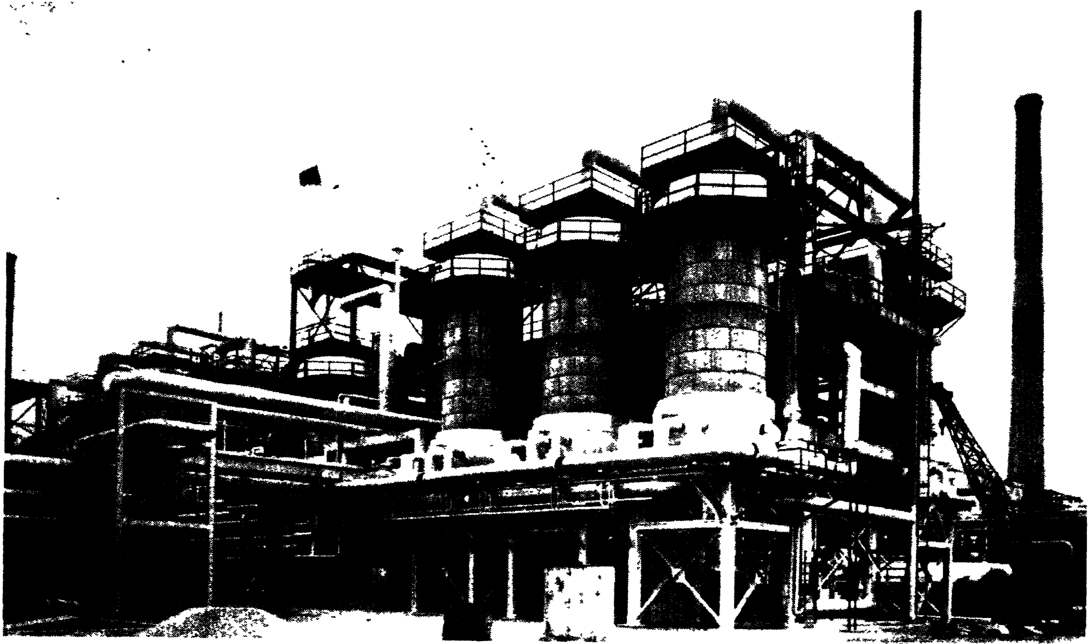


Courtesy Socony-Vacuum Oil Co

A Houdry Catalytic Cracking Plant.

THE AMAZING PETROLEUM INDUSTRY

By

V. A. KALICHEVSKY
RESEARCH AND DEVELOPMENT LABORATORIES, SOCONY-VACUUM OIL CO., INC., AUTHOR OF "MODERN METHODS OF REFINING LUBRICATING OILS," CO-AUTHOR OF "CHEMICAL REFINING OF PETROLEUM"

REINHOLD PUBLISHING CORPORATION
330 WEST FORTY-SECOND ST., NEW YORK, U. S. A.
1943

Printed in the United States of America by
HADDON CRAFTSMEN, INC., SCRANTON, PA.

Preface

Petroleum is one of the basic commodities which enters into our everyday life. Millions of people depend directly or indirectly on the "flowing gold" of the world, and nations are waging bitter wars for rich oil fields vital to their existence. Thousands of chemists and engineers devote their entire lifetime to petroleum research in order to improve our living standards; as a result of their work, thousands of useful substances have been made available to the public. Thus the petroleum industry has become highly specialized.

This book has been written in answer to the demand for a brief popular outline of the existing petroleum manufacturing processes. Such an outline should be of assistance to college students, to young engineers beginning their careers in the petroleum industry, and to persons already connected with it but not directly engaged in production or refining of oil. For these reasons the discussion is presented in an elementary form, omitting technical details.

The author wishes to express his gratitude to Dr. J. B. Rather in charge of the General

Laboratories of the Socony-Vacuum Oil Co., Inc., for permission to publish this book and for the encouragement received in the course of its preparation; to Mr. G. G. Hawley of the Reinhold Publishing Corporation for critically reviewing and correcting the manuscript; and to Miss Kira V. Kalichevsky for proof-reading and compiling the index.

V. A. Kalichevsky

Woodbury, N. J.
Oct. 1, 1942

Contents

CONTENTS

Chapter 1

Introduction

Petroleum is probably the most important substance in the world today next to those which are necessary to sustain life itself. Much of the strategy of the present war is dictated by its presence or absence; without it airplanes, ships, warships, tanks and all other moving machinery would be helpless. To extract the last ounce of power locked up in its molecules, scientists have developed many ingenious methods of refining petroleum, that is, of purifying and improving it, as a result of which modern "high-octane" aviation fuels have been made possible. The importance of these in the modern world is self-evident, but the margin between a very good and an excellent gasoline may not be so generally appreciated. It is an established fact that a difference of only 13 points in octane number made possible the defeat of the Luftwaffe by the R.A.F. in the Fall of 1940. This difference, slight as it seems, is sufficient to give a plane the vital "edge" in altitude, rate of climb and maneuverability that spells the difference between defeat and victory. The extra power may also be translated into greater load capacity for bombs, freight or passengers. A glance at the figures given below will indicate the difference.

100 Octane vs. 87 Octane Gasoline in Airplane Performance *

	87 Octane	100 Octane
Max. speed at 2,750 rpm	236 mph	260 mph
Altitude for max. speed	15,700 ft	17,300 ft
Cruising at 60% max. power	192 mph	211 mph
at height of	15,700 ft	17,300 ft
Rate of climb at sea level	1,490 ft/min	2,180 ft/min
Time of climb to 6,500 ft	4.2 min	2.9 min
Time of climb to 13,000 ft	8.0 min	5.6 min
Service ceiling	31,800 ft	35,700 ft
Absolute ceiling	32,800 ft	36,700 ft

* The Institution of Automotive Engineers, Australia; *The Modern Engineer,* July 20, 1941.

Non-technical people may be inclined to ask, What is this mystery about octane numbers, catalytic gasolines, cracking, and all the other odd terms that are constantly encountered whenever petroleum is mentioned? The following chapters are devoted to a simple explanation of these questions about petroleum and its products; of cracking and its importance in converting otherwise valueless substances into high-grade gasolines; of refining, which frees gasoline from foreign substances which interfere with its proper "performance"; and of numerous other phases of the oil industry.

INTRODUCTION

It must constantly be borne in mind that petroleum is not one substance but a vastly complicated mixture of many substances. The molecules of some of these are of such a shape that they will burn quite well in an automobile engine; others are of somewhat different shape, burning very poorly and leaving a large deposit of carbon in the cylinders; still others are so formed that they will scarcely burn at all. The problem facing petroleum chemists has been first to separate out those molecules which give the best performance, and secondly to rearrange the others so that they too will be efficient. A large number of transformations is possible; these are carried out by various so-called "cracking" processes, which means merely that large, complex molecules too unwieldly for gasoline engines are broken up and rearranged into suitable forms. Heat and pressure are used in the older cracking methods; newer ones make use of substances called catalysts, the mere presence of which greatly increases the speed of a reaction and makes possible a superior product. The simple addition of hydrogen to the molecules has done much to make modern aviation fuels possible.

