft. (it can be computed from Fig. 39).

$$d_2(d_1 - d_2) = 0.0148(50 - 0.0148) = 0.74$$

The constant C for a surface tension of 20 is about 700 (Fig. 146). The allowable mass velocity, $W = 602$.

$$\text{Cross-sectional area of tower} = \frac{119{,}400}{602} = 198 \text{ sq. ft.}$$

The diameter is 15.9 ft. with no factor of safety. (The actual tower that was used for these conditions was 17 ft. in diameter.) The linear velocity corresponding to the foregoing is 11.3 ft. per second.

Tower Equilibrium and Number of Trays.—The direct application of equilibrium equations, involving vapor-pressures and mol fractions of components, to the design of oil columns is hopelessly involved and is not a satisfactory or safe method of design.

Several attempts have been made to employ simplifying assumptions which would reduce the complex system to the essential mechanism of a binary mixture and thereby permit of a practical calculation of the number of theoretical plates required for a definite separation of components. One of the methods[14] consists of (1) selecting a narrow-boiling fraction near the "cut-point" between the fractions separated, (2) considering this as an ordinary component with the same average volatility as a pure hydrocarbon of corresponding boiling-point, and (3) calculating

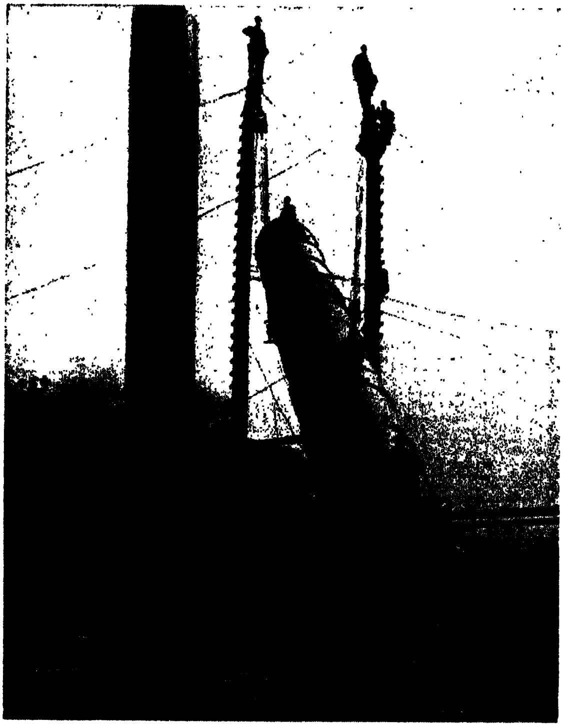

FIG. 147.—Erecting a bubble-tower. (*A. J. Smith Engineering Company.*)

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[14] LEWIS and WILDE, *Trans. Am. Inst. Chem. Eng.*, **21**, 99 (1929).

the number of plates required to secure a satisfactory distribution of the arbitrary component between distillate and residue. The calculations consist of computing material balances and equilibrium relationships from plate to plate. This method is unsatisfactory because the calculated results vary with the fraction chosen as the arbitrary component.[15] Another method which has been proposed[16] employs graphical integration of an equilibrium equation, applied to the true-boiling-point curve of the vapor distillate or liquid residue. The liquid or vapor in equilibrium with the material represented by the true-boiling-point curve is calculated and the analysis is continued from plate to plate down (or up) the column until a residue (or distillate) of the desired composition is produced.

All such methods, when applied to petroleum oil columns, indicate that the separation of marketable oil products is a relatively easy separation. Perhaps two or three perfect equilibrium contacts are sufficient for the separation of most petroleum products.

Because of the difficulties involved in the theoretical design of columns for complex mixtures and also because of the use of multiple-draw columns, petroleum towers are usually designed by relying on plant experience. As an approximation the number of trays (22-in. spacing) between fractions that may be used are shown on page 467.

Fractionation is more effective at low pressures than at high pressures because of the larger difference in the vapor-pressures of the components at a low pressure. This probably accounts for the relatively few plates that are used in many vacuum plants, although the wide tray spacing that is normally used accounts in part for the lesser number of trays.

As indicated earlier in the chapter, fractionation is disturbed in the multiple-draw column because the lower boiling products pass the plates in the column from which the high-boiling products are withdrawn. Thus side-draw products are bound to contain low-boiling materials, and no amount of fractionation can completely eliminate this difficulty. These light components are customarily removed from the side-draw products by the use of auxiliary steam stripping columns. Each of the side-draw products is allowed to

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[15] Lewis and Smoley, *A.P.I. Bull.*, **11** (1), Sec. 3, 73 (1930).

[16] Brown and Caine, *Trans. Am. Inst. Chem. Eng.*, **21**, 91 (1928).

flow through about four bubble plates in the steam stripping column. Although the stripping column usually appears to be about as tall as the main fractionating column, in reality it consists of separate distinct columns, one above another, and a separate stripper is used for each side-draw product. Steam is admitted to each stripping column, and the vapor (steam and a small amount of light material) from each stripper is allowed to pass back into the main column at the tray above the side-draw plate. Thus the steam stripper governs the initial boiling-point or flash-point of the product but the degree of fractionation which is obtained in the main column governs the end-point.

Operation	Materials	Plates between fractions
Steam, atmospheric	Gasoline and kerosene	5–6
	Gasoline and naphtha	4–5
	Naphtha and kerosene	4–5
	Kerosene and gas oil	4–5
	Gas oil and wax distillate	3–5
	Stripping plates	4–5
	Gas oil and vaporizer	2–3
Cracking	Pressure distillate and recycle	7–9
Brightstock solution	Naphtha and gas oil	4–5
	Gas oil and neutral	5–6
	Neutral and feed plate	3–5
	Stripping plates	4–5
Lubricating oil	Gas oil and wax distillate,* vacuum	2–3†
	Wax distillate and overhead cylinder stock, atmospheric	7–10
	Wax distillate and overhead cylinder stock, vacuum	3–4†

* Often separated by partial condensation.
† At wide tray spacing (30 in.).

The use of internal stripping sections is becoming more and more common. The stripping tower is smaller than the main tower, and hence it can be built within the main tower.

Steam strippers are designed in the same manner as fractionating columns. In determining the diameter, the volume of the steam is all that is usually considered.

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CHAPTER XXII

CRACKING PROCESSES

Although the commercial practice of cracking functions by the principles outlined in Chap. XVII, it has not been guided to a large extent by these principles. As is so often the case in industrial development, commercial improvements have preceded the development of theory. Perhaps the greatest hindrance to rapid commercial development has been difficulties in the fabrication of materials which could withstand the high temperatures and pressures necessary in most cracking processes. Today it is hard for us to realize the inadequacy of the materials and fabrication facilities which were available when cracking was first commercially attempted in about 1910. At that time, steam boilers could hardly be operated at pressures exceeding 80 to 100 lb. per square inch and at such pressures the boiler had to be fabricated and tended with the greatest care or the pressure could not be maintained. Obviously, the advantages of operating at a pressure of 1,000 to 1,500 lb. per square inch or at a temperature exceeding 900°F. could not, at that time, be given serious consideration.

Although a large number of processes were developed or proposed during the decade 1910–1920, most of these have not survived. The one process which was practiced on a large scale was the Burton process. This process was developed by the Standard Oil Company of Indiana and was used extensively by many of the Standard companies. The first commercial-size Burton still was operated in about 1913, and by 1920 several hundred Burton stills were in operation. In general, the Burton process consisted of heating a charge of oil to about 700°F. After reaching 700°F., the temperature was gradually raised to a final temperature of 775 to 810°F. Additional oil was added during heating from 700 to 800°F. and the still was on-stream from 24 to 30 hr. The cracked distillate amounted to 60 to 65 per cent but the distillate contained only about 50 per cent of end-point gasoline. About 35 per cent of residual fuel oil was also produced. The operation was conducted in a 10 by 30-ft. pressure shellstill. The products were condensed under the pressure of the still.

Many other processes were attempted during this same period but most of them are not important today. For a detailed discussion of these processes and the patents under which they operated, refer to "Motor Fuels" by Leslie[1] and "American Petroleum Refining" by Bell.[2]

Modern cracking processes are expected to produce a large yield of gasoline, produce little coke, and be able to operate for a long period of time before cleaning is necessary. The formation of coke is necessarily related to the length of operation because the unit must be shut down to remove the coke. The percentage of time that the unit is in active operation is referred to as the cycle-time-efficiency. For example, if the unit can operate for 45 days and then requires 5 days for shut-down, cleaning, repair, and time to get on stream, the cycle efficiency is 90 per cent. The expense of shut-down time is so great that it is usually more economical to sacrifice some yield than to have a poor cycle efficiency. This accounts, in part, for the relatively small amount of coking that is practiced. The yield by cracking is much greater if coke, rather than fuel oil, is produced but the cost of operating a coking plant is great.

Cracking processes may be generally classified as follows:

1. *Viscosity Breaking.*—A short-time decomposition, usually conducted at low cracking temperatures (830 to 870°F.), for the purpose of reducing the viscosity or pour-point of a heavy straight-run fuel oil.
2. *Mixed-phase Cracking.*—Most of the widely known processes are classed as mixed-phase processes. The name liquid-phase, which is often used, is a misnomer because in most processes some vapor generation occurs. The purpose is the production of antiknock gasoline and a greater total yield of gasoline from crude oil.
3. *Reforming.*—A cracking process that utilizes a straight-run gasoline or naphtha as a charging-stock. The cracked distillate has a much higher octane-number than the charging-stock. The feasibility of the process depends upon the market demand for high-octane fuel. A high temperature must be employed.

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[1] Leslie, E. H., "Motor Fuels," Chemical Catalog Company, Inc., New York, 1923.

[2] Bell, H. S., "American Petroleum Refining," 2d ed., D. Van Nostrand Company, Inc., New York, 1930.

4. *Vapor-phase Cracking.*—These processes are usually more expensive than the liquid-phase processes but the gasoline is highly antiknock and can be sold at a premium as a blending stock.
5. *Coking.*—The operating of coking involves nothing more than a cracking process in which the time of cracking is so long that coke is produced as the bottoms product. Special means of collecting and removing the coke must be provided.

Cracking Plant Design.—The major difference between liquid or mixed-phase and vapor-phase cracking is the pressure that is used. In the liquid-phase and mixed-phase processes, the pressure is usually held above 350 lb. per square inch. This pressure is above the critical pressure of most of the hydrocarbons that are found in cracking-stocks (and products) and hence a very dense phase, whether it be liquid or a mixture of liquid and vapor, is produced. The density of the vapor, if any is formed, is high and hence little or no stratification of the mixture occurs at the velocities that are maintained in the cracking-tubes of the pipe-still. A lower pressure may result in a separation of liquid and vapor, and the liquid that sticks to the walls may be decomposed into coke. There are other differences between liquid and vapor-phase processes such as the types of stocks that may be cracked and the temperature-pressure-relation. The liquid and mixed-phase operations are characterized by the use of a relatively low temperature and high pressure, whereas the vapor-phase operations are characterized by a relatively high temperature and a low pressure.

In vapor-phase processes, the pressure is normally less than 100 lb. per square inch (often 35 lb.) and a pure vapor-phase is produced. The time in the cracking-tubes is short because of the great volume of material and hence the temperature must be higher than for liquid or mixed-phase operation. The importance of a *homogeneous phase* must again be stressed. If any liquid particles are present in the vapor, they will be thrown to the tube walls and cause the formation of coke.

The time of cracking in modern processes ranges from about 1 sec. for some vapor-phase processes to about 200 sec. for liquid-phase processes. Such short times as these must be carefully controlled and hence most modern processes are arranged so that the hot cracked material can be suddenly cooled by means of the charge-stock or fuel oil from the process. This operation is referred to as *quenching*.

Another factor which is vital in the operation of many cracking systems is the production and cracking of only *clean distilled stocks.* If a residual product is to be cracked, the gas oil that it contains is distilled from it in a topping operation; this topping may be conducted in the cracking plant itself or the system must be arranged so that only straight-run tar is cracked. The cycle efficiency is usually much higher if only distilled stocks are cracked. Unless a cracking-pipestill is carefully designed, coke will be deposited in the tubes and will cause a shut-down after about a week if a residual stock is passed through the tubes. Even coking processes depend upon a clean stock for heating the coke chamber (Fig. 157).

Although the cracking of a distilled stock is advantageous from the standpoint of the cycle-time-efficiency, the yield of pressure distillate is usually slightly smaller than when a *residual* or *black stock* is cracked. If a distilled stock is produced from a black charging-stock, a part of the charging-stock is not thoroughly cracked, and therefore the yield is smaller. Likewise, the tar that is produced by cracking only the distilled part of a black charging-stock tends to have a high viscosity and the yield of distillate must be less in order to produce a tar of suitable viscosity. If the difficulties of heating and cracking a black stock in the cracking-tubes can be solved, the cracking of the entire black stock in the tubes is advantageous. The Dubbs process is one of the few processes that has been able to avoid serious coking of the tubes when cracking a black stock.

If a black stock is cracked in the tubes, it is always advantageous to separate the cracked tar that is produced in the cracking reaction and allow none of it to enter the cracking-tubes during recycling.

The use of a quench-stock, the production of a homogeneous phase, and the cracking of stocks that contain no cracked tar are details which are not easily recognized in flow diagrams of processes, but close inspection reveals that almost all successful processes utilize these principles. The flow diagrams that are given later in the chapter are those that are usually given for the different processes, but many refiners have modified the operation of the processes so that the aforementioned principles can be utilized.

The velocity (hot) of the oil-vapor mixture in the cracking-tubes must exceed about 10 ft. per second or coke will be deposited. Most processes maintain a velocity of 11 to 14 ft. per second (hot). Higher velocities would be advantageous except that the pressure-drop becomes prohibitive. Thus if a pressure of 450 lb. is to be held at the outlet of the still, the charging pressure, at a velocity of 13 ft. per second, will be about 850 lb. per square inch. As coking takes place, the charge-pressure rises to over 1,000 lb. per square inch. The rate of heat absorption in the pipestill usually ranges from 10,000 to 14,000 B.t.u. per square foot of projected area (3200 to 4500 B.t.u. per square foot outside diameter surface). These low rates can be produced in the radiant section by using a large amount of radiant surface, by using flue-gas recirculation, or by using large amounts of excess air. Part of the convection section may be used for the cracking zone but the exact location in the convection section cannot be easily determined. Some engineers believe that cracking must take place at a constant or slightly rising temperature or coke will be deposited.

Volume of Stock at Cracking-temperature.—In analyzing cracking plant operation or in designing cracking-still equipment, the estimation of the volumes at cracking conditions always proves troublesome. The exact volume cannot be computed but fair approximations can be made. The problem is really not so serious as it might seem because the exact volume or velocity is not necessary. This is true because a small change in the cracking-temperature will compensate for a large error in the computed time in the cracking zone or in the velocity that is used. In other words, during operation, the cracking-temperature can always be adjusted through a temperature range of 15 or 20° and this adjustment allows for a range of about 90 per cent in the cracking time. [Eq. (62), page 330]. The time in the cracking zone can easily be computed within an accuracy of 90 per cent.

An examination of critical data for petroleum products suggests several important facts concerning the volume at cracking conditions. The critical temperature of the mixed stock that is found in the cracking zone is seldom less than 875°F. Thus at cracking-temperatures of 900 to 950°F. the critical temperature is not greatly exceeded. In the case of a pure compound, the material cannot exist as a liquid if the critical temperature is exceeded. With mixtures, a different condition arises. A range of critical temperature is found and complete vaporization does not occur at the so-called critical temperature. However, some vapor generation probably does occur at the conditions that are encountered in liquid-phase processes.

If vapor generation does occur, the vapors will not occupy a great volume or, in other words, the total volume will not be greatly increased by the vaporization. The critical pressure of petroleum products ranges from about 125 lb. for gas oil to about 500 for gasoline. Thus any vapor that is produced will be very dense or will occupy a relatively small volume at the pressures used in cracking processes. The gas is the material that would be generated if anything is generated. Table 67 was computed as a comparison of the effect of vapor generation on the volume of the cracking-stock (Example 75). The table was computed for a process operating at a temperature of 900°F. and a pressure of 400 lb. per square inch, when the recycle ratio was 2 to 1.

TABLE 67.—EFFECT OF VAPOR GENERATION ON THE VOLUME OF CRACKING-STOCK

Per cent of gas generated	Approximate barrels of material at 900° and 400 lb. per sq. in. per barrel of charge-stock			
	Recycle stock	Liquid products	Gas	Total
0	0.98	1.66	....	2.64
25	0.98	1.13	0.55	2.66
50	0.98	0.73	1.11	2.82
100	0.98	0.46	2.22	3.66

Thus the volume at cracking conditions changes by only about 38 per cent if all of the gas is generated.[3] If the cold velocity (60°) is 5 ft. per second, the velocity at 900° with 50 per cent of the gas generated will be about 5 × 2.82 or 14.1 ft. per second.

Example 75. Estimation of Volume at Cracking Conditions.—A plant produces the following materials:

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[3] The author estimates that not more than half of the gas is generated at 900° and 400 lb.

Basis: 100 gal. of stock.

Material	Per cent by volume	A.P.I.	Lb. per gal.	Total lb.
Pressure distillate	50.0	53	6.385	319.2
Cracked fuel oil	43.0	11	8.27	356.0
Gas (by difference)	27.6*	....	3.0*	82.8
Stock	100.0	24	7.58	758.0
Recycle†	200.0	17.1		

* Approximate, see Example 62 (page 335).

† Two parts of recycle (17.1 A.P.I.) are used per barrel of stock.

At 60°F. and with 25 per cent of gas generated:

Gal. of pressure distillate, fuel oil, and 75 per cent of gas,

$$93 + 0.75 \times 27.6 = 113.7$$

Lb. per gal. of pressure distillate, fuel oil, and 75 per cent of gas,

$$\frac{758 - 0.25 \times 82.8}{113.7} = 6.5$$

This corresponds to a gravity of 49.7 (sp. gr. = 0.78).

At 900°F. (see Fig. 39, p. 118):

Vol. of pressure distillate, fuel oil, and 75 per cent of gas,

$$113.7 \times \frac{0.78}{0.26} = 340 \text{ gal.}$$

Volume of 25 per cent of gas (Example 11, $P_R = 0.59$; $T_R = 2.38$; $V_R = 15$ and; mol wt. = 32) = 167 gal.

$$\text{Volume of recycle stock (Fig. 39)} = 200 \times \frac{0.95}{0.643} = 296 \text{ gal.}$$

Total volume of 300 gal. of stock and recycle, at 900°:

$$340 + 167 + 296 = 803 \text{ gal.}$$

Bbl. of material at 900° per bbl. of charge-stock = $^{803}/_{300}$ = 2.66 (Table 67).

CRACKING PROCESSES

There is a striking similarity between all of the widely used modern cracking processes. Many processes crack only a clean distilled stock, and the hot stock from the pipestill tubes is quickly cooled by a quench-stock. Other processes have reaction chambers or soaking drums by which the capacity and yield are increased, but drums and chambers are not necessary unless coke is to be produced. The arrangement of the equipment, *i.e.*, stills, towers, evaporators, etc., is different for the several processes but the fundamentals of the processing are much the same in all of them.

Following the establishment or discovery of these fundamentals, the development of modern cracking processes may be directly traced to the development of suitable construction materials. Lyman C. Huff[4] says,

> Among these are large, forged-steel and electric-welded vessels, such as reaction chambers and dephlegmators, heavy seamless-steel tubing in iron-pipe sizes, alloy steel tubing, welded pipe joints, metal-to-metal high-pressure flange joints, alloy-steel studs and bolts, alloy-steel forgings and castings, high-temperature and high-pressure cast and forged-steel valves and fittings, high-temperature and high-pressure pumps (handling oil up to 800°F. and 1,500 lb. pressure), fans for circulating flue gases at high temperatures (1100 to 1200°F.), high-temperature insulating materials and many others.

Of almost equal importance was the formulation of the theories of heating and the application of these theories in the plant, so that mild absorption rates could be maintained in the pipestill. Obviously, the modern cracking processes could not have been developed without developing the pipestill.

In the following pages, only those modern cracking processes which have found wide application will be discussed. If any processes of merit have been neglected, it is not because their merits have not been recognized, but simply because they have not as yet been widely used. In a book of this size all of the promising processes cannot be discussed. The most widely used processes are the Dubbs, the so-called Tubestill, the Cross, the Gyro, the Tank-and-Tube, and the Holmes Manley. The Jenkins, deFlorez vapor-phase, Isom, and Gulf processes are less widely used.

Tubestill Process.—Among the latest developments in cracking processes is what may be called the Tubestill process. This process is so named because the major piece of equipment is a high-pressure high-temperature tubestill. Practically all of the cracking takes place within the furnace tubes so that no

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[4] *Oil Gas J.*, Oct. 9, 1930, p. 138.

reaction chambers are required. The success of the process is largely due to the production of a clean distilled cracking-stock which can be cracked with the production of little or no coke. A small amount of decomposition also takes place in the evaporator (Fig. 148) or flash drum, but this decomposition is not important, except as it aids in reducing the viscosity of the pressure-still tar and in producing additional clean recycle stock. The vapor heat exchangers shown in Fig. 148 are a source of difficulty and the use of an additional pipestill heater is a better arrangement.

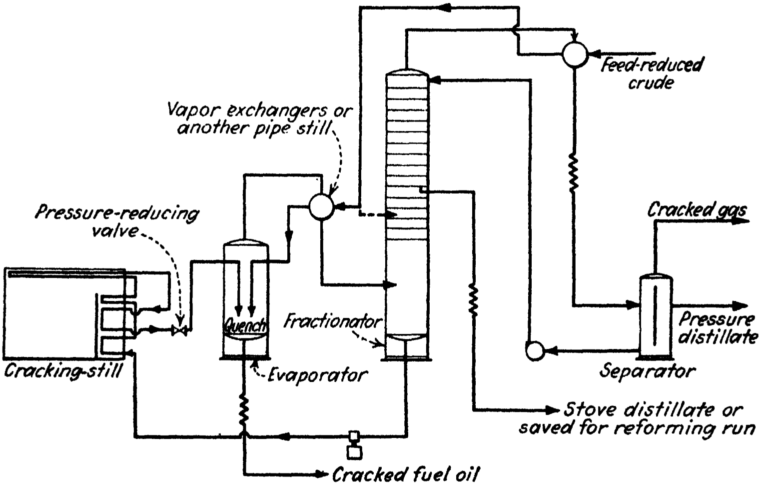

FIG. 148.—Tubestill cracking process.

The Tubestill process will be discussed in more detail than other processes, not because it is more important than other processes, but because it is well adapted for an explanation of the operation of cracking.

In order to crack the oil in the short length of time during which it passes through the tubes, a high temperature is necessary. The pipestill outlet temperature is about 890 to 940°F. depending on the stock, and the time for cracking is only 2 or 3 min. At these rapid rates of cracking it is necessary to quickly lower the temperature. This is accomplished at the point marked "quench" in Fig. 148 by mixing the charging-stock with the cracked material from the pressure-still. Mixing in this manner is a perfect means of heat-exchange, and hence the maximum amount of heat contained in the pressure-still product is recovered and utilized in vaporizing the charging-stock.

Continuous operation for periods of 3 months is common, although the operation is often prematurely terminated by the formation of coke within the tubes. In maintaining long cycles of operation, the condition of the charge to the furnace is of prime importance. If this stock contains any tar by imperfect separation in the fractionating tower, coking proceeds immediately, and after 6 hr. of operation on a dirty charge-stock the tubes will often be badly coked and the operation must be halted. A low conversion per pass, 18 per cent or less, aids in reducing coke formation. Thus the process is vitally dependent on "clean circulation."

Although many of these plants operate on a gas oil charging-stock, it is becoming more and more common to charge a reduced crude stock. Thus the topping of gas oil from reduced crude oil is accomplished within the cracking plant itself but only the gas oil is exposed to cracking conditions. The viscosity of the tar, when charging gas oil, is relatively low, but it may be too high for market specifications if reduced crude oil is the charging-stock. This difficulty may be remedied by lowering the evaporator temperature and producing less gasoline or by providing a longer soaking time (viscosity breaker) in the evaporator. A vaporizer temperature higher than 820°F. will usually cause the deposition of coke in the evaporator.

The cracking-tubes may be in the convection or radiant section but in either case the rate of heat input should be kept below about 13,000 B.t.u. per square foot of projected area per hour. Furthermore, the hot velocity should be maintained at 10 ft. per second or higher. An outlet pressure of 400 to 700 lb. per square inch is maintained at the outlet of the pipestill. Lower pressures result in the formation of coke and, though we know little of the phase condition at such temperatures and pressures, it is usually conceded that some vapor generation takes place even at a pressure of 700 lb. per square inch. A pressure-drop of 300 to 800 lb. per square inch occurs through the pressure-still, so that inlet pressures of 700 to 1,200 lb. per square inch are common. Twin-simplex, compound steam cylinder pumps or crank-and-flywheel steam engine pumps are commonly used (Fig. 149). Multistage centrifugal pumps have also been used (Fig. 150). The conversion-per-pass usually ranges from 14 to 20 per cent.

This process has been used for vapor-phase cracking without changing the fundamentals of the process. However, the outlet temperature is much higher (1050 to 1100°) and the outlet pressure must be reduced to 30 to 50 lb. per square inch so that substantially a pure vapor-phase exists in the cracking-tubes. Milder rates of heating and higher recycle ratios must be used. Difficulty arises because cracking starts to occur before vaporization is complete and coke is deposited in some section of the still.

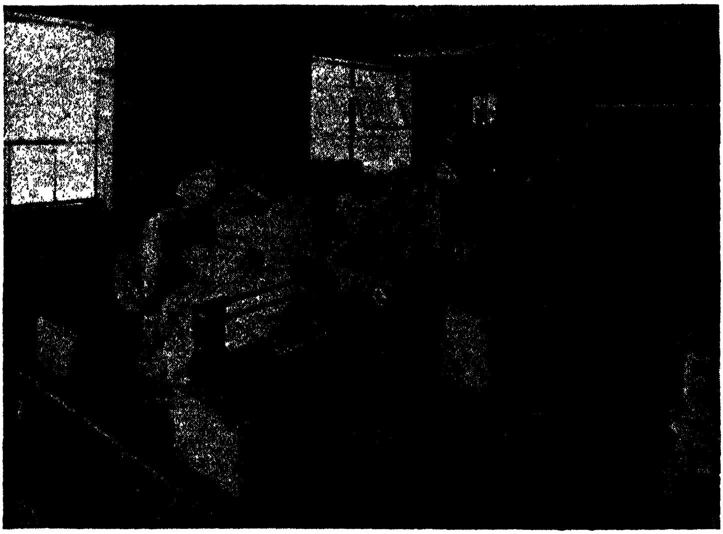

Fig. 149.—Installing a Wilson Snyder twin-simplex compound pump for high temperatures and pressures. (*A. J. Smith Engineering Company.*)

The best known continuous coking processes are like this process except that coke drums are substituted for the evaporator vessel of the Tubestill process (Fig. 157).

One of the advantages claimed for the Tubestill process is the long cycle of operation. Shut-downs for the removal of coke are expensive and hence the longer the operating period over which the expense of a shut-down can be distributed, the greater is the economy of the operation. These plants often operate on an

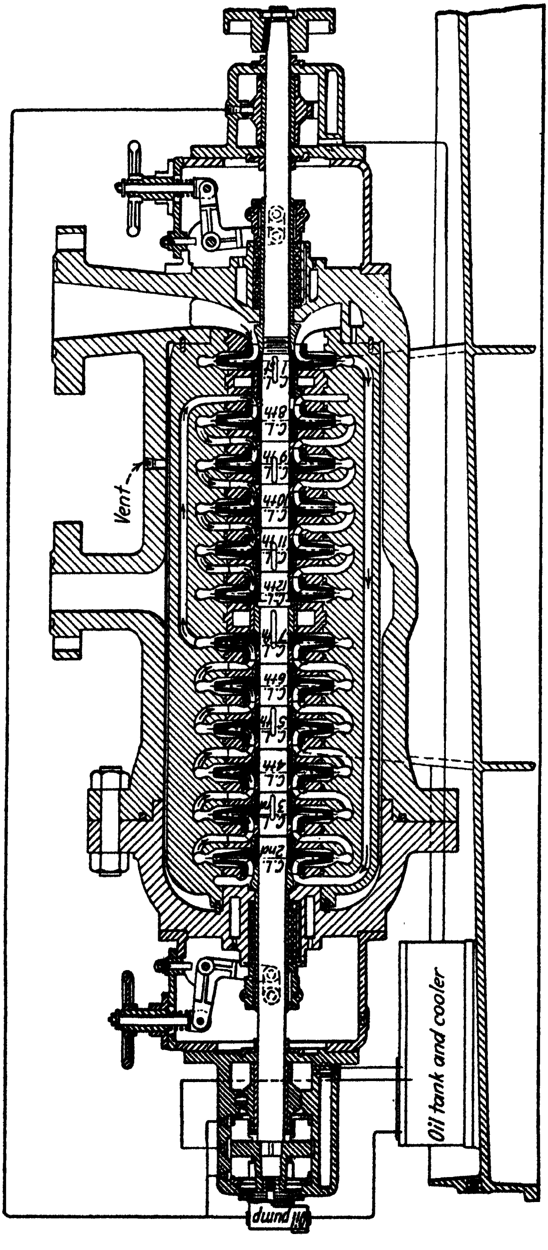

FIG. 150.—Twelve-stage hot oil centrifugal pump for oil at a temperature of 850°F. and a pressure of 1,500 lb. per square inch. (*Byron Jackson Pump Company.*)

average cycle efficiency of more than 97 per cent, although a more common figure is 93 per cent.

In processing topped or reduced crude oil, the maximum yield of gasoline is largely dependent upon the properties of the pressure-still tar. If too high an evaporator or vaporizer temperature is used or if the time in the evaporator is too short, the tar may be a solid asphaltic material which is awkward to handle and cannot be marketed. In processing gas oil, this difficulty seldom arises because the tar consists almost entirely of cracked tar which has a lower viscosity. However, an evaporator temperature of about 820°F. cannot be exceeded because coke will be deposited in the evaporator. The large yield of 56.5 per cent of end-point gasoline shown in the third operation of Table 68 indicates the increased yields that are possible with a high evaporator temperature. In this operation, approximately 80 per cent of the topped crude oil was vaporized. However, this operation was not entirely successful because coking occurred within two weeks and the tar had a furol viscosity of over 1,200 sec. at 122°F. In processing reduced crude oil, it is sometimes necessary to use a second pipestill for heating the reduced crude oil. The evaporator temperature may not be high enough with the vapor heat exchangers alone.

TABLE 68.—YIELDS BY THE TUBESTILL PROCESS

Charging-stock	A.P.I.	Per cent gasoline	Per cent tar and P.D. butts	Evaporator or vaporizer temperature, °F.	Recycle ratio	Pressure at outlet	Temperature at outlet, °F.
1. M.C. topped crude........	23.9	49.5	47.8	780	2.5:1	750	901
2. M.C. topped crude........	23.9	38.0	60.8	730	1.6:1	700	915
3. M.C. topped crude........	23.9	56.5	41.7	807	2.7:1	400	914 (low cycle efficiency)
4. Calif. gas oil.............	18.5	51.0	42.0				
5. M.C. topped crude........	26.0	42.0	38.0	780	.....	low	1100 (vapor-phase)
6. 38 per cent M.C. topped crude...............	20.2	49.8	48.7	758	2.3:1	400	890
62 per cent M.C. gas oil..	28.3						

Dubbs Cracking Process.—This process is used widely by independent companies and also by many large companies. An advantage of the process is its great flexibility in meeting all types of operation. Almost any charging-stock, including naphtha, distilled fuel oils, light and heavy residue oils, waste wax stocks, and even semi-solid asphalts, may be processed. The operation may be conducted for the production of tar or coke and large yields of distillates if such an operation is economical.

Figure 151 indicates the three most common methods of operation.[5] With *nonresiduum operation* the oil that is charged to the system is converted entirely to pressure distillate, fixed gas, and coke. High yields of gasoline are produced but the cycle-time-efficiency is low because the operation must be interrupted for the removal of coke.

However, two reaction chambers can be used so that one is being emptied while the other is "on-stream." In this manner, nonresiduum runs of as long as 98 days have been conducted. The coke is sometimes removed from the reaction chamber by means of a special steel cable which is laid in spiral form, from the top to the bottom of the chamber. At the end of the run the cable is pulled through the bottom manhole, cutting through the coke and breaking it so that it may be removed through the manhole of the chamber. A conveying system or small cars are used to collect the coke under the manhole and deliver it to storage. Drills are also used to cut the coke from the reaction chamber.

Flashing operation is practiced for the production of fuel oil instead of coke. Lower yields of gasoline are obtained but the cycle of operation is much longer. The viscosity of the tar can be regulated, to some extent, by the height of oil held in the chamber or, in other words, the length of time during which the tar is allowed to decompose or soak. If a very heavy stock is charged, then the *Low-level operation* is used. In this type of operation, the tar is not allowed to crack to pitch or coke but is drawn from the chamber almost immediately. The gasoline yields are smaller than by either of the other types of operation but the length of run is long.

Another type of operation, termed *full-flashing*, has been introduced recently. In this type of operation, the stock from the furnace enters the reaction chamber at the top and leaves at the bottom. The liquid and vapor from the reaction chamber

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[5] Huff, L. C., *Trans. A.S.M.E.*, **52**, *Petroleum Mech. Eng. Division*, p. 65 (1930).

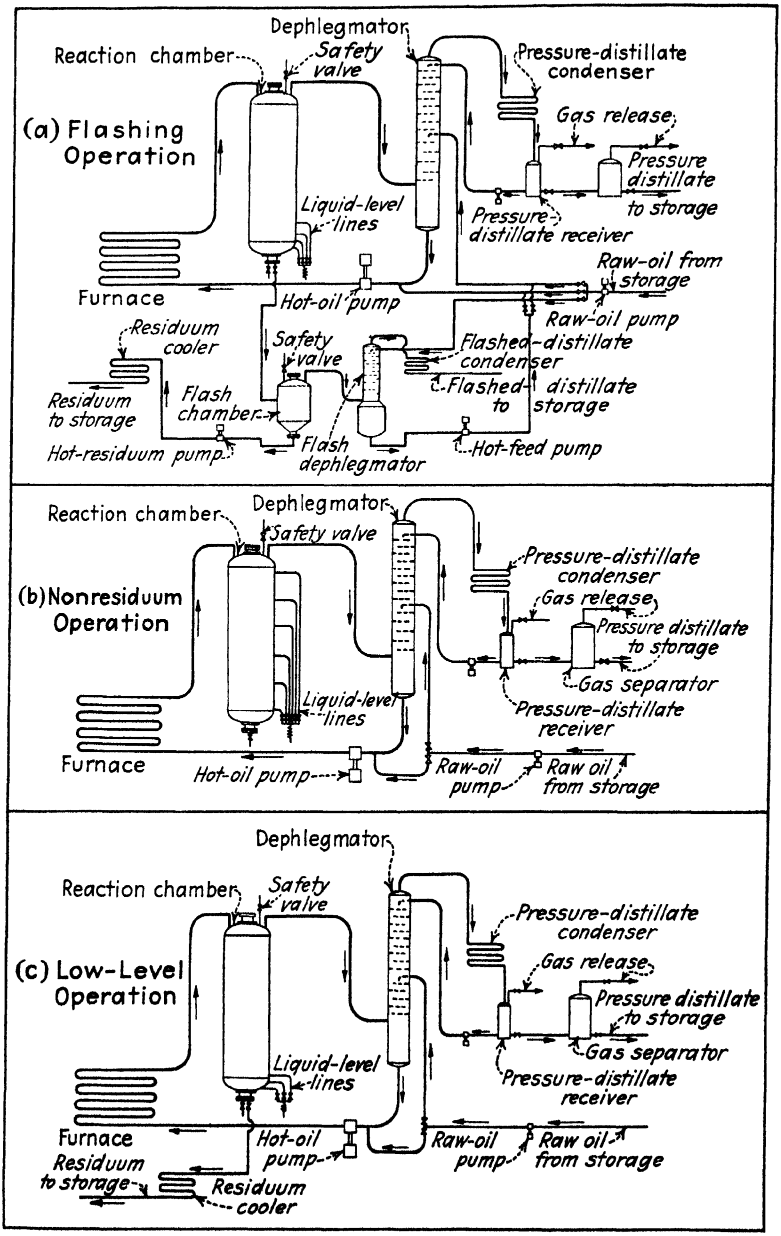

FIG. 151.—Diagrams of Dubbs process: (*a*) flashing operation, (*b*) nonresiduum operation, and (*c*) low-level operation. (*Universal Oil Products Company.*)

are flashed into the base of a combined flash chamber and fractionating tower. The feed to the plant is introduced part way up the tower and the combined feed- and recycle stock is withdrawn just above the flash chamber and it is charged, while still hot, to the cracking-still. The downward travel of the material through the reaction chamber permits the vapor to be soaked for a relatively long time but the liquid passes rather quickly to the flash chamber. The cracked tar is withdrawn from the flash chamber.

Table 69 indicates yields by the three common methods of operation. The operating conditions for various stocks range as follows:

Operating pressure on chamber.....	140– 355 lb. per sq. in.
Transfer temperature to chamber...	876– 969°F.
Vapors to dephlegmator...........	825– 865°F.
Vapors to condenser...............	450– 530°F.
Combined feed to heating-tubes....	745– 820°F.
Furnace, above tubes..............	1260–1630°F.

TABLE 69.—DUBBS CRACKING PROCESS

Charging-stock	A.P.I.	Per cent gasoline 437 end-point	Per cent tar and P.D. butts	Lb. coke per bbl.	Operating pressure	Cycle-eff.*	Type of operation	Reference
West Tex. fuel oil..............	21.8	60.55	12.58	56.0	185	0.80	Nonresiduum	[5]
Mixed M.C. and W. Tex. fuel oil.	20.7	62.0	12.24	74.9	150	0.77	Nonresiduum	[5]
Pa. gas oil....................	37.8	72.8†	9.2	29.7	267	0.89	Nonresiduum	[5]
Calif. fuel oil..................	18.5	36.4‡	54.5	0.115	171	0.90	Flashing	[5]
Mixed M.C. and W. Tex. fuel oil.	20.0	44.29	50.21	0.39	200	0.82	Flashing	[5]
M.C. topped crude.............	24.0	44.38§	53.53	......	153	0.86	Flashing	[5]
Mixed M.C. gas oil and P.D. butts	33.1	64.93	24.2	......	273	0.88	Flashing	[5]
Calif. gas oil..................	32.1	61.8	28.2	0.009	300	0.88	Flashing	[5]
Mex. gas oil....................	26.9	56.08	32.36	......	280	0.96	Flashing	[5]
West Tex. residue..............	21.4	37.15	61.23	0.026	180	0.88	Low level	[5]
Calif. residue..................	18.6	34.76	58.11	......	175	0.90	Low level	[5]
M.C. kerosene..................	39.3	74.9	6.5	......	354	....	....	[6]

* Assuming 12-hr. shut-down for nonresiduum operation and 48 hr. for other types of operation.