In speaking of molecules the word "shape" has been used purposely. As will be explained in detail in the next chapter, all petroleum molecules consist of atoms of carbon and hydrogen which are linked together in different ways. Some are in the form of long chains of carbon atoms, with hydrogen atoms attached at both sides and on the ends; in others the carbon molecules are arranged in a hexagonal ring, the hydrogens being attached at various points around the perimeter. It is by replacing these hydrogen atoms with atoms of other types, or by changing the positions of the hydrogens relative to the carbons that chemists have been able to create super-powerful motor fuels, as well as thousands of other useful products from the mother substance petroleum.

The first step in separating the constituent parts of crude oil is distillation. This is done by applying heat; when the boiling point of one of the components, for example, ordinary gasoline, is reached the substance vaporizes just as water does, at its boiling point, and is then condensed in a separate container or chamber. This is known as "straight-run" distillate. The heating of the oil is continued until the boiling point of the next component is reached; and this process is carried on until the highest-boiling components have been distilled off. The remainder is either asphalt, paraffin wax, or a combination of the two, depending on the source of the crude oil. In technical language, the various substances thus obtained are called "fractions," and the process is known as fractional distillation. The principal fractions of petroleum are gasoline, naphtha, kerosene, lubricating oil, fuel oil and residue (asphalt or paraffin).

The quantity of the various fractions present in the crude oil does not necessarily correspond to their consumption by the public. However, lighter fractions may be obtained from the heavier fractions by cracking. The modern cracking processes are also of vital importance for manufacture of high-grade gasolines. It is therefore plain that by their research and ingenuity petroleum chemists have nearly doubled the effective petroleum reserves of the world in the last 15 years. An idea of the miracles they have performed in juggling the molecules around to produce more and more efficient types of gasolines may be gained by careful reading of the succeeding chapters.

The magnitude of the production end of the petroleum industry may be visualized by the fact that this country has at the present time about 400,000 oil wells yielding 1,350,000,000 barrels of crude oil per year. Production of natural gas is approximately 2,500,000,000,000 cu. ft. per year. The deepest well drilled in 1938 by the Continental Oil Company is 15,004 ft., while the deepest producting well is 13,266 ft. However, the average depth per well is only 2,861 feet.

The petroleum industry employs over 1,100,000 men, and pays more than $1,500,000,000 taxes, which is larger than the total wages of the oil workers. The world production of petroleum is about 2,150,000,000 barrels. In the United States 42.6% of the total energy used for heating and power generation is derived from petroleum and natural gas.

Chapter 2

The Production and Nature of Petroleum

How to Strike Oil

Petroleum is found below the surface of the earth in the form of oil pools, which are really vast volumes of sand mixed with crude oil. The oil is prevented from escaping to the surface and evaporating by the presence of superimposed layers of rock or clay structures which act as protective covers; indeed this fact accounts for the name "petroleum," meaning "rock oil." Existence of certain underground structure such as that shown in Figure 1, is therefore necessary if an oil reservoir is to form. Geologists, who are always looking for new oil pools, try to ascertain in their surveys the existence of such

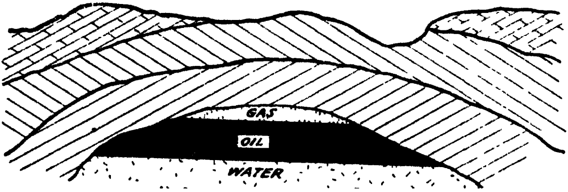


FIGURE 1. Imaginary cross-section of an oil pool. Note the dome-shaped layers of rock and sail.

favorable structures below the earth's surface. This is now done in a variety of ways.

In his search for a new oil field the geologist starts with an investigation of the general contour of the country. He tries to decipher from the surface indications the underground structure of the region where he is working. This he does either by actually surveying the region in the old-fashioned manner, or by taking pictures of the surrounding territory from an airplane. The second method has grown rapidly in importance in recent years because it is both rapid and cheap. Whenever possible, the geologist tries to supplement the survey with observations of oil and gas seepages. However, mapping of the territory is only a preliminary step in this work because the results are usually insufficient for arriving at definite conclusions about the structure of the earth many thousand feet below the ground. Oil and gas seepages also may be misleading. Nevertheless, such a preliminary survey serves as a rough indication of the most probable areas which should be chosen for more extensive examinations.

As the second step in this exploratory work, the geologist tries to ascertain the subsurface structure by the more precise methods which have been developed by the branch of science known as geophysics. Of the geophysical methods, the seismic method has proved to be the most valuable. In applying it, the geologist must secure a good supply of explosives. At a certain selected point he sets off a charge large enough to produce a sound of considerable intensity. The sound wave travels not only horizontally, but also downward through the ground until it meets a dense layer of minerals, from which it is reflected back to the surface. The geologist records the reflected vibrations with very sensitive instruments located at various distances from the point of the explosion. By intricate mathematical calculations he is then able to ascertain the location of the subterranean structures from which the wave was reflected.

A number of other geophysical methods of investigating the structures below the earth's surface have been proposed, but they are of much less importance than the seismic method. They are either less reliable or involve large expenditures without adding anything of value to the information obtained by the seismic method. The gravimetric method measures deviations in the direction of the force of gravity which normally points toward the center of the earth. Presence of dense formations close to the observation point results in deflecting the force of gravity, thus providing some insight into the underground structure. The electrical method attempts to measure differences in the conductivity of an electric current through various layers of minerals. However, these as well as a number of other methods, such as magnetic, radioactive and chemical, have failed to become of real importance to the oil geologist except under some special circumstances.

After completing the preliminary survey, the geologist begins to draw subsurface maps in order to visualize the underground structure. He tries to discover the existence of conditions which make possible the formation of oil pools. In the course of these studies he may drill a few so-called core wells. The core wells are of small diameter and shallow, and penetrate only a short distance below the surface. However, they may give valuable information regarding position of certain layers of minerals and of angles which they form with the earth's surface. A new very helpful branch of science has been developed in this connection; this is known as micro-paleontology.

Micro-paleontology teaches one to recognize various forms of microscopic plant or animal life which existed on the earth millions of years before the arrival of man. The nature of these microscopic beings changed with the age of our planet. As the years went by, one species after another became buried under the ground in superimposed layers, or strata, according to their age. After the core wells are drilled, the geologist tries to compare the remains of various species which he happens to find in different layers. This permits him to make further correlations of the underground structure and to arrive at the best possible site for an oil well.

This is about all a geologist can do before actual drilling is started. His preliminary survey cannot tell him whether any oil is present under the ground; it can only indicate the existence of favorable structures, thus minimizing, but not eliminating the possibility of error. Good luck is still a prime necessity in locating an oil pool, and the chances of drilling a so-called dry hole are always present. However, the chances of finding oil are considerably improved by geological surveys; and this is by no means a small achievement, because the cost of drilling is very high.