† 425°F. end-point.

‡ 410°F. end-point.

§ 428°F. end-point.

The Dubbs process is one of the few processes that can successfully crack a black or residue stock in pipestill tubes without

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[6] EGLOFF *et al.*, *Oil Gas J.*, Apr. 16, 1931, p. 30.

undue formation of coke in the tubes. The process is able to crack a black stock in the tubes and still maintain a high cycle efficiency. For this reason, higher yields are generally claimed for the Dubbs process.

Cross Cracking Process.—The Cross process is one of the widely used processes. A reaction chamber is provided (Fig. 152) which allows the process to be operated for maximum yields and the formation of coke. If two reaction chambers are provided, the operation may be conducted semi-continuously by using one reaction chamber while the other is being cleaned. Some refiners report that less coke is produced if the stock is withdrawn from the bottom of the reaction chamber. Perhaps this allows a soaking of the vapor as in the full-flashing operation of the Dubbs process. The Cross process in its original form is used so little today that yields and operating conditions will not be presented.

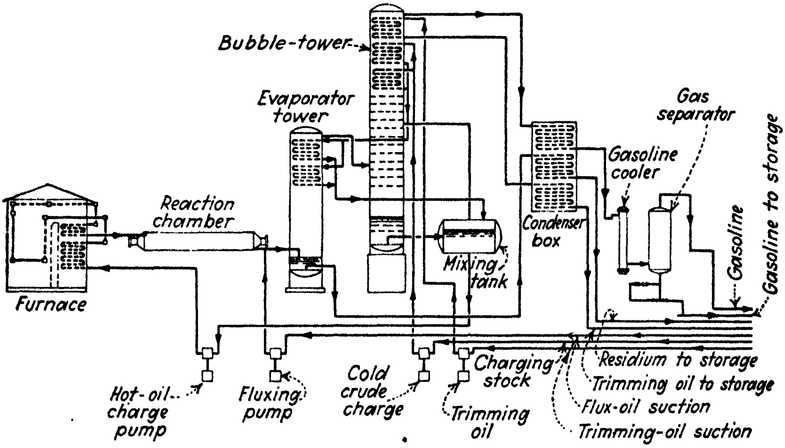

FIG. 152.—Cross cracking process. (*Gasoline Products Company.*)

The modernization of existing Cross plants has been taking place continually. In most instances, these plants have been changed to systems which are essentially the same as the tubestill process (Fig. 148) that has already been described.

Other Liquid-phase Processes.—The Tube-and-Tank and the Holmes Manley processes are used to process a large quantity of oil but they are used by only a few of the larger companies. These processes operate most successfully on clean gas oil cracking-stocks although fuel oil has been used as the cracking-stock for both of the processes. Figures 153 and 154 are diagrams of these processes.

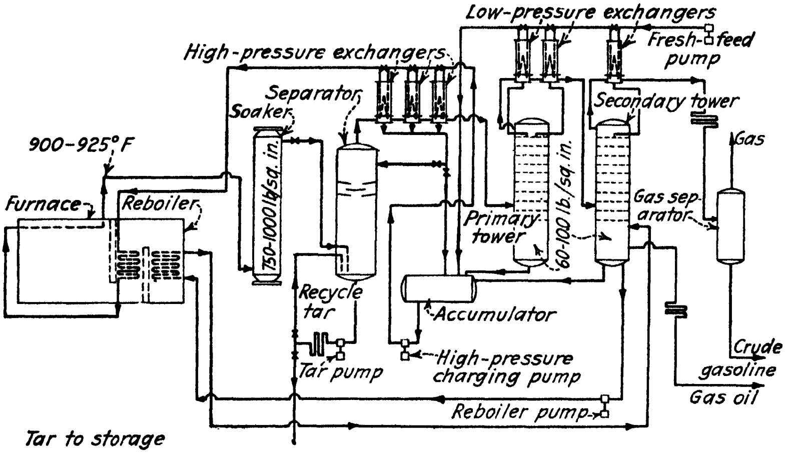

FIG. 153.—Tube-and-Tank high-pressure cracking process. (*Gasoline Products Company.*)

Vapor-phase Processes.—The Gyro process was one of the first processes successfully to overcome the difficulties of cracking

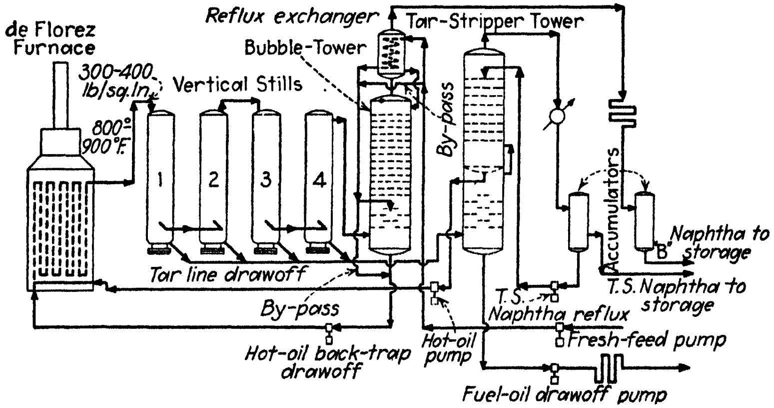

FIG. 154.—Holmes Manley cracking unit. (*Gasoline Products Company.*)

in the vapor-phase. Major among these difficulties had been the formation of coke, the short length of the operating period, and difficulties in treating the distillate. At the same time, a large amount of gas was produced and until recently the yield of gasoline by vapor-phase processes was relatively low. In the Gyro process, the formation of coke is now largely avoided by the production of a pure dry vapor.

At present the Gyro process compares favorably with the common liquid-phase processes in cost of operation, length of cycle, and yields. Figure 155 indicates that any charging-stock may be used and that the equipment is simple and flexible. However, only the gas oil distilled from the charge-stock is cracked. The finished gasoline often has an octane-number of 85 or more which is in general higher than the octane-number of the gasoline produced by other processes. The gas is of a highly unsaturated nature and may become of great importance as a raw stock for the manufacture of chemicals. An important mechanical advantage is the relatively low pressure that is used. The pressure at the evaporator is 10 to 40 lb. per square inch[7] and at the pipestill outlet the pressure is about the same and only great enough to force the product through the fractionating and condensing system.

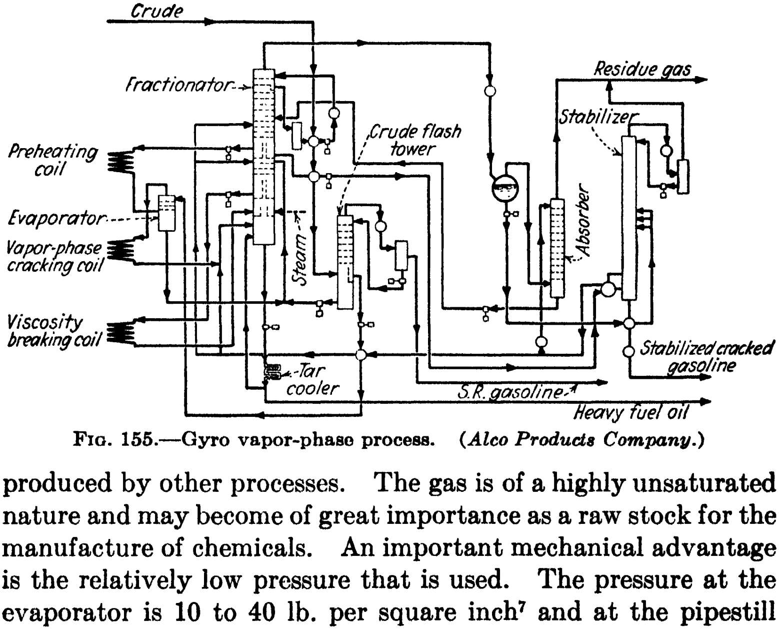

FIG. 155.—Gyro vapor-phase process. (*Alco Products Company.*)

Common operating temperatures are still-outlet temperature, 1150°F.; oil from economizer, 700°F.; and temperature at evaporator, 600°F. The cycle efficiency of the Gyro process is reported to be over 96 per cent when operated with normal stocks.

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[7] WAGNER, C. R., Vapor-phase Cracking, *Petroleum Eng.*, November, 1929.

The deFlorez process differs from most other processes mainly because of the cylindrical type of pipestill that is employed. Although this type of still is somewhat more expensive than an ordinary still, it is just what is necessary in order to get the mild and uniform heating conditions that are advantageous in any cracking operation. The vapor leaving the still is at a temperature of 1050 to 1100°F. and the pressure at the still outlet is 40 to 100 lb. per square inch. The cycle efficiency is not so good as for the Gyro process. Notice the similarity in Figs. 156 and 148.

Table 70 shows yield data for these two processes. A relatively large amount of gas is produced in vapor-phase processes and hence gasoline absorption and stabilizer systems are usually employed in conjunction with them (Fig. 156).

TABLE 70.—YIELDS BY VAPOR-PHASE PROCESSES

Charging-stock	A.P.I.	Gasoline, per cent	Tar, per cent	Gas, per cent	Process	Reference and notes
Still bottoms...	15	40.9	45.3	10.9	Gyro	[10]
Topped crude..	27	57.0	30.9	11.9	Gyro	[10]
Gas oil.........	30–34	75.1	11.4	12.5	Gyro	[10]
Pa. gas oil......	.....	63.8	14.1	26.8	Gyro	[10]
M.C. gas oil....	.....	67.0*	....	20.0	deFlorez	[8] (coking)
Pa. gas oil......	.....	61.4*	7.9	29.2	deFlorez	[9]
Calif. gas oil....	.....	53.89*	18.7	26.97	deFlorez	[9]
Venezuela crude	.....	36.40*	56.0	6.10	deFlorez	[9]

* Probably yields of untreated distillate.

Other vapor-phase processes are the Pratt[11] and the true vapor-phase[12] processes.

Coking.—The production of coke is accomplished by lengthening the time of cracking. The equipment that is used in modern semi-continuous processes is much the same as used in cracking processes except that drums, chambers, or reaction vessels must be provided for the accumulation of the coke. Several coke

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[8] SWANSON, P. F., *Oil Gas. J.*, Mar. 5, 1931, p. 95.

[9] DEFLOREZ, L., A New Type of Cracking Unit, 10th Ann. Meeting A.P.I., Chicago, December, 1929.

[10] *Ref. Nat. Gaso. Mfr.*, February, 1932, p. 116.

[11] Introduce New Type Vapor Phase Unit, *Oil Gas J.*, Oct. 16, 1930, p. 38.

[12] SACHS, A. P., *Ref. Nat. Gaso. Mfr.*, January, 1930, p. 70.

drums are usually provided so that several of them can be emptied while another is on-stream. At least three coke drums are

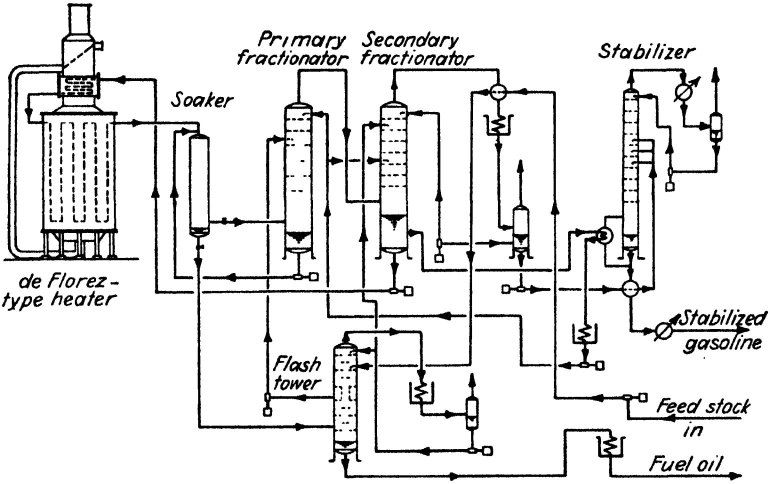

Fig. 156.—DeFlorez process running to fuel oil. (*Gasoline Products Company.*)

necessary because time is required to dry the coke and difficulties frequently arise in the removal of the coke.

Semi-continuous cokers were not successful for many years because the black tarry stock was exposed to cracking conditions

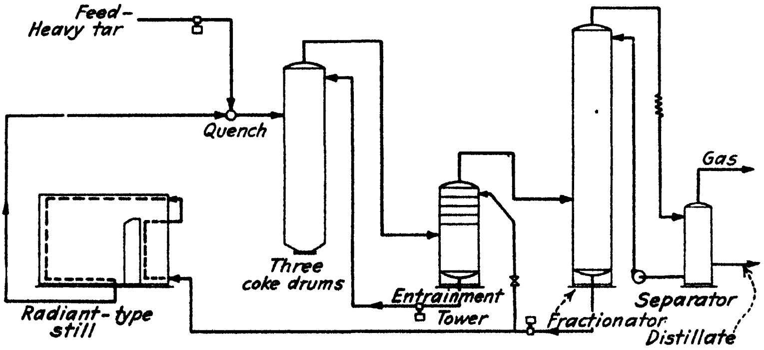

Fig. 157.—Semi-continuous coking system.

in the tubestill. Most of the processes that are now successfully operating are of the general type shown in Fig. 157. A clean distilled stock is produced from the coke drum, along with gas and distillate, and this distilled stock is recycled through the furnace, coke drum, and back to the fractionating system. The small entrainment tower is provided to insure that no black material gets into the furnace charge-stock. The temperature in the coke drum is sustained entirely by the recirculating stream. Much of the cracking occurs in the pipestill tubes but the drum is necessary to prolong the time and for the accumulation of coke.

Again it will be noted that the process is similar to the Tubestill process shown in Fig. 148. It differs from the Tubestill process because coke drums replace the evaporator of the Tubestill process. The entrainment tower would probably be an advantage in the Tubestill process. Normally no heat-exchange is used because the cold charge-stock is usually viscous and the exchangers tend to become plugged.

Viscosity-breakers.—In Chap. XVII the cracking reaction was shown to be very complex and it was shown that intermediate distillate products such as gas oil and kerosene are produced, as well as pressure distillate, gas, and tar. Furthermore, the properties of the tar produced during cracking are entirely different from the properties of straight-run tar. Particularly, the viscosity and pour-points of cracked tars are lower. Thus a small amount of cracking is often practiced for the purpose of lowering the viscosity or pour-point of an unsalable residue. Plants for conducting this process consist simply of a pipestill, a fractionating system, exchangers, condensers, and coolers. The oil is heated from 830 to 875°F. and a yield of 5 to 15 per cent of pressure distillate is produced. Some gas oil is distilled with the distillate and it is either saved for subsequent cracking or, if it is dirty, it may be mixed with the fuel oil from the process. Table 71 shows the viscosity reduction and lowering of the pour-point by a "viscosity-breaking" operation. The tests were conducted in a pressure bomb.[13]

In addition to the foregoing use of the term viscosity-breaker, it is also used to designate a unit for the purpose of distilling and cracking a heavy residue for the production of a gas oil stock. If a heavy residue (8 to 15 A.P.I.) is distilled without cracking, the operation is expensive because either large amounts of steam are required or a vacuum must be maintained. Furthermore, the

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[13] Tests by Dr. S. Born and the author in the laboratories at the University of Tulsa (1933).

gas oil product may be viscous or waxy. If this gas oil product is to be used as a cracking-stock, decomposition will do no harm, and the distillation may be conducted more cheaply and satisfactorily by heating to high temperatures and allowing some decomposition to take place. In this way a 70 per cent yield of 14 A.P.I. gas oil has been obtained[14] from an 8 to 10 A.P.I. residue. This was accomplished by heating the stock to about 900°F. in a pipestill heater and flashing the heated oil in a simple fractionating tower. The residue was a brittle bituminous material which could be powdered and fired as a fuel. The same results, if accomplished by vacuum or steam, would be uneconomical. Such units are simple distillation equipments differing from normal topping stills only in the design of the furnace, which should be designed for a mild rate of heating. Usually the oil is heated only to 850 to 875°F. because higher temperatures cause coke to be deposited in the tubes.

TABLE 71.—VISCOSITY-BREAKING TESTS

Stock	Cracking temp., °F.	A.P.I.		Viscosity			Pour-point, °F.		Distillate	
		Before	After	Before	Test method	After	Before	After	Per cent	A.P.I.
Fuel oil	830	26.3	25.9	18	Furol at 122	14.2	55	0	18.0	45.0
Residual fuel oil	845	18.8	18.5	193	Furol at 122	49.0	65	55	21.6	46.8
Gas oil	840	25.3	18.5	337	Say. at 100	253.0	75	15	38.2	49.9
Gas oil	837	25.3	24.2	337	Say. at 100	108.0	75	0	17.0	58.4
Reduced crude	850	22.0	28.4	92	Say. at 210	.....	87	..	0.0	

Reforming Units.—The demand for premium antiknock fuels has become so great that the disposal of the straight-run gasoline, which must be produced in distilling crude oil, has become a problem. Straight-run gasoline normally has an octane-number of about 50. The octane-number of competitive and premium fuels in 1933 was 65 to 69 and 75 to 80 respectively. Since most cracked fuels have octane-numbers between 70 and 90, it is apparent that larger amounts of cracked gasoline must be produced, more compounds such as tetraethyl lead must be used,

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[14] Viscosity Breaker, *Ref. Nat. Gaso. Mfr.*, July, 1932, p. 431.

or some means of disposal must be found for the straight-run fuel. The industry has attempted to solve this problem by the development of reforming units in which the straight-run gasoline or the heavier part of the straight-run gasoline is cracked to produce a material having a higher octane-number.

The yields that may be expected are somewhat greater than from heavier cracking-stocks. Commercial yields are 60 to 85 per cent for charge-stocks ranging from heavy kerosene to gasoline. However, the yield is not entirely dependent on the charge-stock because the yield may be greatly changed by the extent of cracking that is practiced. As an example, Egloff and Nelson[15] report the following commercial results when cracking 17.9 A.P.I. topped Smackover crude at 200 lb. per square inch and at 935°F.

Gasoline			Residue			Gas and loss, per cent
Yield	A.P.I.	Octane-number	Yield	A.P.I.	Universal Saybolt vis. and 122°F.	
39.0	57.1	80	58.4	8.7	159	2.6
45.2	57.0	80	48.0	4.8	357	6.8
48.8	55.3	80	46.0	2.6	637	5.2
50.2	55.6	80	44.8	0.7	1,411	5.0
63.1	55.1	80	None	Coke	.....	36.9 (and coke)

These data are not for a reforming operation but they do indicate the effect of the amount of cracking that is practiced. These authors conclude that it is not economical to top the light gasoline and reform the naphtha separately, because the yields and the octane-number are substantially the same if the entire gasoline is reformed. These results are not entirely in agreement with the results of LeRoi and Ferguson (page 309).

LeRoi and Ferguson[16] conclude that the yield of a given octane-

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[15] Cracking Light and Heavy Oils, 3d Midyear Meeting, A.P.I., Tulsa, May, 1933.

[16] Developments in Naphtha Reforming . . . , 3d Midyear Meeting, A.P.I., Tulsa, May, 1933.

number product is greatest by a once-through operation, *i.e.*, by passing the stock through a heating coil only. Smaller yields are obtained in passing the stock through a coil and soaker, and still smaller yields are obtained by recycling. They find the capacity of a given equipment is greater at higher pressures. Data on the yields by reforming are given in Table 72. Goldtrap[19] also reports higher yields of a given octane-number gasoline when higher pressures are used. A discussion of the octane-number obtained by reforming will be found in Chap. XVII.

TABLE 72.—YIELDS BY REFORMING

Stock	A.P.I.	Octane-number of stock	Cracking temp.	Cracking pressure	Yield gaso.	Octane-no. of gaso.	Process	Reference
Pa. gasoline	58.7	40	....	.....	83.7	76	Dubbs	17
Pa. naphtha	52.7	30	....	.....	84.4	76	Dubbs	17
Pa. kerosene	46.1	..	....	.....	81.2	75	Dubbs	17
Naphtha Cracked naphtha	47–50	..	1010	350	....	72	Quench process*	
Cracked naphtha	.....	..	998	350	....	69	Quench process*	
Cracked naphtha	.....	..	1010	330	....	70	Quench process*	
Naphtha	51.0	..	925	1,000	82.0	70	Tube and Tank	18
Pa. gasoline	64.6	50	1000	400	76.7	75	Dubbs	15
Pa. naphtha	54.9	31	950	500	73.5	76	Dubbs	15
Joiner and E. Tex. gasoline	58.7	56	950	500	84.4	75	Dubbs	15
Joiner and E. Tex. naphtha	58.7	56	950	500	88.1	71	Dubbs	15
E and W. Tex. gasoline	61.3	59	995	450	85.8	73	Dubbs	15
M.C. gasoline	59.8	42	975	500	82.3	70	Dubbs	15
M.C. naphtha	53.5	34	1000	500	75.5	75	Dubbs	15
W. Tex. gasoline	58.1	61	950	750	87.4	78	Dubbs	15
W. Tex. naphtha	51.5	52	950	750	80.4	78	Dubbs	15

* Separate reforming coils.

Combination Topping and Cracking Plants.—There has been a great development during the last few years of combined cracking, topping, reforming, viscosity-breaking, and gas absorption plants. This has been possible because of the more thorough knowledge of cracking-plant design and because of the large amount of heat that is available in high-temperature cracking processes.

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[17] EGLOFF and NELSON, *Oil Gas J.*, Jan. 7, 1932, p. 22.

[18] MCCONNELL, E. B., *Ref. Nat. Gaso. Mfr.*, May, 1931, p. 95.

[19] Increasing Octane Values . . . , *Ref. Nat. Gaso. Mfr.*, April, 1932, p. 281.

Topping can be accomplished in equipment similar to that shown in Fig. 148, except that an additional pipestill heater is usually required because of the large volume of crude oil charge-stock. If it is advisable not to mix the straight-run and cracked distillates, a separate tower is required. Reforming of straight-run naphtha is often conducted by passing the material, while it is still hot, through a separate cracking coil in the main cracking furnace. The customary gas absorption systems are used for the cracked gas, but heat for the stripper is obtained by circulating a part of the hot furnace charge-stock. The pressure distillate and wild gasoline is sometimes stabilized and again heat is obtained from the furnace charge-stock. Diagrams of several combination plants of this kind are given by Armistead.[20]

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CHAPTER XXIII

NATURAL GASOLINE

Casinghead gasoline first attracted commercial attention in about 1904 in the Pennsylvanian oil district. By 1920 the value of natural-gasoline products was estimated to be over $75,000,000 per year, but during that year and 1921 the industry suffered a serious relapse because of the general economic stress but more directly because of the unscrupulous sale of casinghead-kerosene blends as gasoline during the previous decade. At that time the manufacturers formed the National Gasoline Manufacturers' Association and by scientific investigations and publicity have been able to reestablish the respect of the buying public. Properly manufactured natural gasoline has properties which make it of definite usefulness as a motor fuel, particularly when blended with regular gasoline. The low boiling-range of natural gasoline or its tendency to vaporize easily makes it an admirable motor fuel for cold weather when ordinary gasoline may fail to ignite properly. However, casinghead or raw natural gasoline contains dissolved gases and is not satisfactory as a motor fuel because the gases are evolved at engine temperatures, causing vapor-lock in the feed system. Today the properties of natural gasoline, particularly the vapor-pressure, are closely regulated, so that the refiner can safely take full advantage of the superior properties of blended motor fuels. Even pure natural gasoline is sold by some refiners as a motor fuel. Furthermore, natural gasoline has a higher octane rating than straight-run gasoline. Approximately 7.5 per cent[1] of the total gasoline sold in 1932 consisted of natural gasoline.

The lighter hydrocarbons such as propane, isobutane, and butane, which may be removed from raw natural gasoline during its processing, are finding a relatively wide use as so-called bottled gas and as stocks for the manufacture of city gas. During the five years from 1926 to 1931, the production of liquefied petroleum

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[1] Approximately 10 per cent in 1930.

gas increased about fortyfold. The liquefied gas is shipped under pressure and is allowed to expand when ready for use. Inasmuch as the heating value of the pure gas is unnecessarily high, it is often mixed with air. The following tabulation[2] indicates the cheapness of butane gas as compared with a normal manufactured gas.

Comparative Prices of Butane and City Gas

Cost of Butane at Burner, Cts. per Gal. (Delivered Price)	Equivalent Value of 530 B.t.u. City Gas, Cts. per 1,000 Cu. Ft.
8.0	41.4
7.5	38.8
7.0	36.2
6.5	33.6
6.0	31.0
5.5	28.4
5.0	25.9
4.5	23.3
4.0	20.7
3.5	18.1
3.0	15.5

In 1930 the number of butane-air plants for the manufacture of city gas has been estimated as 60 and as many more were under construction. Commercial butane is also used to enrich the low-heating-value manufactured gases. As well as centralized plants of this kind, many rural dwellers are burning bottled or liquefied gas in kitchen ranges and lamps.

Although the design and operation of natural-gasoline absorption and stabilization plants have been handled largely by production engineers, there is no real difference in principle between these plants and those used in the refinery. The principles underlying all distillation and absorption operations are much the same and the design of natural-gasoline equipment may be considered as a part of the design fundamentals outlined in previous chapters. However, natural gasoline and natural gas can be accurately analyzed and hence the design of natural-gasoline equipment can be approached in a more precise manner than the design of heavy oil equipment.

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[2] Oberfell, G. G., *Proc. 10th Ann. Meeting Nat. Gaso. Mfr.*, 1931.

General Processing Plan.—The processing involved in the manufacturing of finished products from natural gas consists mainly of two operations, *viz.*, absorption and stabilization.

1. *Wet* natural gas or a gas containing relatively large percentages of compounds higher in molecular weight than propane is processed to produce *dry* natural gas and *raw or wild natural gasoline.* The raw gasoline may be separated from the wet gas by (*a*) adsorption by charcoal, (*b*) compression, (*c*) absorption in a mineral absorption oil, or (*d*) a combination of the compression and absorption processes. Although all of these processes have been used, most modern plants are combination compression and absorption plants. Modern absorbers operate between 35 and 500 lb. per square inch.
2. Stabilization of the raw natural gasoline. Raw gasoline as obtained above usually contains 10 to 30 per cent of methane, ethane, and propane. These dissolved gases cause the gasoline to be highly volatile and they must be removed before the gasoline can be shipped or marketed as a stable product. Stabilization is nothing more than fractionation for the removal of these light, high-vapor-pressure components. Since the fractionator must be refluxed with almost pure liquid propane or butane, the operation must be conducted under pressure.

In the past a stable gasoline has been produced by the process of "weathering," which consisted of allowing the wild gasoline to stand in open tanks at prevailing atmospheric temperatures until the dissolved gases had escaped. Although a stable product can be obtained in this manner, a serious loss of gasoline occurs because the light components carry a large percentage of the heavier components with them when they vaporize. This method of stabilizing has been abandoned.

Some plants have been built for stabilizing the pressure distillate from cracking units. Inasmuch as pressure distillate is collected under pressure and in the presence of cracked gas, it also contains from 5 to 10 per cent of material lighter than butane and must be either stabilized or mixed with naphtha to reduce its vapor-pressure. However, the stabilization of pressure distillate is expensive because of the large volume of stock that must be handled.

A simplified flow diagram of the complete absorption, stripping, and stabilization operation is given in Fig. 158. The compressors which are used to create the pressure in the absorption tower are not shown. Figure 118 shows much the same arrangement except that control instruments are shown. The wet gas is compressed and admitted to an absorber column. This column and also the stripper and stabilizer are of the conventional bubble-plate type of construction although the tray spacing is usually not over 18 in. In the absorber, the wet gas flows countercurrently to an absorption oil and leaves the top as a dry natural or refinery gas. The rich absorption oil flows through exchangers, in which heat is exchanged with the hot lean absorption oil, through a steam heater, and into the stripping column. Some fractionation as well as stripping may be accomplished in the stripper or still, and hence heat is supplied at the bottom by a steam reboiler and reflux is used at the top. Wild or raw natural gasoline and steam pass overhead, and some of the light constituents cannot be condensed. These are cycled back into the absorber. The wild gasoline is pumped through heat exchangers to the stabilizer (fractionator or rectifier) and stable natural gasoline and dry gas are produced. The stabilizer is a typical fractionating column with a steam reboiler. Sometimes it is more economical to allow some gasoline hydrocarbons to escape in the residue gas from the stabilizer and cycle this gas through the absorber than to do an exact job of fractionation in the stabilizer.

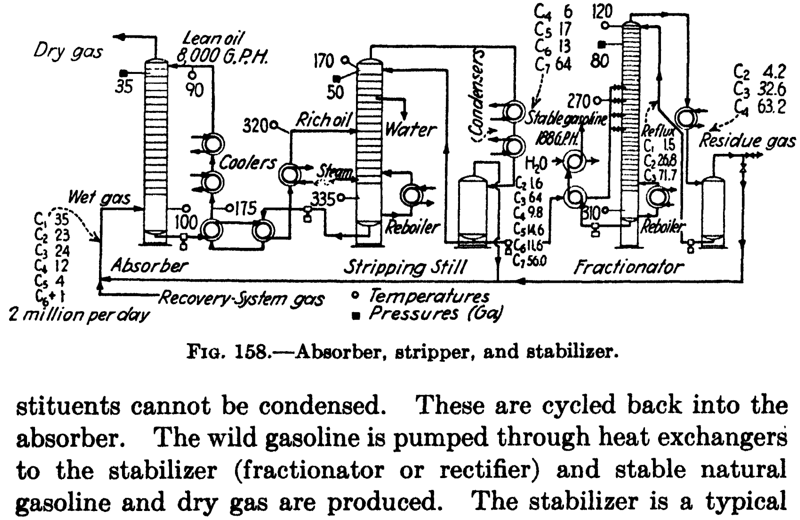

FIG. 158.—Absorber, stripper, and stabilizer.

Natural and Refinery Gases.—Almost all of these gases are of such a composition that they can be profitably processed for the manufacture of natural gasoline. Prior to 1915 a gas containing less than 7 gal. of stable natural gasoline per thousand cubic feet was called a dry gas and in general was not considered as suitable for processing. Since that time the value of natural gasoline has increased and the methods of recovering the gasoline

TABLE 73.—ANALYSES OF GASES

Material	From	Approx. gal. gaso.† per 1,000 cu. ft. of gas	Analysis, per cent by volume										
			CH_4*	C_2H_6	C_3H_8	C_3H_6	iC_4H_{10}	C_4H_{10}	C_4H_8	iC_5H_{12}	C_5H_{12}	$C_6H_{14}+$	Others
1. Dry gas..........	Stabilizer	1.1	77.9	10.04	8.61	.....	2.6	0.85					
2. Dry gas..........	440-lb. absorber	0.334	86.56	8.67	3.92	.....	0.36	0.47	...	0.2			
3. Dry gas..........	52-lb. absorber	0.724	60.77	19.83	17.12	.....	1.21	0.97	...	0.10			
4. Dry gas..........	18-lb. absorber	2.86	18.66	27.24	45.10	.....	6.0	3.0					
5. Dry gas..........	Absorber and stabilizers	1.93	45.19	23.26	23.2	.....	5.83		...	0.23		....	H_2S 2.29
6. Dry gas..........	Compressers and coolers	0.79	81.04	9.74	5.46	.....	1.35	1.3	...	0.5	0.25	0.36	
7. Dry gas..........	59-lb. absorber	0.495	92.1	1.9	4.5	.....	0.6	0.7	0.2				
8. Dry gas..........	53-lb. absorber	0.655	76.7	10.5	8.8	.....	1.1	0.5	0.4				
9. Dry gas..........	An ave. of 45‡	0.535	85.9	6.31	7.74	.....	0.78	0.69	0.16				
10. Dry cracked gas...	Stabilizer	1.6	64.5	16.0	6.7	1.9	2.9		1.3	0.6			H_2 2.9, C_2H_4 2.9
11. Dry cracked gas...	Gyro	3.54	38.81	13.15	3.68	13.5	6.43			2.47			C_2H_4 20.31
12. Dry cracked gas...	Gyro absorber	......	44.4	10.3	2.95	12.0	.....	.....	...	....	....	....	C_2H_4 30.35
13. Wet ref. gas.......	Vapor recovery	6.07	46.78	16.51	18.8	.....	4.44	7.77	...	2.76	1.51	1.43	
14. Wet ref. gas.......	Raw gaso. tanks	11.03	7.17	15.21	34.72	.....	10.88	23.16	...	4.29	3.02	1.55	
15. Wet ref. gas.......	Vapor recovery	5.41	41.62	20.91	19.72	.....	9.05		...	4.43		2.09	H_2S 2.18
16. Wet nat. gas......	....	2.21	85.3	1.6	6.8	.....	1.5	1.4	...	3.4			
17. Wet nat. gas......	....	5.53	70.0	5.9	5.7	.....	2.3	3.1	...	9.9			
18. Wet nat. gas......	An ave. of 45‡	2.23	79.8	6.48	6.22	.....	1.35	2.33	...	2.97			
19. Wet cracked gas...	15-lb. separator	6.6	33.1	21.8	16.7	4.5	7.1		2.8	5.5		3.3	Air 3.1, C_2H_4 1.3
20. Wet cracked gas...	Gyro stabilizer	21.33	4.2	.....	.....	27.1	66.45			0.64			C_2H_4 1.6
21. Wet cracked gas...	Gyro stabilizer	5.13	11.37	12.35	.....	44.87	13.86			1.99			C_2H_4 15.56

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* N_2, CO_2, O_2, etc., usually counted as CH_4.

† Butanes and heavier.

‡ The wet gases of 18 yielded the dry gases of 9.

have been so improved that almost all natural gas containing more than 2 gal. of gasoline per thousand cubic feet is being processed, and gases that contain only 0.3 gal. per thousand cubic feet may be economically handled. Table 73 shows analyses of various natural and refinery gases.

Brewster[3] reports analyses of refinery gases from topping, cracking, rerunning, and coke stills. The crude oil contained 30 per cent of gasoline, and an additional 30 per cent of gasoline was produced by cracking. About 20 per cent of the original oil was coked. Table 74 shows the composition and amounts of these gases.

TABLE 74.—AMOUNT AND COMPOSITION OF REFINERY GASES

	Crude stills	Coke stills	Dry gas from cracking	P.D. release gas	Auto tar plant	P.D. rerun stills	Total
Cu. ft. per bbl. of crude	7	26	100	37	20	10	200
Approximate mol. wt.	51	32	23.8	40.5	28.2	52	31
Approximate gal. C_5 + per 1,000 cu. ft.	7.4	5.1	0.8	3.5	1.2	8.2	2.5
Analysis:							
CH_4	5	47	68	18	53	4	49.13
C_2H_6	12	15	15	24	20	10	16.81
C_3H_8	30	16	11	31	16	30	17.46
C_4H_{10}	34	9	4	18	8	35	10.23
$C_5H_{12}^+$	19	13	2	9	3	21	6.37

In estimating the gasoline content of a wet gas the following tabulation will be of value. The figures represent the approximate number of gallons of liquid that can be obtained from 1,000 cu. ft. of each of the compounds.

Propane	26.6
Butane	31.4
Isobutane	32.4
Pentanes	36.3
Hexanes	41.2
Hexanes and heavier	43.0 (an average)
Normal heptane	46.2
Normal octane	51.0

For the olefin hydrocarbons the foregoing figures may be reduced by about 10 per cent. Propane is not considered as a

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[3] *Oil Gas J.*, June 19, 1930, p. 46.

recoverable gasoline product unless bottled gas is to be manufactured.

Example 76. Gasoline Content of Natural Gas.—A wet gas contains 10 per cent of butanes, 5 per cent of pentanes, and 2 per cent of hexanes and heavier.
Basis: 1,000 cu. ft. of the natural gas.

$$\begin{array}{lrr}
 & & \text{Gal.} \\
\text{Gasoline from butanes} = \frac{10}{100} \times \cancel{1000} \times \frac{31.8}{\cancel{1000}} & = 0.1 \times 31.8 & = 3.18 \\
\text{Gasoline from pentanes} & = 0.05 \times 36.3 & = 1.81 \\
\text{Gasoline from hexanes+} & = 0.02 \times 43.0 & = \underline{0.86} \\
\text{Recoverable stable gasoline per 1,000 cu. ft. of gas} & & = 5.85
\end{array}$$

Table 75 indicates the analyses of common gasoline products. Commercial butane, bottle gas, and pressure distillate are also shown.

Properties of Natural Gasoline.—Natural gasoline has a higher octane-number than normal straight-run gasoline. Alden[4] finds that the antiknock properties of natural gasoline can be best correlated against vapor-pressure. Table 76 shows the approximate relationship between octane-number and Reid vapor-pressure for Mid-Continent natural gasolines.

TABLE 76.—OCTANE-NUMBER VERSUS REID VAPOR-PRESSURE

Reid Vapor-pressure at 100°F.	Octane-number, Original Waukesha Unit, 212°F. Jacket
4	57.3
10	64.6
14	69.6
18	73.3
22	76.2
26	78.4
30	80.0

Alden also finds that the octane-number of natural gasoline is increased more by the addition of a given amount of tetraethyl lead than are the octane-numbers of other gasolines. Furthermore, the octane-number of natural gasoline is decreased less, when the engine jacket temperature is increased from 212 to 350°F., than the octane-number of other gasolines, and this is particularly true when compared with the decrease for cracked fuels.

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[4] ALDEN, R. C., *Oil Gas J.*, Jan. 21, 1932, p. 22.

TABLE 75.—ANALYSES OF GASOLINE PRODUCTS

Material	From	A.P.I.	V.P., lb. per sq. in.	Analysis, per cent by volume (gas)							
				CH_4	C_2H_6	C_3H_8	iC_4H_{10}	C_4H_{10}	iC_5H_{12}	C_5H_{12}	$C_6H_{14}^+$
1. Raw gasoline	Absorber	94.5	....	0.08	1.51	12.12	8.76	29.33	48.2		
2. Raw gasoline	Absorber	....	....	....	1.83	12.57	32.75		29.98		22.87
3. Raw gasoline	High-press. abs.	92.2	60	0.03	2.27	17.29	9.38	23.33	47.7		
4. Raw gasoline	High-press. abs.	92.2	50	0.04	1.78	16.03	8.81	26.95	5.54	12.24	28.61
5. Raw gasoline	High-press. abs.	91.8	51	....	1.9	17.08	10.23	25.54	45.25		
6. Raw gasoline	Absorber	....	....	....	0.72	13.69	4.74	23.71	10.43	21.19	25.07
7. Raw press. dist	150–200 lb. separator	....	....	0.91	3.08	6.71	8.74		8.36		72.2
8. Raw press. dist	25-lb. separator	....	....	....	0.73	3.16	6.06		6.36		83.69
9. Raw press. dist	Cross	....	....	....	0.35	2.36	5.66		6.7		84.93
10. Raw press. dist	Holmes Manley	....	....	0.45	3.7	6.31	7.62		8.5		73.42
11. Stabilized gaso	Stabilizer	85.6	....	....	....	0.10	0.10	32.6	67.2		
12. Stabilized gaso	Stabilizer	89.0	29	....	....	0.11	32.94		40.07		26.88
13. Stabilized gaso	Stabilizer	77.8	18.7	....	....	.....	1.02	17.55	13.67	15.06	52.7
14. Stabilized gaso	Stabilizer	78.7	17.2	....	....	.....	1.73	16.13	11.58	19.33	51.23
15. Stabilized gaso	Stabilizer	74.7	11.5	....	....	.....	.....	9.97	90.03		
16. Stabilized gaso	Stabilizer	....	....	....	....	0.51	4.42	24.06	13.18	18.19	39.64
17. Commercial butane	Stabilizer	....	65	....	....	5.0	20.0	75.0			
18. Commercial butane	Stabilizer	0.581*	....	....	0.04	3.32	18.1	75.8	2.74		
19. Commercial propane†	Stabilizer	....	....	....	2.0	98.0					

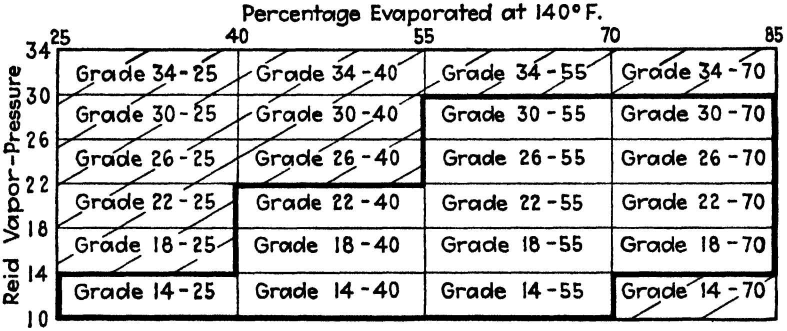
* Specific gravity 60/60.

† Per cent liquid volume.

Specifications.—The official specifications of the Natural Gasoline Manufacturers Association of America, effective Jan. 1, 1932, are as follows:

1. Reid vapor-pressure	10 to 34 lb.
2. Percentage evaporated at 140°F	25–85
3. Percentage evaporated at 275°F	Not less than 90
4. End-point	Not higher than 375°F.
5. Corrosion	Noncorrosive
6. Doctor test	Negative, "sweet"
7. Color	Not less than plus 25 (Saybolt)

In addition to the foregoing, natural gasoline is divided into 24 possible grades on a basis of vapor-pressure and percentage evaporated at 140°F. These grades are shown in Fig. 159.



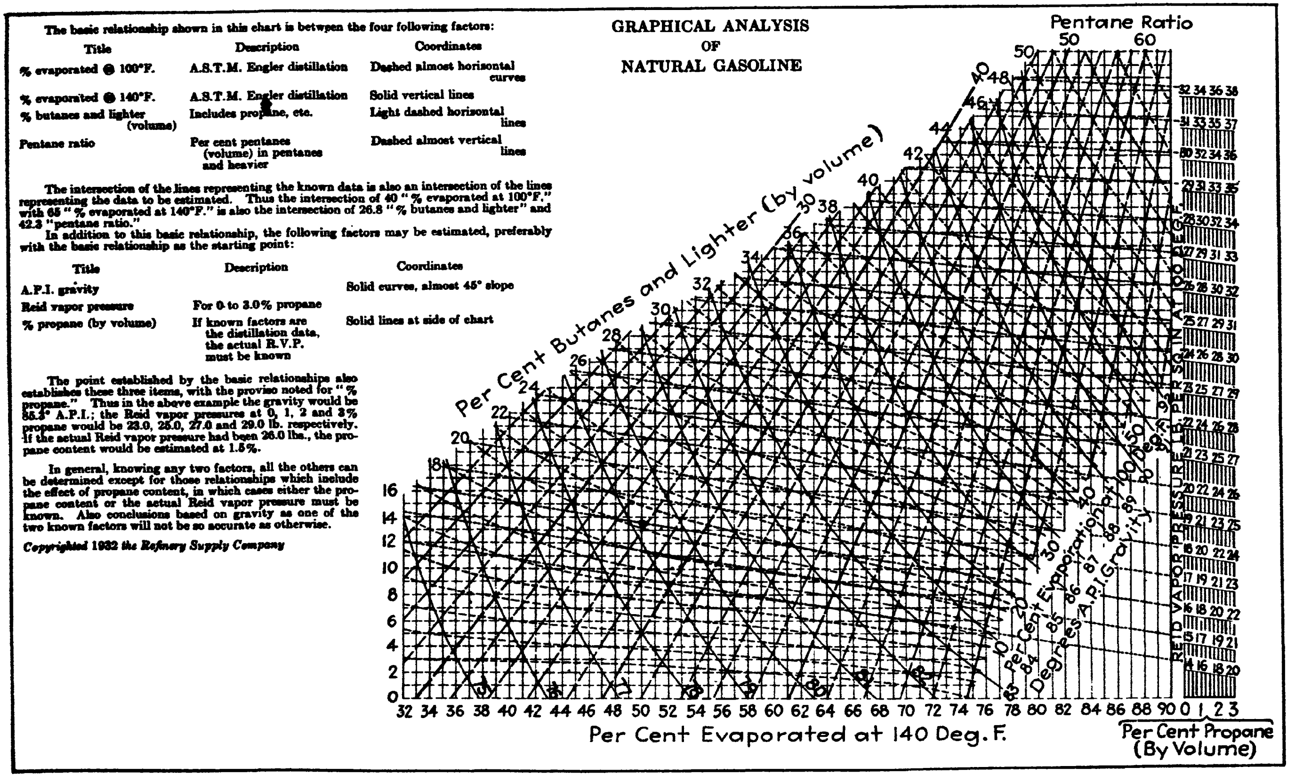
34	Grade 34-25	Grade 34-40	Grade 34-55	Grade 34-70
30	Grade 30-25	Grade 30-40	Grade 30-55	Grade 30-70
26	Grade 26-25	Grade 26-40	Grade 26-55	Grade 26-70
22	Grade 22-25	Grade 22-40	Grade 22-55	Grade 22-70
18	Grade 18-25	Grade 18-40	Grade 18-55	Grade 18-70
14	Grade 14-25	Grade 14-40	Grade 14-55	Grade 14-70

FIG. 159.—Grades of natural gasoline. The most common grades are outlined in the block.

The grades of gasoline that are widely used fall within the 13 grades that are outlined in Fig. 159. The approximate compositions of the different grades of gasoline can be estimated from Fig. 160. The use of this figure can be best illustrated by means of an example.

Example 77. Relation of Composition and Physical Properties of Natural Gasoline (Fig. 160).—A natural gasoline has a Reid vapor-pressure of 16, it contains no propane, and 50 per cent of it distills at 140°F. What are its approximate composition, its gravity, and the percentage evaporated at 100°F.?

The percentage evaporated at 140° is located along the base line and the vapor-pressure is located among the Reid vapor-pressure axes on the right, using the 0 per cent propane axis. These two lines cross at the circle point



GRAPHICAL ANALYSIS
OF
NATURAL GASOLINE

The basic relationship shown in this chart is between the four following factors:

Title	Description	Coordinates
% evaporated @ 100°F.	A.S.T.M. Engler distillation	Dashed almost horizontal curves
% evaporated @ 140°F.	A.S.T.M. Engler distillation	Solid vertical lines
% butanes and lighter (volume)	Includes propane, etc.	Light dashed horizontal lines
Pentane ratio	Per cent pentanes (volume) in pentanes and heavier	Dashed almost vertical lines

The intersection of the lines representing the known data is also an intersection of the lines representing the data to be estimated. Thus the intersection of 40 "% evaporated at 100°F." with 65 "% evaporated at 140°F." is also the intersection of 26.8 "% butanes and lighter" and 42.3 "pentane ratio."

In addition to this basic relationship, the following factors may be estimated, preferably with the basic relationship as the starting point:

Title	Description	Coordinates
A.P.I. gravity		Solid curves, almost 45° slope
Reid vapor pressure	For 0 to 3.0% propane	
% propane (by volume)	If known factors are the distillation data, the actual R.V.P. must be known	Solid lines at side of chart

The point established by the basic relationships also establishes these three items, with the proviso noted for "% propane." Thus in the above example the gravity would be 85.3° A.P.I.; the Reid vapor pressures at 0, 1, 2 and 3% propane would be 23.0, 25.0, 27.0 and 29.0 lb. respectively. If the actual Reid vapor pressure had been 26.0 lbs., the propane content would be estimated at 1.5%.

In general, knowing any two factors, all the others can be determined except for those relationships which include the effect of propane content, in which cases either the propane content or the actual Reid vapor pressure must be known. Also conclusions based on gravity as one of the two known factors will not be so accurate as otherwise.

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FIG. 160.—Graphical analysis of natural gasoline. (*Refinery Supply Company, Tulsa, Okla.*)

on the diagram. This intersection point is then located with respect to the other axes in the figure giving properties as follows:

A.P.I. gravity	79.2	(curved lines reading along base and to right)
Per cent evaporated at 100°F	18.5	(rather flat curving lines reading to right)
Per cent butanes and lighter	13.5	(horizontal lines reading at left)
Per cent pentanes in pentanes and heavier	35.5	(converging straight lines reading at top)

ANALYSIS

Propane	0.0	Pentanes (35.5%)	30.7
Butanes	13.5	Hexanes+ (100 − 35.5)	55.8
Pentanes+	86.5		86.5

Tentative specifications for the liquefied petroleum gases, propane and butane, are given by Legatski.[5] The vapor-pressure specifications are limited to some extent by the vessels (tanks and cylinders) that are available for transportation. The water content must be limited because the water becomes frozen and clogs the vaporizing apparatus during expansion. The water that is permitted amounts to about 10 parts of water vapor per million. The sulfur content is listed as two groups of compounds because sulfide stenches are often used to impart a characteristic odor to the gas so that leaks can be located.

Blending of Natural Gasoline.—The composition of natural gasoline greatly affects its vapor-pressure. This is inferred in Figs. 159 and 160. The reason for the powerful effect of composition on vapor-pressure is the great differences in the vapor-pressures of the low-boiling components. The vapor-pressure of propane is very high and hence a small amount of propane will greatly increase the total vapor-pressure. If butane is substituted for propane (by good fractionation), the resulting gasoline has a much lower vapor-pressure. These relations are given graphically by Kremser.[6] Figure 161 shows the gallons of a heavier hydrocarbon component that may be substituted for a gallon of a lighter component without changing the vapor-pressure of the total material.

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[5] *Oil Gas J.*, May 19, 1932, p. 44. Tests are described.

[6] Midyear Meeting A.P.I., Tulsa, June 3, 1932.

For each gallon of propane that is present in a 14-lb. gasoline, about 5.35 gal. of butane or 3.5 gal. of isobutane may be substituted for the propane without changing the vapor-pressure (Fig. 161). Stated in the reverse, this means that the total yield of 14-lb. gasoline can be increased by about 4.35 and 2.5 per cent respectively by substituting butane or isobutane for propane. However, butane and isobutane must be available in sufficient quantity in the raw gasoline. Thus a thorough elimination of the lightest component of a raw gasoline by good fractionation in the stabilizer is a profitable operation unless the separation is a particularly difficult one. For summer blending requirements, a high-pentane-content gasoline is desirable, but during the winter a high-butane gasoline may be used.

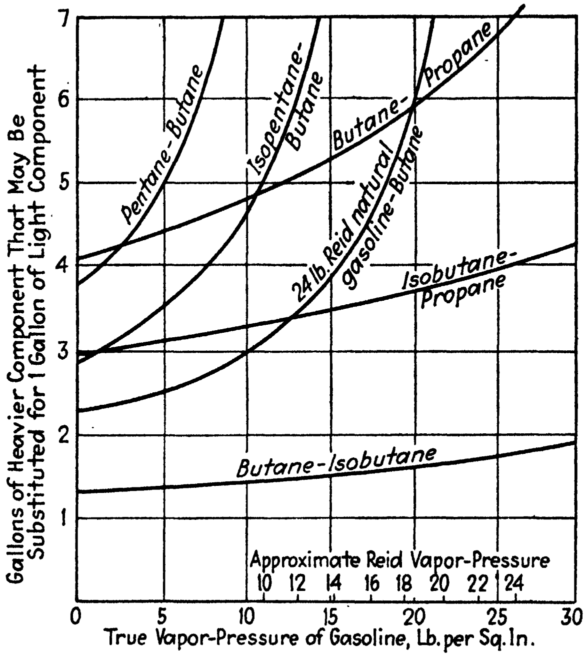

FIG. 161.—Amount of a natural-gasoline component that can be substituted for another component without changing the vapor-pressure. (*Kremser, Oil Gas J.*)

The boiling-range of naphtha and natural-gasoline blends can be closely approximated by averaging the material boiling up to a given temperature, in the ratio of the quantity of each blending agent that is used. The method is exact for fractionating distillations but it is not perfect for distillations such as the A.S.T.M. distillation. If the entire distillation range is desired, the calculations can be more easily accomplished by graphical methods. The curve of the blend will be spaced from the curves of the two blending stocks by a distance along the percentage axis which is inversely proportional to the amount of each blending agent.

Example 78. Boiling-range of Blends.—A naphtha contains 18 per cent of material boiling to 200°F. and a natural gasoline, 70 per cent. If the two stocks are blended 20:80, *i.e.*, 20 volumes of natural gasoline to 80 volumes of naphtha, how much of the blend will distill at 200°?

$$\begin{array}{rl} & \text{Per Cent} \\ 0.80 \times 18 = & 14.4 \\ 0.20 \times 70 = & 14.0 \\ \hline \text{Material boiling to } 200^\circ = & 28.4 \end{array}$$

An illustration of the graphical method is not justified, but the following equations will clarify the operation to be followed in a graphical solution.

$$\text{Per cent in blend, boiling to } 200^\circ = 18 + {}^{20}\!/_{100}(70 - 18) = 28.4$$

or

$$\text{Per cent in blend, boiling to } 200^\circ = 70 - {}^{80}\!/_{100}(70 - 18) = 28.4$$

The vapor-pressure of blends can be estimated in much the same manner except that mol percentages rather than volume percentages must be used. The method is accurate when true vapor-pressures are used, but it is not exact when using the Reid vapor-pressure.

Example 79. Vapor-pressure of Blends.—Naphtha and natural gasoline are to be blended. The properties of the stocks are

Stock	Vapor-pressure	A.P.I.	Lb. per gal.	Mol. wt.
Naphtha	6	57	6.25	119
Natural gasoline	18	72	5.79	90

What is the vapor-pressure of a 20:80 blend?

Basis: 1 gal. of blend.

		mols	mol per cent
Naphtha...............	$\frac{0.8 \times 6.25}{119}$	= 0.042	76.5
Nat. gasoline............	$\frac{0.2 \times 5.79}{90}$	= 0.0129	23.5
		0.0549	100.0

Partial vapor-pressure of naphtha....... 0.765 × 6 = 4.6

Partial vapor-pressure of nat. gaso....... 0.235 × 18 = 4.2

Vapor-pressure of blend = 8.8 lb. per sq. in.

The octane-number and the specific gravity (not A.P.I.) of blends are also proportional to the amount of each stock in the blend and the properties of the stocks.

NATURAL-GASOLINE PLANT DESIGN AND OPERATION

Although the design of natural-gasoline absorbers, strippers, and stabilizers (fractionators) is essentially the same as the design methods outlined in other chapters, the mechanism of handling these computations is facilitated because an exact analysis, showing the percentage of each hydrocarbon, is usually available. However, the computations are involved because so many components must be handled at the same time.

Raoult's law and Dalton's law are the basis for most of these computations. These laws are discussed in detail on pages 243 and 244 and in Example 43. At high pressures Raoult's law is not valid, and equilibrium constants must be used. These constants are presented in Figs. 73 and 74 and are discussed on pages 245 and 246 and in Example 44. Computations of the equilibrium relations of complex mixtures such as natural gasoline are involved because of the many components. These relations are discussed on pages 253 and 254 and Example 45. The fundamentals of fractionation, absorption, and stripping are treated in Chap. XV.

Absorbers and Strippers.—The performance of absorbers can be most easily understood by means of a mathematical study.[7] In an equilibrium plate the relation between the composition of the vapor leaving the plate and the liquid overflowing from the plate may be expressed as follows:

$$y_n = Kx_n \tag{43}$$

[7] Souders and Brown, *Ind. Eng. Chem.*, **24**, 519 (1932).

in which y_n is the mol fraction of a particular component in the vapor leaving any plate or the nth plate; x_n is the mol fraction in the overflow liquid; and K is a constant which may be determined from Figs. 73 and 74 or by Raoult's law.

By a material balance (Fig. 88),

$$L(x_n - x_{n-1}) = V(y_{n+1} - y_n) \tag{70}$$

in which L is the total mols of pure absorber oil; V is the total mols of dry gas; the subscript $n - 1$ refers to the plate above the nth plate; and $n + 1$ to the plate below.

Substituting $\frac{y_n}{K}$ for x_n, and $\frac{y_{n-1}}{K}$ for x_{n-1},

$$\frac{L}{KV}(y_n - y_{n-1}) = y_{n+1} - y_n \tag{71}$$

The factor L/KV is commonly referred to as the *absorption factor.*

Let

$$A = \frac{L}{KV} = \text{absorption factor} \tag{72}$$

Solving Eq. (71) for y_n and substituting Eq. (72),

$$y_n = \frac{y_{n+1} + Ay_{n-1}}{1 + A} \tag{73}$$

For a *single-plate absorber:*

$$y_1 = \frac{y_2 + Ay_0}{1 + A} \tag{74}$$

in which y_1 is the mol fraction of the component in the gas that leaves the top plate of the absorber and y_0 is the mol fraction of the component in the gas that is in equilibrium with the entering oil (or the oil flowing from the hypothetical zero plate which is above the top plate).

For a *two-plate absorber:*

$$y_2 = \frac{y_3 + Ay_1}{1 + A}$$

Substituting the value of y_1 and solving for y_2,

$$y_2 = \frac{y_3(A + 1) + A^2 y_0}{A^2 + A + 1}$$

For a *three-plate absorber,*

$$y_3 = \frac{y_4(A^2 + A + 1) + A^3 y_0}{A^3 + A^2 + A + 1}$$

or

$$y_3 = \frac{\frac{(A^3 - 1)}{(A - 1)} y_4 + A^3 y_0}{\frac{(A^4 - 1)}{A - 1}}$$

or

$$y_3 = \frac{(A^3 - 1)y_4 + A^3(A - 1)y_0}{A^4 - 1}$$

For an *absorber with n plates,*

$$y_n = \frac{y_{n+1}(A^n - 1) + A^n(A - 1)y_0}{A^{n+1} - 1} \tag{75}$$

and because

$$y_n = Kx_n$$

$$x_n = \frac{y_{n+1}(A^n - 1) + A^n(A - 1)y_0}{K(A^{n+1} - 1)} \tag{76}$$

A material balance over the entire absorber gives

$$A(y_n - y_0) = y_{n+1} - y_1 \tag{77}$$

Solving Eq. (77) for y_n and setting it equal to y_n from Eq. (75)

$$y_1 = y_{n+1}\left(\frac{A - 1}{A^{n+1} - 1}\right) + y_0 \frac{(A^{n+1} - A)}{(A^{n+1} - 1)} \tag{78}$$

in which y_{n+1} is the mol fraction of the component in the entering rich gas or gas arising from the hypothetical plate below the bottom or n plate.

This is a general statement of the absorption equation which was derived by Kremser,[8] although the formulation herein given was published by Brown.[7] The equation may be arranged in a more convenient form thus:

$$\frac{A-1}{A^{n+1}-1} = 1 - \frac{A^{n+1}-A}{A^{n+1}-1}$$

Rearranging Eq. (78),

$$\frac{y_1 - y_{n+1}}{y_0 - y_{n+1}} \quad \text{or} \quad \frac{y_{n+1} - y_1}{y_{n+1} - y_0} = \frac{A^{n+1}-A}{A^{n+1}-1} \tag{79}$$

where $(y_{n+1} - y_1)$ = actual change in composition of gas.
$(y_{n+1} - y_0)$ = maximum change in composition of gas that would occur if an infinite number of plates were used or if the gas leaving the top of the absorber were in equilibrium with the lean oil.

An equation for stripping can be derived in a similar manner:

$$\frac{x_e - x_n}{x_e - x_{n+1}} = \frac{S^{n+1}-S}{S^{n+1}-1} \tag{80}$$

where x_n = mol fraction of component in liquid leaving stripper (lean).
x_e = mol fraction of component in liquid entering stripper (rich).

$$S = \frac{KV}{L} = \frac{1}{L/KV} = \frac{1}{A}. \tag{81}$$

If steam is used for stripping, as is the case in gasoline plant strippers, $x_{n+1} = 0$ and Eq. (80) reduces to

$$\frac{x_e - x_n}{x_e} = \frac{S^{n+1}-S}{S^{n+1}-1} \tag{82}$$

These two fundamental equations [Eqs. (79) and (80)] are expressed graphically in Fig. 162. The figure may be used by determining the value of the factor $(y_{n+1} - y_1)/(y_{n+1} - y_0)$, or $(x_e - x_n)/x_e$, and noting the value of A (or S). The

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[8] *Nat. Petroleum News*, May 21, 1930, p. 43.

quantity of absorption oil or steam may be obtained from A or S as explained in the following paragraph.

Absorption and Stripping Factors.—The common method of expressing the amount of absorption oil is gallons of oil per 1,000 standard cubic feet of gas (60°F., 14.7 lb.). With these units the absorption factor can be expressed as follows:

$$A = \frac{L}{KV} = \frac{3.156dG}{KM} \tag{83}$$

or if Raoult's law holds

$$A = \frac{3.156dG\pi}{PM} \tag{84}$$

where d = sp. gr. of absorption oil.
G = gal. of absorption oil per 1,000 cu. ft. of gas.
K = equilibrium constant (Figs. 73 and 74).
M = mol. wt. of absorption oil.
P = vapor-pressure of component, lb. per sq. in. abs.
π = total pressure in absorption tower, lb. per sq. in. abs.

The stripping factor may be expressed in a similar manner.

$$S = \frac{1}{A} = \frac{KV}{L} = \frac{KWM}{150d} \quad \text{or} \quad \frac{PWM}{150d\pi} \tag{85}$$

in which W is the pounds of steam per gallon of oil.

In determining the oil-to-gas ratio for an absorber, it is customary practice to decide how much of a certain low-boiling component (usually butane) can be allowed in the final gasoline and to compute the absorption factor and the oil circulation for this component. The other components will also be absorbed and to varying extents, depending upon their vapor-pressures or equilibrium constants. The amount of absorption is inversely proportional to the vapor-pressure [Eqs. (83) and (84)]. Thus the absorption factor is different for each component even though the oil circulation is the same for all. For several components, *i.e.*, 1, 2, 3, etc.,

$$A_1 : A_2 : A_3 = \frac{1}{K_1} : \frac{1}{K_2} : \frac{1}{K_3} \tag{86}$$

After the A for the governing or key component is determined, the values of A and the amount of absorption of each of the other components can be obtained from Eq. (86). The reverse is true of stripping; *i.e.*, the amount of stripping is directly proportional to the vapor-pressure of the component in question. For an absorption factor of 1 ($A = 1$) for normal butane, the factors for other components in a low-pressure absorber are about as follows:[8]

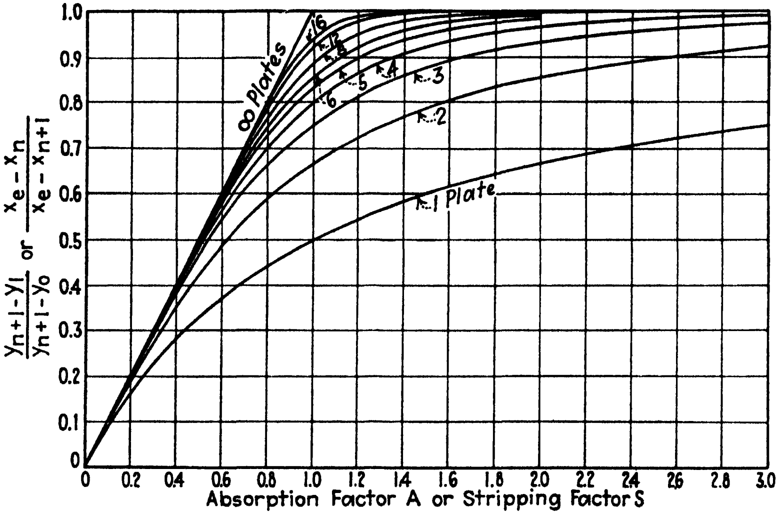

FIG. 162.—Relation of number of equilibrium plates to absorption and stripping factors. (*Dr. G. G. Brown and Ind. Eng. Chem.*)

Component	Absorption Factor A
C_3H_8	0.25 of factor for butane
iC_4H_{10}	0.67 of factor for butane
C_4H_{10}	1.0 of factor for butane
iC_5H_{12}	2.67 of factor for butane

This relation is only approximate because it varies with temperature.

The full significance of the factor $(y_{n+1} - y_1)/(y_{n+1} - y_0)$ in Fig. 162 is frequently overlooked. The expression $y_{n+1} - y_1$ is nearly equal to the amount of component that is removed from the gas; *i.e.*, it is the difference between the concentration in the incoming and outgoing gas.[9] The expression in the denominator, $y_{n+1} - y_0$, represents the maximum amount of component that could be removed if the outgoing gas were in equilibrium with the incoming lean oil. If the absorption oil contains none of the component under consideration; *i.e.*, $x_0 = 0$ (therefore $y_0 = 0$) the factor $(y_{n+1} - y_1)/(y_{n+1} - y_0)100$, is nearly[9] equal to the percentage recovery of the component in the absorber. For practical purposes, it may be considered as the fraction of the component that is absorbed. Likewise, $(x_e - x_0)/x_e$ is nearly[9] equal to the fraction of the component that is removed from the oil by the stripper. Thus if we desire to absorb 99 per cent of the isopentane from a gas, the value of $(y_{n+1} - y_1)/(y_{n+1} - y_0)$ is nearly 0.99, if the lean oil contains no isopentane. Or if we wish to strip 99 per cent of a component from the oil with steam, the value of $(x_e - x_n)/x_e$ is nearly 0.99. The application of Fig. 162 to the design or analysis of an absorber is by no means as complicated as the mathematical derivation herein presented. The use of Fig. 162 can be most ably presented by means of the examples which follow this discussion.

An examination of Fig. 162 shows the relation between the absorption factor and the percentage of component that is absorbed. Consider the line for five theoretical plates (Fig. 162).

No. of theoretical plates	Fraction below which the absorption factor and the fraction absorbed are equal*	Absorption factor* required to absorb about 99% of a component
1		
2	0.1	
3	0.3	
4	0.4	3.0
5	0.5	2.2
6	0.55	1.9
8	0.6	1.5
12	0.7	1.3
16	0.8	1.2

* Approximate.

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[9] It is not exactly equal to the amount of component removed because the total number of mols of gas changes as it passes through the absorber (Example 29, page 196). If the compositions were given as mols of component per mol of dry gas, then the expression would exactly represent the mols of component removed, per mol of dry gas.

This line approaches the line for infinite plates, as the absorption factor is decreased, until at 50 per cent absorption or $(y_{n+1} - y_1)/(y_{n+1} - y_0)$, the value of A is nearly 0.5 (about 0.505). In other words, at low percentages absorbed, the percentage absorption and the absorption factor are numerically the same. The number of plates that are used also affect the location of the point at which A is substantially equal to the percentage absorbed. Likewise the number of plates is related to the absorption factor that must be used to absorb substantially all of a component. These relations are shown in the tabulation given on page 515.

Example 80. Oil Rate for Low-pressure Absorber.—A 26–70 grade of finished gasoline is to be produced from a gas of the following composition:

Component	Volume Per Cent
C_3H_8	7.15
iC_4H_{10}	1.39
C_4H_{10}	2.55
iC_5H_{12}	1.34
$C_5H_{12}+$	1.98

The absorber is to operate at 90°F. and at a pressure of 50 lb. per square inch absolute. The absorption oil has a specific gravity of 0.83 and a molecular weight of 160. The oil is completely stripped of isopentane, but it contains 0.0005 mol fraction of pentane plus. The absorber has 16 actual plates.

How much oil should be recirculated and what will be the approximate composition of the raw gasoline?

A 26–70 grade of gasoline will contain about 33 per cent of butanes and lighter. If 99 per cent of the isopentane is absorbed, enough butanes will be absorbed to provide the 33 per cent that is required in the finished gasoline (Fig. 160).

Considering isopentane (key component),

$$y_1 = \text{mol fraction is residue gas} = \frac{0.01 \times 0.0134}{(1 - 0.0134) + 0.01 \times 0.0134} = 0.000136$$

$$\frac{y_{n+1} - y_1}{y_{n+1} - y_0} = \frac{0.0134 - 0.000136}{0.0134 - 0} = 0.9898$$

For practical calculations it is customary to use the value of

$$(y_{n+1} - y_1)/(y_{n+1} - y_0)$$

as the percentage absorbed, or in this case 99 per cent.

The plate efficiency will be about 50 per cent and hence the column will behave as if it consisted of eight theoretical plates. The absorption factor, to recover 99 per cent of a component, when eight plates are used, is about

1.5 (Fig. 162). The equilibrium constant for isopentane at 90°F. and 50 lb. is about 0.37 (Fig. 74*b*).

$$\text{Gal. oil per } 1{,}000 = \frac{AKM}{3.156d} = \frac{1.5 \times 0.37 \times 160}{3.156 \times 0.83} = 33.8$$

The equilibrium constant for butane is about 0.9 (Fig. 73*c*) and hence the absorption factor for butane is

$$A_{\text{butane}} = 1.5 \frac{0.37}{0.9} = 0.615$$

and the absorption of butane (Fig. 162) is about 61 per cent. The gallons of butane absorbed per 1,000 cu. ft. are

$$0.0255 \times 31.4 \times 0.61 = 0.488$$

All of the components were studied in the same manner, as shown in the following tabulation:

Component	Mol fraction	Gal. per 1,000 cu. ft.	Equi. constant at 90° and 50 lb.*	Absorption factor	Percentage of each component that is absorbed (Fig. 162)	Gal. absorbed per 1,000 cu. ft.	Percentage composition of raw gasoline
C_3H_8	0.0715	1.9	2.8	0.2	20	0.38	16.35
i-C_4H_{10}	0.0139	0.45	1.2	0.46	46	0.206	9.0
C_4H_{10}	0.0255	0.8	0.9	0.615	61	0.488	21.0
i-C_5H_{12}	0.0134	0.5	0.37	1.5	99	0.495	21.35
C_5H_{12} plus	0.0198	0.75	0.24	2.3	100	0.75	32.3
						2.319	100.00

* Not corrected by use of Deviation Factor (p. 520).

The analysis of the raw gasoline is not exact because some of the propane and butanes will be lost in the stripper and a little ethane (neglected) will be present in the raw gasoline.

The approximate analysis of the finished stable gasoline can be estimated as shown at the top of page 518:

ANALYSIS OF STABLE GASOLINE

Component	Gal.	Percentage, liq. vol.
Butanes	0.613	33.0
Isopentane	0.495	26.6
Pentanes +	0.75	40.4
Recovery of 26–70 gasoline	1.858	100.0

Gal. of pentanes and heavier........$0.495 + 0.75 = 1.245$

Gal. of butanes......................$1.245 \times \frac{0.33}{0.67} = 0.613$

Excess butanes.......$(0.206 + 0.488) - 0.613 = 0.081$ gal.

Example 81. Steam Rate for Stripper.—The oil from Example 80 is to be stripped to a pentane plus content of 0.0005 mol fraction. Ten actual plates or about five equilibrium plates will be used. The temperature in the stripper is about 250°F. and the pressure about 30 lb. abs.

The mol fraction of pentane plus in the rich oil must be computed. Basis: 1,000 cu. ft. of gas.

All of the pentane plus is absorbed in the oil.

Mols pentane +..................$\frac{0.75 \times 1{,}000}{36.3 \times 379} = 0.0542$ (Example 80)

Mols oil....................$\frac{33.8 \times 0.83 \times 8.33}{160} = 1.46$ (Example 80)

Total mols rich oil per 1,000 cu. ft............ .. $= 1.514$

Mol fraction $C_5H_{12}^+$ in rich oil.............$\frac{0.0542}{1.514} = 0.0358$

Fractional reduction of pentane:

$$\frac{x_e - x_n}{x_e} = \frac{0.0358 - 0.0005}{0.0358} = 0.987$$

The S corresponding to this reduction of pentane when using five plates (Fig. 162) is about 2.55. A more exact figure can be obtained by a trial and error solution of Eq. (82).

See Eq. (85).—The K for pentane plus at 250°F. (Fig. 74c) at 30 lb. is about 4.5. More exact computations of K could be used and also for S but exactness is not justified because of the approximation of the plate efficiency (50 per cent), and the fact that strippers, as used in gasoline plants, are fractionators as well as strippers.

$$W = \frac{150Sd}{KM} = \frac{150 \times 2.55 \times 0.83}{4.5 \times 160} = 0.441 \text{ lb. steam per gal. oil}$$

Thus the pounds of steam per 1,000 cu. ft. of gas are

$$0.441 \times 33.8 = 14.9$$

The steam rate could be greatly decreased by raising the stripping temperature.

High-pressure Absorbers.—High-pressure absorbing equipment is being more and more widely used. The reasons for this trend are (1) the amount of absorption oil is decreased and (2) the capacity of the absorber column is increased. However, these two savings must pay for the additional cost of compression and for the extra cost of the high-pressure equipment.

The effect of pressure on the oil recirculation can be illustrated by a study of the absorption equation [Eq. (83) or (84)]. Raoult's law is not greatly inaccurate up to pressures of 80 lb. absolute and hence changes in K or P are eliminated if Raoult's law is assumed to be valid. This leaves only two variables in Eq. (84), the pressure and the oil recirculation. For a given absorption oil, a fixed number of plates, a constant temperature, and a fixed recovery (or value of A), the relation of oil recirculation to pressure is

At 35 lb.

$$G_{35} = \frac{APM}{3.156d} \times \frac{1}{\pi} = \frac{\text{a constant}}{35}$$

At 80 lb.

$$G_{80} \cdots\cdots\cdots\cdots = \frac{\text{a constant}}{80}$$

Thus the recirculation at 80 lb. in terms of the recirculation at 35 lb. is approximately

$$G_{80} = {}^{35}\!/_{80}G_{35} = 0.437G_{35}$$

The oil recirculation is inversely proportional to the pressure so that, if 50 gal. of oil are necessary at 35 lb., only 21.8 gal. are required at 80 lb.

At higher pressures the foregoing does not hold because two factors are variables [Eq. (83)]. The oil recirculation is directly proportional to K, but K is dependent on the pressure. As an example, the values of K at 35 and 500 lb., for pentane, are about as follows:

K at 85° and 35 lb. = about 0.3 (Fig. 74*c*)
K at 95° and 500 lb. = 0.07

$$G_{500} = \frac{0.07}{0.3}G_{35} = 0.224G_{35}$$

Thus if 50 gal. is required at 35 lb., only 11.2 gal. is required at 500 lb. This is far from being inversely proportional to pressure, which shows only 3.5 gal. required, and serves to emphasize the danger in applying Raout's law at high pressures.

It will be noted that a higher absorption temperature was used at 500 than at 35 lb. So much gasoline is absorbed in a small amount of oil, in the 500-lb. absorber, that the latent heat of condensation becomes an important factor and raises the oil temperature. In ordinary absorbers, little or no rise in oil temperatures occurs, but in high-pressure absorbers, or when a very rich gas is absorbed at a low pressure, the temperature rise amounts to 10 to 20°F. The equilibrium constants given in Figs. 73 and 74 may be used in all natural-gasoline computations but a correction factor which Dr. Brown[10] calls the deviation factor must be applied to the equilibrium constants because oil solutions are not ideal solutions. The deviation factor is large if the percentage of the component in the mixture is small and it is also larger for methane and ethane than for the heavier hydrocarbons. Approximate values of the deviation factor[10] are as follows:

Mol per cent in liquid	Approximate deviation factors		
	Methane	Ethane	Heavier hydrocarbons
0	2	1.5	1.35
20	1.16	1.15	1.102
40	1.095	1.085	1.065
60	1.055	1.05	1.04
100	No correction necessary		

The equilibrium constants should be multiplied by the deviation factors.

In designing high-pressure columns only one major difference arises. The computation is conducted as in Example 80 except that some gasoline is condensed during compression to the high pressure. Equation (46) (page 254) can be used to determine the amount condensed, and the method of computation is much the same as given in Example 45.

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[10] Brown and Katz, Vapor Pressure and Vaporization of Petroleum Fractions, *Ind. Eng. Chem.*, **25**, 1373 (1933).

Example 82. Condensation during Compression.—A lean natural gas is to be compressed from 30 to 500 lb. per square inch absolute and cooled to 80°F. before it enters the absorber. The analysis of the gas is

CH_4	79.8
C_2H_6	6.5
C_3H_8	6.2
iC_4H_{10}	1.4
C_4H_{10}	2.3
iC_5H_{12}	1.6
$C_5H_{12}+$	2.2

What is the final composition of the gas and condensate, and the amount of condensate?

Basis: 100 mols or volumes of gas.

Equation (46) must be solved by trial and error because V (or L) is not known until the computation is complete.

A value of V is assumed, L is found from V, and Eq. (46) is filled in. The solution of the equation gives the actual V and, if it is not the same as the assumed value, a new assumption must be made.