Drilling the Well

After the geologist has chosen the location for an oil well, drilling begins. This is almost always done by using a rotating drill which insures good speed of penetration into the ground. However, in some instances it may be necessary to resort to the old method of drilling with a falling bit. The bit is alternately raised and then allowed to fall from a distance, crushing the ground and gradually forming a hole. The method is slow and is applied only when the well must be sunk through layers of hard minerals that cannot be penetrated by a rotary drill. The cutting surfaces of the drills are often studded with diamonds, as this is the hardest substance known, and has great cutting power.

While the well is being drilled, the geologist continues to investigate the subsurface structure by taking occasional samples of the materials loosened by the drill. He tries to determine whether drilling progresses according to his predictions, and whether the well passes through mineral layers which were assumed to be present from the preliminary surveys.

In general, drilling a well is a long and tedious task, although the time has been considerably shortened during the last few years. Many different problems may confront the driller which he must solve in order to complete his undertaking successfully. He may, and usually does, strike sands carrying water that may flood the well. The penetration of such underground waters into the well is prevented by applying cement around the metal tube, or casing. This casing is almost always forced into the hole to add strength to the walls of the well. The driller may strike layers of sand which are unable to hold their weight, and he must modify his drilling methods to overcome such difficulties. Occasionally he loses the drill in the hole because of the failure of the cable from which it is suspended, or for some other reason. The drill must be fished out before work can be resumed.

The driller is also careful to make provisions to keep the drill cool and to lift the mineral particles loosened by the drill to the surface of the earth. He achieves this by continually pumping through the hole the so-called drilling mud, which consists of water and clay, and may contain some additional substances. The purpose of drilling mud is chiefly to support the walls of the well and prevent them from caving in when drilling through strata where water and soft soil are encountered. The driller likewise makes use of the long, heavy columns of drilling mud to keep the well under pressure. This is important, because considerable pressure may exist in some places below the earth's surface and much damage may be done to the well and equipment in the case of a blow-out. In drilling through sands which carry water, the pressure exercised by the mud column should be high enough to keep water out of the well and to plaster the walls, thus permitting continuation of drilling. If the weight of the mud column is insufficient for this purpose, the driller adds to the mud very finely divided heavy materials, such as certain compounds of barium, etc. The numerous problems involved in selecting composition of drilling mud have stimulated extensive investigations and have led to the development of novel methods for preparing the mud and thus insuring its proper functioning.

Drilling wells under water is entirely practicable and is being carried out on the Gulf Coast and off the coast of California as well as in many shallow lakes and bayous in Louisiana. Vast areas of rich oil deposits lying close to shore are thus reached.

Getting Out the Oil

When the well is completed and the oil pool discovered, the problem of bringing the crude oil to the surface arises. In some instances, particularly in the newer fields, the oil begins to flow by itself because of the pressure under which it is stored under the ground. This pressure is due to the large quantities of natural gas which are dissolved in or associated with the crude oil. Occasionally the pressure is so high that the well blows out and a fountain of oil, or "gusher," starts spraying into the air. Terrible fires may occur if the oil becomes ignited, and such fires are extremely difficult to fight; they may burn for months and even years. However, this can be avoided by taking precautions while the well is being drilled.

As the well grows older, the pressure of the gas begins to decline and the oil stops flowing. Artificial means must be devised to bring it to the surface. A number of methods have been developed to accomplish this; they are applied with varying degrees of success in different oil fields. The use of mechanical pumps is quite common. More modern methods employ the so called air- or gas-lift. Air or natural gas, *i.e.*, gas which accompanies the crude oil, is pumped into the bottom of the well through a pipe inside the casing and allowed to escape through the circular space between the pipe and the casing. As the air or gas rises to the surface, it carries certain quantities of the crude oil with it.

When the oil field becomes depleted, the quantity of gas associated with each volume of oil begins to decrease. This happens because gas finds its way through the sand and up to the surface of the earth faster than the liquid. This is highly undesirable because gas in the crude oil serves several useful purposes in securing maximum oil recovery. The oil must travel to the bottom of the well over quite a distance through the sand. This process is slow but is speeded up by the gas associated with the oil. Gas liberated at the more distant portions of the oil pool drives the oil toward the well where the pressure is lower. Furthermore, solutions of gas in oil are much less viscous than the oil itself. For this reason they penetrate through the sands considerably faster than oil containing no dissolved gas. The loss of gas from the oil therefore results in the decline of crude oil production.

Various methods are employed for improving the productivity of oil sands. The oil fields may be repressured, *i.e.*, large quantities of gas or air may be pumped into certain wells in order to raise the pressure in the oil pool. In many fields it is common to pump the gas back into the wells as soon as it is separated from the oil. This serves to prolong the life of the oil field because the waste of gas is held at a minimum. It is better to use gas than air because air can supply only the driving force, whereas gas not only supplies the driving force but also makes the oil thinner and more fluid. However, in older oil fields the supply of gas is already exhausted and air is the only cheap gas at hand.

The same driving force might be supplied by pumping water into certain wells. This method is used with much success in the Pennsylvania oil fields. Water displaces oil from the sand pores and drives it toward the wells, which are reserved for pumping it to the ground. In some instances the wells are placed under vacuum to increase the effective force of the gas for pushing the oil toward the well. The choice between these various methods depends to a great extent on the characteristics of the oil field, and requires considerable study to insure returns.

After a pool is discovered, a number of wells are sunk into the ground to increase the recovery of oil. The field development may proceed in an orderly or in a haphazard manner. This depends to a large extent on whether the field is in the hands of one or many individual owners and on what agreements were reached concerning its exploitation.

The oil in the pool is not stationary but migrates toward the point of least pressure. It is, therefore, possible to pump the oil from somebody else's property. To offset this, the individual owners begin to drill as rapidly as possible, so that they may secure the maximum share in production. The oil is lifted to the ground with the utmost possible speed and with complete disregard for the conservation of natural gas and for the total ultimate oil recovery. This practice should be condemned, as it is wasteful and tends to demoralize the oil market, because crude is produced in larger quantities than may be absorbed by the existing transportation and refining facilities. As a result, with a few possible exceptions, everybody loses.

If the exploitation of an oil field proceeds in a systematic manner, and to the credit of the oil industry this is now quite usual, wells are drilled so as to insure maximum ultimate recovery of oil and maximum returns on the investment. In general, the total recovery of oil improves with the number of wells, other conditions being equal, but the quantity of oil recovered per well declines. This shows that the number of wells and their spacing are of much importance in arriving at the best economic solution in the development of a field.

The spacing of oil wells depends on the depth of the oil sands and on a number of other factors which must be carefully studied and scrutinized. From this brief discussion it is also obvious that for the best conservation of our natural resources oil-field development should be carried out by large petroleum companies and not by small individual concerns.

How Long Will our Petroleum Resources Last?