TABLE 77.—TRIAL-AND-ERROR SOLUTION FOR EXAMPLE 82

(1)	(2)	(3)	(4)	Assume $V = 96$, $\frac{L}{V} = 0.0416$		Assume $V = 97$, $\frac{L}{V} = 0.0309$		(9)
Component	Values of G, mols	Values of K at 500 lb. and at 80°F.	$K \times G$, (2) × (3)	(5) $\frac{L}{V} + K$	(6) Values of V, (4) ÷ (5)	(7) $\frac{L}{V} + K$	(8) Values of V, (4) ÷ (7)	Mols gaso. (2) − (8)
CH_4	79.8	5.7	455.0	5.74	79.3	5.73	79.4	0.4
C_2H_6	6.5	1.1	7.15	1.14	6.27	1.13	6.33	0.17
C_3H_8	6.2	0.46	2.85	0.502	5.68	0.491	5.8	0.4
iC_4H_{10}	1.4	0.22	0.31	0.262	1.18	0.251	1.23	0.17
C_4H_{10}	2.3	0.16	0.368	0.202	1.82	0.191	1.93	0.37
iC_5H_{12}	1.6	0.071	0.114	0.113	1.01	0.102	1.12	0.48
$C_5H_{12}+$	2.2	0.052	0.115	0.094	1.22	0.083	1.38	0.82
Total	....	.....	....	.....	96.48	.....	97.19	2.81

As an example, the amount of methane that remains uncondensed will be computed:

Assume $V = 96$, then $L = (100 - V)$ or 4.

$$\frac{L}{V} = \frac{4}{96} = 0.0416$$

K_1 for CH_4 at 80° and 500 lb. (Fig. 74*a*) is 5.7.

$$K_1G_1 = 5.7 \times 79.8 = 455$$

$$\frac{L}{V} + K_1 = 0.0416 + 5.7 = 5.74$$

$$\frac{K_1G_1}{\frac{L}{V} + K_1} = \frac{455}{5.74} = 79.3 \text{ volumes of } CH_4 \text{ uncondensed}$$

The deviation factors were not used because they would complicate the calculations unduly.

The other hydrocarbons were computed in a similar manner as shown in Table 77. Upon totaling the volumes of each of the hydrocarbons, column (6), the total is 96.48 rather than 96 as assumed. A second solution is shown in columns (7) and (8), based on an assumed V of 97. The check (97.19) is a reasonable one and the actual value of V will doubtless be about 97.3. The final column (9) shows the mols of gasoline that are condensed.

The compositions of the residue gas and the condensate are as follows:

Component	Mols, or volume per cent	
	Residue gas	Condensate gasoline
CH_4	81.68	14.23
C_2H_6	6.52	6.05
C_3H_8	5.97	14.23
iC_4H_{10}	1.27	6.05
C_4H_{10}	1.99	13.16
iC_5H_{12}	1.15	17.08
$C_5H_{12}+$	1.42	29.2

The amount of methane and ethane absorbed would be considerably less if the deviation factors mentioned on page 520 were used and these factors should be used in exact work.

The residue gas, as shown above, is the material that would be processed in a high-pressure absorber.

Construction of Absorbers and Strippers.—The diameter of an absorber can be determined by the methods that are outlined in Chap. XXI. The linear velocities that are used are usually lower than for other bubble-towers. There are several reasons for the low velocity:

1. The temperature is low (increases density).
2. The trays are usually closely spaced.
3. Entrainment is kept at a minimum.
4. The pressure is relatively high (increases density).
5. The oil rate is high.

The most important of these, in reducing the velocity, is probably the high oil rate. Kallam and Steward[11] report that the allowable velocity for low-pressure absorbers decreases with the oil-to-gas ratio approximately as follows:

Oil-to-gas Ratio, Gal. per 1,000	Velocity, Ft. per Sec.
10	1.0
20	0.9
50	0.7
100	0.5
500	0.2
1,000	0.12

They do not state if different towers were used or if the downspouts were increased in size to care for the additional oil circulation.

The details of tray design, tray spacing, etc., were discussed in Chap. XXI.

Stabilizer Design.—No entirely satisfactory method of designing stabilizers has been proposed. Several methods have been used but they are so complicated by the large number of components and trial-and-error methods that they are not practical. Perhaps the best design method is that proposed by Brown and others.[12]

Stabilizers are built with a large number of trays (often more than 30) and for high reflux rates (often a reflux ratio of more than 8:1). If designed in this manner, the unit will be flexible enough to take care of almost any condition that may arise. In fact, a stabilizer is frequently operated for the production of several gasolines of greatly different vapor-pressure, and hence a flexible unit is exactly what is needed.

The pressure at which a stabilizer should operate can be estimated by a trial-and-error solution. The partial-vapor-pressure of a component in the liquid reflux is equal to the partial-pressure of that component in the vapor:

$$y = Kx \tag{43}$$

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[11] *Ref. Nat. Gaso. Mfr.*, November, 1929, p. 62.

[12] Brown, Souders, Nyland, and Hesler, *Ind. Eng. Chem.*, **27**, 383 (1935).

When the proper pressure (or series of K's) is selected, the sum of the mol fractions in the liquid (x's) is equal to 1. Example 83 illustrates this calculation.

The number of plates in the stabilizer can be computed in much the same manner except that the pressure is known and the temperatures on the various plates are unknown. By working from plate to plate, usually starting at the feed plate, the composition of the overflow liquid and the vapor can be traced until the proper composition is attained. The method is impractical except as a rough guide and it is tedious because a trial-and-error solution is required for each plate.

Example 83. Stabilizer Pressure and Composition of Reflux. A raw gasoline has the following composition:

CH_4	0.03	iC_4H_{10}	9.38
C_2H_6	2.27	C_4H_{10}	23.33
C_3H_8	17.29	$iC_5H_{12}+$	47.77

A 26–70 grade of gasoline is to be produced. The temperature of the cooling water is 83°F. and hence the condenser temperature will be about 90°F. What is the approximate fractionator pressure? The deviation factors will not be used so that the computation will be less complicated.

A 26-70 grade of gasoline contains about 30 per cent of butane. The mols and mol fractions of the components in the residue gas are about as follows:

Component	Moles	Approximate mol per cent in residue gas
CH_4	0.03	0.09
C_2H_6	2.27	7.1
C_3H_8	17.29	54.21
i and n C_4H_{10}	12.3*	38.6
Total	31.89	100.0

* i and n $C_4H_{10} = (9.38 + 23.33) - (47.7 \times \frac{30}{70})$.

$y = Kx$, for each component. If the proper pressure is used, the sum of the x's is equal to 1 (Figs. 73 and 74).

The final assumption can be more easily estimated by interpolating or extrapolating than by reading new values of K, because the charts cannot be read accurately.

$$\text{Pressure} = 100 - \frac{1.321 - 1.0}{1.321 - 1.026}(100 - 65) = 62.0 \text{ lb.}$$

The pressure is greatly increased if the condenser temperature is 100 rather than 90°.

(1) Component	(2) Vapor y	Assume 150 lb.		Assume 100 lb.		Assume 65 lb.	
		(3) K at 90°	(4) (2) ÷ (3)	(5) K at 90°	(6) (2) ÷ (5)	(7) K at 90°	(8) (2) ÷ (7)
CH_4	0.0009	15	0.00006	20			
C_2H_6	0.071	3	0.236	3.8	0.187	4.8	0.147
C_3H_8	0.5421	1.1	0.492	1.5	0.361	1.9	0.285
C_4H_{10}	0.386	0.38	1.015	0.5	0.773	0.65	0.594
Total	......	.....	1.743	....	1.321	....	1.026

The composition of the reflux, as mol percentage, is given in column (8) of the tabulation.

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CHAPTER XXIV

CHEMICAL AND CLAY TREATMENT

With few exceptions all petroleum products must be chemically treated in some manner in producing finished market products. The impurities that must be removed are usually present in the crude oil but some are also produced during the refining operations of distillation, cracking, etc. Some of the purposes of chemical treatment are as follows:

1. To improve the color.
2. To remove sulfur.
3. To improve the odor.
4. To remove gumlike, resinous, and asphaltic substances.
5. To improve the stability upon exposure to air or light.
6. To eliminate corrosive materials.
7. To change properties of the oil, such as the viscosity-index, carbon residue, etc.

Most stocks do not need to be improved in all of these respects but some stocks, such as pressure-still distillate that is produced from sulfur-bearing crude oil, must be treated for many of the above purposes.

Although many chemicals are used for refining, *sulfuric acid* is by far the most useful and generally used chemical. Sulfuric acid treatment improves the color, removes sulfur, reduces the gum content, improves the stability of light distillates, and to some extent improves the odor. It is also used to improve the color of lubricating oils and sometimes wax. For "sour" sulfur-bearing light distillates, the *doctor treatment* must be used. This treatment consists of agitating the oil with a little sulfur and an alkaline solution of sodium plumbite. The odoriferous mercaptans, hydrogen sulfide, and elementary sulfur, are removed. A newer treatment for somewhat the same purpose is the *hypochlorite process,* in which the oil is agitated with an alkaline solution of sodium or calcium hypochlorite. Solutions of *sodium hydroxide* are usually used after acid treatment to neutralize the excess acid and to remove sulfonic acids and other organic acids, as the sodium salts. Used alone, it removes hydrogen sulfide and to some extent the mercaptans or thioalcohols. Sodium hydroxide, when used to neutralize acid-treated lubricating oils, often gives troublesome emulsions, and hence *neutralizing clays* and *ammonia* are being more widely used for this purpose. The color of lubricating oils is improved by percolation through adsorbent clays or by contacting the oil, after acid treatment, with clay at a high temperature. In addition to these, there are many other chemicals and processes such as the clay vapor-phase processes for cracked gasoline, the zinc chloride and the copper sulfate treatments for light distillates, and the Edeleanu solvent process. During 1933 a widespread development of *solvent treating* or *extraction* processes took place. In general, these processes aim to separate the high- and low-viscosity-index hydrocarbons by selective absorption.

SULFURIC ACID TREATMENT

Sulfuric acid has been used since the first days of the oil industry, and even before that, for treating coal oil. No generally useful substitute for acid has been found but a serious study of new methods of conducting acid treatment is now being made.

The action of sulfuric acid on the several series of hydrocarbons is different for each series. The *n*-paraffins and naphthenes are only slightly attacked by 93 per cent acid (66 Bé.) at room temperature. At higher temperatures and at higher concentrations of acid they are attacked, and particularly those isomers that have several side-chains. Whereas straight-run gasolines are composed largely of paraffin and naphthene hydrocarbons, sulfuric acid is an excellent treating agent for them if any treatment is necessary. The aromatic hydrocarbons, such as benzene and its homologues, are only slightly attacked by 93 per cent acid but toluene and xylene are more readily attacked than benzene. The aromatic hydrocarbons cause lamp oils to burn with a smoky flame. For the removal of aromatics, 93 per cent and higher strengths of acid are useful and sometimes even fuming acid is necessary.

The unsaturated hydrocarbons, such as the olefins, diolefins, and acetylenes, are readily attacked by sulfuric acid even at strengths as low as 75 per cent. The olefins tend to polymerize to di- or higher polymers, some of which[1] are highly resistant to further action by the acid. Cracked gasoline contains olefins in considerable quantity and their polymerization may account in part for the increase in end-point during acid treatment. High temperatures and high concentrations of acid favor polymerization, and low temperatures and low concentrations favor the formation of alkyl acid sulfates, neutral esters, and secondary and tertiary alcohols. The higher alcohols and dipolymers and to some extent the acid alkyl sulfates dissolve in the distillate and upon redistillation the acid alkyl sulfates decompose, yielding alcohols, sulfur dioxide, etc., and cause trouble with the color, stability, and gum content of the gasoline. The acid alkyl sulfates are dissolved by a caustic wash, after acid treatment, but the neutral esters are not, and at temperatures above 285°F. they decompose. Diolefins cause the formation of tars, a loss in color, and the formation of "gum" during storage.[1]

Sulfuric acid also removes resinous or asphaltic substances which may be present by poor fractionation, entrainment, or a small amount of cracking. These materials tend to inhibit the crystallization of wax, and hence acid treatment often raises the pour-point. Oxygen compounds, such as naphthenic acids and ketones, and substances such as alcohols and aldehydes that are formed by high-temperature oxidation are dissolved by sulfuric acid, but when diluted with oil their removal is never complete. Nitrogen bases similar to quinoline or pyridine, which are produced in small quantities during distillation, are easily dissolved in dilute acid.

Many sulfur compounds are present in petroleum but not many of them have been isolated or studied. The action on mercaptans will serve as an illustration of the action of acid:

$$\begin{aligned} \mathrm{RSH} + \mathrm{H_2SO_4} &= \mathrm{RSHSO_3} + \mathrm{H_2O} \\ \mathrm{RSH} + \mathrm{RSHSO_3} &= \mathrm{(RS)_2SO_2} + \mathrm{H_2O} \\ \mathrm{(RS)_2SO_2} &= \mathrm{R_2S_2} + \mathrm{SO_2} \end{aligned}$$

The final disulfide products are partly dissolved in the acid sludge. Strong acid (93 per cent or stronger) is necessary to remove mercaptans but such large quantities of acid are required that

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[1] BROOKS and HUMPHREY, *J. Am. Chem. Soc.*, **40**, 822 (1918).

"sweetening" is seldom practiced in this manner. Alkyl sulfides, disulfides and sulfates, and most sulfur compounds are removed by 93 per cent or stronger acid but the acid alkyl sulfates dissolve to some extent in the oil.

The rate[2] of action of sulfuric acid on the various impurities appears to be somewhat as follows: (1) nitrogen compounds such as amines, amides, and amino acids, (2) asphaltic substances, (3) olefins, (4) aromatics, and (5) naphthenic acids.

Concentration of Acid.—Sixty-six Baumé[1] or 93 per cent acid finds the most general use. However, for treating light distillates to color only, a more dilute acid may be advantageous.[3] For most other purposes, such as removing combined sulfur, improving the burning qualities of kerosene, and removing tar from lubricating oils, a 93 per cent or stronger acid should be used. For lubricating oil, 98 per cent acid is also widely used.

The loss of oil to sludge increases as high concentrations of acid are used so that in general the most dilute acid that is suitable should be used. The following data by Potthoff[4] indicate for pressure distillate the larger sludge loss and total loss (sludge and polymerization) which occur by using strong acid.

Lb. acid per bbl.	Sludge loss		Total loss	
	66° acid	60° acid	66° acid	60° acid
5	1.8	1.6	2.8	2.2
10	3.5	2.7	5.3	3.9
20	8.0	4.7	11.3	6.3

Weir, Houghton, and Majewski[5] have conducted experiments with a light lubricating oil stock (289 viscosity at 100°F.) which show the following effect of acid strength:

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[2] PYHÄLÄ, E., *Petroleum*, **9**, 1506 (1928).

[3] KALICHEVSKY and STAGNER, "Chemical Refining of Petroleum," p. 51, Chemical Catalog Company, Inc., New York, 1933.

[4] Purification of Pressure Distillate, *Oil Gas J.*, Mar. 5, 1931, p. 141.

[5] Control of Color . . . Treating, *Ref. Nat. Gaso. Mfr.*, December, 1930, p. 89.

Lb. acid per bbl.	Sludge loss with these strengths of acid			
	75%	86%	93%	98%
6.25	0.7	0.92	1.75	2.35
12.5	1.1	1.6	2.3	3.1
31.3	1.3	1.95	3.1	4.15

Thus with small amounts of acid, such as those customarily used in treating distillates, the sludge losses are small and, although the loss increases with the strength of acid, it is of such a magnitude that the effect of acid concentration may be almost neglected. However, for quantities of acid exceeding 10 lb. per barrel, the loss caused by using strong acid begins to be important. The exact strength of acid that should be used depends entirely upon the impurities that must be removed, the types of hydrocarbons found in the oil, and the final color that is desired. Strong acid (93 to 103 per cent), when used at relatively low temperatures, is effective in removing combined sulfur and removing aromatic hydrocarbons from burning-oils (and transformer oils) but, in general, the color of the product, when fuming acid is used, is not good because oxidation of some of the less stable compounds occurs.

Cooke and Hayford[6] report the following effect of acid strength on the removal of sulfur by the Stratford contactor centrifuge process.

Strength of Acid, Per Cent	Per Cent Sulfur in Treated Distillate
80	0.2
93	0.17
95	0.13
98	0.09
100	0.075
104	0.07

For improvement of color, an acid of 93 per cent strength is recommended; but if the combined sulfur is low, an acid of only 85 per cent strength may be advantageous. Weak acid is also useful in removing nitrogen bases and for improving the color

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[6] Distillate Treating, Part II, *Ref. Nat. Gaso. Mfr.*, April, 1934, p. 130.

without removing unsaturated compounds. The concentration of acid that is most suitable for a particular stock can only be ascertained by laboratory and plant-scale experiments.

Quantity of Acid.—Enough acid must be used to improve the color and remove impurities, but an excess over this amount may result in a poorer color and a loss of aromatic and unsaturated hydrocarbons as well as a waste of acid. If acid is applied to lubricating oils in too large doses, the oil may be discolored by "burning." The remedy is to use the acid in small charges and keep the oil cool. The treatment of spray oils, medicinal oils, and sometimes wax is accomplished by adding fuming acid in 25 or 30 lb. per barrel charges and using as much, in some cases, as 200 lb. of acid per barrel.

The quantity of acid that is commonly used is about as follows:

Natural gasoline—Usually none but occasionally 2 lb. per barrel.
Straight-run gasoline—0 to 3 lb. per barrel.
Pressure distillate—To improve the color, normally 1 to 4 lb. per barrel. For high-sulfur oils and oils from naphthene-base crude oils the quantity may be much more. Some distillates cannot be economically desulfurized with acid.
Solvents—0 to 5 lb. per barrel. High-sulfur stocks are seldom used in solvent manufacture.
Kerosene—1 to 15 lb. but as much as 75 lb. per barrel for the kerosene from some naphthene-base crude oils.
Lubricating oils—0 to 60 lb. per barrel. Pennsylvanian oils usually require no acid treatment, mixed-base oils more, and asphalt-base oils the higher figure. Vacuum-distilled stocks require less acid than residual stocks. The acid required for lubricating oils is intimately connected with the amount of percolation or contacting that is practiced.

Cooke and Hayford[6] find that the desulfurization is directly proportional to the amount of acid that is used.

Amount of Acid, 98 Per Cent, Lb. per Bbl.	Per Cent Sulfur in Treated Distillate
5	0.165
8	0.142
11	0.117
14	0.095

Temperature of Treatment.—The temperature at which the treatment is conducted is one of the most important factors. Although the temperature for a particular stock should be determined by experiment, the following considerations are useful as a guide:

Polymerization losses are greater at higher temperatures, so that unless polymerization is desired, as in rare cases when the sludge is to be utilized, lower temperatures are desirable.

High temperatures favor the removal of aromatic and unsaturated hydrocarbons and the removal of resinous asphaltic materials. Thus naphthenic kerosenes and solvents are usually refined at a relatively high temperature unless the removal of sulfur is also necessary.

Lower temperatures produce a better color in the product and are favorable for the removal of sulfur compounds. Sludge losses are slightly higher at lower temperatures but as the quantity of acid that is required is also less, the actual sludge loss is not greatly affected. In treating lubricating oils at low temperatures the viscosity of the oil may be so great that settling is slow and the separation is imperfect. This results in too long a contact time and a loss in color, and hence lubricating oils are usually treated at relatively high temperatures. Table 78 illustrates the effect of temperature on color when a kerosene stock is treated with 17.5 lb. of acid per barrel (99 per cent acid).[7]

TABLE 78.—EFFECT OF TEMPERATURE ON COLOR

Temperature, °F.	Acid sludge, g. per l.	Arbitrary color scale, mm.
32	61.6	193.0
41	62.0	166.5
50	62.5	143.0
59	63.5	112.5
68	64.3	89.5
77	64.8	80.5
86	65.2	52.0
95	65.8	Yellow
104	66.0	Yellow
113	66.4	Yellow
122	67.0	Yellow

The effect of the temperature of treating upon sulfur removal[3] is illustrated by Table 79. The cracked-gasoline stock contained

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[7] ZALOZIECKI, R., *Chem. Ztg.*, 875, 1895.

0.39 per cent sulfur and 90 per cent of the treated material was distilled with steam.

TABLE 79.—EFFECT OF TEMPERATURE ON SULFUR REMOVAL*

Acid strength, per cent H_2SO_4	Treating temp., °F.		H_2SO_4, net lb. per bbl.	Loss to sludge, per cent	Engler dist. of neutral oil to 400°F., per cent	Sulfur in steam dist., per cent
	Initial	Max.				
103	88	98	10	5.2	90.5	0.26
103	80	98	20	6.7	88.0	0.19
103	86	102	30	10.0	....	0.16
103	80	104	40	12.0	....	0.14
103	74	106	60	16.0	80.3	0.10
103	7	20	10	5.2	92.0	0.32
103	2	20	15	6.0	91.5	0.17
103	7	23	20	9.0	88.0	0.10
103	2	25	30	10.4	87.0	0.06
93	93	102	10	4.2	91.5	0.25
93	84	97	20	5.8	88.5	0.21
93	78	96	30	8.3	....	0.16
93	76	101	40	13.3	....	0.14
93	84	102	60	16.7	81.5	0.10
93	10	16	10	4.2	93.5	0.34
93	8	18	20	5.8	92.5	0.25
93	5	20	30	10.0	91.0	0.12
93	0	21	40	10.8	90.0	0.07
93	5	28	60	15.8	....	0.04

* Courtesy of Union Oil Company of California.

The temperatures that are commonly used for various treating operations are as follows:

Straight-run gasoline—70 to 90°F. If large quantities of acid are required, it may be practical to go to lower temperatures.

Cracked gasoline—60 to 90°F. If heavy treats are required, temperatures of 25 to 30°F. are recommended although temperatures of 40 to 50° may be more economical[8] (Table 79).

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[8] Standard Oil of California, Brazilian Pat. 5,667 (Jan. 23, 1929), and other patents.

Kerosene—90 to 130°F. If the oil is to be redistilled, a higher temperature may be economical. Robinson[9] finds that low temperatures are better.

Lubricating oil stocks—Customary temperatures[10] are given in Table 80.

Cylinder stock—130 to 170°F.[10] and 150 to 180°F. if treating is conducted before dewaxing.

TABLE 80.—TEMPERATURE FOR TREATING LUBRICATING OILS

Viscosity of oil at 100°F., sec.	Temperature of oil when acid is added, °F.	Temperature of oil and wash water during washing and settling, °F.
50	70– 80	110–120
75	80– 90	120–130
100	85– 95	130–140
150	90–100	140–150
200	95–105	150–160
300	100–110	155–165
500	105–115	160–170
1,000	110–120	165–175
1,500	110–120	165–175
2,000	115–125	170–180

The cold-treating methods have many advantages from a treating standpoint but the refrigeration requirements are enormous. The practicability of low-temperature treating must be carefully investigated and a stock must be very difficult to treat before cold methods can be adopted.

Contact Time.—Two factors are involved in considering the contact time. Prolonged contact of acid-sludge and oil results in a poorer color and less stability, but too short a time may prevent a complete utilization of the acid. Furthermore, the time of contact is intimately associated with the fineness of dispersion of the acid throughout the oil and the time required to separate the sludge.

Straight-run and cracked gasolines are contacted with acid for less than a minute in continuous-treating systems. A short

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[9] ROBINSON, C. L., U.S. Pat. 910,584 (Jan. 26, 1909).

[10] KAUFFMAN, H. L., *Ref. Nat. Gaso. Mfr.*, May, 1927, p. 59.

contact time is particularly advantageous for cracked gasolines in order to minimize polymerization and sulfonation of the oil. The time of contact is sometimes held to only a few seconds by mechanical contactors[11] and the settling time is eliminated almost altogether by centrifugal means. Continuous processes for treating lubricating oils are being investigated[12,13,14] and a short time of contact (10 min.) is found to be advantageous. These short-contact processes all claim to reduce the amount of acid that is required and to facilitate the control of the treating operation.

In the older method of batch agitation, the time of contact is much longer. For light distillates the time of air agitation ranges from 15 to 40 min. Kerosene normally requires 30 or 40 min. and for lubricating oils the time may be 90 min. The time required to settle the sludge in an agitator ranges from a few minutes for gasoline to as long as 15 hr. for very viscous stocks.

Laboratory control tests are necessary in finding the best conditions for treating. An excellent method for the control of lubricating oil treating is outlined by Weir, Houghton, and Majewski.[5]

Octane-number.—The loss in octane-number by acid treating is not large for normal quantities of acid. Born and Wilson[15] have studied three pressure distillates by treating under conditions comparable to those used in the respective plants from which the distillates were obtained. Table 81 gives their results.

Wirth, Kanhofer, and Murphy[16] present similar data except that the total loss in octane-number was divided into the loss due to (1) evaporation and loss of light hydrocarbons during steam distillation, (2) polymerization and solution during treating, and (3) heavy hydrocarbons remaining as a residue upon

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[11] STRATFORD, C. W., *Nat. Pet. News*, Mar. 12, 1930, p. 32F.

[12] JONES, L. D., Use of Centrifuge in Acid Treating Petroleum Stocks, *Ref. Nat. Gaso. Mfr.*, June, 1934, p. 224.

[13] WALKER, R. C., Continuous . . . Centrifugal Separation . . . , *Ref. Nat. Gaso. Mfr.*, June, 1934, p. 228.

[14] TRESCOTT, L. C., Sludge, *Ref. Nat. Gaso. Mfr.*, May, 1934, p. 172.

[15] *Nat. Petroleum News*, Apr. 5, 1933, p. 23.

[16] *Oil Gas J.*, July 3, 1933, p. 13.

distillation. The first of these gave losses in the octane-number of 0 to 2, the second gave losses of 1 to 2.5, and the third was negative, or the octane-number increased by 0 to 1 owing to the elimination of heavy ends. Their results are comparable with those given in Table 81.

TABLE 81.—EFFECT OF ACID TREATMENT ON OCTANE-NUMBER

Lb. acid per bbl.	Octane-numbers* for				
	Distillate *A*		Distillate *B*		Distillate *C*
	66°Bé.	62.5°Bé.	66°Bé.	62.5°Bé.	66°Bé.
0	70.0	70.0	68.5	68.5	67.4
1	68.9	69.0	67.3	67.4	66.1
2	68.2	68.3	66.6	66.8	65.7
3	67.7	67.8	66.2	66.4	65.1
5	67.1	67.3	65.8	65.9	64.7

* 30-B Ethyl engine, 212°F. jacket temperature, 15 deg. spark advance.

SWEETENING TREATMENTS

Mercaptans and elementary sulfur are not removed from distillates by the ordinary treating processes. The so-called sweetening treatments are used to remove these substances. Mercaptans impart a foul odor to the distillate and elementary sulfur (in the presence of mercaptans) causes the distillate to be corrosive. Hydrogen sulfide is also removed in the doctor treatment but it may also be removed by a caustic wash. The two common sweetening processes are the doctor and the hypochlorite treatments.

The *doctor treatment* consists of agitating the oil with a little sulfur and with alkaline sodium plumbite solution. Reactions for the process are as follows:

$$2RSH + Na_2PbO_2 = (RS)_2Pb + NaOH$$
$$(RS)_2Pb + S = R_2S_2 + PbS$$

Most of the lead sulfide settles but the disulfides dissolve in the oil to some extent. Inasmuch as disulfides decompose at elevated temperatures,[17] the doctor treatment should preferably be conducted after the final distillation of cracked distillates. Elementary sulfur in the gasoline is removed by these reactions; but if an excess (about 20 per cent more than required for the reaction) of sulfur remains in the oil, the oil will be corrosive. The presence of lead sulfide, even added, facilitates the sweetening process and oxygen is also advantageous.[18] Hence air agitation is an advantage in doctor sweetening. The doctor treatment is always difficult to control and hence the chemistry of the process must be considered for each particular distillate.[18] Gasolines that contain much free sulfur sometimes require the addition of mercaptans or sour distillates before the doctor treatment because mercaptans are necessary in completing the reactions with sulfur.

The concentration of the sodium hydroxide solution should be 12 to 30°Bé. (8 to 24 per cent). Lead oxide or litharge (PbO) is dissolved in the caustic solution before it is mixed with the oil. The solubility of lead oxide in caustic soda increases with the gravity of the solution, being about 1 per cent in a 12°Bé. solution and about 3 per cent in a 30°Bé. solution. About 0.05 lb. of lead oxide is consumed per barrel of cracked gasoline. Rhombic or lump sulfur should be used because flowers of sulfur is not sufficiently soluble in oil. Continuous-treating equipments are generally used, but batch treatment with air agitation has the advantage of regenerating the lead sulfide and decreasing the amount of sulfur that is required. Sometimes a better color gasoline is obtained by using the caustic solution from a hydrogen sulfide wash in making the doctor solution.[19]

Spent doctor solution is often recovered or used over again by adding more litharge to the solution and carrying the sulfide in suspension. Some refiners oxidize the lead sulfide as a caustic slurry, by heating to 150 to 175°F. and blowing with air which converts the sulfide to plumbite.[20]

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[17] Excepting ethyl and propyl disulfides. Faragher, Morrell, and Comay, *Ind. Eng. Chem.*, **20**, 527 (1928).

[18] BORN, S., Chemical Reactions . . . , *Petroleum Eng.*, August, 1931, p. 149.

[19] ROWSY and WHITEHURST, *Oil Gas J.*, Dec. 29, 1927, p. 250.

[20] *Chem. Met. Eng.*, **38**, 76 (1931); also D. F. GERSTENBERGER, *Petroleum Eng.*, January, 1930, p. 167.

Lead sulfide itself may be used as a sweetening agent for certain distillates.[21] The lead sulfide molecule absorbs or holds many molecules of sulfur compounds, such as alkyl sulfides and mercaptans, but the mechanism of the action is not entirely clear.

Sodium or calcium *hypochlorite sweetening* has found extensive use in the treating of natural gasoline and straight-run gasoline but it is seldom used for cracked products or high-boiling oils. With dilute hypochlorite a mild oxidation takes place, thus:

$$2RSH + NaOCl = R_2S_2 + H_2O + NaCl$$

With more concentrated solutions,

$$RSH + 3NaOCl = RSO_3H + 3NaCl$$

Likewise for sulfides,

$$R_2S + NaOCl = R_2SO + NaCl$$

and

$$R_2S + 2NaOCl = R_2SO_2 + 2NaCl$$

Elementary sulfur is not attacked and hydrogen sulfide is oxidized to water and free sulfur. The sulfones (R_2SO_2), such as ethyl and propyl sulfones, can be removed by washing with water but the higher molecular-weight sulfones are not soluble in water.

Sodium hypochlorite is commonly prepared by bubbling chlorine gas through a 10 per cent solution of sodium hydroxide. The temperature should not be over 95°F. or chlorates may be produced. A water-cooled cast-iron vessel may be used but steel is satisfactory. The stock solution is diluted to about 0.34 *N* when ready to use. The quantity of solution required, measured in terms of chlorine, amounts to 1 to 15 lb. of chlorine per 1,000 gal.

Calcium hypochlorite is more convenient to use and is somewhat cheaper than sodium hypochlorite. The solution may be prepared as above, with lime and chlorine, but bleaching powder is often more convenient. A 0.34 *N* solution is satisfactory. The Mathieson Alkali Works has a special chlorinated calcium compound sold as H.T.H. which contains about 65 per cent of

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[21] MORRELL and FARAGHER, *Ind. Eng. Chem.*, **19**, 1045 (1927).

chlorine. The quantity of H.T.H. required is usually between 1 and 5 lb. per 1,000 gal. of gasoline, and three to five times as many pounds of a good grade of bleaching powder is required.

The hypochlorite process partially oxidizes hydrogen sulfide to free sulfur, so that a precaustic wash is sometimes used to remove hydrogen sulfide. In fact, a caustic wash materially reduces the chemical that is needed in the hypochlorite treat. Little or no sludge is produced so that the process is particularly suited to the processing of natural gasoline.

REFINING BY ADSORPTION

Various mineral clays, earths, and artificial mineral adsorbents are used to improve the color of oils and remove asphaltic or resinous material. In general, three methods are followed: (1) percolation through a long column of coarse clay, (2) contact at a high temperature with finely powdered clay, and (3) contact in the vapor-phase with loosely packed clay. The percolation method is the oldest method and in many ways is not so satisfactory as contact treatment, but in other ways, particularly its flexibility, it is a desirable method. The application of vapor-phase treating is limited to the treatment of the lighter distillates, particularly cracked gasoline, because higher boiling oils cannot be easily kept in the vapor state. The contact process is now used for neutral oils, gasoline, and diluted cylinder stocks.

The removal of coloring matter from oils by clay appears to be governed by the adsorption isotherm of Freundlich.[22] This may be stated as

$$\frac{X}{M} = aC^{\frac{1}{n}}$$

or in logarithmic form

$$\log \frac{X}{M} = \log a + \frac{1}{n} \log C$$

where X = units of impurity removed.
M = quantity of adsorbent used.
C = concentration of the impurities in the oil or vapor, in equilibrium with the solid adsorbent.

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[22] WALKER, LEWIS, and McADAMS, "Principles of Chemical Engineering," 2d ed., p. 645, McGraw-Hill Book Company, Inc., New York, 1927.

a and n = constants which depend upon the characteristics of the adsorbent, oil or vapor, and solvent if one is used.

Thus decolorizing data yield straight lines if X/M is plotted against C on logarithmic graph paper. The equation may be used to compare several clays but this is about the limit of its usefulness, because the value of the constants is usually unknown. L. L. Davis[23] presents a study of five clays in the treatment of a lubricating oil. He found the reciprocal of the Tag Robinson color was a satisfactory measure of the impurities. For comparing the efficiency of two clays on a particular oil, the foregoing equation may be arranged in a more convenient form by dividing one equation by the other, thus

$$\frac{M}{M'} = \frac{a'}{a}C^{\left(\frac{1}{n'}-\frac{1}{n}\right)} \quad \text{or} \quad bC^{\left(\frac{1}{n'}-\frac{1}{n}\right)}$$

Table 82 shows the efficiencies of the five clays.[23]

TABLE 82.—COMPARISON OF CLAYS

Tag Robinson color	Efficiencies as per cent of Riverside earth				
	Riverside, Tex., Fuller's earth	Natural, Utah	Treated German clay, dry form	Treated Tex. clay, pulp form	Treated Calif. clay, pulp form
½	100	120	120	170	285
1	100	130	133	235	400
1½	100	140	140	240	465
2	100	150	150	245	500

Many factors are involved in the efficiency of decolorizing, such as the kind of oil, the kind of treatment it has undergone, the kind of solvent, if any is used, and the presence of sludge or tarry material, and hence, a fair cataloguing of clays in the order of efficiency cannot be made. In the selection of a clay, examinations of the clays that are available in the vicinity should be made in the laboratory. As an indication of the differences in clays

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[23] *Ref. Nat. Gaso. Mfr.*, March, 1928, p. 90.

note Table 83 by Dunstan.[24] He examined the decolorizing power of the adsorbents using a 0.25 per cent solution of crude asphaltic oil in benzene.

TABLE 83.—COMPARISON OF DECOLORIZING MATERIALS

Material	Cc. of colored solution decolorized by 1 g. of clay	Approximate bbl. per ton
Alumina	60	342
Fuller's earth I	30	171
Bauxite I	30	171
Bauxite II	25	142
Bauxite III	20	114
Ignited peat	15	85
Bone charcoal	14	80
Bog iron ore	12	68
Fuller's earth II	10	57
Ferric oxide	10	57
Ball clay	8	45
Fuller's earth III	8.5	47
Fuller's earth IV	4	23
China clay	2	11.5
Kieselguhr	2	11.5

The more important groups of adsorbents are (1) fuller's earth, (2) bentonite, (3) various clays, (4) bog iron ore, and (5) bauxite and alumina. These are often sold under trade names such as "Palex," "Filtrol," "Floridin," and "Kontak." The chief sources of bleaching clays in the United States are Georgia, Florida, southern Illinois, Texas, Colorado, Utah, Nevada, Arizona, and southern California, although suitable clays are found in many other states.[25] Some are used in the natural state, except for drying and crushing, but others are burned, washed with water, steam, hydrochloric, or sulfuric acid. The treated clays usually have a greater decolorizing power but the treatment is expensive. Most clays can be reactivated by burning and some by washing with solvents.

In general, the hydrocarbons are adsorbed in the following order: unsaturates, aromatics, naphthenes, and paraffins. However, the high-molecular-weight hydrocarbons are adsorbed

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[24] MORRELL and EGLOFF, reference, *Oil Gas J.*, Jan. 28, 1932, p. 22.

[25] NUTTING, P. G., *Ind. Eng. Chem.*, Anal. Ed., **4**, 139 (1932).

more readily and this doubtless accounts for most of the decolorizing action. Thus the specific gravity, viscosity, and color of the stream of oil from a percolation filter increase as more and more oil flows through the filter, and the first oil will be of a much lower gravity and viscosity[26] than the parent stock. Resinous and asphaltic substances are actively adsorbed. Little of the sulfur is adsorbed and hence clay-treating methods are seldom used for desulfurization.

SOLVENT EXTRACTION

Between 1930 and 1934 the viscosity-index of motor oils was forcefully brought to the attention of refiners by advertising. The solvent extraction processes were developed in order to produce high-viscosity-index oils from mixed-base and naphthene-base stocks. Some of these processes improve the color but the main object is the removal of the low-index hydrocarbons.

Solvent extraction processes are still in the development stage, although a capacity of about 25,000 bbl. per day will soon be in operation (1936), and hence they cannot be completely discussed. Two general types of solvents are used: (1) a single solvent which dissolves either the high- or the low-index material and (2) two solvents, one of which dissolves the high-index oil and the other the low-index oil. The separation of high- and low-index material is never perfect and the effectiveness of the solvents differs in this respect.

Some of the solvents that have been used are

1. Sulfur dioxide.
2. Sulfur dioxide-benzol.
3. Phenol.
4. Dichlorethyl ether (Chlorex).
5. Furfural.
6. Nitrobenzene.
7. Propane-cresylic acid (Duo-Sol).
8. Nitrobenzene-sulfuric acid.
9. Crotonaldehyde-acrolein.
10. Aniline oil.
11. Propane.

The action of some of these solvents is illustrated in the following tabulations. No attempt should be made to compare the

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[26] KAUFFMAN, H. L., *Ref. Nat. Gaso. Mfr.*, April, 1928, p. 74.

processes in the order of value by means of these tabulations because they are not comparable.

The solubility of 100 index and 0 index oil in acetone, nitrobenzene, and Chlorex is as follows:[27]

	Approximate solubility, cc. per 100 cc. solvent at		
	50°F.	65°F.	80°F.
Nitrobenzene 100 index	15.5	20.5	25.5
Acetone:			
100 index	1.7	2.7	3.7
0 index	5.0	7.5	11.0
Chlorex 100 index	1.5	2.5	3.8

The properties of the extracts and raffinates of several solvents are shown in Table 84.

PRACTICE OF TREATING

The foregoing discussion of the chemistry and fundamentals of treating was so involved that the manner of conducting these processes and the equipment that is used could not be discussed. Many different arrangements of equipment have been successfully used and the diagrams that are shown in the following pages are not necessarily the best ones for all oils or all conditions.

Natural Gasoline.—About three-fourths of all of the natural gasoline that is manufactured in the United States is treated by the hypochlorite process. The treating equipment is simple because practically no sludge is produced and the chemical is easily handled. If bleaching powder (or H.T.H.) is used, the plant consists merely of a chemical solution tank, a mixer, and a settler.

Figure 163 shows a hypochlorite treater for using bleaching powder or H.T.H. The gasoline is normally sprayed through the treater and the hypochlorite chamber is not used. When the chemical is spent, the valves that are shown in the diagram can be opened and the solution is pumped through the chamber to dissolve additional chemical. The chamber can be opened and refilled with chemical without molesting the treating operation.

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[27] Page, Buchler, and Diggs, *Oil Gas J.*, Apr. 20, 1933, p. 14.

TABLE 84.—PROPERTIES OF RAFFINATES AND EXTRACTS BY SOLVENT EXTRACTION

	Yield per cent	Viscosity-index	Gravity, A.P.I.	Pour-point, °F.	Reference
1. Original stock	....	77.5	25.8	0	27
Chlorex:					
Raffinate	74.8	104	28.5	5	27
Extract	25.2	5.4	18	−10	27
Nitrobenzene:					
Raffinate	51.1	104.5	29.8	5	27
Extract	48.9	54.1	21.8	−10	27
Acetone:					
Raffinate	79.2	89.4	27.7	0	27
Extract	20.8	49.8	19.8	−15	27
Phenol					
2. 70 viscosity Coaligna oil—stock	....	− 50	15.9	25	28
Raffinate	24.7	74	26.2	− 5	28
3. Mid.-Cont. Brightstock—stock	....	80	24.1	0	28
Raffinate	72.8	96	27.3	15	28
4. Mid.-Cont. Wax stock (144 vis.)—stock	....	71	19.8	70	28
Raffinate	67.8	103	25.8	70	28
Furfural					
5. Van Zandt. Lube stock (68 vis. at 210)—stock	....	81	22.3	115	29
Raffinate	78.5	95	26.6	110	29
Extract	21.5	−163	7.6	60	29
6. Residuum Gulf Coast—stock	....	3	17.1	35	29
Raffinate (acid treated)	49.7	64.5	23.1	0	29
Extract	50.3	− 80	13.7	40	29
Duo-Sol					
7. Hendricks long resid	....	....	16.8	....	30
Propane Extract	49.3	100	27.6	5	30
Sulfur dioxide					
8. Gulf Coast Dist.—stock	....	23	20.8	....	31
SO_2 raffinate	84	53	23.7	....	31
SO_2 benzol (75–25) raffinate	74	63	25.3	....	31
9. Mid.-Cont. Neutral oil—stock	....	86	26	....	31
SO_2 raffinate	88	94	29	....	31
SO_2 benzol (85–15) raffinate	83	101	29.9	....	31
Crotonaldehyde-acrolein					
10. Mid.-Cont. Pressed dist.—stock	....	66	25.2	20	32
Primary product*	81	96	30.4	35	32
Secondary product*	8.5	25.5	19.0	15	32
11. Treated Calif. Resid—stock	....	47	19.9	....	32
Primary product*	55	90	25.1	....	32
Secondary product*	31.5	9.5	17.8	....	32

* An extract also produced.

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[28] STRATFORD, POKORNY, and HUGGETT, *Ref. Nat. Gaso. Mfr.*, November, 1933, p. 458.

[29] MANLY, MCCARTY, and GROSS, *Oil Gas J.*, Oct. 26, 1933, p. 78.

[30] ANON., Duo Sol Process, *Petroleum Eng.*, October, 1933, p. 27.

[31] KAIN, W., *Ref. Nat. Gaso. Mfr.*, November, 1932, p. 553.

[32] POOLE and WADSWORTH, *Ref. Nat. Gaso. Mfr.*, November, 1933, p. 412.

The chemical is added once a day through the top of the settling tank and the solution is recirculated, as required, through the mixing column. Simple mixing devices which utilize the gasoline supply through an aspirator cone, for sucking the solution into the system, have been successfully used.[33]

If hydrogen sulfide is present in more than traces, the gasoline should be first washed with water or caustic. From 1 to 4 lb. of H.T.H. or 4 to 25 lb. of bleaching powder per 1,000 gal. of gasoline is normally required (see page 549 for the design of mixers, settlers, etc.).

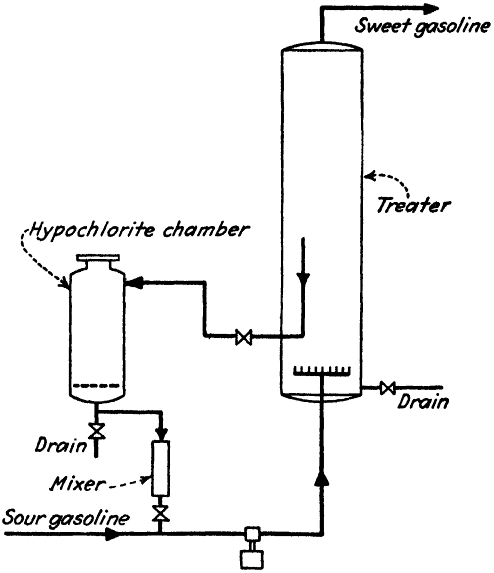

FIG. 163.—Hypochlorite sweetener for using bleaching powder.

Straight-run Gasoline.—A caustic wash or a doctor sweetening treatment is all that is normally required for straight-run gasoline and some of these gasolines require no treatment at all. This is particularly true if it is to be mixed with low-color cracked gasoline or is sold as a dyed gasoline. Figure 164 is a diagram for doctor sweetening. In simple caustic treatment, the foregoing diagram can be modified to eliminate the sulfur chamber and the

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[33] Treating Natural Gasoline . . . , *Ref. Nat. Gaso. Mfr.*, July, 1933, p. 278.

continuous feed of chemical. The caustic settling tank can be charged once daily (or less often) with fresh caustic and circulated until it is spent. If the gasoline is unstable, a filtration through coarse fuller's earth is often helpful.

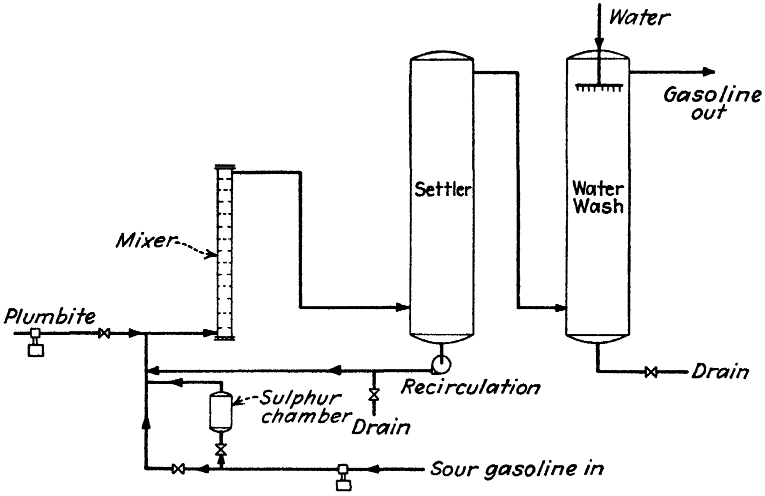

FIG. 164.—Doctor or plumbite sweetener.

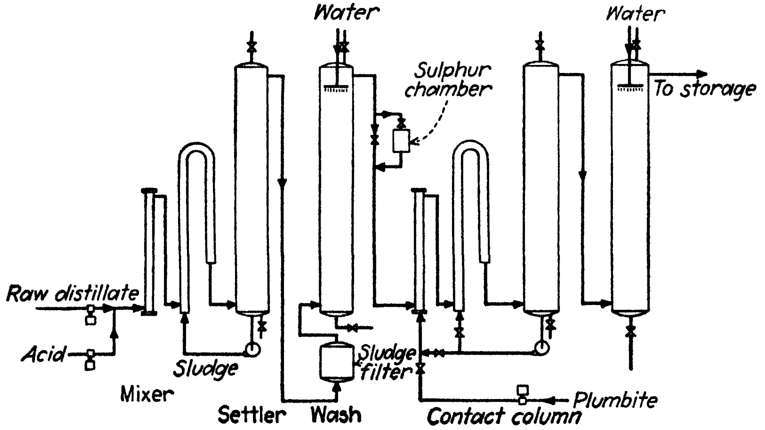

FIG. 165.—Continuous pressure distillate treater.

Occasionally the sulfur content is so high that acid treatment must also be used and the general manner of handling such a gasoline may be found under the next topic.

Sweetening may also be conducted in a batch system by using an agitator. The advantageous effect of air agitation upon the sweetening is recognized but the vapor losses may be great.

Pressure-still Distillate.—The common method of treating cracked products is by acid treatment, steam distillation, and doctor sweetening. Acid treatment is usually conducted at prevailing temperatures in a continuous treater and neutralizer, but if the gasoline does not turn sour upon distillation the treating may be simplified to an acid treatment and plumbite treatment in one operation (Fig. 165). Some refiners find that a double doctor treatment, one before and one after distillation, aids in removing sulfur. This amounts to the treatment shown in Fig. 165, followed by distillation and by a treatment as in Fig. 164.

Other modifications of the continuous-settler type of system are sometimes useful. The arrangement of equipment for two of these are

A. Sludge-circulation Treatment.
   1. Baffle column for pressure distillate and acid sludge.
   2. Sludge settler. Sludge to waste.
   3. Mixing columns for fresh acid.
   4. Acid settler, sludge to 1.
   5. Sludge filter.
   6. Water wash.
   7. Caustic mixers.
   8. Caustic settler.
   9. Water wash.

B. Split plumbite.
   1. Plumbite or caustic mixers.
   2. Settler.
   3. Water wash.
   4. Acid mixers.
   5. Settler.
   6. Water wash.
   7. Plumbite mixer.
   8. Settler.
   9. Water wash.

For high-sulfur oils, method B usually suffices but occasionally the sulfur is not completely removed. Sometimes this may be remedied by applying the acid in several doses of about 2 or 3 lb. per barrel each and using a presludge treat before applying any acid. Some high-sulfur distillates require 20 lb. of acid per barrel.

Some refiners[34] have found that neutralization and coagulation with clay is more satisfactory than settling and neutralization with caustic. The use of a Hardinge clarifier is reported.[34] The sludge is collected on a bed of sand and revolving paddles continually scrape the sticky sludge from the top of the filter. The thickness of the bed is finally so decreased that new sand must be added.

The design of *mixing columns* is normally based on the pressure-drop that is available for mixing. A total pressure-drop of 30 lb. per square inch is sufficient to give effective mixing and many refiners find that mixing is effective at much lower pressure-drops. The particular type of mixer is not important but intimate contacting must be attained. At the same time, many refiners report that too intimate a mixing gives difficulty in the settling and suggest only a pump and several sharp angle turns for mixing. Among the types of mixers that are used are square-angle bends, orifice-plate columns, baffle-plate columns, perforated buckets, various mechanical mixers operated by motors, jet or nozzle mixers, and pumps. Irwin[35] describes a multiple-cone type of mixer and the computation of the pressure-drop through the mixer. Mechanical mixers usually consist of a shaft with blades attached. Pumps give fair mixing, particularly centrifugal and rotary pumps, but additional mixers and baffle columns for prolonging the time are usually used. An ingenious use of a centrifugal pump for mixing is mentioned by Morrell and Bergman.[36] The impeller of the pump is cut down to about half diameter and the impeller is reversed in the case.

The *orifice column*[36] is widely used for mixing. The friction loss through an orifice may be computed by the orifice formula [Eq. (12), page 172]. The pressure-drop as given by this formula is the differential pressure between the tap connections and is not the permanent loss in head. With an average discharge coefficient of 0.65, the permanent loss is about 95 per cent of the pressure differential. With these figures and with velocity used as barrels per hour, the following formula results:

$$\text{Bbl. per hr.} = 17.8D^2\sqrt{\Delta h} \tag{87}$$

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[34] WILLSON, C. O., *Oil Gas J.*, Dec. 18, 1930, p. 38.

[35] *Oil Gas J.*, July 19, 1934, p. 10.

[36] *Chem. Met. Eng.*, 3 articles, **35**, 210; 291; 350 (1928).

D = dia. of orifice hole, in.
Δh = pressure-drop across one plate, expressed as head of liquid in ft.

The accuracy of this equation is influenced by the arrangement of the orifice hole or holes and by the ratio of the area of orifice holes to the area of the pipe, but great accuracy in the design of a mixing column is not justified. In general, the ratio of pipe area to the total orifice area may range from 3 to 10 and still be satisfactory. Inasmuch as the equation is to be used for only approximate results, Table 85 will prove to be a useful simplification. The figures within the block are the pressure-drops normally employed. The feet of liquid may be converted to pounds per square inch by the following relation (see also Fig. 52, page 171):

$$\text{Lb. per sq. in.} = (\text{ft. of fluid}) \times (\text{sp. gr.}) \times 0.433$$

or

$$\text{Lb. per sq. in.} = \frac{\text{ft. of fluid}}{2.148 + 0.01623\,(\text{A.P.I.})} \qquad (88)$$

TABLE 85.—PRESSURE-DROP THROUGH ORIFICE MIXERS

Bbl. per hr.	Pressure-drop for each orifice plate, expressed as ft. of liquid for the following areas of orifice (total), sq. in.						
	0.4	0.6	0.8	1.0	3.0	6.0	10.0
10	1.2	0.54					
20	4.7	2.15	1.11	0.52			
40	18.8	8.6	4.45	2.08	0.35		
60	42.2	19.3	10.0	4.67	0.8		
100	.....	53.7	27.7	13.0	2.22	0.57	
150	.....	.....	62.5	29.2	5.0	1.29	0.45
200	.....	.....	.....	52.0	8.9	2.3	0.79
300	.....	.....	.....	.....	20.0	5.2	1.78
500	.....	.....	.....	.....	.....	14.2	4.95

The mixing column may be assembled by welding, by cutting slots at 1-ft. intervals and on opposite sides of the pipe. The plates are cut with a recess on one side (as thick as the pipe) so that one side of the plate fits against the inside of the pipe and the other side extends through the slot so that it can be welded. Another way to assemble the column is to use flanged spools with a plate between each spool. The plates may also be strung on rods, spot-welded, and slipped into the column from the end.

If a longer time of contact is desirable, so-called *contact columns*, or time columns may be used. These are attached after the mixing columns as shown in Fig. 165. Time columns may consist of large pipe with half-moon baffles or orifice plates having large holes. In arranging mixing equipment, no low points in which the chemical may collect, should exist, because the liquid tends to surge in slugs into the settling equipment.

If the chemical is injected by gravity feed or from a pressure feed-tank, the rate of feed can be controlled with a valve and no metering device is necessary. If blow-cases are used, the chemical must be measured as it is added. The most common method of metering is by orifice meters. Morrell and Bergman[36] present orifice charts but Eq. (12) (page 172) may be used for approximate calculations. Usually the actual rate of flow is not important but it is necessary to know that the flow is the same from day to day. The treater often estimates the material handled by a blow-case by noting the time and the pressure during the admission of acid.

Example 84. Design of Orifice Mixer.—Acid is to be mixed with 8,000 bbl. per day of 53 A.P.I. pressure distillate. A pressure-drop of 25 lb. per square inch is permissible.

$$\text{Bbl. per hr.} = \frac{8{,}000}{24} = 334$$

Use about 7 sq. in. of orifice holes or openings.
Use a pressure-drop, feet of fluid (Table 85), of about 5.5 ft.

$$\text{Pressure-drop, lb. per sq. in., per plate} = \frac{5.5}{2.148 + 0.01623(53)} = 1.83$$

$$\text{Number of plates} = \frac{25}{1.83} = \text{about } 14$$

Use a pipe having about five times the orifice area or 30 sq. in. Use standard or extra heavy 6-in. pipe with a transverse area of 28.9 sq. in.

		Sq. In.		Sq. In.
Approximate layout of plates:				
six 1¼-in. holes	6 × 1.227 = about	7.37		
or twelve ⅞-in. holes	12 × 0.601 = about	....		7.22
and $\frac{1}{16}$-in. clearance around one side of plate.....	=	0.42		0.42
Total opening, sq. in.	=	7.79	or	7.64

The plate will be 6.07 in. in diameter with a $\frac{1}{16}$-in. recess around half of the circumference.

If the plates are spaced 1 ft. apart, the total length of the mixing column will be about 16 ft.

The exact *settling time* that is required must be determined for each treating operation. In general, caustic and water mixtures settle more rapidly than acid sludge or "pepper." Ten or fifteen minutes often suffices for caustic or doctor settlers but an hour may be required for settling acid sludge. The settlers are usually about 40 ft. high and range in diameter from 2 to 10 ft. In large-diameter tanks, a gentle circulation takes place and tends to spoil the separation. The sprays for water-wash tanks are usually of welded pipe in the form of a cross or six-legged star with $\frac{1}{8}$-in. holes drilled on the same side of each pipe in the star. These sprays, all pointed in the same direction, give a gentle rotating motion to the oil in the tank. The sprays are placed several feet below the oil outlet. Horizontal settling tanks are more effective than vertical settlers of the same capacity. This is due to the lower vertical velocity in the horizontal settler. The velocity of the fluid in the settler should not exceed about 3 ft. per minute. A higher velocity will require a greater time for settling.

Example 85. Design of Settlers.—A tank for settling caustic from 12,000 bbl. of oil per day may be designed as follows:

Caustic or doctor settler:

Allow 30 min. of time and use a vertical tank 40 ft. high.

$$\text{Vol. of oil per hr.} = \frac{12{,}000}{24} \times \frac{42}{7.5} = 2{,}800 \text{ cu. ft.}$$

$$\text{One-half of this} = \frac{2{,}800}{2} = 1{,}400 \text{ cu. ft. to be handled in 30 min.}$$

$$\text{Cross-section area of settler} = \frac{1{,}400}{40} = 35 \text{ sq. ft.}$$

Dia. = about 6 ft. 10 in.

If 40-ft. tanks are not convenient, then two 20-ft. tanks connected in series can be used.

Acid sludge settler:

Allow 1 hr. and use a 40-ft. tank.

Cross-section area = 35 × 2 = 70.0 sq. ft.

Dia. = about 9 ft. 6 in.

Concentrated sulfuric acid, acid sludge, and caustic solutions do not attack steel rapidly, but dilute acid reacts violently so that water-wash tanks after acid-settling tanks must be lead lined. The caustic settlers and caustic water-wash tanks are also frequently lined with lead although lead linings are not really necessary. Self-lubricated cocks, such as the Merco-Nordstrom or MacGregor, should be used on the chemical lines. Steel pipe is used for all connections except the drain lines from acid-water-wash tanks. These lines should be of lead-lined pipe or chromium alloys. The drains should have air or steam connections into them so that they can be "blown-out" in case they become plugged with sludge or scale.

QUICK-CONTACT AND QUICK-SETTLING PROCESSES

These methods are attracting more and more attention. Whether they are used for distillates or lubricating oils, the advantages that are claimed are the smaller amount of acid that is required, the control which the processes afford, the advantages of continuous operation, and the smaller sludge losses.

A flow diagram of the Stratford contactor centrifuge process is shown in Fig. 166. The high-sulfur pressure distillate[6] is pumped from the caustic wash tanks to the contactor in which it is mixed for 1 or 2 sec. by means of a rotating shaft with blades and fixed baffles. The oil is immediately transferred to the centrifuges and the entire time of treatment including contacting, transfer, and separation of the sludge may be less than 4 sec.

The acid stage oil is then delivered to caustic treaters or contacted[37] with 200–300 mesh clay for a few minutes and filtered in Sweetland presses. The short time aids in avoiding polymerization of the valuable olefin hydrocarbons and thus allows the use of acid for desulfurizing high-sulfur cracked distillates without destroying the antiknock properties of the gasoline. At one time the development of quick-contact processes was at a standstill because the gum was not thoroughly removed, but this difficulty has apparently been solved.

The use of centrifuges is also being promoted for the treating of lubricating oils.[12,13] In general, the oil is heated and mixed with acid for about 10 min. by a mechanical mixer and/or a reaction tank. It is then "soused" with water to prepare the sludge and discharged through the centrifuges. The sludge accumulates in a

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[37] TRIVALS, *Ref. Nat. Gaso. Mfr.*, May, 1932, p. 312.

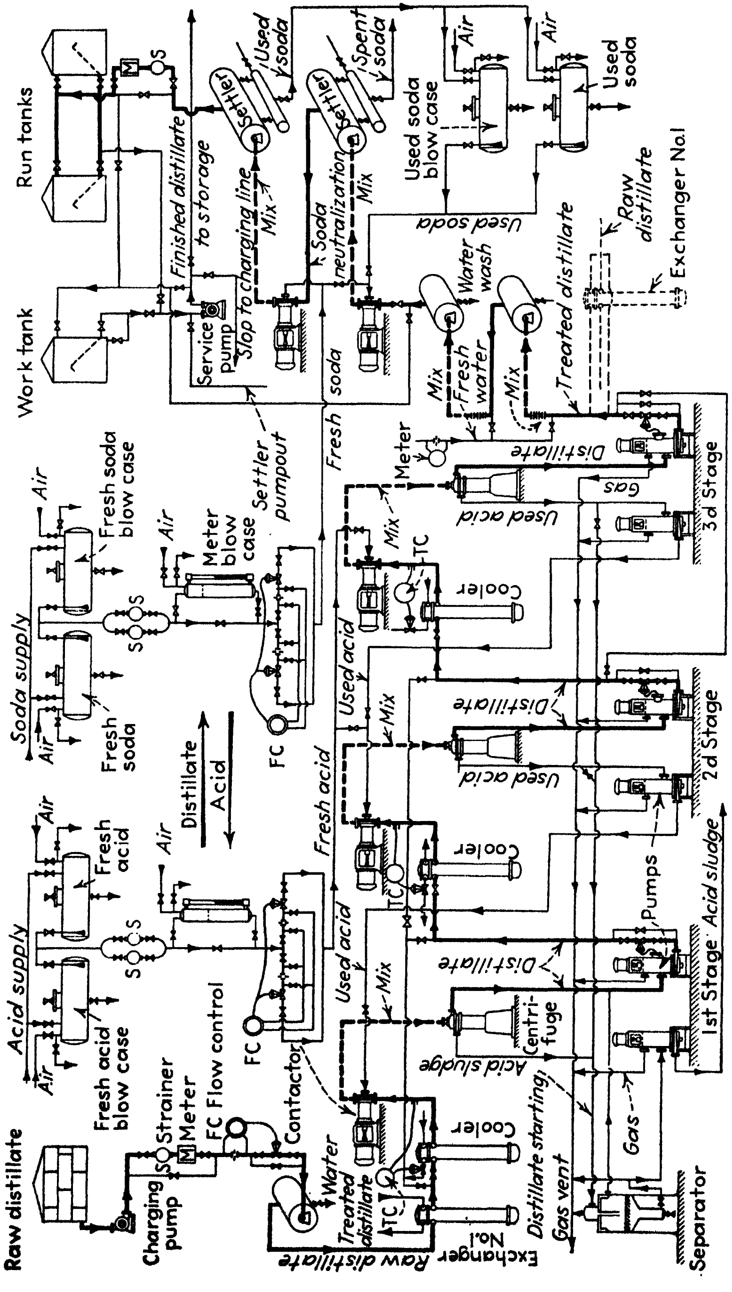

FIG. 166.—Stratford centrifuge treating system. (*Stratford Engineering Corporation.*)

hopper and is continuously pumped to fuel oil mixing tanks or to an acid recovery system. The acid is sometimes added in two portions, one portion as outlined above and a second dose at the centrifuge itself. The latter dose of acid aids in producing a fluid sludge. In one plant the sludge was removed from the bowl of the centrifuge by means of hot fuel oil. The properties of lubricating oil sludge vary so widely[14] that each continuous lubricating oil treater is a new problem. Cylinder stock has been treated in some of these plants without dilution. Figure 167 shows the centrifuges in a lubricating oil treating plant.

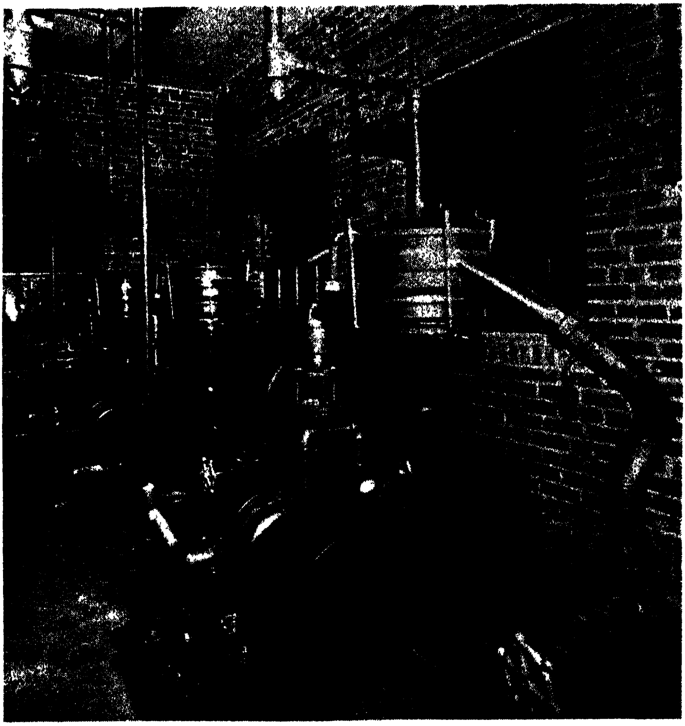

FIG. 167.—Centrifuges used in treating lubricating oil with acid. (*A. J. Smith Engineering Company.*)

The success of continuous treatment of lubricating oils always depends upon a method for removing the sludge. Cone settlers have been used to some extent[14] for the separation of the sludge. The settler is a conical bottom tank. The sludge accumulates continuously in the bottom of the cone and the oil overflows continuously from the entire periphery of the top of the cone. Thus the oil is skimmed from the top of the settler without causing currents in the fluid as a connection in the side of the cone would do. Obviously the settler must work or the sludge will plug the bottom of the cone and halt the treating operation.

CLAY PROCESSES FOR CRACKED DISTILLATES

The *Gray vapor-phase*, the *Osterstrom liquid-phase*, and the *Stratford continuous* processes are the outstanding examples of clay processes for treating cracked distillates. They cannot be applied to high-sulfur distillates because they remove little, if any, sulfur but they are effective and cheap for many cracked distillates. The principles underlying the three processes are the same. Most of the diolefin and other gum-forming hydrocarbons are removed, but other hydrocarbons are only slightly attacked. Most low-sulfur distillates can be successfully treated but the distillates from some California oils have given difficulty with color stability. The vapor-phase process is not usually applied to distillates from vapor-phase cracking processes because the action is too vigorous and results in the removal of valuable hydrocarbons such as the olefins. The Osterstrom process was developed to meet this need. The approximate daily capacities that are handled by these processes indicate their usefulness; the Gray vapor-phase process, more than 100,000 bbl.[38] per day; the Stratford process, 30,000 bbl.;[38] and the Osterstrom, 20,000 bbl.[38]

In the *Gray process*, the vapor from the cracking tower is taken through towers that are packed with clay. Polymerization occurs and a polymer liquid, containing a large percentage of gasoline, collects in the bottom of the tower (Fig. 168). The polymers may be injected into the bubble-tower or evaporator of the cracking system so that the gasoline is recovered and the pure polymer either finds its way into the tar or is recracked. The vapor passes on to the condensers and is a finished product except for sweetening.

[38] Gray, by independent refiners; Stratford, by Imperial Oil Co., Ltd.; Osterstrom, by Pure Oil Co. respectively.

Goode[39] reports that the color and gum content of the gasoline is governed to some extent by the vapor-velocity and the depth of the bed of clay. Using 30, 15, and 7½ tons of clay in the same tower, he found that the color was 30, 25, and less than 21 for the three charges of clay, and the gum content 25, 33, and more than 74 mg. Several refiners have reported that the removal of gum becomes more effective as more and more gasoline vapor is put through the tower. The color of the product decreases slightly as the run proceeds until it suddenly becomes very poor and the clay must be removed. The clay may be burned but most refiners feel that it is cheaper to not bother with reburning. A 30–60 mesh clay is commonly used but 60–90 clay is used by some refiners. The following earths have been widely used: Attapulgus, Floridin, Ohmstead (Ill.), and heavy Texas earths.

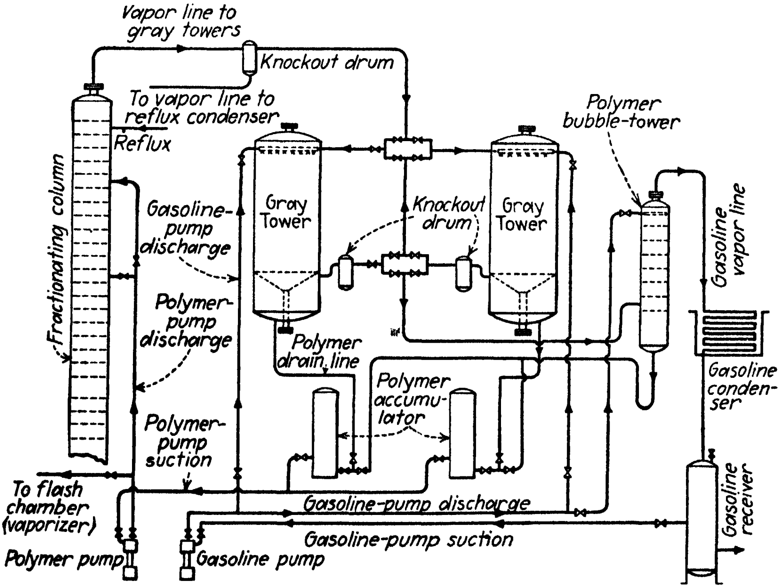

Fig. 168.—Diagram showing series-parallel arrangement of Gray towers. (*Gray Processes Corporation.*)

The throughput per ton of clay is often 3,000 to 5,000 bbl. and one plant is reported to have processed 20,000 bbl. for each ton of

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[39] *Ref. Nat. Gaso. Mfr.*, December, 1931, p. 79.

clay. The yield per ton of clay is greatly increased by eliminating entrainment in the gasoline vapor line. One refiner uses a mist extractor for this purpose. When the Gray process can be used, it is certainly an economical and convenient method of treating. The clay chambers range in size from 6 to 16 ft. in diameter and in height from 25 to 40 ft. The only disadvantage of the process is the minor one that the extent of treating cannot be easily changed or controlled for the production of several grades of gasoline.

In the *Stratford process* the vapor ascends the treating tower countercurrently to a stream of descending clay slurry. The spent clay slurry is continuously settled in cone bottom tanks and dried continuously with hot flue gas and a vacuum. About 1,000 bbl. of distillate can be treated per ton of clay but the gallonage varies because the amount of slurry can be regulated to obtain different degrees of treating. The flexibility of the process is one of its main advantages.

In the *Osterstrom process* the cracked distillate is heated, as a liquid, in a conventional pipestill to about 500 to 600°F. It flows under pressure (no vaporization) through a bed of adsorbent, such as 30–90 mesh fuller's earth, and back into a short coil in the pipestill. It issues from the still at a temperature high enough to cause vaporization when the pressure is released. The vapor is fractionated to end-point in a tower and the polymer is separated as a bottoms product. The high temperature facilitates the action of the clay so that as much as 70,000 bbl. of gasoline have been treated per ton of clay. However, vapor-phase gasoline is seldom treated to the high colors that are required in other gasolines.

Kerosene.—The quantity of kerosene that is manufactured in most refineries is relatively small, and hence batch agitators are still widely used. The batch agitator is nothing more than a large mixing and settling tank. Cylindrical shells with conical bottoms having a pitch of 4 to 6 in. per foot are used. Connections are provided for injecting chemicals, for introducing wash water through sprays, and for an air-line with which to mix or "roll" the chemical and the oil. Although large vapor losses occur with air agitation of distillates, the mechanical methods of mixing, using a circulating pump or paddles, are not entirely satisfactory because of the time required for complete mixing. A lead lining weighing 8 to 10 lb. per square foot is provided. Lead is a ductile material and hence it should be supported at intervals of about 8 in. by reinforcing bars. The lead lining is placed in position by "burning." The support bars are then bolted through the lead to the steel shell and a strip of lead is burned over each bar and its bolts, so that no steel is exposed. Hard or antimony lead (94 Pb-6 Sb) is gaining in favor because of its greater strength.[40]

The batch treatment of kerosene varies greatly depending upon the characteristics of the raw stock. For normal kerosenes the acid requirement is 3 to 6 lb. per barrel but kerosenes that are rich in aromatics may require 30 lb. per barrel, part of which may be fuming acid. One Pennsylvanian refiner[41] reports the successful use of hypochlorite in treating kerosene but such a treatment is probably unfit for most kerosene stocks. A typical batch acid treatment for kerosene is as follows:

1. Agitate with acid 30 min. Often the acid is split into a small dose of "water-acid," and after this is drained the main acid is admitted.
2. Settle ½ to 1½ hr.
3. Spray with water for two 15-min. periods and drain.
4. Spray with soda and wash with water, 15 to 30 min. Drain.
5. Wash with water, 15 min. at about 100°F.
6. Settle 45 min. to 2 hr.

In the manufacture of prime kerosene from naphthene-base crude oils the following elaborate procedure may need to be used:

1. Agitate with water acid (1 lb.), 15 min.
2. Settle. Drain.
3. Three treats of 8 lb. each of fuming H_2SO_4; settle and drain after each.
4. 3 lb. treat with 66°Bé. acid. Drain.
5. Three washes with water, agitating during wash, 15 min. each.
6. Neutralize with 6 lb. of 12°Bé. caustic.
7. Settle and drain.
8. Two washes with water, 15 min. each.
9. If color not satisfactory, filter through fuller's earth or agitate with about 0.4 lb. of earth.

Methods of improving the color are (1) redistillation with steam as with pressure distillate and (2) filtration through fuller's earth. Continuous methods of acid treating kerosene are in operation in many Mid-Continent refineries. The treating of

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[40] Hiers and Sowers, *Petroleum Eng.*, February, 1931, p. 194.

[41] Kirkwood, G. M., *Petroleum Eng.*, February, 1932, p. 108.

kerosene from mixed-base and paraffin-base oils is usually not a difficult operation.

LUBRICATING OILS

There is such a wide variety of heavy oil stocks, and the treatments that are used differ so greatly, that only a few general operations can be discussed. Oils are treated with acid, filtered through clay in percolation filters, contacted with clay at a high temperature, or treated by solvent extraction methods. Pennsylvanian stocks can usually be finished by percolation or clay contacting without acid treatment, but other oils usually require acid treatment.

The acid treatment of lubricating oil stocks is usually conducted in batch agitators. However, note the discussion of continuous lubricating oil treaters (page 553). Inasmuch as the characteristics of oils vary greatly and the details of treating various oils are so different, the operations can be best explained by a list of the steps that may be followed:

Application of acid.

1. Water acid, 66°Bé., 2 to 12 lb.
2. Agitate ½ to 2 hr.
3. Settle 1 to 2 hr. and drain.
4. Acting acid, 66°Bé., 20 to 60 lb. Often applied in several doses, settling and draining off sludge between each dose.
5. Agitate 1 to 3 hr.
6. Settle 1 to 6 hr.
7. Agitate gently and sprinkle with water until sludge gathers into lumps.

Neutralization in another agitator.

8. Spray with caustic (3 to 10°Bé.) agitating gently until neutral.
9. Spray with hot water.
10. Settle 6 to 15 hr., taking care not to drain much of the emulsion. Often an emulsion is formed that cannot be separated without introducing acid again.
11. Repeat washing and settling (9 and 10) several times and occasionally as many as twelve times.

Brightening.

12. Heat to 120 to 160°F. with steam coils in open pan, or
13. Heat and blow with air, or
14. Agitate with dry Sil-o-Cel, etc., and filter.

Neutralization with caustic or soda is a troublesome operation because of the frequent formation of emulsions. Often these emulsions are of such stability that only a repeated acid treatment will cause a separation. For this reason, neutralization is being more and more frequently accomplished by the use of clay, as in the contact process, and with ammonia.

Contact Filtration.—The most common method of neutralizing with clay is the contact process. Although neutralization occurs, the process also effectively decolorizes the oil. Contacting is usually practiced on oil that is in the "acid-stage" or, in other words, oil that has been treated with acid but not neutralized. The clay is rendered more effective if the oil is acid.

The process is practiced at 220 to 650°F. but most refiners contact diluted cylinder stocks at 475°F. and neutral oils at 220 to 320°F. Occasionally lower temperatures are used but such an operation should be classed as neutralization. The acid-stage oil is mixed with 200 or 200–300 mesh clay and the mixture is heated in a pipestill to the aforementioned temperatures. The hot oil is then allowed to settle for a short time and the "fines" (clay dust) are filtered from the oil in Sweetland or similar presses. Sometimes a short percolation filter is used to aid in the removal of the fine clay. The clay is not usually recovered although experiments are constantly being made in an effort to reactivate the clay by solvent methods. Figure 169 illustrates the general equipment in a contact plant.

The more viscous oils, such as cylinder stock, are usually acid treated and contacted in solution. The solution contains between 50 and 75 per cent of a high initial boiling-point naphtha. The naphtha usually has a boiling-range of 160 to 400°F. Dilution is necessary for the subsequent operation of centrifuge dewaxing and it also simplifies the handling of the stock during the acid treating and contacting operations. In addition, Trescott[14] reports that the amount of dilution vitally affects the losses during acid treatment. In treating a Mid-Continent residuum (U.S. 130 at 210) with 30 lb. of acid per barrel, the losses were as follows:

Per Cent Naphtha in Solution	Per Cent Treating Loss
None	31
25	23
50	14
75	14

The decrease in loss is doubtless due to the fact that less oil is contained in the sludge if the stock is diluted. The neutral oils are usually contacted without diluting them. However, they must be heated to a sufficiently high temperature to cause them to be fluid.

Although the contact process yields excellent products, it may be more expensive[42] than percolation, particularly if an efficient clay-burning system is available. However, the cost of installing a complete percolation system is great, and contacting is probably the cheaper method for a new installation. In the contact process, the amount of clay that is required ranges from 5 to 25 per cent of the weight of the oil. This amounts to 15 to 80 lb. per barrel.