Much has been written lately on the possible shortage of petroleum in the near future. Such claims should be disregarded, however, as political propaganda and not as true statements of fact. Certainly, and this is true of every natural resource, the time must come when crude oil will be more or less completely exhausted, but we have no indications that this will occur during the life of the next few generations. We should not permit our natural resources to go to waste, but we must also be careful not to impose unwarranted restrictions which may cripple the petroleum industry. Besides, commercial methods are already known for producing substitutes for crude oil from sources other than petroleum. These methods are successfully applied in countries such as Germany or Italy, where petroleum is scarce. Our vast resources of shale from which oil may be recovered by heating, are still untouched. Coal can be converted into petroleum-like products. These methods of manufacturing liquid fuels are expensive, but entirely practical if the price of *crude oil rises above a certain level. Our worries* about the future oil supply are, therefore, superfluous. We might just as well fear that oxygen will disappear from the atmosphere because of its tremendous consumption by the industries, and that we will suffocate in the resulting atmosphere of nitrogen!

What Is Petroleum?

To most of us the word "petroleum" is associated with a vile-smelling, dirty, thick liquid from which we should keep away if we want to stay clean. We can hardly believe that a substance of such an uninviting nature can be converted into a vast number of extremely valuable products, each very different from the others, and retaining none of the objectionable characteristics of the crude oil. This transformation is brought about by refining processes, which have undergone many basic changes in the course of the last few decades. These processes involve the use of huge installations which are both complicated and dramatic in appearance.

There are many different kinds of crude oil, which vary in their composition from one locality to another. For example, Pennsylvania crude is quite different from Texas or California crude, in spite of the fact that they might ap-

pear to a superficial observer to be identical. Some crudes contain larger or smaller quantities of a black, semi-solid material familiar to everybody as asphalt. Others, which are usually lighter in color, congeal readily, but begin to flow with ease after they are heated above a certain temperature. When such crudes are cooled they deposit a light-colored, crystalline or semi-crystalline substance which is nothing more or less than ordinary paraffin wax. Still other crudes contain both asphalt and paraffin. Consequently, crude oils are classified as being either asphalt-base, paraffin-base, or mixed-base.

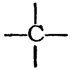
This classification has survived up to the present time and is quite common among refinery men. However, it is far from being satisfactory because it fails to explain the real nature of the different crudes. Petroleum consists largely of various carbon and hydrogen compounds which differ widely in their properties. The relative quantities of the various compounds present in a crude determine the chemical nature of the oil with which asphalt and wax are associated. Chemists came gradually to realize that no two crude oils are alike, thus making correct classification almost an impossibility. This also means that each crude presents its own problems, particularly when attempts are made to rework it into high-grade products. Some crudes may be well fitted for certain specific purposes, but others may be worthless in this respect, or yield products of inferior characteristics irrespective of the method employed in refining them. The person in charge of a refinery is, therefore, very careful in selecting the source of his crude oil if he wants to maintain uniformity of production.

Hydrocarbons: Chain and Ring Types

Chemically the crude oils may be considered as mixtures of various compounds of carbon and hydrogen which are known under the general name of *hydrocarbons*. In addition, they may contain compounds of sulfur, nitrogen or oxygen, but for purposes of simplicity the latter may be regarded as impurities. Although hydrocarbons consist of only two elements, they vary widely in their properties depending on the *number* of the carbon and hydrogen atoms and their *arrangement* in the molecule. In general they may be divided into two major classes: straight-chain (aliphatic) and ring (naphthenic and aromatic). A brief description of these classes is necessary to understand some of the recently developed refinery processes which begin to approach the domain of organic chemistry.

When atoms combine to form a chemical molecule, each carbon atom is capable of holding or attaching to itself *four* hydrogen atoms, or their equivalent. When it does so, the carbon atom is said to be *saturated*. The attractive force holding the atoms together, and indicated by a straight line, is called a bond, or linkage. The nature of this attractive force is too complicated to be discussed here, as it would lead too far afield.

This may be represented by the following symbols:



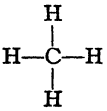
$$\begin{array}{c} | \\ -\mathrm{C}- \\ | \end{array}$$

Carbon atom
(4 bonds)

$\mathrm{H}-$

Hydrogen atom
(one bond)

Therefore the simplest chemical compound containing carbon and hydrogen is:



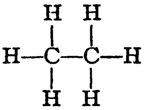
$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

or CH_4

Methane (saturated)

This hydrocarbon is called *methane*. It constitutes by far the largest proportion of the so-called natural gas which is found in the oil fields and which is closely associated with petroleum.

The next simplest hydrocarbon, which is also a gas, contains two carbon atoms joined to each other in the following manner:

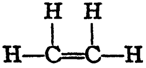


$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H \qquad \text{or } C_2H_6$$

Ethane (saturated)

This gas is known as *ethane*, and is also one of the constituents of natural gas. In this case each carbon atom holds three hydrogens, the fourth being replaced by the second carbon atom. Further members of this series of saturated hydrocarbons are formed in a similar way, with more carbons and hydrogens extending out in a straight-chain structure; thus a large and important group of saturated hydrocarbons is built up. This "straight-chain" group is often referred to as *aliphatic* hydrocarbons.

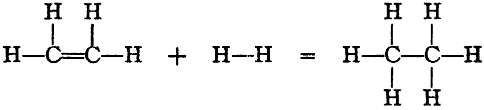
In the above compounds the carbon atoms are united between themselves by only one dash, which is considered as representing one chemical bond. However, a very large group of hydrocarbons contain atoms which are joined by two or more chemical bonds. This may be visualized from the following picture of the simplest member of this series:



$$H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H \qquad \text{or } C_2H_4$$

Ethylene (unsaturated)

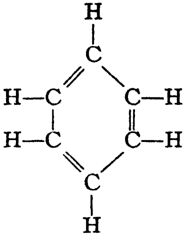
This hydrocarbon is called ethylene and is also a gas. The term "unsaturated" is applied to such hydrocarbons, because one of the bonds between the two carbon atoms is free to attach itself to some other element if it becomes available; thus the double bond becomes two single bonds, and a saturated molecule is formed. For instance, if available hydrogen is present, ethylene may add a molecule of hydrogen by means of the free bond, and form ethane. The reaction may be presented graphically as follows:



$$\mathrm{H{-}\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}{-}H \;+\; H{-}H \;=\; H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H}$$

C_2H_4 + H_2 = C_2H_6
Ethylene *Hydrogen* *Ethane*

Another equally important series of hydrocarbons is known as the *aromatic* group, so-called because of their characteristic odor. These differ radically from the straight-chain or aliphatic group. They contain six carbon atoms forming a closed *ring* with double bonds between each second pair of carbon atoms. The simplest member of this series is the very well known substance benzene, or benzol. Graphically the benzene molecule may be represented as follows:

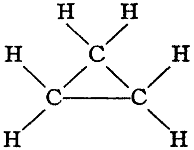


or C_6H_6

Benzene (unsaturated)

The complexity of the aromatic series of hydrocarbons may be visualized if we try to imagine the number of substances than can be formed by replacing one or more of the hydrogen atoms with other groups containing both carbon and hydrogen, as was shown in connection with the saturated hydrocarbons, or with other elements. Such "benzene derivatives" may be numbered in the thousands. Although the aromatic hydrocarbons contain double bonds, they are much less reactive than the unsaturated straight-chain hydrocarbons previously described.