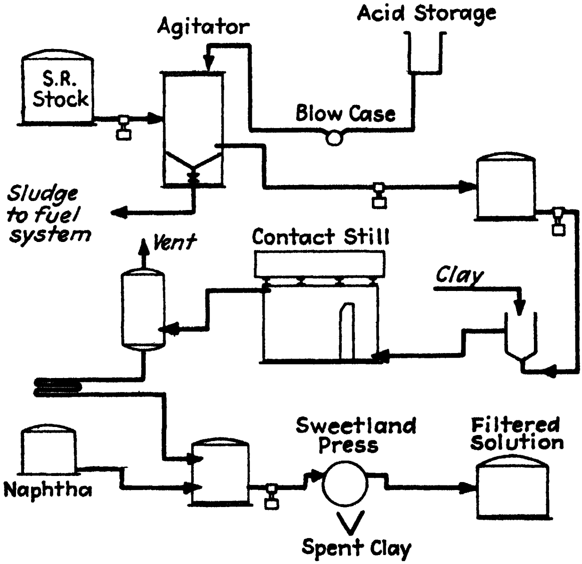

FIG. 169.—Diagram of contact clay treating process.

Clay is sometimes used as a neutralizer for treated pressure distillate or treated neutral oils. In the treatment of neutrals the neutralization is accomplished at temperatures that are just high enough to cause the oil to be fluid. Trivals[37] reports the use of clay for cracked distillates. The clay was removed in pres-

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[42] DAVIS, L. L., *Ref. Nat. Gaso. Mfr.*, March, 1928, p. 90.

sure leaf-type filters. About 1 to 5 lb. of clay was required to neutralize the acid. A 200-mesh clay was used. The problems and methods of handling clay filter cake are discussed by Trescott.[43] A Sweetland press is shown in Fig. 170.

Percolation.—Percolation was the original method of decolorizing lubricating oils and until recently no other method of using clay was widely employed. Gurwitsch[44] says,

> The advantage of filtration consists in the better utilization and smaller expenditure of the adsorbent to produce a given degree of decolorization . . . the oil comes successively into contact with a great number of very thin layers of the adsorbent, the filtration is equivalent to an extremely fractionated mixing, and so its effect on the reversibly adsorbed substances must be greater than that of mixing, even when carried out in several operations with equal quantities of adsorbent.

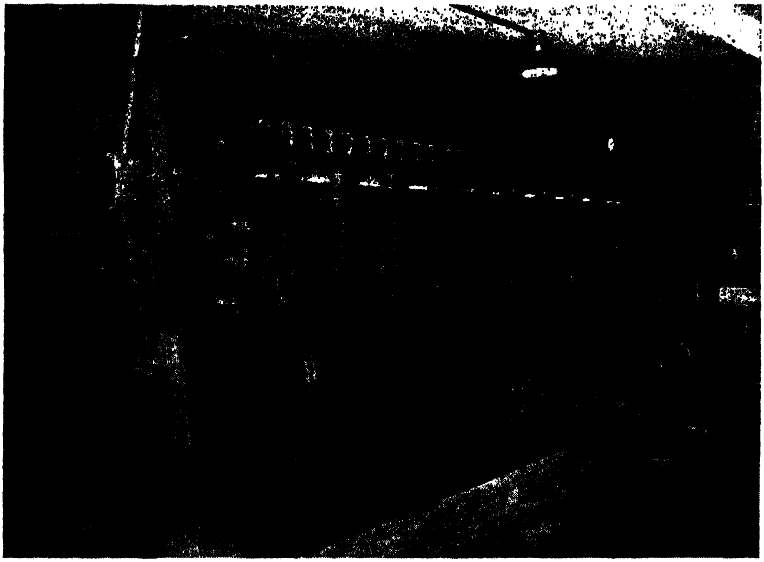

FIG. 170.—Sweetland filter press for removing fine clay. (*A. J. Smith Engineering Company.*)

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[43] *Ref. Nat. Gaso. Mfr.*, February, 1934, p. 54.

[44] "Scientific Principles of Petroleum Technology," 2d ed., D. Van Nostrand Company, Inc., New York, 1924.

Regarding the percolation method, Funsten[45] says,

> Thus, percolation permits the manufacture of a wide variety of oils at one time. White oils or petrolatums of varying degrees of refinement can be processed with it equally as well as cylinder oils. . . . Specialties can be made at little, if any, extra cost by selection of proper cuts from the filter stream. Waxes, gasoline, kerosene and furnace oil can be clarified with revivified percolation clay at extremely low cost, since yields are very large in this type of work.

In general, for gravity flow, the longer the packed column the greater the bleaching action, the coarser the earth the less the bleaching, and the higher the temperature the less the bleaching (other conditions being comparable). Bauxites and fuller's earth are used almost entirely. The efficiency as a function of particle size is somewhat as follows:

Mesh	Per Cent Efficiency
60–90	100
30–60	87
16–30	72

However, a 30–60 mesh material is most commonly used because it can be more easily handled. Although the temperature should not be so high that the oil drains through the clay with only a short time of contact, nevertheless viscous lubricating oil stocks must be heated or the rate of percolation will be hopelessly slow. Operating conditions[45] for a 1,000-cu. ft. filter are as follows:

Stock	Saybolt viscosity	Temp. of filtration, °F.	Rate of filtration, bbl. per hr. for a 1,000-cu. ft. filter	Pressure filtration,* lb. per sq. in.
Light spindles	Up to 200 at 100°	80–100	5–25	0–25
Heavy spindles	200–500 at 100°	100–140	5–15	0–25
Overhead or residual cylinder stock	100–160 at 210°	160–200	2–10	15–50
Naphtha solutions of cylinder stock	....	100–130	30–50	5–15
Petrolatums	100–160 M.P.†	25° above M.P.†	5–20	0–15
Waxes	100–160 M.P.†	25° above M.P.†	5–20	0–15

* Pressures in the higher range are required where 60–90 mesh earths are used.
† Melting-point.

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[45] *Ref. Nat. Gaso. Mfr.*, June, 1934, p. 201.

The stock may be acid treated before percolation but it is usually neutralized before it enters the filters. The percolators should be insulated to promote a constant rate of flow. The clay is washed with 56 A.P.I. or lighter naphtha to remove the oil from the clay. The filter is then steamed and the clay can be removed by allowing it to flow from the bottom of the percolator. The clay may be revivified by burning it at a temperature of about 1100 to 1200°F.

The throughput of percolators cannot be definitely stated because of the differences in stocks, differences in clays, and the degree of decolorization that is practiced. In a general way, 8 to 21 bbl. of finished-color motor oils can be filtered per ton of clay. For lighter finished colors, the capacity ranges from 4 to 8 bbl. per ton, and for darker finished oils, such as dark-red oils and cylinder stocks, as much as 25 bbl. per ton may be filtered. Funsten[45] reports that rates of 40 to 50 bbl. per hour can now be obtained. As high as 32 bbl. per ton of cylinder stock in the form of 50-50-600° stock solution has been filtered through new clay. Reburning decreases the efficiency of decolorizing. The average efficiency of mixed clay that has been burned from one to six times is about 60 per cent. In general, the clay may be burned six to eight times in Moore, Brockway, Rotary, and Kuebler burners and as many as forty times in the Nichols-Herreshoff burner. However, it is not usually economical to burn the clay more than ten or fifteen times in the Herreshoff burner.

In general, the refiner uses new clay for light-colored low-viscosity lubricating oils, and the heavy oils with a darker allowable color are decolorized by this same clay after it becomes unfit for decolorizing light oils. Thus the various used clays progress through the plant in a countercurrent manner so that the new earth meets light-colored stocks and the nearly spent earth meets dark-colored stocks.

Solvent Extraction.—These processes are still in such a state of development that a presentation of flow diagrams and the equipment that is used would be of little value. The following references give this information concerning the processes as they are now used:

1. Propane—Stockman, L. P., *Oil Gas J.*, Apr. 16, 1934, p. 6.
2. Chlorex—Bahlke, Brown, and Diwiky, *Oil Gas J.*, Oct. 26, 1933, p. 60; also Williams, D. B., *Ref. Nat. Gaso. Mfr.*, June, 1935, p. 283.

3. Nitrobenzene—Ferris, Myers, and Peterkin, *Ref. Nat. Gaso. Mfr.*, November, 1933, p. 435.
4. Phenol—Stratford, Moor, and Pokorny, *Oil Gas J.*, Mar. 30, 1933, p. 8.
5. Edeleanu—Cottrell, O. P., *Ref. Nat. Gaso. Mfr.*, November, 1933, p. 432.
6. Furfural—Manley, McCarty, and Gross, *Oil Gas J.*, Oct. 26, 1933, p. 78; also Bryant, Manley, and McCarty, *Oil Gas J.*, May 6, 1935, p. 50.
7. Crotonaldehyde and acrolein—Poole and Wadsworth, *Ref. Nat. Gaso. Mfr.*, November, 1933, p. 412.
8. Duo-Sol—Max B. Miller, *Oil Gas J.*, Oct. 12, 1933, p. 11; also Malcolm H. Tuttle, *Oil Gas J.*, May 23, 1935, p. 13.
9. Extraction principles—A. W. Nash, *Oil Gas J.*, Mar. 30, 1933, p. 52.
10. General development—W. T. Ziegenhain, *Oil Gas J.*, Mar. 29, 1933, p. 44.

Wilson and Keith[46] report that it is cheaper to refine oils by combined solvent treating and dewaxing than by the customary methods. However, the costs of operation are now in such an experimental stage and the manner of conducting the processes differs so greatly that little can be said of the actual costs.

It appears that the future development of solvent processes will depend on the following factors:

1. The advertising value of the processes.
2. The practical superiority of the oils when used in the engine.
3. The yield of high-grade product and the means of disposing of the inferior material.
4. The amount of solvent that is lost or used.
5. The development of combined dewaxing and extraction processes which use the same solvent.

The development of solvent processes tends to erase the old crude oil marketing system by which some crude oils were classed as oils for lubricant manufacture. By solvent methods, the original properties of the oil can be changed so that a uniform grade of oil can be manufactured from a wide variety of crude oils.

The general principles of solvent extraction are discussed in Chap. XV. However, many practical difficulties arise during the application of these principles to an oil system.

Only one of the many solvent processes will be discussed. The Duo-Sol process was selected not because it is necessarily the best process but because it affords an excellent opportunity to study the different factors that are involved. This process involves the use of two immiscible solvents, one of which (propane)

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[46] Economic Aspects of Solvent Refining of Lubricating Oils, *Ref. Nat. Gaso. Mfr.*, July, 1934, p. 252.

dissolves paraffinic hydrocarbons, and the other (cresylic acid) dissolves naphthenic hydrocarbons. The two solvents are used in a countercurrent system of flow and the feed is introduced at an intermediate point in the flow system. The oil is completely dissolved by the two solvents. In one end of the extraction system the outgoing cresylic acid solution is stripped of paraffinic material by pure propane, and in the other end the outgoing propane solution is stripped of naphthenic material by pure cresylic acid. Thus, a true countercurrent stripping operation is maintained although the extraction is conducted as a series of countercurrent batch contacting and settling operations. A diagram of the process is shown in Fig. 171. The extractor is not shown in detail. It consists of nine settlers or compartments. The heavy cresylic acid solution is pumped from one compartment to the next and the propane solution is also pumped but in a countercurrent manner. The feed is introduced in compartment 3 nearest the end at which propane is introduced.

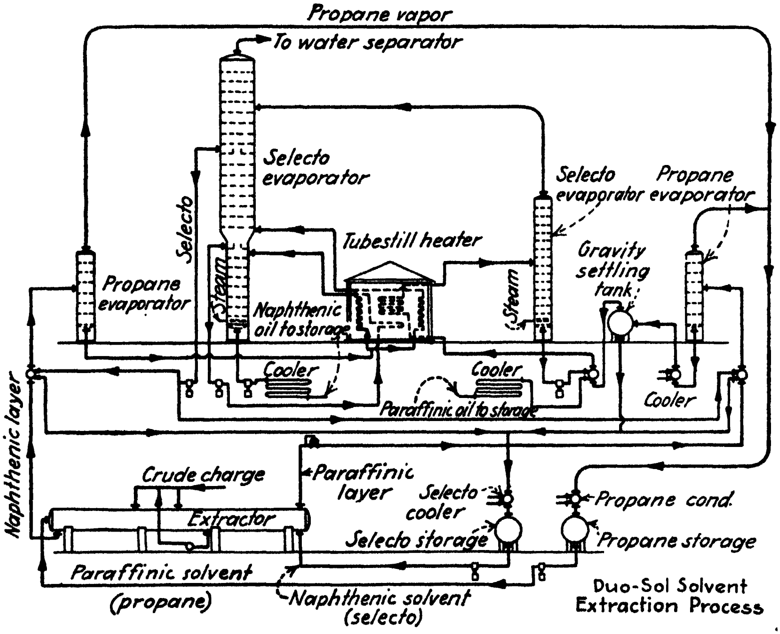

FIG. 171.—Diagram of Duo-Sol process. (*Max B. Miller and Company, Inc.*)

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CHAPTER XXV

DEWAXING

The solid materials that are found in high-boiling petroleum oils can be classified into two general types, *viz.*, crystalline wax and amorphous wax. Crystalline wax is found in wax distillate (paraffin oil), and amorphous wax or petrolatum is found in cylinder stock. In reality, both materials are crystalline but the crystals in the petrolatum stock tend to be small, so that the petrolatum behaves physically as a colloidal or jelly-like material. The crystalline nature of all waxes is evidenced by the several newly developed solvent dewaxing processes. In these, the so-called amorphous wax can be successfully collected on filters.

The crystalline wax that is found in wax distillate can be filtered from the oil, but amorphous wax is sticky and it quickly plugs the pores of a filter cloth.

Composition of Paraffin Wax.—The waxes extend throughout the entire boiling-range of the lubricating oil stocks. Attempts to separate wax from oil by fractionation have met with no success. Buchler and Graves[1] have studied the wax-bearing stocks of Salt Creek, Wyo., crude oil. All of these stocks, paraffin wax, slop wax, petrolatum, and sucker rod wax, were found to consist mainly of the same series of hydrocarbons, and these authors concluded that the waxes consist of the normal paraffin series. They also isolated a material which they call "soft wax" and they attribute the different pressing characteristics of wax stocks to the amount of soft wax that each stock contains. They believe that paraffin distillate contains small amounts of soft wax, and petrolatum stocks contain a large amount. Ferris, Cowles, and Henderson[2] have also made a thorough examination of wax stocks by the repeated crystallization of high- and low-melting-point waxes. They obtained

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[1] The Petroleum Waxes, *Ind. Eng. Chem.*, **19**, 718 (1927).

[2] Composition of Paraffin Wax, *Ind. Eng. Chem.*, **21**, 1090 (1929).

six different melting-point waxes. Part of each of these waxes came from both high- and low-melting-point wax stocks and hence it is clear that some of the same hydrocarbons are present in both high- and low-melting-point waxes. They found no soft wax, as reported by Buchler and Graves. The six waxes ranged in melting-point from 84 to 140°F. and all had approximately the same boiling-point. These authors conclude that petroleum waxes consist mainly of normal paraffin hydrocarbons and that the rest of the material consists of isomeric branch-chain hydrocarbons. They believe that no unsaturated or cyclic compounds are present. Clark and Smith[3] studied the wax fractions that were prepared by Ferris and others[2] by X-ray diffraction patterns, and they concluded that the wax consisted of about 65 per cent of *n*-paraffin hydrocarbons and at least 20 per cent of isoparaffin materials.

Crystallization of Wax.—Three theories have been proposed to explain the manner in which wax crystallizes or fails to crystallize. Zaloziecki[4] proposes the proto-pyro-paraffin theory which states the existence of an amorphous wax which probably consists of branch-chain hydrocarbons. This amorphous material decomposes into a crystalline variety upon heating at mild cracking temperatures. This theory was probably developed because, at that time, a so-called "cracking distillation" was thought to be necessary if a pressible wax distillate was to be obtained. Gurwitsch[5] suggests that the crystalline behavior of wax stocks is dependent upon the properties of the crystallizing medium. If the oil is viscous, the crystals will be small and an amorphous wax results; whereas if the oil is fluid, the crystals are large and a pressible type of wax results. In addition, he believed that bituminous or high-boiling materials inhibit the crystallization of wax. It is found that a careful separation of high-boiling asphaltic materials by fractionation does cause the formation of a more crystalline wax. The third theory of wax crystallization, that of Buchler and Graves,[1] has already been discussed. Jones and Blachly[6] attribute the differences in the waxes to the presence

[3] *Ind. Eng. Chem.*, **23**, 697 (1931).

[4] *Z. angew. Chem.*, **3**, 126, 318 (1888).

[5] "Scientific Principles of Petroleum Technology," 2nd ed., D. Van Nostrand Company, Inc., New York, 1924.

[6] *Ind. Eng. Chem.*, **21**, 318 (1929).

of impurities, perhaps the soft wax of Buchler and Graves,[1] which results in different surface-tension properties.

Perhaps all of the theories that are outlined above are related, in part, to the crystalline condition that a wax may exhibit. A more complete study of wax crystallization is given on page 580, under the heading of pressibility of wax stocks.

Three crystalline forms of wax are generally recognized, *viz.*, plate form, needle form, and mal or imperfect crystal formations. The plate form of crystal is necessary for good pressing characteristics but the needle form is necessary for the sweating operation. The plates apparently "roll up" or fold into the needle type of crystals. Davis and Campbell[7] have studied the crystalline structure of 13 fractions of wax oil. The fractions were obtained by a true-boiling-point distillation of a Mid-Continent wax distillate. The properties of the fractions are given in Table 86.

TABLE 86.—FRACTIONS OF WAX OIL

Fraction No.	Per cent of crude at end of fraction	Universal vis. at 100	Temperature, °F., at cut point, approx.		Pour-point, °F.	Per cent wax by weight	Melting-point of wax, °F.	Crystalline structure
			At 3 mm.	At 760 mm.				
1	58.2	40	358	680	3	0	...	None
2	60.4	51	377	700	35	7.2	96	Few plates
3	62.6	66	402	727	53	9.1	106	Plates
4	64.8	75	420	752	58	9.3	112	Plates
5	67.0	89	442	773	66	7.4	124	Plates
6	69.2	115	460	789	76	10.8	128	Plates
7	71.4	152	478	813	85	10.1	132	Partly malform
8	73.6	200	499	832	89	9.7	137	Partly malform
9	75.8	258	520	862	95	9.2	142	Malform
10	78.0	330	541	886	98	8.7	145	Malform
11	80.2	400	567	915	102	9.5	145	Malform
12	82.4	480	598	950	105	6.8	145	Malform
13	84.6	470	625	978	108	5.2	149	Plates

The clean-cut crystals appearing in fraction 13 were probably due to decomposition during the distillation of the last fraction.

The fractions were blended together as follows: 1 to 6 inclusive, 1 to 7, 1 to 8, etc., including all the cuts. The size of the crystals was progressively smaller and smaller as cuts were added, but

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[7] *Oil Gas J.*, May 25, 1933, p. 49.

with the exception of blends 1 to 12 and 1 to 13 the crystalline size and form were satisfactory. The approximate end-points, at atmospheric pressure, of the blends were as follows: 780, 798, 819, 830, 851, 872°F., and for the two unsatisfactory blends (1 to 12 and 1 to 13) 893 and 921°F. Thus it appears that wax oils having end-points exceeding about 860°F. are not satisfactory and many refiners have found it advisable to limit the end-point to 835°F. Nevertheless, other factors, such as the characteristics of the oil, the degree of fractionation, the viscosity, and the amount of cracking, doubtless alter the allowable end-point for a pressible stock.

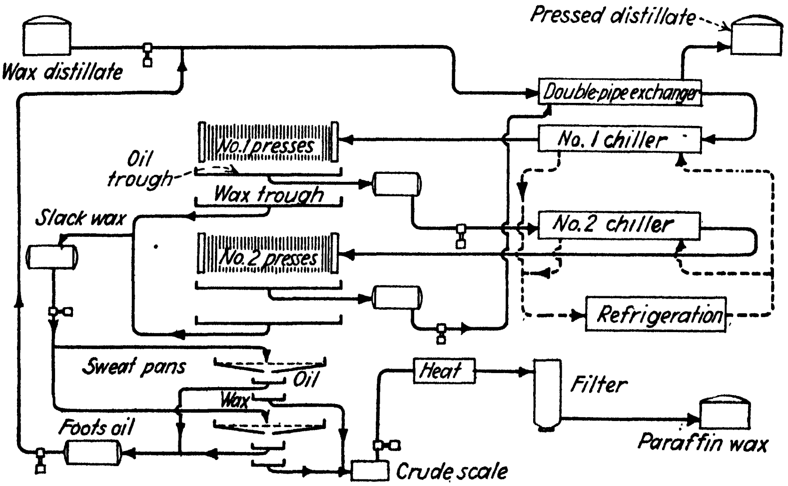

FIG. 172.—Diagram of the operations of pressing and sweating (double pressing).

Pressing and Sweating.—Most refiners now (1936) use the pressing and sweating processes for removing and producing wax from wax distillate but solvent processes are attracting attention. A mixture of wax and oil, called slack wax, is obtained from the filter presses, and the slack wax is frozen into a cake and allowed to warm slowly so that the oil drains from the cake. Figure 172 shows the general processing scheme for conducting these two operations. Most modern plants, particularly when manufacturing low cold-test oils, use direct expansion of ammonia for chilling the stock but many older plants circulate brine through the chillers.

The double-pipe chilling machine has been adopted almost exclusively for chilling wax oil. This machine is constructed much as a double-pipe cooler except that a revolving-screw or ribbon-type conveyor turns in the inner pipe. The conveyor scrapes the congealed wax from the walls of the pipe and moves it through the machine. The common size of chiller has a 6-in.-diameter inside pipe and an 8-in.-diameter outside pipe. The chilling machine is built of several sections or lengths of pipe arranged in stacks usually five to eight sections high. The conveyors for each stack (or for two stacks) are actuated by a common chain drive. Thus 24 sections of chiller can be arranged in four stacks, each stack 6 sections high, and with two chain drives. Sometimes the conveyors are actuated by a single motor so that if one section should freeze or plug the large motor will have sufficient power to break the wax in the frozen section. However, this practice often causes damage to the machine and it is usually necessary to take a frozen chiller out of service and warm it.

The rate of cooling is greatly dependent upon the effectiveness of the scrapers, particularly the amount of mixing that occurs. If the scraper fits poorly, the rate of heat-transfer drops to the low values of 2 or 3 B.t.u. per sq. ft. per °F. per hr. With closely fitting scrapers that mix the wax into the oil, rates of 16 B.t.u. have been recorded. Commonly accepted values of the transfer rate are

Type conveyor	Cooling conditions	Transfer rate, B.t.u. per °F. diff. per hr. per sq. ft.
Screw..........	Brine circulation	4–5
Screw..........	Direct expansion	7–10
Ribbon.........	Direct expansion, nonturbulent flow	8–12
Ribbon.........	Direct expansion, turbulent flow and recirculation	15

Thus a section of chiller having a surface of 55 sq. ft. will be able to cool 12 to 18 bbl. of wax oil per day through the customary range in temperature. The higher capacity is for chilling the oil to 10 to 15°F. when some heat-exchange is used, and the lower capacity is for cooling to 15°F. without exchangers or to 0° with exchangers. Manufacturers of refrigeration equipment should be consulted concerning an actual installation.

Two kinds of plates are used for filtering the chilled wax oil. One is a recess type of plate (permanent ring) and the other consists of a flat plate and a spacer ring (loose-ring type) (Fig. 173). It is claimed that the blanket on the permanent ring plate is worn by the tool that is used to pry the plates apart. The loose-ring plate is less expensive but the riveted spreaders must be removed each time that the canvas is replaced, and many refiners feel that the ring involves needless handling. Plates are manufactured in diameters of 27, 36, and 48 in. but the 48-in. plate is used almost exclusively. Each plate has a hole in the center which allows the chilled oil to flow through the entire length of the press to every plate. Special canvas (12-0) filter cloth is sewed around each plate and in the loose-ring type the "blanket" is also fastened to the plate by riveted spreaders. The wax remains on the cloth and the oil flows down the plate and around the edge of the plate to the bottom. The pressure at the end of the pressing operation seldom exceeds 450 lb. per square inch and the common "drying-off" pressure is 350 lb. Ten or twelve plates require a foot of length and the presses are normally assembled with 250 to 500 plates in a press. The capacity of the press is greatly dependent on the properties of the wax oil, such as the wax content, the crystal structure, and the pressing temperature (page 581). For a normal stock that contains 5 to 8 per cent of wax and for single-pressing operation, one or two 48-in. plates are required for each barrel of Pennsylvania oil that is pressed per day, and two or three plates are required for a Mid-Continent oil. Even lower capacities are common with double-pressing operation or if the stock contains a large amount of wax. The amount of slack wax that is obtained from the presses is far greater than the 5 to 8 per cent of finished wax and may in some cases amount to 30 per cent of the wax distillate.

Low-pour-point oils are becoming more and more common. These oils require a low pressing temperature and the rate of filtration is much slower. In general, the stock should be chilled to 5 to 10°F. below the desired pour-point for single-pressing

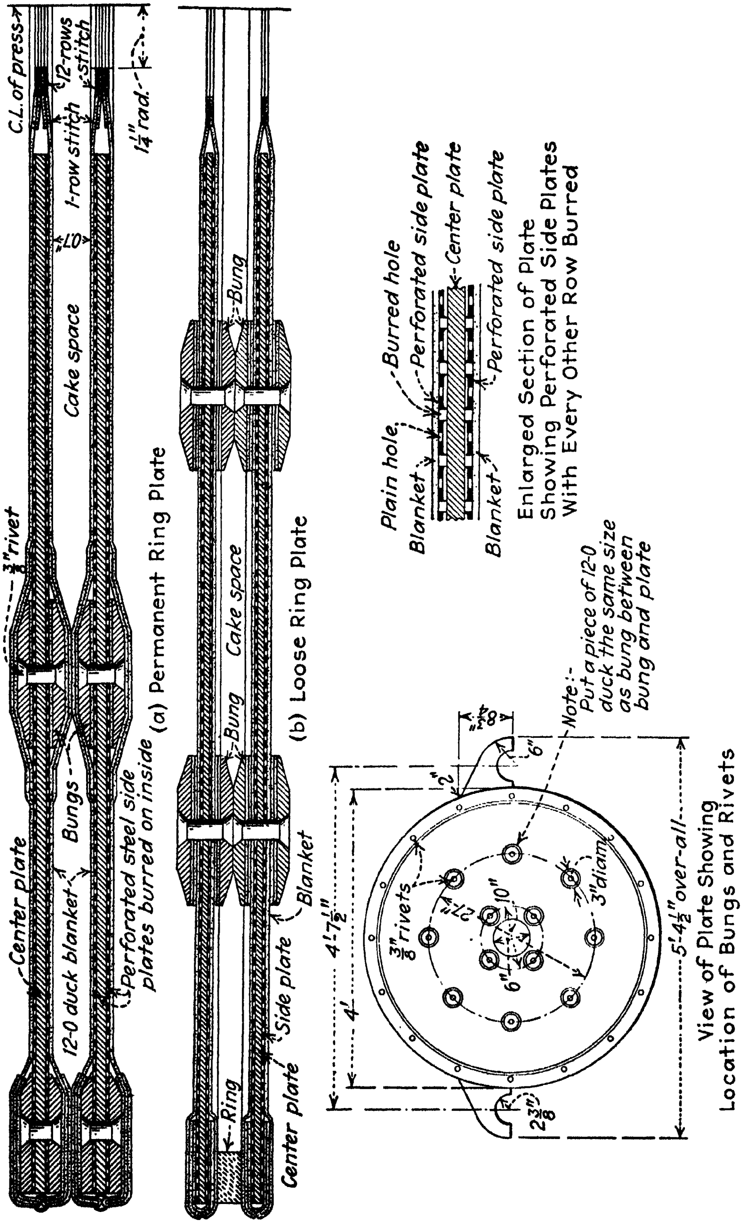

FIG. 173.—Details of filter plates. (*a*) Permanent-ring type; (*b*) loose-ring type. (*Carbondale Machine Company.*)

operation, but for a double-pressing operation the stock need not be chilled to such a low temperature. One refiner reports that zero-pour-point oils can be obtained by pressing at +5°F. and another reports a temperature of −8°F. The difference doubtless arises because of differences in the fractionation of the stocks and in the crystalline condition. Direct expansion of ammonia is advantageous for the obtainment of these low temperatures. When brine is used as the cooling medium, two temperature differences are involved, and the ammonia temperature must be much lower than when direct expansion is used.

The operation of *sweating* consists of cooling the slack wax to a congealed mass and slowly heating it to temperatures of 100 to 140°F. The wax is heated in long shallow pans, usually about 10 ft. wide, 40 or 50 ft. long, and sufficiently deep to hold a 5- to 7-in. cake of wax. A flat perforated metal sheet or a 50-mesh screen lies across the bottom of the pan. A pipe coil for cooling and heating lies just above the screen. The pans are arranged, one above another, in stacks of about eight and housed in a building or oven. The oven has steam coils along the walls to aid in maintaining uniform temperature conditions within the oven.

In conducting a sweating operation, cold water is turned into the pans up to the screen, cold water is circulated through the coils above the screen, and slack wax is pumped into the pan. The wax solidifies into a cake and the water is withdrawn, leaving the cake on the screen. The temperature is then gradually increased by circulating warmer and warmer water through the coils in the cake, and by passing steam through the coils on the walls of the oven. If the wax is in the proper condition, it gathers into well-defined needle crystals and the oil sweats or drips from the wax cake. The oil is called foots oil and it may be returned directly to the wax distillate or it may be resweated for the recovery of additional wax and a less waxy foots oil. Often the oil from the wax cake is collected in two portions, the first, foots oil, and the second, *intermediate wax*. In making 118°F. melting-point wax, the intermediate wax may be resweated with the slack wax, but more frequently it is sweated separately. The intermediate wax from a high-melting-point sweating operation often contains as much as 50 per cent of slack wax. The resweating of intermediate wax can be economically conducted in a tank which contains several layers of water coils, because the wax sweats nicely and a very thick cake is possible. Very low-melting-point waxes are usually made by resweating the foots oil.

The rate of heating is greatly dependent on the uniformity of temperature within the cake. With circulating water as the main heating medium, the total time for the sweating cycle is about 30 or 40 hr. The exact time depends upon the melting-point of the wax that is being produced, the crystalline characteristics, and the uniformity of temperature throughout the cake. For 110 to 112°F. melting-point wax, only 24 to 36 hr. are required, but for 120°F. wax the time is 35 to 45 hr. The use of automatic temperature-control instruments is an advantage in maintaining a uniform cycle of heating.

The total time for the sweating cycle is not proportional to the melting-point of the wax because about 16 hr. is required for the charging, cooling, and melting operations. The melting-point of the crude scale wax is about the same as the maximum temperature attained in the sweating operation. The resweating of intermediate wax does not take so long because the cake is more porous. L. D. Wyant[8] has made a systematic study of wax sweating. He concludes:

1. Super chilling the wax cake before starting to sweat does not increase the yield or quality of wax produced.
2. Extremely slow chilling allows or causes paraffin wax to segregate into patches or blocks throughout the slack wax cake.
3. In chilling a wax cake before starting it to sweating, all the material should be chilled to at least a complete semi-solid mass; however, additional chilling is a loss of time in cycling.[9]
4. No advantage compatible with the cost is gained by extremely rapid chilling.
5. Local over-heating, if of only a few (2 or 3) degrees difference, has an appreciable effect on a sweating wax cake.
6. Water coils arranged so heated water can circulate through the sweating wax cake decreases the cycling time required for sweating.

In a study of the recovery of wax that was obtained by several Mid-Continent refiners, he found that the recovery of wax varied

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[8] Separation of Wax from Distillate, *Oil Gas J.*, Oct. 2, 1924, p. 224.

[9] Author's note: Most refiners find that the wax cheese must be perfectly solid before starting the sweating operation or the yields are poor.

greatly. Based on the wax recoverable by solvent methods, the efficiency of the sweating operation ranged from 23 to 85 per cent and averaged about 50 per cent. Paraffin wax is a very valuable product, particularly if a large match and candle market is available.

The crude scale has a slightly yellow color. This discoloration may be removed by treating the molten wax with acid (or sometimes dilute caustic solution) in an agitator, but filtration through fuller's earth is all that is normally required.

Pressibility of Wax Stocks.—The rate at which wax stocks can be pressed is of prime importance to the refiner. By slight changes in the operating conditions, a wax distillate may be produced which presses very slowly or cannot be pressed at all.

Some factors that affect the pressibility of a wax oil are

1. Viscosity.
2. Fractionation.
3. Distillation range.
4. Wax content.
5. Crystal structure.
6. Extent of cracking.

Viscosity.—The pressing qualities of wax oils from the same crude oil are somewhat dependent on the viscosity. The higher the viscosity, the slower the rate of pressing. Wax oils that are pressed without dilution usually have a viscosity between 55 and 75 sec. Saybolt at 100°F. Higher viscosity oils[10] have been pressed but usually they are diluted with heavy naphtha to a viscosity of about 60 sec. The use of naphtha permits the use of single-pressing for stocks that would otherwise require double-pressing.

The viscosity at the pressing temperature is of more interest than the viscosity at 100°F. Davis and Campbell[7] report viscosities at the pressing temperature of 1,200 to 2,100 sec. (Table 87).

The pressing qualities of a distillate are also dependent on other factors than the viscosity, so that the several factors must be considered collectively. The proper viscosity for a particular distillate must be determined in the plant by a consideration of the several factors and by conducting plant experiments.

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[10] A 110 viscosity distillate is being pressed without dilution by one company.

TABLE 87.—PRESSING TESTS

Pressing stock No.	1	2	3	4	5	6		7
Gravity, A.P.I.	34.2	32	31	31.4	31.7	31.6		
Flash point, °F.	90	170	360	280	320	315		
Viscosity of distillate at 100°F.	63	70	94	66	68	75		100
Cold test, °F.	66	68	74	42	56	80		
Distillation-range at 40 mm., °F.								
Initial boiling-point	....	256	450	256	312	306		
10 per cent	344	312	476	395	394	416		
20	466	350	493	416	426	445		
30	494	473	509	436	453	469		
40	511	498	525	461	479	491		
50	527	518	541	490	503	513		
60	544	539	557	524	523	533		
70	564	561	573	557	543	554		
80	588	585	593	590	562	580		
90	622	611	615	625	590	616		
End-point	648	632	637	643	625	652		
End-point, 760 mm. approx	862	844	849	859	835	870		
Wax content, per cent	8.75	6.75	7.66	1.58	5.77	4.8		
Melting-point of wax, °F.	118	123	123	119	124	123		
Per cent raw 200 vis. neutral	50	48	50	51	33	39		
Pressing characteristics:								
Pressing temp.	−18	−8	−10	−5	−6	+8	−5	15
Vis. at 100°F.:								
Distillate	63	70	94	66	68	75	75	100
Pressing stock	55	70	58	66	68	75	66	100
Dewaxed oil	57	76	63	68	74	82	69	114
Viscosity at pressing temp. approx	1,400	2,100	1,350	1,380	1,800	1,200	1,400	1,800
Pressing rate, bbl. per plate per day	0.43	0.43	0.41	0.4	0.37	0.35	0.3	0.45
Fractionation	....	....	....	....	Poor	Poor		
Crystal formation	Good	Good	Good	Fair	Poorly formed	Very small		

Fractionation.—The degree of fractionation plays an important part in the pressing qualities of an oil.[11] The quantity of material boiling above 800°F., and particularly the "tail" of poorly fractionated material in the oil, affects the pressing rate greatly. A poorly fractionated stock may press more slowly than a well-fractionated product that has a much higher end-point because of minute quantities of very high-boiling material. Dunmire[11] concludes that fractionation is more necessary in producing a pressible distillate than cracking. Fractionation also affects the centrifuging properties of the cylinder stock, and hence a

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[11] DUNMIRE, H. J., *Nat. Petroleum News*, Apr. 23, 1930, p. 38.

poor separation between the cylinder stock and the wax distillate results in trouble with both of these stocks. For this reason, refiners have sometimes found it necessary to take a "slop" wax cut between these two stocks.

Distillation-range.—This constitutes a valuable method for the laboratory control of the pressing operation. A common method of determining the boiling-range is by the Bureau of Mines vacuum distillation operated at 40 mm. pressure. End-points at 40 mm. pressure of 610 to 640°F. are possible without spoiling the pressibility of the stock. This corresponds to a cut-point of about 840 to 870°F. (atmospheric pressure) on the true-boiling-point distillation curve.[12] It appears that the viscosity of the heaviest part of the wax distillate also affects the pressibility. In general, it should not exceed about 580 sec. at 100°F.

Wax-content.—An abnormally high wax-content usually lowers the pressing rate because the presses must be dumped oftener. At the same time, the wax in the higher wax-content oils often crystallizes better, so that pressing may actually be facilitated in spite of the high wax-content. A method of determining the wax-content is given by Davis.[7] The average wax-content of distillates is about 6 per cent but some stocks contain as little as 1 per cent of wax and others contain as much as 25 per cent.

Crystal Structure.—The crystal structure is perhaps the most important factor that affects the pressibility of a stock, but it is related and dependent on the several other factors that are discussed herein. A means of examining and photographing waxes is described by Davis.[7] Figure 174 shows several characteristic photomicrographs of wax distillate. A stock having very good pressing properties is shown in Fig. 174*a*; a typical stock in *b*; a stock with too high an end-point in *c*; and one which indicates that a small amount of crude oil had leaked into the stock during heat-exchange in *d*. The size of the crystals shown in the figure is of little significance unless they were grown under comparable conditions, because the size depends upon the length of time that they are allowed to grow before the picture is taken.

Cracking Distillation.—Until recently, all refiners prepared their wax stocks for pressing by a so-called "cracking distilla-

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[12] If the wax oil is cracked before pressing, the cut-point may be 30 to 40° higher but the cracking distillation of wax oils is expensive, involves losses of oil, and is no longer widely practiced.

tion." The wax oil was heated for several hours at about 800°F. The wax crystallizes more cleanly from a stock handled in this manner but a loss of lubricating oil occurs and the operation is expensive. Dunmire[11] finds that greater yields of pressible distillate are obtained by cracking the distillate but that even a larger yield is obtained by carefully fractionating the stock.