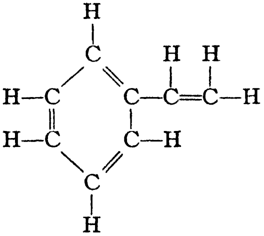
Another group of hydrocarbons, known as *naphthenic* hydrocarbons, is characterized by a ring structure similar to that of benzene, but contains no double bonds and has a variable number of carbon atoms in the ring. The simplest member of this series is cyclopropane which is a gas occasionally found in natural gas; it is sometimes used as an anesthetic.



or C_3H_6

Cyclopropane (saturated)

The complexity of hydrocarbon molecules increases rapidly with increase in the number of carbon atoms. A vast number of hydrocarbons are known which may be classified within more than one group. For instance a compound such as styrene may be considered as being both an aromatic and a straight-chain hydrocarbon.



or $C_6H_5 . C_2H_3$

Styrene (unsaturated)

The Complexity of Petroleum

The foregoing description shows the diversity and the extremely large number of possible combinations of carbon and hydrogen atoms which may exist in a molecule. For all practical purposes it may be considered as infinite. Therefore, it is not astonishing that relatively few of the hydrocarbons present in petroleum have been isolated and identified. This is possible only with the hydrocarbons of a fairly simple nature, like those which constitute the lowest-boiling portions of crude oil. The complex composition of petroleum likewise explains the difficulty of employing it as a raw material for manufacturing various chemicals. With the exception of the few low-boiling hydrocarbons, the hydrocarbons are present in crude oil in very small quantities, or have similar boiling points, thus making their separation practically impossible. However, considerable progress has been made recently in connection with the utilization of the low-boiling hydrocarbons by converting them into valuable by-products or high-grade motor fuels. Commercial processes of this type are new, but represent an important addition to refinery operations.

Chapter 3

Transportation and Storage

Methods

Petroleum may be transported from oil fields to the refineries and from the refineries to the distributing centers by tankers, barges, pipe lines, railroads or motor trucks. The choice between these methods depends on geographical conditions, availability of transportation facilities, quantity of commodities moved, distance, and a number of other economic factors. The following tabulation illustrates the approximate relative costs of shipping petroleum by these various means taking the cost of shipment by water as unity:

Transportation method	Cost per ton-mile
Water	1
Pipe line	9
Railroad	27
Truck	81

Obviously these comparisons are subject to wide variations and should not be used indiscriminately. Of the total crude oil reaching the refineries in 1941, 320 million barrels were transported by water, 939 million barrels by pipe lines and 40 million by tank cars and trucks.

Tankers and Barges

First shipment of American petroleum to Europe dates back to 1861. The oil was sent in barrels, but as early as 1863 an attempt was made to transport it in iron tanks placed within the vessels. In 1885 the forerunner of the present tankers came into existence; the shell of the vessel also served as the shell of the oil-containing compartments. The capacity of this tanker was 25,000 barrels.

Since that time great improvements have been made in tanker design insuring safety from fire hazard and reducing transportation costs. Modern tankers range in capacity from 60,000 to 125,000 barrels, with new tankers under construction capable of loading up to 170,000 barrels of oil.

Diesel engines employing oil as fuel are gradually replacing the older steam-driven engines for propelling tankers. Two or more cargo pumps, each capable of pumping 4,000-6,000 or more barrels of oil per hour, are used for loading and unloading various compartments, which are located on both sides of the tanker with partitions running longitudinally through the middle of the vessel. Provisions are also made for heating heavy oils in order to insure easy pumping.

Special tankers are assigned for shipment of refined and crude oils. This is necessary because the expense of cleaning a tanker previously employed for transporting crude may be as high as $30,000 before it is made suitable for loading refined products. Tankers are run on very strict schedules to reduce to a minimum the time lost in ports. For the same reason the cargo and shore pumps are also of high capacities. The usual speed of tankers is 10-12 knots, but new tankers will be capable of making about 16 knots, which is a considerable improvement. However, in normal times the speed of tankers is adjusted so as to obtain the maximum overall economic performance. Before the depredations of submarines off the Atlantic Coast, our tanker complement was about 500 units, with a gross tonnage of 3 million tons. Whatever the immediate situation may be—and it has been extremely bad—this is about the capacity necessary to keep our nation supplied with fuel oil and gasoline.

Barges are also employed for transporting oil by inland waters. They are smaller than the sea-going tankers because of obvious size limitations imposed by canals and locks. Some of the larger ones have, however, capacities as high as 10,000 barrels or more. Such barges are about 200 ft. long, 35 ft. wide, and draw 11 ft. of water, which makes them unwieldly for inland navigation. Barges may be motor-driven or towed by tugs; their normal speed is only from two to four miles per hour upstream, but may be as high as 10 miles per hour down stream.

Pipe Lines

Attempts to employ pipe lines for transportation of crude oil date back to 1861. However, due to hostility of teamsters, the first pipe line, four miles long, began its successful operation only in 1865. By 1942 approximately 120,000 miles of pipe lines were available in this country, one-half of which were trunk lines, the other half constituting the tributary gathering systems.

Pipe lines are usually buried under the ground. Various precautions are taken to prevent their corrosion by coating the outside with asphalt and other protective coatings, or by encasing them in cement. The laying of pipe lines is a rather slow process. Individual joints must be welded together, and a speed of one mile per day is seldom exceeded. Pumping stations are provided at 30-40 mile intervals or closer, depending on the contour of the country and the type of oil to be pumped.

The size of the pipe determines the capacity of the line. The main trunk lines are usually about twelve inches in diameter, but smaller sizes are employed for the gathering lines. Under normal conditions a twelve-inch line should be capable of moving 50,000-60,000 barrels of oil per day, although this figure is subject to variation depending upon the viscosity of the oil and terrain across which it is pumped. The chief trunk lines at present run from the producing centers of Oklahoma and Texas to refineries near Chicago and New York. A new line is now under construction to relieve the tanker shortage. It extends from Oklahoma to Southern Illinois, whence the oil is transshipped in barges via the Erie Canal.

Careful precautions are taken to prevent contamination of one type of crude with another, although this cannot be entirely avoided. For this reason it is sometimes necessary to employ two parallel lines if intermixing must be avoided.

Besides transporting crude oils, pipe lines are also employed for transporting gasoline and gas. Due to radical differences in the physical properties of these commodities the construction of pipe lines is also different. For these reasons a pipe line suitable for transporting crude oil is not suitable for gasoline and *vice versa,* and at the best a considerable expenditure of money is required to adapt it to another purpose than that for which it was designed.

Railroads

Petroleum is transported by railroads in tank cars. Individual tank cars are usually capable of loading 8,000 or 10,000 gallons of oil, although 6,000-gallon tank cars are also in existence. Occasionally 12,000-gallon tank cars of modern build may be found. Approximately 150,000 railroad tank cars are available in the United States while the number of tank trucks is about half that. In the present state of emergency up to 850,000 barrels of oil are transported daily to the Eastern area by tank cars after the circulation of tankers had been curtailed.

Tank cars may be divided into compartments and some of them are insulated if they carry light products like gasoline. Tank cars employed for transportation of waxes or asphalt are equipped with heating coils to keep the products in a molten state for insuring easy pumping.

Special cars are also available for transporting such products as natural gasoline or liquefied petroleum gases. All these different types of cars are not interchangeable, but are employed for shipment of the products for which they were designed. These are important not only on account of inherent differences in their construction but also for reducing the cost of cleaning.

Motor Transport

The usual combination of a motor truck and a trailer which is seen on the highways has a capacity of about 4,000-5,000 gallons. However, a large number of smaller size trucks are also in operation. This method of transportation is practically never used for moving crude oils, but is confined to the refined products, because of the expense involved. Special trucks are also used for transporting asphalt; these are heated to keep the contents in a liquid state. These trucks are frequently seen on roads under construction.

Storage

Crude oil may be stored in concrete reservoirs often capable of holding several million barrels of oil. These reservoirs are quite common in California. However, in the East the oil is usually kept in steel tanks having capacities ranging from 50,000 to 120,000 barrels. Formerly earthen reservoirs were also employed. Steel tanks are obviously much more expensive, but less oil is lost by evaporation, and they are practically immune to the fire hazard created by lightning.

For storing volatile products like gasoline, steel tanks capable of withstanding slight pressure are employed..This permits the reduction of losses caused by "breathing," that is, contraction and expansion of vapors and air present above the gasoline level on account of temperature fluctuations. The same purpose is sometimes achieved by equipping tanks with floating roofs or other similar devices. For storing very volatile products, like butane, tanks of spherical design are used. In order to minimize as far as possible temperature fluctuations inside the tanks special paints capable of reflecting sunlight are applied to the outside. Aluminum paint is favored by many refinery men.

Chapter 4

Petroleum Emulsions and Natural Gas

Emulsions and How to Break Them

When crude oil reaches the surface it usually contains more or less water, the proportion increasing with the age of the oil field. This happens because water is present at the bottom of the oil pool below the oil level, and when the oil is removed and gas pressure declines, the water gradually works its way up to the well and contaminates the oil stream. The quantity of water in the crude oil may vary from zero or a few per cent to fifty per cent or more, depending on the locality and how old the field is. Some water may also seep in from the water-bearing sands above the oil pool, if sufficient precautions are not taken to seal them off while drilling the well.

Everyone knows that water and oil do not mix under ordinary conditions. However, they may be made to disperse in each other in very fine droplets. Such dispersions are known as oil-field emulsions. To the naked eye these emulsions seem to be quite uniform and homogeneous, but they are usually of a lighter color than crude oil and have a milky appearance. The oil producer is confronted with the problem of separating the oil from such emulsions. This must be done before the crude is shipped to the refineries or pumped to storage. The method of accomplishing this must be cheap, because crude oil is not an expensive commodity.

The most common method of "breaking," or separating, crude oil emulsions is by electrical dehydration. Warm emulsion is passed between two electrodes which carry electric charges of very high voltage. The oil is thus subjected to the action of an electric field of very high intensity and the water droplets become electrified. As opposite charges attract each other, the droplets begin to move toward the electrodes having charges opposite to those of the droplets. When an alternating current is employed, the charge on the electrodes reverses many times per second, causing corresponding changes in the direction in which the droplets are moving. These vibrations finally disrupt the oil film around the droplets, causing the latter to coalesce into larger ones. The larger droplets settle out fairly easily from the oil due to their increased weight.

Another method of breaking emulsions involves the use of chemicals. According to present theory, emulsions consist not only of oil and water but also of an emulsifying agent, that is, a substance that promotes the formation of emulsions. The emulsifying agent concentrates on the surface between the water and the oil, preventing the individual droplets of water from combining. To break the emulsion it is therefore essential to destroy or to neutralize the action of the emulsifying agent. This is made possible because of the fact that some substances cause the formation of emulsions containing oil droplets surrounded by water, while other substances produce emulsions containing water droplets surrounded by oil. It may be readily seen that emulsifying agents responsible for one type of emulsion should have the ability to break the other type of emulsion. This is the principle of the chemical method of treating emulsions.

Both the water-in-oil and the oil-in-water types of emulsions are encountered in the petroleum industry. The water-in-oil type is represented by the oil-field emulsion, and the oil-in-water type is encountered in the course of petroleum refining.

However, application of chemical methods for breaking emulsions is much more complicated in practice than in theory. The nature of the emulsifying agent in oil-field emulsions varies with the crude, thus requiring application of different chemicals for their treatment. A very large selection of such chemicals is available to the petroleum industry. They are manufactured almost exclusively by the Tretolite Company and are sold under the trade name of "Tret-o-lite." The choice between the different samples of Tret-o-lite is made on the basis of experimental work with the emulsion under consideration.

Heating emulsions always reduces their stability, that is their ability to "stay put." The water can also be expelled from the oil by distillation if special stills are employed to prevent foaming. This method is suitable for all types of emulsions, but is little used in practice because of expense and other limitations. Centrifuging and filtering have been recommended as possible alternatives, but they are seldom economical.

Water is not the only impurity in the crude oil which must be removed in order to insure successful processing of the crude in the refineries. Some of the crude oils contain considerable quantities of mineral salts, such as sodium or magnesium chlorides. These mineral salts may form deposits in the distillation equipment or cause corrosion. Their elimination is, therefore, often desirable before the crude is distilled.

Elimination of mineral salts from the crude oil may be affected by washing with water and settling the resulting salt solutions. Difficulties may be encountered in separating these solutions due to formation of emulsions. Such emulsions can be broken in the same manner as oil-field emulsions, as both are of the water-in-oil type. If heating alone is insufficient, processes such as the Petreco Electrical De-Salting Process may be installed. In this process the wash water is separated from the oil by passing the emulsion through an electric field, as in the electrical dehydration method. While the removal of water from oil-field emulsions is always done in the field, desalting is frequently carried out at the refineries, although in many instances it might be more profitable to conduct it in the field also, because of the similarities between the desalting and dehydrating operations.

Natural Gas

As it was pointed out in the previous chapter, natural gas almost always accompanies crude oil. It is composed mainly of methane, which finds little commercial application except for heating purposes or for manufacturing carbon black. However, besides methane, natural gas contains vapors of heavier hydrocarbons, some of which boil within the gasoline range. The recovery of these heavier hydrocarbons is in the hands of the natural gasoline industry.

Hydrocarbons present in natural gas are of the saturated type similar to methane. The greater the number of carbon atoms in the molecule, the higher the boiling point. These hydrocarbons include ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), and the heavier ones in decreasingly smaller quantities.

Little use has been found up to now for ethane, which is a gas similar to methane. However, propane, which is also a gas under normal conditions, may be liquefied by applying considerable pressure. Butane liquefies with still greater ease because its boiling point under normal atmospheric pressure is very close to the freezing point of water. It is the starting point for the manufacture of butadiene, which is the basis of many kinds of synthetic rubbers. Hydrocarbons heavier than butane which are present in natural gas boil within the gasoline range.