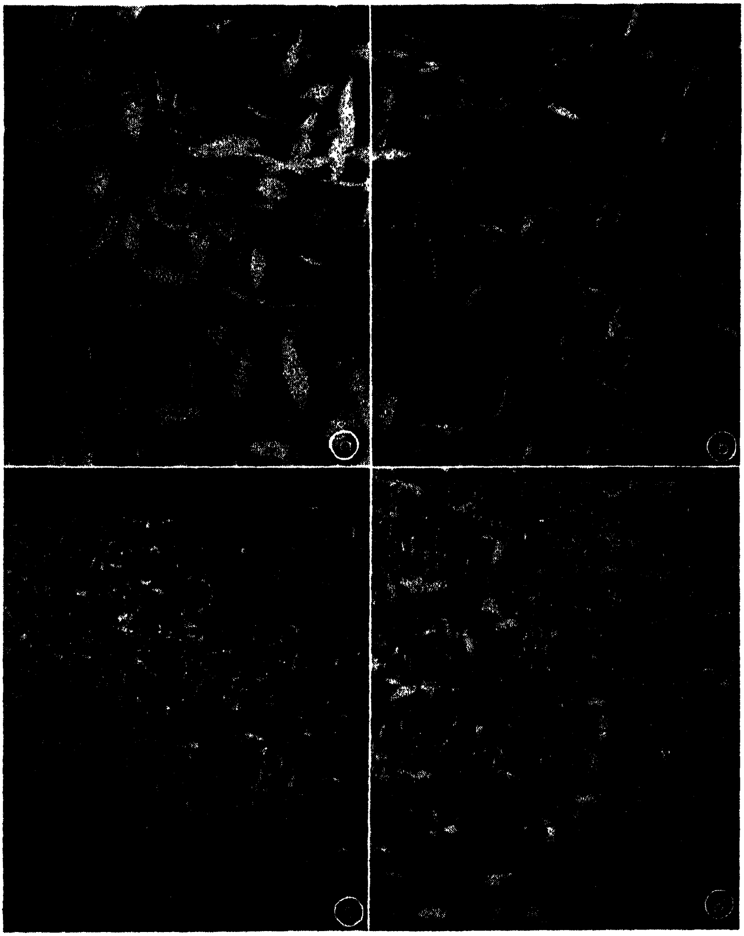

Fig. 174.—Photomicrographs of wax: (*a*) very good; (*b*) typical; (*c*) high end-point; (*d*) crude oil leaked into distillate in exchanger. (*L. L. Davis, Continental Oil Company.*)

During the last 10 years it has been definitely proved that cracking is not necessary in order to produce a pressible distillate. If other factors such as fractionation, viscosity, boiling-range, and crystal structure are satisfactory, the stock will be pressible without a cracking distillation.

In determining the suitability of a stock for pressing, all of the foregoing factors must be considered collectively. In the control of plant pressing operations, the wax oil should be examined for at least the following characteristics: (1) viscosity, (2) boiling-range at 40 mm. pressure, and (3) crystal structure.

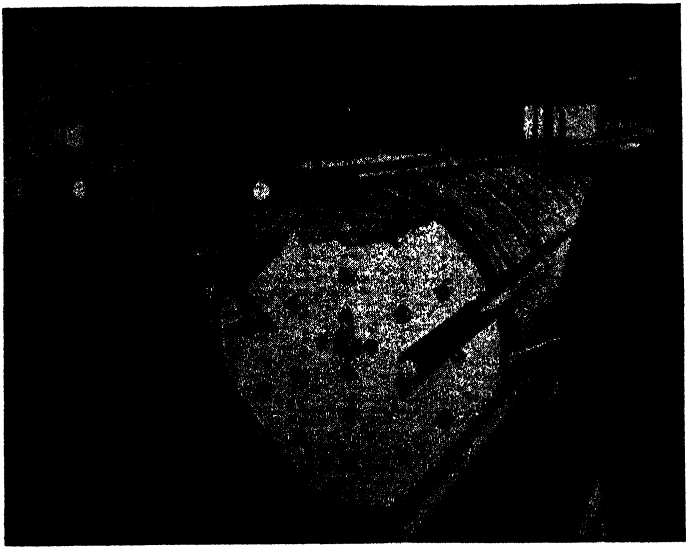

FIG. 175.—"Spudding" a wax press. (*Carbondale Machine Company.*)

Cold Settling and Centrifuging.—These processes have been widely used for the dewaxing of cylinder stock but solvent processes are now claiming attention. The *cold-settling* process was an outgrowth of the experiences of the early Pennsylvania refiners. They allowed their crude oil to stand through the winter in storage tanks. During cold weather, the wax separated and settled to the bottom of the tank so that a partially dewaxed crude oil could be drawn from the top of the tank. The cold-settling process involves the use of large well-insulated settling tanks. Brine coils are suspended in the tanks and by slowly cooling the cylinder stock solution (60 to 70 per cent naphtha) the wax collects and settles to the bottom of the tank. The lowest economical pour-point by this process is about 30°F. and hence the process has been gradually abandoned. However, slow-cooling tanks similar to settling tanks, except that they are used continuously, are used in cooling the solution for the centrifuge process.

The *centrifuge* process of dewaxing is now widely used. The process is illustrated in Fig. 176. The percolated cylinder stock solution, containing about 65 per cent of naphtha, is continuously chilled in slow-cooling tanks to about 10°F. and, if low-pour-point oils are required, the cooling is continued in chilling tanks that are provided with mixing paddles. The latter tanks are usually cooled by direct expansion of ammonia. The rate of cooling in the slow-chilling tanks should be about 3 or 4° per hour, but a more rapid rate of cooling is usually possible after a temperature of 0° has been attained. The temperature difference between the solution and the cooling medium must be kept to less than about 20° in the slow-chilling tanks in order to avoid fouling of the transfer surfaces. If pour-points of 20 to 30°F. are satisfactory, the oil should be cooled to about −10°F. and direct expansion of ammonia is not necessary. For zero-pour-point oils the chilling must be continued to about −45°F., and for some stocks a

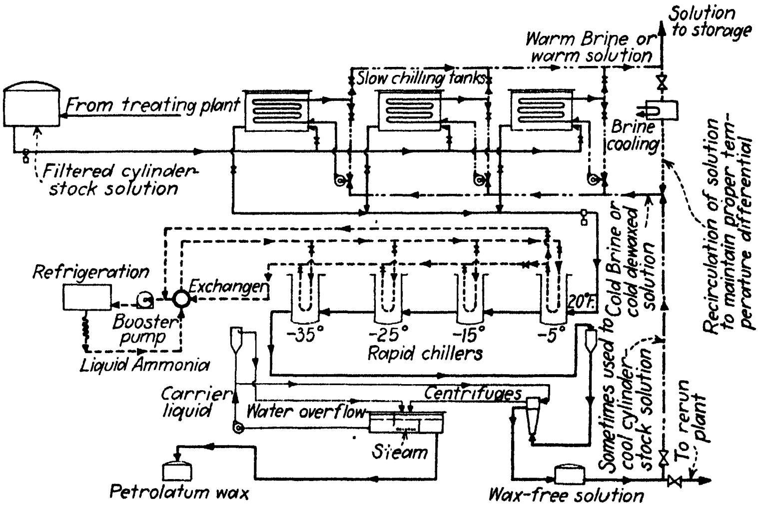

FIG. 176.—Centrifuge process for dewaxing cylinder stock.

temperature of −55°F. may be necessary. The chilled solution is charged to Sharples centrifuges through a constant-head feed device. The centrifugal force separates the wax and oil; the oil from the top and center of the bowl, and the wax from a point lower. Figure 177 shows the arrangement at the top of the machine. A stream of warm water (150 to 180°F.) sprays on the petrolatum to prevent freezing of the wax in the bowl. The dewaxed solution flows directly to storage but the wax solution is separated from the carrier-water in a separator tank. In modern plants it is becoming common practice to use the cold dewaxed oil as the cooling agent in the slow-chilling tanks. In so doing it is sometimes necessary to recirculate some warm dewaxed oil to

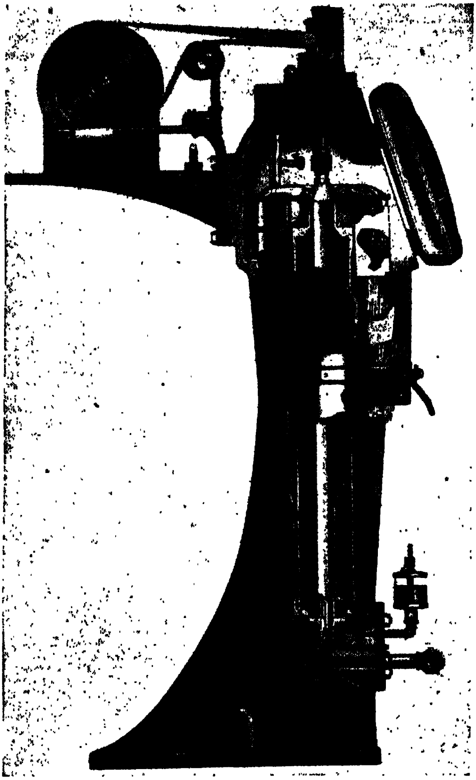

FIG. 177.—Sharples Super-Centrifuge for dewaxing cylinder stock solution. (*Sharples Specialty Company.*)

maintain the proper temperature differential between the two stocks.

The capacity of the Sharples machine is 25 to 45 bbl. per day based on cylinder stock. Thus each machine handles 70 to 180 bbl. per day of solution, depending upon the pour-point of the finished product, the properties of the stock, and the amount of dilution. The machine operates at 17,000 to 19,000 r.p.m. and requires about 1 kw. per hour of power. The refrigeration requirement per machine per day is 5 to 8 tons.

The secret of successful centrifuge operation is the maintenance of uniform operating conditions in the entire plant operation as well as the operation of the centrifuge plant. The stock must be carefully fractionated in the topping or vacuum distillations to eliminate crystalline wax. The rate of chilling should be sufficiently fast to prevent the formation of large crystals, but too fast a rate of chilling will give a petrolatum that is too colloidal to centrifuge properly. High-boiling dark-colored or asphaltic materials inhibit the growth of crystals and a stock whose color is lighter than 1⅛ Tag Robinson will probably give trouble. Some refiners have even added colloidal matter to a distilled cylinder stock to inhibit the growth of crystalline wax. The chilling surfaces must be kept free from wax and the equipment should be designed so that masses of wax cannot accumulate on cooling surfaces, tank bottoms, or lines. A sufficient amount of naphtha must be used to obtain a nonviscous solution at the centrifuging temperature. A solution containing about 70 per cent of naphtha and having a gravity of 44 to 47 is usually satisfactory for producing zero-pour-point oil. In producing very low-pour-point oils it may be necessary to use even more naphtha. In the past, the viscosity of the cylinder stock that could be successfully centrifuged was about 110 sec. at 210°F., but by careful operation it is now possible to operate on a stock whose viscosity is as low as 75 sec. at 210°F. This permits most of the wax distillate to be incorporated in the long residuum cylinder stock.

In order to get proper centrifuging properties, many recirculation schemes have been used. In processing very waxy stocks and some overhead stocks, it is necessary to recirculate some of the dewaxed oil. Other stocks can be centrifuged most successfully by recirculating some petrolatum and in rare cases it has been necessary to add dark-colored material to the stock.

New Dewaxing Methods.—The use of two dewaxing methods, *i.e.*, pressing and centrifuging, has been a source of great expense to refiners. In an effort to lower this expense, much attention is being given to the development of methods by which the entire range of wax-bearing stocks can be dewaxed by a single process. Two general types of processes are being studied. In one of these the combined wax distillate and cylinder stock is pressed or filtered, and in the other the entire wax stock is dewaxed in a centrifuge. With the exception of the filter aid process, all of the proposed processes require the use of a special solvent. The filter aid process relies upon the use of a filter aid material which strengthens and reinforces the wax cake and at the same time keeps it in a porous condition. For those processes that involve filtration, the trend is toward the use of suspended leaf types of presses, such as the Kelly, Vallez, and the Sweetland, rather than the familiar plate-and-frame type that is used in pressing wax distillate. Closed filtering systems are required because the solvents must be recovered or the operation will be an economic failure. In fact, the recovery of the solvent has been a great hindrance to the adoption of new dewaxing methods, and no such process can be highly successful unless the solvent can be effectively recovered and is relatively cheap.

The use of a single dewaxing process for both the high- and low-viscosity wax stocks has many advantages. The cuts that must be produced in a vacuum tower are reduced to gas oil, a lubricating oil stock, and tar; only one type of dewaxing equipment is required; only one rerunning operation is necessary; and the production of several blending stocks will be unnecessary. Lower and lower viscosity stocks are being successfully handled by the centrifuge process but the dewaxing is not entirely satisfactory because of the high cloud-points of the neutral oils.

The processes which are attracting most attention are

1. Pressing by the use of filter aid.[13]
2. Pressing in acetone-benzol solution.[14]
3. Filtering and self-refrigeration in propane solution.[15]
4. Centrifuging in trichlorethylene solution.[16]
5. Centrifuging in ethylene dichloride solution (Barisol process).

[13] Gee, William P., *Ref. Nat. Gaso. Mfr.*, June, 1933, p. 238.

[14] Gover and Bryant, *Ref. Nat. Gaso. Mfr.*, June, 1933, p. 222.

[15] Bahlke, Giles, and Adams, *Ref. Nat. Gaso. Mfr.*, June, 1933, p. 229.

[16] Pester, C. F., *Oil Gas J.*, May 25, 1933, p. 52.

Although some of these processes are being used commercially, they are still in development stages. Some of them will probably be commercially successful but others will not. Any truly successful process must meet the following requirements:

1. The solvent must be cheap so that the replacement of lost solvent will not be expensive.
2. The process should be able to handle the entire range of wax-bearing stocks.
3. The differential between the separating temperature and the pour-point must be low. In other words, the solubility of wax in the solvent should be low.
4. The rate of pressing or centrifuging should be high.
5. The solvent should not be corrosive.

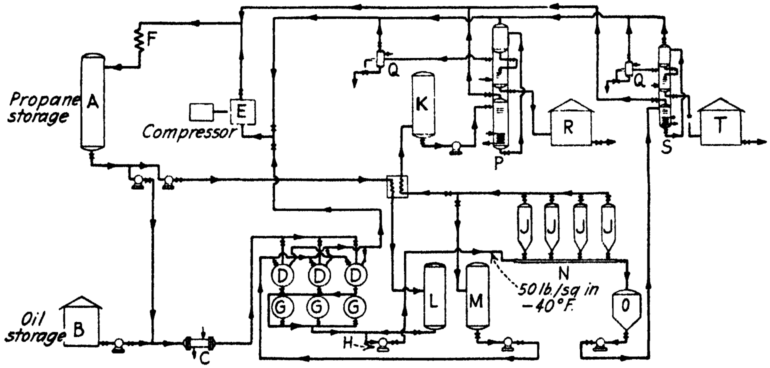

FIG. 178.—Propane dewaxing process. (*Standard Oil Company of Indiana.*)

In addition to these, a heavy solvent is desirable for centrifuging and a noninflammable solvent is advantageous. A solvent which could be used for both dewaxing and solvent extraction would be highly desirable. Propane meets these requirements to some extent. It aids in the elimination of asphaltic material but it is not an entirely suitable solvent from the standpoint of solvent extraction or treating.

The only one of the processes that will be discussed is the *propane self-refrigeration* process. The process is unique because part of the solvent is allowed to evaporate and the entire material is chilled by the refrigeration effect of the evaporation. The advantages of the process are

1. Self-refrigeration.
2. Rapid rates of chilling. The entire operation of filling, evaporating and emptying the chilling vessel requires only about 90 min.

3. Ability to handle all kinds of wax-bearing stocks.
4. High rates of filtration even for viscous oils.
5. A cheap solvent which may be recovered in the regular gas recovery system of the refinery. The make-up solvent requires only a wash with caustic to sweeten it.

A simplified diagram[15] of the process is shown in Fig. 178. The wax stock is dissolved, under pressure, in propane (or butane) in the storage tanks *D* by heating to about 130°F. The solution is then allowed to evaporate and chill itself in the vessels *G* by reducing the pressure to about 50 lb. per square inch. Chilling can be conducted at the rate of 3°F. per minute and the final temperature is about −40°F. The chilling uses about half of the solution. The chilled solution is pumped to the filters *J*, and it can be filtered at the rate of 2 gal. of solution per square foot of filter area per hour for a solution containing 17 per cent of oil; and at a rate of 0.8 gal. per hour for a 35 per cent solution. Heavy stocks seem to filter at about the same rate as light stocks. The solvent that remains in the wax and oil is distilled and fractionated under pressure. Steam may be used for heating the solution. It is usually necessary to add additional propane after the chilling operation to keep the proper ratio between oil and solvent.

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CHAPTER XXVI

ECONOMICS OF DESIGN

The economic feasibility of a processing operation is a factor that cannot be overlooked by the engineer. The most sound and exact processing plan may be absurd from an economic standpoint and many of the sales arguments of engineers must be classed as trifling or economically unsound.

The scientist has been defined as a man that is trained in the organization of common sense. The engineer is a scientist, who is forced by circumstances to employ judgment as well as use organized common sense. Economics enters into every detail of a design and hence it is impossible to illustrate more than a few cases.

COSTS OF PROCESSING

Inasmuch as the operating costs vary widely from plant to plant, no exact data can be presented. Two plants that are operated with the same care and judgment may vary in operating costs as much as 100 per cent. The reason for such differences is easily understood when the following items are considered:

1. Ease of chemical treatment—kind of crude oil.
2. The design of the plant—modern or obsolete.
3. Location—cost of fuel and cost of labor.

These factors explain the wide variation in the operating costs appearing hereafter. The data were taken from actual plant records[1] for a number of plants in all parts of the country. The costs for sales, advertising, general administration expense, depreciation, taxes, and cost of charge stock are not included. All direct charges, such as direct refinery supervision, power, fuel, and materials, are included.

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[1] The author is indebted to Dr. Sidney Born of the University of Tulsa. Many of the plant records were supplied by him. Date of records, 1927–1932.

OVER-ALL REFINING COSTS

Direct cost of refining, not including sales, administration, depreciation, and taxes

Operation	Cts. per Bbl. of Crude
Topping	12–21
Topping and cracking	26–39
Complete	25–52

An analysis of these costs by departments is helpful:

Department	Skimming and cracking, cts. per bbl. of crude	Complete, cts. per bbl. of crude
Simple distillation	3.3	6.2
Cracking distillation	17.2	10.4
Gasoline recovery	0.7	0.4
Oil treating—agitators, sludge, handling, etc	1.5	3.8
Filtering and burning clay	....	4.6
Wax handling	....	2.5
Compounding and grease mfg	....	0.8
Boiler house	3.3	5.2
Miscellaneous	4.3	6.3
Total cost per bbl. of crude	30.3	40.2

For a topping and cracking operation in the Mid-Continent area:[2]

	Cts. per Bbl.
Plant fuel	9.0
Labor	5.7
Depreciation and obsolescence	12.0
Royalty (cracking)	7.0
Maintenance	1.5
Treating	0.8
Total	36.0

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[2] WILLSON, C. O., *Oil Gas J.*, Aug. 4, 1932, p. 8.

Miscellaneous Operating Costs

	Cts. per Bbl.
Light oils	
Cracking, complete	48–90 (finished gaso.)
Acid treatment of light oils, complete	2.2–6 (charge-stock)
Rerunning pressure distillate	6.2–12.9 (charge-stock)
Stripping rich absorption oil	1.5–4 (rich oil)
Loss in acid treating	Per Cent
Pressure benzene	0.8–2.9
Pressure gasoline	0.35–4.0
Gasoline, st. run	0.27–1.03
Naphtha	0.2–1.9
Kerosene	0.18–3.26

The costs for processing heavy oils such as neutral oils and cylinder stock are even less consistent. The great variation in these costs is due to the inherent differences in lubricating oil stocks and the variety of treating and dewaxing operations that must be used. Some stocks require five times as much acid as others.

Heavy oils:	
Rerunning complete	4.1–6.2 cts. per bbl. charge
Acid treating complete	11–43 cts. per bbl. treated
Loss in acid treating	
Non-viscous neutral	2.8–4.9 per cent
Viscous neutral	3.5–12.0 per cent
Residual cylinder stock	18.5–40 per cent
Overhead cylinder stock	11–18 per cent
Contacting in solution	35–62 cts. per bbl. finished stock
Percolation:	
Non-viscous neutral	7.2–36.2 cts. per bbl.
Viscous neutral	15.4–48 cts. per bbl.
Wax	19.4–36.4 cts. per bbl.
Average of straight filtering	18.4–46.4 cts. per bbl.
Solution filtering	27–75 cts. per bbl. of stock
Burning clay:	
Wedge type	$1.22–$4.13 per ton
Rotary type	$0.50–$0.92 per ton
Loss during burning	1.5–2 per cent
Dewaxing:	
Pressing and sweating	13.6–46.8 cts. per bbl. wax distillate
Sweating	41.7–125 cts. per bbl. sweated wax
Barreling and molding wax	7.6–106 cts. per bbl. finished wax
Centrifuging	31.9–164 cts. per bbl. brightstock
Refrigeration	46.3–316 cts. per ton of refrigeration

The amount of steam required and the approximate costs of generating power or heat are given below:

Power costs:	
Steam generation, complete	15.6–30.5 cts. per 1,000 lb. steam.
Heat, by pipestill:	
Without exchangers	21–37 cts. per million B.t.u.
With exchangers	14–30 cts. per million B.t.u.
Fuel required:	
Topping or skimming	7–13.5 per cent of crude throughput
Complete processing	15–23 per cent of crude throughput
Steam required:	
Skimming and cracking	119–185 lb. per bbl. crude
Complete processing	155–230 lb. per bbl. crude
Percolation filter	25,000 lb. per 1,000 cu. ft. filter
Nat. gaso. stripper	1.7–2.5 lb. per gal. gaso.

REALIZATION OF CRUDE STOCKS

The most economical "break-up" of products varies day by day because of fluctuations in the market prices and in market specifications. During one season a plant may be most economically operated for the production of maximum yields of gasoline by topping and cracking, whereas at another time the manufacture of a maximum yield of fuel oil or of particular lubricating oils may be advantageous. Consider the posted market prices for October, 1933,[3] and July, 1928,[4] for Oklahoma, on page 595.

Figure 24 (page 79) is an analysis of a typical 37.3 A.P.I. Mid-Continent crude oil. The yields (Chap. VII) of products from this crude oil and the value of the products per barrel are approximately as shown in the table on page 596.

However, the type or completeness of processing is governed by more factors than the market quotations and the expected yields. Certain crude oils are more suitable for lubricating oil manufacture than others. In fact, some crude oils are so dark that a merchantable long residuum (realization 4) could not be made. Others contain so much wax that 32 to 36 A.P.I., 0 to 15 cold-test gas oil could not be made without undue expense, others are so dark that abnormal quantities of acid would be required, and others contain lubricants of such viscosity-index

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[3] *Oil Gas J.*, Oct. 19, 1933, p. 34.

[4] *Oil Gas J.*, July 5, 1928, p. 148.

that they cannot be marketed. Of even more importance are the market outlets that are available. As an example, few refiners can find a ready market for long residuum or for 190 to 200 viscosity brightstock. However, if a buyer can be located, the manufacture of specialties becomes lucrative.

Material	Oct. 17, 1933, cts. per gal.	July 3, 1928, cts. per gal.
Gasoline, U.S. motor regular	4¾	7.945
Gasoline, 60–62, 400 E.P. regular	5.0	8.143
Gasoline, 60–62, 400 E.P. premium	5⅜	
Naphtha, 50–52, 450 E.P. blending	4¼	7⅝
Stoddard solvent, 300–410	6⅛	
Lacquer diluent, 140–200	8¾	
Kerosene, 41–43	3½	4¾
Kerosene, 42–44	3⅝	5.0
Furnace oil, 32–36, straw	2⅞	2⅝
Furnace oil, 39–41, prime	3.0	
Gas oil, 32–36, cracking	1⅞	2½
Gas oil, 32–36, 0 to 15 cold test	2¼	
Fuel oil, 28–30, 0 to 10 cold test	2.0	2.0
Fuel oil, 20–22	1.3	1.5
Fuel oil, below 16	1.2	
Petroleum coke, lump, and egg	$7.00*	
Neutral oils, 0 to 10 cold test:		
150 vis., 3 color	7¼	8½†
200 vis., 3 color	9.0	10½†
280 vis., 3 color	12.0	16.0†
400 vis., 4 color	14¾	18 (est.)
Steam-refined cylinder stock 600 light green	6¼	8.0
Brightstock:		
190–200 vis. D	24.0	29.0
150–160 vis., D, 0–10 cold test	22¼	
150–160 vis, D, 25–40 cold test	21¼	22.0
White crude scale, 124–126	3½‡	4.0‡
Crude oil, Okla. and Kans., crude at field, 37 A.P.I.	$1.02 per bbl.	$1.31 per bbl.

* Dollars per ton, f.o.b. Chicago refineries.

† Higher cold test.

‡ Cents per pound.

With the refining costs as generally outlined heretofore, the gross profits for the seven processing realizations are estimated as

Realization	Per cent, untreated	Per cent, finished	Value at refinery, dollars per bbl.	
			October, 1933	July, 1928
1. Simple topping:				
Gasoline, 60–62, 400 E.P. regular	28*	27.5	0.577	0.939
Kerosene, 42–44	13	12.5	0.19	0.262
Fuel oil, 28 A.P.I.	58	58.0	0.487	0.487
Loss (assumed)	1	2.0		
Total	....	....	1.254	1.688
2. Topping through gas oil:				
Gasoline, U. S. motor regular	34	33	0.658	1.110
Kerosene, 41–43	4.5	4.5	0.066	0.088
Gas oil, cracking stock	34	34	0.214 (est.)	0.322 (est.)
Fuel oil, 20–22	26	26	0.142	0.164
Loss (assumed)	1.5	2.5		
Total	....	....	1.080	1.684
3. Topping and cracking:				
Gasoline, 60–62, 400 E.P. premium, cracked	57†	55.0	1.01	2.02 (est.)
Kerosene, st. run 42–44	13	12.5	0.19	0.262
Furnace oil, 39–41 straw	4	4.0	0.050	0.050 (est.)
Fuel oil, 8–9	18	18.0	0.091	0.098 (est.)
Loss and gas	8	10.5	Neglect	
Total	....	....	1.341	2.430
4. Long residuum operation:				
Gasoline, 60–62, 400 regular	28	27.5	0.577	0.939
Kerosene, 42–44	13	12.5	0.19	0.262
Gas oil, 32–36, 0–15 C.T.	25	25.0	0.236	0.276 (est.)
S.R. cylinder stock, 100–120 vis., 600 flash	32	31.0	0.814	1.04
Loss (assumed)	2	4.0		
Total	....	....	1.817	2.517
5. Lubricating oil I (vacuum):				
Gasoline, 60–62, 400 regular	28.0	27.5	0.577	0.939
Kerosene, 42–44	13.0	12.5	0.19	0.262
Gas oil, 32–36, 0 to 15 C.T	22.0	22.0	0.208	0.243 (est.)
Neutral, 150 vis., 3 color	5.0	5.0	0.152	0.178
Neutral, 400 vis., 4 color	10.0	9.0	0.557	0.68
Brightstock, 190–200 vis, D	16.6	13.3	1.34	1.62
Solid tar (by vacuum)	4.0	4.0		
Loss, sludge, wax, etc	1.4	6.7		
Total	....	....	3.024	3.922
6. Lubricating oil II (vacuum):				
Gasoline, 60–62, 400 regular	28	27.5	0.577	0.939
Kerosene, 42–44	13	12.5	0.19	0.262
Gas oil, 32–36, 0–15 C.T	22	22.0	0.208	0.242 (est.)
Neutral, 200 vis., 3 color	12	10.2	0.386	0.450
Brightstock, 150–160 vis., D, 0–10 C.T	20	16.5	1.56	1.66 (est.)
Solid tar (by vacuum)	4	4.0	Neglect	
Loss, sludge, wax, etc	1	7.3	Neglect	
Total	....	....	2.921	3.553
7. Lubricating oil III (residuum):				
Gasoline, 60–62, 400 regular	28	27.5	0.577	0.939
Kerosene, 42–44	13	12.5	0.19	0.262
Gas oil, 32–36, 0–15 C.T	19	19.0	0.179	0.208 (est.)
Neutral, 150 vis., 3 color	11	9.4	0.286	0.336
Brightstock, 150–160 vis., D, 0–10 C.T	26	15.8	1.480	1.590 (est.)
Loss, sludge, wax, etc	3	15.8	Neglect	
Total	....	....	2.712	3.335

* Some used to lower initial on kerosene.

† Estimated [Eq. (57)].

follows. The gross profit must care for the general administration, depreciation, sales, taxes, and transportation charges.

Realization	Value of products, October, 1933, dollars per bbl.	Approx. operating expenses, dollars per bbl.	Cost of crude (est.)	Gross profit, dollars per bbl.
1. Simple topping.........	1.25	0.15	1.02	0.08
2. Topping through gas oil.	1.08	0.20	1.02	Loss
3. Topping and cracking...	1.34	0.31	1.02	0.09
4. Long residuum.........	1.82	0.33	1.40*	0.09
5. Lubricating oil I........	3.02	0.39	1.40*	1.23
6. Lubricating oil II.......	2.92	0.37	1.40*	1.15
7. Lubricating oil III......	2.71	0.40	1.40*	0.91

* Estimate—Lubricating crude oils are usually purchased by special contract.

The administration, sales, depreciation, etc., expenses will be at least 10 cts. per barrel, and hence operation is unprofitable for the first four break-ups. In addition, the pipeline charges must be deducted from the gross profits and this charge may range from 10 to 90 cts. per barrel.

COST OF REFINING EQUIPMENT

In estimating the cost of refinery equipment the preferable method is carefully to design the plant, make an approximate plant layout, and itemize in detail the units of equipment that must be purchased. However, difficulties arise in presenting such a method of cost analysis because the unit cost of steel, brick, labor, machines, etc., varies with the current economic conditions. For this reason the following costs are given on an over-all-capacity basis and are only approximate.

Costs based on the over-all capacity are of little value in studying the economics of processing. The small items, which constitute the total cost, are necessary if economy is to be practiced. As an example, the cost of generating steam is only a small part of the total processing cost in a refinery. The steam cost may be twice what it should be and yet fail to attract attention, because it constitutes such a small part of the total cost.

However, if the boiler house is studied separately, the inefficiency in operation may be clearly apparent.

Although changes in wages and the cost of materials are important, the size of the plant affects the dollars per barrel cost much more. Note that a small topping plant may cost $50.00 per barrel daily capacity whereas a 10,000-bbl. plant may cost only $16.50 per barrel.

Equipment	Cost of material, labor, and engineering	Range of capacity
Pipestill:		
Distillation	1,200–2,100 dollars per million B.t.u. absorbed	50–10 million B.t.u.
Cracking	1,400–2,400 dollars per million B.t.u. absorbed	60–15 million B.t.u.
Piping and insulation:		
Topping	2–9 dollars per daily bbl.	10,000–1,000 B.P.D.
Vacuum	4–9 dollars per daily bbl.	3,000– 500 B.P.D.
Cracking	5–10 dollars per daily bbl.	5,000– 500 B.P.D.
Topping plants, no treating	16.5– 60 dollars per daily bbl.	10,000–1,000 B.P.D.
Pressure distillate rerun	13 – 40 dollars per daily bbl.	10,000–1,000 B.P.D.
Vacuum distillation	49 – 84 dollars per daily bbl.	3,000– 500 B.P.D.
Solution rerun	38 – 68 dollars per daily bbl. of solution	5,000–1,000 B.P.D.
Pressed distillate rerun	39 – 72 dollars per daily bbl.	4,000–1,000 B.P.D.
Cracking	70 – 110 dollars per daily bbl.	5,000–1,000 B.P.D.
Wax plant, no rerun	150 – 200 dollars per daily bbl. wax distillate	1,200– 400 B.P.D.
Centrifuging, no rerun	600 –1,500 dollars per daily bbl. finished brightstock	600– 100 B.P.D.
Pump house, condenser on top	41–60 cts. per cu. ft. vol.	
Galvanized-iron buildings	25–30 cts. per cu. ft. vol.	
Heat exchangers	2–4.5 dollars per sq. ft.	

Such general costs as these must be used with extreme care. The lower of the two costs is usually due to the small size of the plant rather than to other factors. In prosperous times, the costs will all be higher, and during times of business depression the costs may drop far below the figures given.

Depreciation Rates.—The rate at which equipment is worn out, destroyed by corrosion, or rendered obsolete by technical development is another factor which cannot be accurately computed. The following figures have been used by well-established companies. The tendency of well-established companies has been to depreciate their equipment before it is really useless and in this manner they have been able to take full advantage of rapid technical advances.

Kind of Equipment	Rate of Depreciation per Year, Per Cent
Storage tanks	3 – 5
Stock tanks	5 –10
Oil lines	5 – 8⅓
Sewerage and traps	7 –25
Tank cars	4 – 5
Repair shop and machine tools	8 –15
Tools	15 –40
Buildings and structures	3 – 8⅓
Loading racks	7½–10
Pumps and compressors	6¼–15
Boilers	6¼–10
Trucks and automobiles	25 –33⅓
Laboratory equipment	20 –35
Distillation equipment	8⅓–15
Cracking equipment:	
Complete	10 –25
Piping	25 –40
Condensers	12½–33⅓
Condenser boxes	5 –10
Condenser coils	10 –25
Tubular condensers	10 –33⅓
Treating tanks, agitators, etc	8⅓–15
Exchangers	6¼–25

Plant Economy versus Investment.—In the selection of equipment, buyers are often guided too greatly by the initial investment cost. Particularly in times of depression, the refiner needs well-designed equipment in order to make a profit. In prosperous times the margin of profit is enough, so that even though ineffective processing is practiced the plant will still show a profit. The plant need not be new or equipped with an array of conveniences, but it must be properly designed and carefully operated. Many highly successful refiners have found it necessary to use old discarded equipment when installing new processes. During poor-profit years, these companies have such low investment charges that they can still manage to make a little profit. However, it seldom pays to use an old equipment which is unsuited for the new purpose or to save money on a new equipment by accepting an inadequate design. For example, an apparent saving of about $1,800 might be made in the cost of a bubble-tower (4,000 bbl. per day crude oil) by using 20 rather than 27 plates. If the 27-plate tower recovers an additional one-half of 1 per cent of gasoline which otherwise would be sold as kerosene, the saving per year at a price of 6 cts. for gasoline and 4 cts. for kerosene, would be

$$4{,}000 \times 42 \times 0.005\frac{(6 - 4)}{100} \times 320 = \$5{,}375 \text{ per year}$$

Thus by a saving of $1,800 in the cost of the tower, a loss of $5,375 of gasoline into kerosene occurred during the first year. In other words, a slight saving in the percentage recovery of products will care for a large investment cost. Likewise, a small saving in labor cost will pay for a large capital investment.

ECONOMICS OF UNIT OPERATIONS

In the following part of the chapter, the economics of several of the most useful unit operations will be discussed as illustrations. As inferred heretofore, the most successful manner of effecting economies is to study each phase or operation of the complete processing scheme independently. By this manner of approach, savings which are of such magnitude that they may be unnoticed in the total processing cost are forcefully brought to attention. The topics that will be discussed are (1) the saving per year due to heat-exchange, (2) the most economical approach between the outgoing heating medium and the incoming cold-stock of an exchanger, or vice versa, (3) the most economical amount of heat-exchange to use with a pipestill, (4) the most economical approach between the flue-gas temperature and the cold oil temperature of a pipestill, and (5) the optimum velocity of flue gas in the convection section of a pipestill.

There is no end to the phases of processing that may be studied in a similar manner. Among the economic studies that have been so studied are (1) the optimum relation between tower diameter and tray-spacing for a bubble-tower, (2) the optimum thickness of insulation to use, (3) the optimum cost of protective coatings for pipelines, etc., (4) the optimum length of pipestill tubes and dimensions of a furnace, (5) the optimum dimensions of a storage tank or pressure vessel, (6) the optimum amount of a valuable component to absorb in a natural-gasoline absorber, (7) the optimum spacing between a series of structural beams, and

(8) the most economical relation between amount of steam and vacuum to use in a vacuum plant.

Economics of Heat-exchange.—The net saving effected by the recovery of waste heat approaches a definite limit in any plant equipment. The value of the heat saved, less the cost of the equipment and the cost of operating the equipment, is the net saving and this approaches a high value for a particular set of conditions and decreases if any of the conditions are changed.

In selecting heat exchangers an important consideration is the most economical "approach" or difference in temperature between the incoming cooling medium and the outgoing heating medium. The maximum recovery of heat occurs if these two streams are at the same temperature, but in practical heat-exchange equipment a difference in temperature must exist. Some of the factors that affect the smaller temperature difference or the so-called approach are

1. Difference in temperature at the hot-end—A large temperature difference at the hot-end of the exchanger allows a smaller approach on the cold-end (or vice versa).
2. The transfer rate—At high transfer rates, the surface required to recover heat is less, so that a closer approach is economical. Except in extreme cases the effect of transfer rate on the economical approach is small.
3. Value of fuel and cost of surface—High fuel prices and cheap surface costs allow a closer approach. The effect of surface cost is important but in the refinery the value of fuel remains almost constant.
4. Time to depreciate equipment—If the depreciation of the equipment is spread over many years, the economic approach is smaller.
5. The relative quantities of the two fluids—If the quantity of one of the fluids is small compared with the quantity of the other, a closer approach is economical. This is also involved in 1.

These variables may be combined in a mathematical expression such as

$$S = 7{,}700C_f - \frac{500{,}000C_s(2 + IY)}{YH\theta} - C_e \qquad (89)$$

where S = net saving, dollars per year when absorbing a million B.t.u. per hr.

C_f = value of heat, dollars per million B.t.u.

C_s = cost of equipment, dollars per sq. ft. of surface.

C_e = cost of repairs and cleaning.

Y = years to depreciate the investment.

I = interest rate divided by 100.

H = transfer rate.
θ = log mean temp. diff.

For the following values $C_f = \$0.15$; $C_s = \$3.00$; $Y = 6$; $I = 0.06$; and $H = 50$; and neglecting the cost of upkeep, the equation takes this simple form:

$$S = 1{,}158 - \frac{11{,}800}{\theta} \tag{90}$$

The most economical approach can be computed for an exchanger by setting up several sets of conditions and computing the net savings as shown in Example 86. The upkeep cost C_e is an important factor and one that should not be overlooked, but it does not have a great effect on the most economical approach.

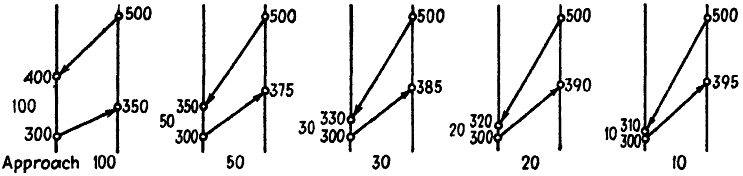

FIG. 179.—Approaches for Example 86.