Propane and its mixtures with butane are now used quite extensively as substitutes for gaseous fuels in the regions where domestic gas is not easily available. In 1922 the quantity of liquefied propane sold as domestic fuel was 222,000 gallons; in 1940 its consumption rose to 57,000,000 gallons. The liquefied gas is pumped under pressure into cylinders and thus transported to the customers. By releasing the pressure the liquefied gases begin to "boil," supplying fuel for domestic or other needs. At the present time the liquefied gas is used not only in individual homes in rural districts, but even in small towns equipped with central gas distributing systems. In addition, certain quantities of liquefied gas are employed as fuel for tractors, trucks, and busses. Liquid hydrocarbons present in natural gas boil within the gasoline range and are sold under the name of "natural gasoline." Previously, this gasoline was known as "casinghead gasoline," but this name is now obsolete. Natural gasoline is somewhat lighter than the gasoline known to the motoring public and representing a blend of various petroleum products including natural gasoline or its equivalents.

Recovery of Fuels from Natural Gas

Several methods have been developed for the recovery of these products from natural gas. The oldest, which is now to a certain extent obsolete, although new improvements may restore its original importance, is the compression method. Natural gas containing hydrocarbons of the desired type is compressed until the gasoline vapors are liquefied. The liquefied portion, or "fraction," is separated from the remaining gas and the gas is returned to the well or disposed off in some other manner. Natural gasoline produced by this method is sometimes referred to as "compression gasoline."

The compression method has been to a very great extent superseded by the absorption method. This method is based on the principle that the heavier hydrocarbons are more easily dissolved by petroleum fractions than the lighter ones. The "wet gas," *i.e.*, natural gas containing gasoline vapors, is intimately mixed with a petroleum fraction, usually a light grade of kerosene or naphtha, in a specially designed absorption tower. Figure 2 illustrates this process. The nature of the hydrocarbons and the extent to which they are dissolved or absorbed by the "absorption oil," is controlled by adjusting pressure, temperature and the rate of flow through the tower. Absorption oil containing the dissolved hydrocarbons and usually referred to as "rich oil" is pumped into another tower and heated to vaporize the absorbed gasoline. The gasoline vapors may be passed to a stabilizer where the lightest fractions, particularly propane, are separated from the rest of the gasoline. The "lean oil," *i.e.*, absorption oil freed from gasoline, is returned to the absorption tower to repeat the cycle. Natural gasoline thus recovered is sometimes called "absorption gasoline."

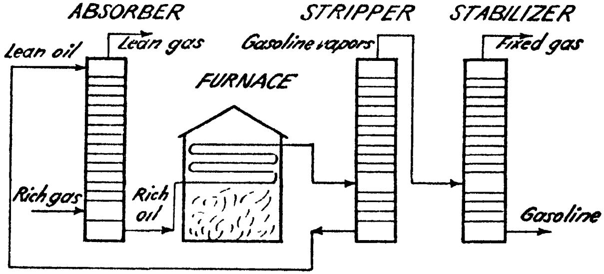


FIGURE 2. Diagram of the absorption method.

A third method, known as the adsorption method, has been also developed to accomplish the same purpose, but its commercial use is quite limited. The method consists in passing natural gas from the wells through towers filled with a solid substance capable of retaining gasoline vapors in preference to the gaseous hydrocarbons. Activated carbon, or charcoal, is usually employed to effect this separation, although silica gel has been recommended for the same purpose. When charcoal becomes saturated with gasoline, the gas is diverted into another tower for a sufficient length of time to permit recovery of gasoline from the charcoal. This is done by blowing steam through it and condensing the gasoline vapors. Three towers are usually required to insure an uninterrupted flow of gas through the plant. Natural gasoline obtained by this process is occasionally referred to as "adsorption gasoline."

Large refineries are equipped with similar plants for the recovery of gasoline vapors from the distillation and cracking units or from storage tanks. Such plants are frequently called "conservation plants" and their products are known as "conservation gasoline." Natural and conservation gasolines often contain considerable quantities of dissolved hydrocarbon gases which tend to evaporate at a much faster rate than the liquid gasoline hydrocarbons. On evaporation, the gases may carry away a large proportion of valuable liquid hydrocarbons, thus causing high storage and handling losses. The presence of dissolved hydrocarbon gases is also undesirable if natural gasoline is used for the preparation of the motor gasoline. Separation of gaseous from liquid hydrocarbons is, therefore, very important in commercial practice. This separation is accomplished by the so-called "stabilization processes" and the resulting gasoline is referred to as "stabilized gasoline."

What is "Fractional Distillation"?

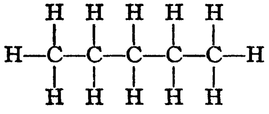
Stabilization of gasoline consists in separating gaseous and liquid hydrocarbons by what is known as fractional distillation. Fractional distillation differs from straight distillation in that the vapors given off are passed through a column containing a number of plates of special design. At each plate the vapors condense and the resulting liquid partially revaporizes. The newly formed vapors ascend to the next upper plate of the fractionating column, while the unevaporated fraction flows downward to the next plate below. After each revaporization the vapors become progressively richer in the low-boiling constituents while the liquid descending the column becomes progressively richer in the high-boiling constituents. The process thus permits separation of the individual gasoline hydrocarbons which have almost the same boiling points.

Stabilization of gasoline results in the reduction of its vapor pressure, *i.e.*, the pressure which is registered when gasoline is confined in a closed vessel under certain prescribed conditions of testing. The desired vapor pressure may be obtained by varying the content of lighter hydrocarbons, for example, propane and butane. In general, propane is an undesirable constituent of gasoline because of its very high vapor pressure; but the presence of certain quantities of butane is often desirable in order to assist vaporization of gasoline in the engine. For this reason, if gasoline contains an excess of butane, this excess may be separated and then added to another gasoline deficient in butane. Such transpositions are not uncommon in manufacturing commercial grades of gasoline in petroleum refineries. When propane is removed, the process is frequently referred to as the "depropanizing process," and the fractionating equipment in which this is accomplished is known as a "depropanizer." When butane is removed, the process is similarly referred to as the "debutanizing process," and the equipment is known as a "debutanizer." If butane is added to gasoline to increase its vapor pressure, the operation is called "repressuring." Under certain conditions propane and butane may be removed from the gasoline as a mixture and butane may be then "depropanized," *i.e.*, separated from propane.

Distillation may be also conducted in the presence of auxiliary substances like alcohols, acetone, phenol, etc. These substances form constant-boiling mixtures with some of the petroleum constituents, thus facilitating their isolation. Processes of this type, known as "azeotropic processes," are now in limited commercial use.

Isomers

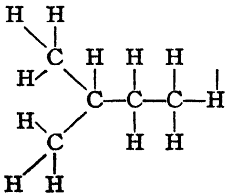
In the foregoing discussion natural gasoline has been regarded as a single commodity. However, with the development of the petroleum industry considerable progress has been made in the utilization of some of its individual constituents. For instance, natural gasoline contains certain quantities of a hydrocarbon known as isopentane which is a valuable component of high-grade gasolines. Although molecules of normal pentane and isopentane are composed of equal numbers of carbon and hydrogen atoms, the difference between the two hydrocarbons may be seen from the following pictorial representation of their chemical structure:



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

or n—C_5H_{12}

Normal pentane



or iso—C_5H_{12}

Isopentane

Substances consisting of the same number and kind of atoms but differing in structure are called *isomers*. Isopentane is thus an isomer of pentane. Commercially isopentane is now isolated from natural gasoline by very careful fractionation. For other purposes, such as for preparation of certain chemicals, a mixture of normal pentane and isopentane may be satisfactory. This shows that the present tendency of the petroleum industry is to utilize the individual compounds present in the gasoline to the fullest possible extent if their separation is possible and commercially practical.