Example 86. Most Economical Approach for Exchanger.—A countercurrent-flow exchanger is to handle one part by weight of a hot fluid at 500°F. and two parts by weight of a fluid at 300°F. What is the most economical approach if the variables are described by Eq. (90)?

$$\text{Savings, dollars per year per million B.t.u.} = 1{,}158 - \frac{11{,}800}{\theta}$$

Repeat, except that the cost of the surface is \$6 per square foot. The equation then becomes $1{,}158 - \frac{23{,}600}{\theta}$. This is exactly equivalent to lowering the transfer rate to 25 if C_s is still \$3 (see Fig. 179 for the approaches).

Assume that the specific heats of the two materials are equal.

Basis: 1 year of operation, and 1,000,000 B.t.u. absorbed per hour when the approach is 100°F.

Approach, °F.	Saving per million, \$3 surface	Relative No. of B.t.u. transferred	Actual savings, \$3 surface	Actual savings, \$6 surface
100	1,062	1	1,062	966
50	1,014	1.5	1,520	1,300
30	971	1.7	1,650	1,330*
20	931	1.8	1,670*	1,270
10	866	1.9	1,640	1,090

* Maximum saving.

Several curves, computed as in Example 86, are shown in Fig. 180. The curves are not plotted against the same cost scale, and hence they are not comparable except as a means of comparing the most economical approach. They were all computed for the conditions that were used in Eq. (90), except for the variations as shown in the tabulation below Fig. 180. In Fig. 180, curves 1 and 2 (also 5 and 6) may be compared for the effect of surface costs; curves 3 and 4 for effect of relative temperature difference

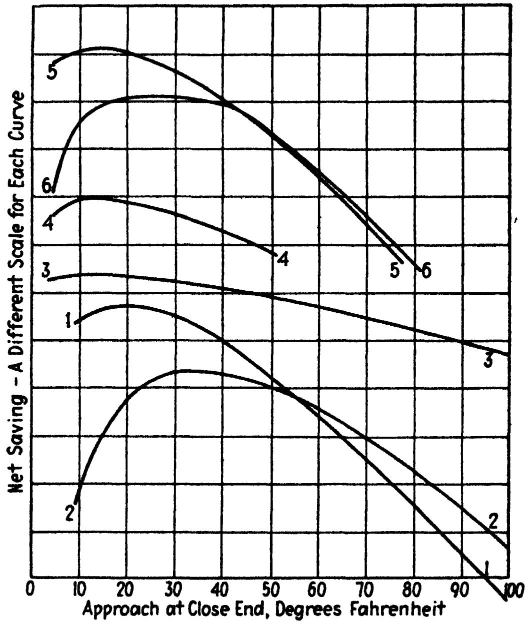

FIG. 180.—Most economical approach temperatures for exchangers. The conditions are:

Curve	Conditions	Temperature, °F.		Quantities by wt.		Economical* approach, °F.
		Hot fluid	Cold fluid	Hot fluid	Cold fluid	
1	None changed	500	300	1	2	20
2	Surface $6 per sq. ft.†	500	300	1	2	35
3	None changed	800	100	1	4	10
4	None changed	800	400	1	4	13
5	Depreciation in 2 years	800	400	1	4	15
6	Depreciation in 2 years, surface $6	800	400	1	4	25

* The cost for upkeep is not included in the depreciation time.

† Equivalent to an *H* of 25, if C_s is $3.00.

at hot-end; and curves 4 and 5 for rate of depreciation (current upkeep not included).

The over-all economy of installing exchangers involves other parts of the plant equipment as well as the exchangers themselves. If exchangers are installed in conjunction with a pipestill, a smaller still may be required because less heat is absorbed in the still, but the flue gases will leave at a higher temperature and hence more heat will be lost in the gas. At the same time, less cooling surface and less cooling water will be required for the condensers and coolers of the plant, because the products are partly cooled by heat-exchange. The particular amount of heat-exchange that is economical may be determined by comparing the total costs of absorbing heat in the pipestill and exchangers, and then removing it again in the coolers. Costs of generating heat in a 20,000,000-B.t.u. simple pipestill distillation unit are approximately as follows:

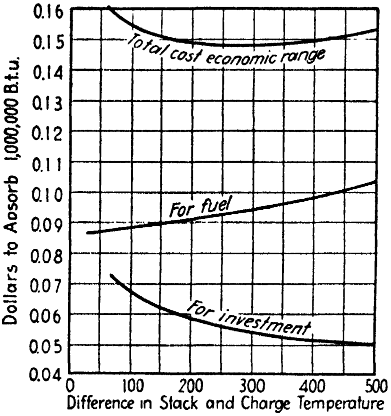

FIG. 181.—Most economical stack-gas temperature for a pipestill.

Pipestill	Cents per million B.t.u.	Saving, dollars per year
Without exchangers	23	
With exchange to 300°F.	17.3	7,220
With exchange to 500°F.	14	13,820
With exchange to 550°F.	14.6	13,200

In this particular case it is not economical to heat the oil by exchangers to a temperature higher than 500°F.

Flue-gas Approach in Pipestills.—In general, the efficiency for a pipestill should not be so high as for a boiler. Oil is usually at 300 to 500°F. before it enters the pipestill but the feed-water for a boiler may enter the economizer at a temperature as low as 60°F. Thus a pipestill operates most economically at an efficiency of 70 to 75 per cent but a boiler may operate at 80 to 85 per cent.

The flue gases should leave the pipestill at a temperature about 300°F. higher than the charge-stock temperature. A closer approach requires a much larger convection section, and a larger approach allows such a large heat loss to the stack that the expenses again rise. These relations are illustrated in Fig. 181. The figure was computed for a radiant type of pipestill absorbing about 10,000,000 B.t.u. per hour, fuel cost 40 cts. per barrel, and depreciation in 6 years at an interest rate of 6 per cent.

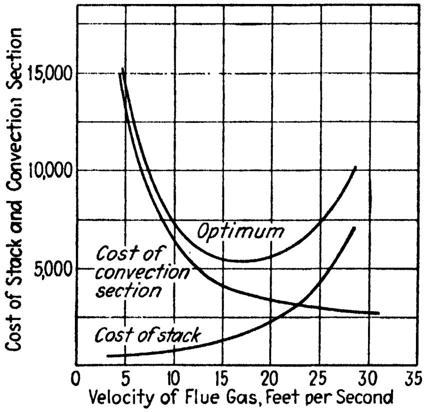

Fig. 182.—Most economical flue-gas velocity in convection section of pipestill.

Although a saving of ½ ct. per million B.t.u. does not sound large, it amounts to about 3.5 per cent of the cost of generating heat and for a 20,000,000 B.t.u. still amounts to $1,500.00 per year.

The optimum velocity for flue gases in the convection section of a still can be computed in a similar manner. As the velocity is increased, the surface in the convection section becomes smaller but the friction loss becomes greater, and a taller stack must be provided. These factors affect the cost of the convection section and stack as indicated in Fig. 182.

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CHAPTER XXVII

TYPICAL DESIGN CALCULATION

The design of petroleum equipment is complicated by the complex composition of petroleum oils. Many features of a design defy exact computation and such cases must be met by the judgment and experience of the design engineer. The factors of judgment and experience cannot be completely eliminated and hence the success of the design depends, to a large degree, upon the experience of the designer.

These are the facts concerning the design of petroleum equipment. However, successful equipment can be designed, even though the calculations are not perfect, because a well-designed plant can be operated to overcome the inadequacies in the design information.

Outline of Computations.—In this chapter, a continuous pipestill topping plant will be designed. A more complicated plant would be more interesting to many engineers, but the calculations would be so involved that they would be almost useless to most readers.

TABLE 88.—YIELDS AND PROPERTIES OF PRODUCTS

Material	Per cent	A.P.I.	Notes
Loss*	0.5	....	About 7 cu. ft. of gas per bbl. (Table 74)
Gasoline	31.0	60.2	A.S.T.M. end-point about 392 (Fig. 28)
Kerosene	10.0	43.0	A.S.T.M. end-point about 493 (Fig. 28)
Gas oil	26.0	34.9	By difference
Reduced crude	32.5	22.5	Viscosity at 210°F., about 107 (Fig. 183)
Crude oil	100.0	38.6	Fig. 183

* Consider as a gas which has a molecular weight of 45.

The Mid-Continent crude oil shown in Fig. 183 is to be topped for the production of gasoline, kerosene, gas oil, and reduced crude oil, as shown in Table 88.

Obviously, the selection of products depends upon the market demands and sales opportunities that are available. Although products having particular specifications must be produced in the unit, the designer has little need for more detailed specifications than the general information which is given in Table 88. However, the designer can build a flexible plant and thus permit the plant operator to produce any reasonable specifications that may be desired.

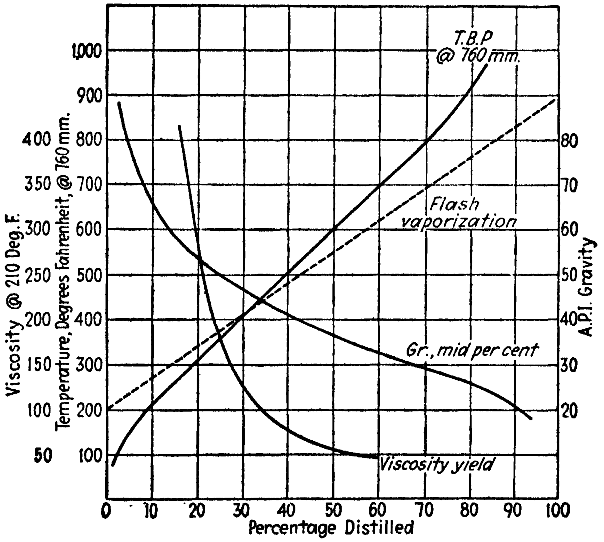

FIG. 183.—Mid-Continent crude oil—38.6 A.P.I.

The design computations can be organized somewhat as follows:

1. Obtain a list of the desirable products from the plant management or the marketing department.
2. Obtain a comprehensive laboratory evaluation of the stock. An analysis, such as shown in Fig. 183, is satisfactory, but if possible the desired products should be produced in the laboratory and examined by routine tests. This is not always convenient because many combinations of products may be contemplated.

3. Analyze the evaluation curves of the stock for the yields of products and if possible produce and examine the products in the laboratory (Chaps. V, VI, VII and IX).
4. Prepare a table of the quantities, weights, and oft-used properties of the several stocks (Table 89).
5. Prepare a tentative flow-diagram of the process. This may be modified as the design progresses to meet unforeseen conditions (Fig. 184).
6. Design the fractionating tower, determining tower temperatures and diameter.
7. Design heat-exchange system by an economic study of each exchanger. Compute the temperature of the stock as it arrives at the pipestill.
8. Design the pipestill.
9. Design the condensers, coolers, stripper, etc.
10. Estimate steam, water, and power requirements.

In a complete computation of this kind, many figures are used over and over again in the computations. Time and confusion may be avoided by tabulating these figures, as in Table 89, at the start of the work.

TABLE 89.—USEFUL QUANTITIES AND PROPERTIES
2,000 bbl. per day

Material	Per cent	A.P.I.	Lb. per gal.	Gal. per hr.	Lb. per hr.	50 per cent boiling-point, °F.	Mol. wt.†
Loss	0.5	....	0.119*	17	70‡	...	45
Gasoline	31.0	60.2	6.14	1,085	6,660	258	109
Kerosene	10.0	43.0	6.75	350	2,360	460	178
Gas oil	26.0	34.9	7.08	910	6,450	635	260
Reduced crude	32.5	22.5	7.65	1,138	8,710		
Crude	100.0	38.6	6.93	3,500	24,250		

* Density, pound per cubic foot at 60°F.

† Fig. 38.

‡ $\frac{2,000 \times 7}{379} \times \frac{45}{24} = 70.$

The general conditions are as follows:

Capacity	2,000 bbl. per day
Temperature of crude oil	90°F. (ave.)
Temperature of cooling water	75°F. (ave.) to 95°F. (max.)

Steam pressure	150 lb. per sq. in. gage; saturation temp., 366°F.
Corrosion	The crude is classed as a sweet oil and contains only 0.1 per cent of sulfur

The flow-diagram of the process is shown in Fig. 184. This diagram shows only the major items of equipment and it is not intended to indicate anything concerning the size or mechanical design of the equipment.

FRACTIONATOR SYSTEM

The design of the fractionation system may be outlined as follows:

1. Draw the flash-vaporization curve of the crude oil unless this curve is included in the laboratory analysis (Figs. 75 and 76).
2. Estimate the amount of steam that is required for stripping.
3. Estimate the temperatures and pressures at all important points in the tower. Adopt the number of plates to be used between cuts (page 467).
4. Compute a heat-balance and determine the amount of reflux.
5. Compute the diameter of the tower.

The flash-vaporization curve was computed as follows (Figs. 76 and 183):

70 per cent on T.B.P. curve = 788°F.
10 per cent on T.B.P. curve = 204°F.

584°F.

Slope of T.B.P. curve = $\frac{584}{60}$ = 9.73
Slope of flash curve (Fig. 76) = 7.0
50 per cent on T.B.P. = 598°F.
50 per cent on flash curve (Fig. 76) = 550°F.
100 per cent on flash curve = $550 + 50 \times 7 = 900$°F.
0 per cent on flash curve = $550 - 50 \times 7 = 200$°F.

This curve is plotted as a straight-line vaporization curve in Fig. 183. With freak stocks, the curvature of the flash curve should be computed as explained in Example 46.

The amount of steam that will be required to strip the kerosene, gas oil, and reduced crude oil can be estimated from the figures given on page 358. Table 90 summarizes the steam quantities.

TABLE 90.—STEAM FOR STRIPPING

Material	Lb. steam per gal.	Gal. per hr. of material	Lb. steam per hr.
Kerosene	0.3	350	105
Gas oil	0.5	910	455
Reduced crude	0.5	1,138	569
Total	...	.....	1,129

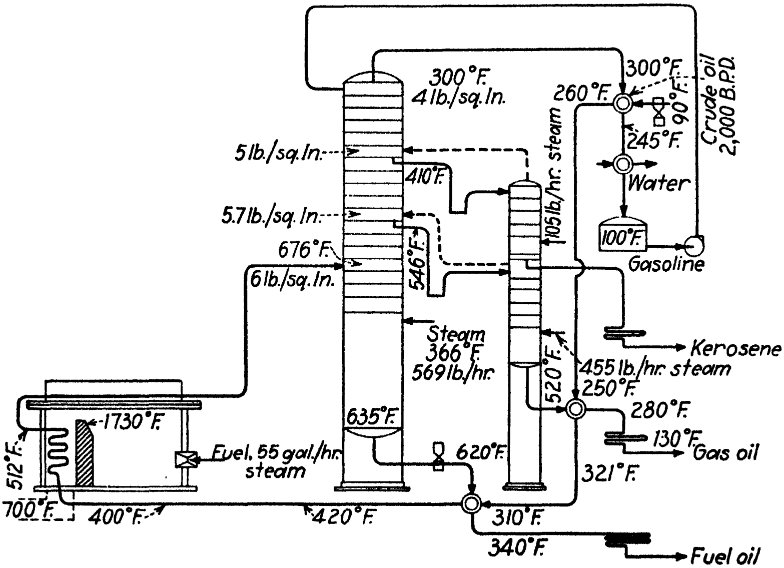

FIG. 184.—Diagram of topping plant.

The number of plates can be estimated from the tabulation on page 467. The following number of plates will be used:

	No. of Plates
Gasoline to kerosene	6
Kerosene to gas oil	5
Gas oil to vaporizer	3
No. of plates above vaporizer	14
Stripping plates	4
Total No. of plates	18

The pressure at the top of the topping tower is seldom more than 4 lb. per square inch gage. The pressure-drop per plate is discussed on page 455. The pressures in the tower and the amount of steam at various points will be approximately as follows:

Position	Pressure,* lb. per sq. in.	Lb. steam
At top plate	4	1,129
At kerosene plate	5	1,024
At gas oil plate	5.7	569
At vaporizer	6.1	569

* Top velocity approximately 2.5 ft. per second (see computed velocity, page 615).

Vaporizer Temperature.—The vaporizer temperature, as obtained from the flash curve at 760 mm., must be corrected for the tower pressure and for the effect of steam. The gasoline, kerosene, gas oil, and loss amount to 67.5 per cent.

Vaporizer temperature at 760 mm. (flash curve) ...... 670°F.

Pressure at vaporizer ..... $760 + \frac{6.1}{14.7} \times 760 = 1{,}075$ mm.

Mols of gasoline (Table 89) .... $\frac{6{,}660}{109} = 61.1$

Mols of kerosene .... $\frac{2{,}360}{178} = 13.3$

Mols of gas oil .... $\frac{6{,}450}{260} = 24.8$

Total mols vapor .... = 99.2

Mols steam .... $\frac{569}{18} = 31.6$

Total mols vapor and steam 130.8

Partial-pressure of oil $= \frac{99.2}{130.8} \times 1{,}075 = 815$ mm.

Vaporizer temperature at tower conditions, by correcting 670°F. to 815 mm. by means of Fig. 45, is 676°F.

Tower Temperatures.—This tower, the stock that is being processed, and the quantities of steam are normal. Under these conditions, the side-draw temperatures may be estimated from Fig. 142. In cases in which the conditions are not normal, the method outlined in Example 72 must be used.

The tower temperatures and corresponding latent heats are approximately as follows:

	°F.	Latent heat†
Top temperature	300*	123
Kerosene drawplate	410	109
Gas oil drawplate	546	92
Bottoms product	635	

* Check later (see page 614).

† Table 8.

The bottoms temperature cannot be estimated as accurately as the other temperatures. However, it is not of great importance because it does not properly belong in the tower balance and is only included in the tower balance as a factor of safety. Most of the cooling of the bottom material in the tower is caused by these factors:

1. Vaporization of a part of the bottoms by steam.
2. Heat losses through the tower shell.
3. Heat used to raise or lower the temperature of the steam.

Table 32 (page 261) indicates that the liquid material from the vaporizer contains about 10 per cent of material that boils below the flash temperature. The vaporization of this 10 per cent of material uses some heat but the greater part of the cooling is due to the other two factors. The cooling due to vaporization can be computed by balancing the heat of vaporization against the sensible heat loss which it causes; the cooling (or heating) due to steam may be computed by a heat-balance; and the cooling due to losses through the walls of the tower can be computed by the resistance theory as given in Examples 36 and 39. For this tower, the cooling of the bottom product is approximately as follows:

	°F.
Due to vaporization	12
Due to heat losses	13
Due to heating of steam	15

Thus the *bottoms temperature* is approximately 636°F.

HEAT-BALANCE OF TOWER

Temperature datum, vaporizer temperature or 676°F. (Figs. 33 and 34)

		B.t.u. per Hr.
Cooling gaso. (vap.)	6,660(676 − 300)0.59 =	1,480,000
Cooling kero. (vap.)	2,360(676 − 410)0.6 =	376,000
Cooling gas oil (vap.)	6,450(676 − 546)0.63 =	530,000
Cooling reduced crude* (liq.)	8,710(676 − 635)0.77 =	275,000
Cooling steam*	1,129(366 − 300)0.5 =	37,000
Total sensible heat		2,698,000
Condense kero.	2,360 × 109 = 258,000	
Condense gas oil	6,450 × 92 = 593,000	
Total latent heat	851,000 =	851,000
Reflux heat		3,549,000

* Actually, these heats have already been accounted for in computing the bottoms temperature, but most designers include them as a factor of safety. If they are not included, then the bottoms temperature should be considered as 676°F. and the steam temperature as 676, 410, and 546°F. for the amount of steam that enters the system at the vaporizer, kerosene plate, and gas oil plate respectively.

With the reflux available at 100°F., the amount of cold reflux per hour is

$$\text{Lb. cold reflux} \ldots\ldots\ldots \frac{3{,}549{,}000}{123 + (300 - 100)0.58} = 14{,}850$$

$$\text{Gal. cold reflux} \ldots\ldots\ldots \frac{3{,}549{,}000}{239} \times \frac{1}{6.14} = 2{,}420$$

$$\text{Gal. cold reflux per gal. product} \ldots\ldots\ldots \frac{2{,}420}{1{,}085} = 2.23$$

Check on top temperature:

$$\text{Mols reflux and product} \ldots\ldots \frac{14{,}850 + 6{,}660}{109} = 197$$

$$\text{Mols steam} \ldots\ldots\ldots \frac{1{,}129}{18} = 63$$

$$\text{Total mols} \ldots\ldots\ldots 260$$

$$\text{Partial-pressure} \ldots\ldots \frac{197}{260} \times \left(760 + \frac{4 \times 760}{14.7}\right) = 732 \text{ mm.}$$

The 100 per cent point on the flash-vaporization curve of the gasoline is approximately 315°F. When corrected to 732 mm., the temperature is about 312°F. However, by Table 61 the computed top temperature is usually about 3 per cent high. Hence the top temperature would be 312 × 0.97 = 302°F. The assumed top temperature was 300°F. and this is a satisfactory check.

Diameter of Tower.—The allowable mass velocity of the vapors at the top of the tower can be computed from Eq. (69). The constant C can be obtained from Fig. 146. At a tray spacing of 22 in., which allows a manhole on each tray, the value of C is about 590.

The density d_1 of the gasoline at 300°F. may be obtained from Fig. 39:

$$\begin{aligned} \text{Sp. gr. at } 60 &= 0.738 \\ \text{Sp. gr. at } 300 &= 0.632 \\ d_1 = 0.632 \times 62.4 &= 39.4 \text{ lb. per cu. ft.} \end{aligned}$$

The density d_2 of the vapor at 300°F. and 4 lb. gage will be computed by the perfect gas laws:

		Mols	Lb.
Internal reflux	$\dfrac{3{,}549{,}000}{123 \times 109} =$	264.7	28,800
Gasoline product	=	61.1	6,660
Steam	$\dfrac{1{,}129}{18} =$	62.7	1,129
Total at top		388.5	36,589

$$\text{Volume at top} = 388.5 \times 379 \times \frac{760}{520} \times \frac{14.7}{18.7} = 169{,}000 \text{ cu. ft. per hr.}$$

$$d_2 = \frac{36{,}589}{169{,}000} = 0.216 \text{ lb. per cu. ft.}$$

$$\text{Mass velocity } W = 590\,[0.216(39.4 - 0.216)]^{0.5} = 1{,}720 \text{ lb. per sq. ft. per hr.}$$

Cross-sectional area of tower	$\dfrac{36{,}589}{1{,}720} =$	21.2 sq. ft.
Factor for overcapacity		2.5
Area used		23.7 sq. ft.

Use a diameter of 5 ft. 6 in.

This corresponds to a linear velocity of $\dfrac{169{,}000}{23.7 \times 3{,}600} = 1.98$ ft. per sec.

HEAT-EXCHANGE SYSTEM

The number of products that may be used to heat the charge-stock is an economic problem. It usually pays to install condensing exchangers for the overhead product and reflux, because of the large quantity of heat that is available in these materials and because the transfer rate is relatively high in condensing equipment. In the case of kerosene, an exchanger may not be economical because the kerosene stream is small and the cost per unit of surface rises. Heat exchangers are usually used on the gas oil stream and other high-boiling distillate streams because of the high temperature. The same holds true for the bottoms product, except that the viscosity may be so high that an exchanger is not economical and because such stocks often contain suspended solid matter. Bottoms exchangers are not usually used for viscous stocks unless a pump is provided for the bottoms product.

In general, the exchangers are purchased from manufacturing companies and these companies are asked to design the exchange-system. However, the plant engineer must not depend entirely on the computations from these manufacturers. For this reason, the following approximate design of the heat-exchange system, is suggested.

The feed-stock should be routed through the exchangers as follows:

1. Gasoline and reflux condenser exchanger.
2. Kerosene exchanger.
3. Gas oil exchanger.
4. Reduced crude exchanger.

The temperatures in these exchangers will be developed during the computations and are shown in Fig. 185.

Gasoline Condensing Exchanger.

Lb. of gasoline and reflux = 14,850 + 6660 = 21,510
Lb. of steam = 1,129

Using an approach of 40°F. on the hot end of the exchanger, the heat that can be absorbed is

$$24{,}250(260 - 90)0.52 = 2{,}140{,}000 \text{ B.t.u. per hr.}$$

This amount of heat will condense about half of the gasoline and reflux and require an outlet temperature, for the gasoline, of about 245°F.

A check on the amount of heat that is removed follows:

Cool half of vapor and the condensate from it	$\frac{21,510}{2}(300 - 245)\frac{0.63 + 0.48^*}{2} =$	331,000
Cool vapor that does not condense	$\frac{21,510}{2}(300 - 245)0.475 =$	281,000
Cool steam	$1,129(300 - 245)0.5 =$	31,000
Condense half of vapor	$\frac{21,510}{2} \times 128 =$	1,380,000
		2,023,000

* Average specific heat of vapor and liquid.

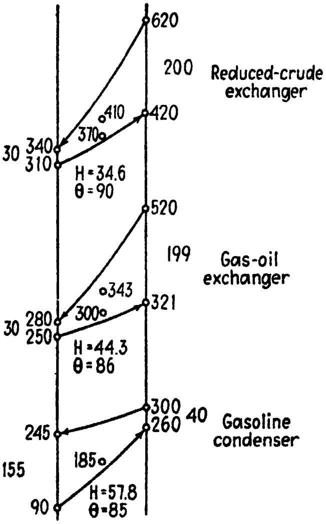

FIG. 185.—Temperatures in heat-exchange system.

This check is sufficiently close.

Transfer Coefficients.—The crude oil will pass through the tubes, and a velocity of 4 ft. per second will be possible because of the pressure that is available.

The average film-temperature of the crude oil will be about 185°F. The viscosity of the crude oil, at this temperature is about 1.2 (Fig. 49). Film transfer rate for crude oil, in 1-in. tubes, is about 240 (Fig. 122).

The gasoline, reflux, and steam will be cooled on the outside of the tubes. The condensing coefficient will be about 140 (Table 50).

The approximate fouling conditions are as follows:

Crude oil in tubes	5.0 (Fig. 125)
Gasoline in shell	1.0
Total fouling factor	6.0

Over-all Coefficient.

$$H = \frac{1}{\frac{1}{240} + \frac{1}{140} + 0.006} = \frac{1}{0.0173} = 57.8$$

Larger temp. diff. = about 155
Smaller temp. diff. = about 40
Log mean temp. diff. (Fig. 67) = 85°F.

$$\text{Surface} = \frac{2{,}140{,}000}{85 \times 57.8} = 435 \text{ sq. ft.}$$

Factor for overcapacity = 55 sq. ft.

Use 490 sq. ft.

Kerosene Exchanger.—This exchanger may not be economical because of the small amount of kerosene and because the crude oil is now at about 260°F. The crude oil will be cooled a little between exchangers, and the kerosene will be cooled a little by the stripper.

Oil	Lb.	Approx. temp.
Kerosene	2,360	385
Crude	24,250	250

An approximate design was made, showing that the exchanger would be very small and would cost about $400. It would hardly pay for itself in two years and this, along with its small size, indicates that it would not be a good investment.

Gas Oil Exchanger.

Oil	Lb.	Approx. temp. after stripper, etc.
Gas oil	6,450	520
Crude	24,250	250

Using an approach of 30°F., the amount of heat that is exchanged is about as follows:

$$6{,}450(520-280)0.645 = 24{,}250(321-250)0.58 = 1{,}000{,}000 \text{ B.t.u.}$$

Gas oil Crude oil

log mean temp. difference = 89°F.
The transfer-rate conditions will be about as follows:

Oil	Approx. film. temp.	Viscosity*	Side	Approx. velocity	Film rate†	Fouling factors
Gas oil.........	343	0.85	Shell	1	74	2
Crude..........	300	0.6	Tube	4	325	4

* Fig. 49.
† Figs. 122 and 123.

$$H \text{ for gas oil exchanger} = \frac{1}{\frac{1}{74} + \frac{1}{325} + 0.006} = 44.3$$

$$\text{Surface} = \frac{1{,}000{,}000}{89 \times 44.3} = 254 \text{ sq. ft.}$$

$$\text{Factor for overcapacity} = 36$$

Use 290 sq. ft.

Bottoms Exchanger.

Oil	Lb.	Approx. temp.
Reduced crude......	8,710	620
Crude.............	24,250	310

Many plant men contend that bottoms exchangers give more trouble than they are worth. If the bottoms stock is dirty or the exchanger is not periodically cleaned, then this is doubtless true, but under proper conditions and with careful supervision bottoms exchangers can be successfully used. In this case a bottoms exchanger would doubtless be justified.

Using an approach of 30°F., the duty of the exchanger would be

$$8{,}710(620-340)0.69 = 24{,}250(420-310)0.627 = 1{,}680{,}000 \text{ B.t.u.}$$

Reduced crude oil Crude oil
log mean temp. diff. (Fig. 67) = 90°F.

The transfer-rate conditions will be about as follows:

Oil	Approx. film temp., °F.	Viscosity	Side	Approx. velocity	Film rate	Fouling factors
Reduced crude...	410	2.3	Shell	2*	74	10
Crude..........	370	0.4	Tube	4	365	3
						13

* Pump on reduced crude oil.

$$H = \frac{1}{1/74 + 1/365 + 0.013} = 34.3$$

If the reduced crude oil were not handled by a pump, the overall rate would be only about 26.

$$\text{Surface} = \frac{1,680,000}{90 \times 34.3} = 545 \text{ sq. ft.}$$

$$\text{Factor for overcapacity} = \underline{\ 75\ }$$

Use 620 sq. ft.

Water Coolers and Condensers.—The design of these equipments is much the same as for the exchangers and hence only one cooler, the gas oil cooler, will be designed. A tubular type of cooler will be used.

The gas oil is available at 280°F. from the exchanger and it will be cooled a few degrees in the transfer line. However, the cooling will be neglected and considered as a further factor of safety. The flash-point of the gas oil will be above 160°F. and hence it need not be cooled to lower than about 130°F. The water will be sent through the tubes. It will not be heated to over 125°F. because scale may be deposited.

Duty of Gas Oil Cooler.

$$\underset{\text{Gas oil}}{6,450(280 - 130)0.53} = \underset{\text{Water}}{W(125 - 95)1.0} = 512,000 \text{ B.t.u.}$$

$$W = \text{lb. water} = 17,100$$

$$\text{Gal. water} = \frac{17,100}{8.33} = 2,055 \text{ gal. per hr.}$$

Transfer-rate conditions will be as follows:

	Approx. film temp.	Vis-cosity	Side	Approx. velocity	Film rate*	Fouling factor
Gas oil..........	165	3.7	Shell	1	41	4
Water..........	...	...	Tube	5	610	3

* Fig. 123 and Table 49.

$$H = \frac{1}{\frac{1}{41} + \frac{1}{610} + 0.007} = 30.3$$

$$\text{log mean temp. diff.} = 81$$

$$\text{Surface} = \frac{512{,}000}{30.3 \times 81} = 209 \text{ sq. ft.}$$

$$\text{Factor of overcapacity} = \underline{\ 21\ }$$

Use 230 sq. ft

PIPESTILL HEATER

The crude oil will arrive at the pipestill at a temperature of about 410°F. It must be heated to a temperature sufficiently high to vaporize, by flash vaporization, 67.5 per cent of the crude oil. This requires a temperature of about 676°F. at the vaporizer at a pressure of 6.1 lb. per square inch absolute (page 612).

The temperature at the outlet of the still will be somewhat higher than 676°F. because of the adiabatic vaporization that occurs in the transfer line to the tower. The outlet temperature can be computed with fair accuracy but the outlet temperature is not important and in this case it will not be computed.

Pipestill Duty.—In computing the heat that will be absorbed in the pipestill, it is not necessary to know the pressure in the still or the outlet temperature, because the same amount of heat is required by any route, if the initial and final conditions are the same for each route (Examples 9, 31, and 32).

Assume that vaporization of the products occurs at the following arbitrary temperatures because the heat data are most accurate at these conditions and because some of the heat quantities have already been computed. However, the latent heats must be picked accordingly.

Oil	Temperature, °F.	Latent heat (Table 8)
Gasoline	410	106
Kerosene	410	109
Gas oil	546	92

			B.t.u. Per Hr.
Sensible heat:			
Gas*	70(676 − 410)0.68	=	12,600
Gasoline (vap.)	6,660(676 − 410)0.615	=	1,090,000
Kerosene (vap.)	2,360(676 − 410)0.6	=	376,000
Gas oil (liq.)	6,450(546 − 410)0.69	=	605,000
Gas oil (vap.)	6,450(676 − 546)0.628	=	527,000
Reduced crude	8,710(676 − 410)0.7	=	1,620,000
Total sensible heat			4,230,600
Latent heat:			
Gasoline	6,660 × 106 =	706,000	
Kerosene	2,360 × 109 =	258,000	
Gas oil	6,450 × 92 =	594,000	
Total latent heat		1,558,000 =	1,558,000
Total pipestill duty			5,788,600

* Consider the gas as a 150 A.P.I. material in estimating specific heat.

Heat-balance of Still.—The approach between the temperature of the stack gas and the temperature of the feed-stock should be about 290°F. (Fig. 181). The stack gas temperature would then be 410 + 290 or 700°F.

The furnace could be fired with 25 per cent excess air but general operation is nearer 40 per cent excess air. With this amount of excess air and burning some of the reduced crude oil as a fuel, the loss due to the temperature of the stack gases amounts to about 18 per cent (Fig. 57).

The heating operation is not a difficult one and hence the radiant section can be designed for a radiation factor of 0.45 (Table 55). This corresponds to a radiant-absorption rate of about 30,000 B.t.u. per square foot of projected area per hour (Fig. 133).

The losses through the walls, etc., of the still amount to about 3 per cent from the radiant section and 2 per cent from the convection section (Table 57).

The efficiency of the still is 100 − 18 − 5 = 77 per cent.

The heat-balance of the furnace is about as follows:

Heat quantity	Per cent of net H.V.	Heat, B.t.u. per hr.
Heat input	100	7,510,000
Wall losses	5	376,000
Stack loss	18	1,350,000
Radiant absorption	45	3,380,000
Convection absorption (by diff.)	32	2,404,000

Convection-section.—If all of the gasoline is vaporized in the convection-section, the oil is at approximately 512°F. as it leaves the convection-section:

$$6660 \times 106 + 24{,}250(x - 410)0.685 = 2{,}404{,}000$$

$$x = 512°\text{F.}$$

The flue gas that enters the convection-section still contains 100 − 45 − 3 or 52 per cent of the net heating value of the fuel. Figure 57 shows that the temperature of the gas at the bridgewall will be approximately 1,730°F. The furnace temperature that is recorded in plant operation is lower than this, but it is usually measured at another point.

$$\text{Larger temp. diff.} = 1{,}730 - 512 = 1{,}218$$

$$\text{Smaller temp. diff.} = 700 - 410 = 290$$

$$\text{log mean temp. diff.} = \frac{1{,}218 - 290}{\ln \dfrac{1{,}218}{290}} = 646°\text{F.}$$

The convection section will be designed for an average flue-gas velocity of 15 ft. per second. With tubing that has an outside diameter of 4 inches, and with an average flue-gas temperature of about 1120°F., the over-all convection coefficient is about 7.3 (Table 56).

$$\text{Convection surface} = \frac{2{,}404{,}000}{7.3 \times 646} = 510 \text{ sq. ft. outside surface}$$

$$\begin{array}{ll} \text{Factor for overcapacity} & \underline{\ 60} \\ & \text{Use } 570 \text{ sq. ft.} \end{array}$$

Radiant Section.

$$\text{Radiant surface} = \frac{3{,}380{,}000}{30{,}000} = 113 \text{ sq. ft. projected area}$$

$$\begin{array}{ll} \text{Factor for overcapacity} & = \underline{17} \\ & \text{Use } 130 \text{ sq. ft.} \end{array}$$

In computing the tube diameters, the data given in Chap. XX will be useful. However, the tube layout and structural design of the still will not be given herein because these details are too complicated to be presented in a discussion of this kind.

Fuel Required.—The net heating value of a 22.5 A.P.I. fuel is about 17,800 B.t.u. (Fig. 55 and Table 23).

Fuel

$$\frac{7{,}510{,}000}{17{,}800} = 422 \text{ lb. per hr.}$$

or

$$\frac{422}{7.65} = 55 \text{ gal. per hr.}$$

One burner could be used, but two small ones would be more satisfactory.

Steam for atomizing (Fig. 59),

$$422 \times 0.3 = 127 \text{ lb. per hr.}$$

WATER REQUIRED

The several products leave the coolers at almost the same temperature as the crude oil enters the plant and hence the heat that must be removed by cooling water is almost equal to the heat that is added to the oil in the pipestill. When the water is at its maximum temperature of 95°F.,

$$\text{Approx. gal. of cooling water} = \frac{5{,}788{,}600}{(125 - 95)8.33} = 23{,}200 \text{ gal. per hr.}$$

This is a maximum figure because some of this heat is lost through the insulation of the equipment.

STEAM REQUIRED

Reciprocating steam pumps would be used for the charge-stock and the reduced crude oil. The steam required for these pumps would be guaranteed by the pump manufacturers but simple approximations can be had, as follows:

The charge pump will operate at a pressure sufficiently high to force the oil through the exchangers, the pipestill, and into the fractionating tower. The charge-pressure will be about 160 lb. per square inch gage. The charge-pressure could be computed as in Example 50 (see also page 431).

A simple manner of getting the steam consumption of a pump is to consider that the volume of oil that is pumped is the same as the volume of steam that is required if the pressures are the same, and except for the inefficiency of the pump. If the pressures are not the same, then the volume of steam that is used will be inversely proportional to the pressure. In this manner, the approximate steam consumption at an over-all efficiency of 50 per cent is

The specific volume of 150-lb. gage pressure steam is 2.76.

$$\frac{3{,}500}{7.5} \times \frac{160}{150} \times \frac{1}{0.5} \times \frac{1}{2.76} = 360 \text{ lb. per hr.}$$

In a similar manner the steam required for the bottoms pump, when pumping at 40 lb. per square inch, is about

$$\frac{1{,}138}{7.5} \times \frac{40}{150} \times \frac{1}{0.45} \times \frac{1}{2.76} = 32.5 \text{ lb. per hr.}$$

Approximate Steam Requirements

	Lb. per hr.
For pumps	382
For stripping (process steam)	1,129
For burners	127
Total	1,638

With the feed-water at 130°F. and with saturate 150 lb. gage steam, the boiler horsepower corresponding to 1,638 lb. per hour is about 54.

Summary.—The design as herein presented is inadequate in many respects. However, each design depends greatly upon the particular plant conditions that are encountered and upon a multitude of practical details. These details cannot be presented without becoming involved in a hopelessly tedious discussion and one that would be uninteresting to most readers.

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SUBJECT INDEX