Commercial Uses of Methane

After removing propane and heavier hydrocarbons, the remainder of the natural gas consists almost exclusively of methane with a small admixture of ethane. Little commercial use has been found for either of these hydrocarbons except as fuel. However, such utilization depends on the proximity of large towns or factories close to the oil fields, which is not usual. Natural gas is quite generally used as fuel for household heating purposes in and near the East Texas and Louisiana fields. For this reason the gas is most frequently returned under the ground in order to maintain pressure in the oil field, or burned to prevent a possible fire hazard if the gas is released to the atmosphere. Fortunately the latter practice is now being gradually discontinued.

Considerable research has been devoted to commercial utilization of methane, but up to now all efforts in this direction have met with a very limited success. The largest quantity of methane is consumed by the carbon black industry. For the preparation of carbon black the gas is burned so as to produce the greatest possible quantity of smoke. The smoke, which represents fine particles of carbon suspended in the air, is collected on cool metal surfaces. The resulting deposits are scraped off and sold as carbon black. However, not all the numerous grades of carbon black can be obtained in this way. Some of them must be prepared by burning certain special oil fractions and not the gas, in order to obtain products of desired quantity. In general, preparation of carbon black is a very wasteful process. The quantity of recovered carbon is sometimes as low as one per cent of the total carbon present in the burned gas. Carbon black finds its greatest use as a reinforcing agent in auto tires and other rubber products; it is also widely used in the manufacture of printing inks, phonograph records and paints.

Methane may be employed for the manufacture of hydrogen. This is accomplished by heating it to very high temperatures at which it decomposes into carbon and hydrogen. This utilization of methane is usually connected with the operation of hydrogenation plants, which is described later. In most instances the methane produced in processing crude oil at the refineries is sufficient to meet the demand of the hydrogenation plants without resorting to the use of natural gas.

Attempts have also been made to utilize methane for preparation of certain chemicals, such as acetylene, but the expense involved and the rather limited use of the resulting products are often unfavorable for extensive commercial development of such processes.

Chapter 5

Gasoline and Crude Oil Distillation

Consumption and Properties of Gasoline

By far the largest quantity of crude oil is utilized as fuel, particularly for manufacturing gasoline. This may be visualized from the following table which shows the quantities of various products obtained to every 1000 barrels of gasoline produced:

Gasoline	1000 barrels
Kerosene	104 barrels
Lubricants	45 barrels
Asphalt and road oils	57 barrels
Fuel and gas oils	851 barrels
Wax	2.4 barrels
Miscellaneous products	139 barrels
Loss	51 barrels

However, the relative quantities of these materials are not necessarily representative of profits derived from their sales, because the margin of profit per unit volume of product sold varies within wide limits. The margin is considerably greater for products approaching the class of specialties than for those sold as fuel.

About one-half of the crude is consumed for operating automobiles; this was true at least up to the beginning of 1942, but it certainly will not be so for the duration of the war. The average yearly consumption has been about 750 gallons of crude per vehicle. The relative quantities of the various petroleum products used by the motorists may be approximated as follows:

Gasoline	1000 barrels
Motor oil	20 barrels
Transmission and differential oils	2 barrels
Chassis greases	1 barrel

Due to the importance of gasoline manufacture for the petroleum industry, the processes developed for this purpose are discussed first.

As it is generally known, gasoline is in practically every instance not a virgin petroleum stock but a blend of different materials which are obtained by a variety of manufacturing methods. A high-grade commercial gasoline must boil within certain prescribed limits in order to insure complete vaporization in the carburetor, where the gasoline vapors are mixed with air to form an explosive mixture. This property of gasoline is frequently referred to as *volatility*. In addition to these general boiling-limit requirements, it is important that certain quantities of gasoline vaporize within smaller temperature ranges than the overall limits permit. Compliance with these specifications insures good starting of the motor, high mileage and freedom from vapor-lock, that is, vaporization of gasoline in the feed lines leading from the gasoline tank to the carburetor which interferes with the gasoline feed. Vapor pressure of gasoline must be also below certain limits to prevent vapor-lock and excessive losses in storage.

What Makes an Engine Knock?

Another important property of gasoline is its anti-detonating, or antiknocking quality. When the same gasoline is employed in different engines, its performance varies depending on the so-called compression ratio of the engine. Compression ratio expresses the ratio between the maximum and minimum amount of space which gases occupy in the cylinder after and before explosion. For instance, if the space taken up by the gases after the explosion is six times that before the explosion, the compression ratio of the engine is 6:1. Gasoline begins to knock, or detonate, when the compression ratio of the engine exceeds certain limits. These limits are different for different gasolines even if the two gasolines are similar in most of their physical properties.

When detonation occurs, the motor emits a characteristic metallic sound familiar to all motorists who have tried to make steep hills in high gear. Detonation is due to improper combustion of fuel, and is accompanied by loss of power and overheating of the engine. While detonation is always harmful, it is infinitely more disastrous in airplane than in automobile engines because the rapid rise in temperature may cause expansion, or "freezing," of cylinder heads and pistons, thus disabling the motor.

Detonation may be avoided by employing engines having low compression ratios; this is undesirable, particularly with airplane engines, because high compression ratios decrease gasoline consumption, permit the use of lighter-weight engines for the same power output, and have a number of other advantages over low compression ratios. However, nothing is gained by employing gasolines of high antiknock qualities in low-compression engines because the gasoline has no opportunity to exhibit its superior performance in comparison with other gasolines.

What is Meant by Octane Number?

The antiknock characteristics of gasoline are expressed in terms of *octane numbers*. The octane number refers to standard mixtures of two pure chemical substances. One of these substances is iso-octane (this is a misnomer, because the hydrocarbon chosen for this standard is not iso-octane of the correct chemical nomenclature, but another isomer of octane, 2,2,4-dimethylpentane); the other is normal heptane. As iso-octane has exceptionally good antiknocking characteristics, it was assigned an octane number of 100. Normal heptane, on the contrary, detonates very easily and its octane number in the same arbitrary manner has been assumed to be zero. By mixing these two substances in all proportions, a series of fuels is obtained covering the whole scale of possible gasoline mixtures; this series is exact, and may be easily reproduced. It is therefore used as a standard with which various gasolines are compared. On this basis an octane number of 70, for instance, refers to a blend containing 70 per cent by volume of iso-octane and 30 per cent by volume of normal heptane. As was already mentioned, the octane number is a very important property of gasoline and is, therefore, included in gasoline specifications.

Other Requirements of High-grade Gasoline

Gasoline must be stable under service conditions and in storage; that is, it must not change in any way with the passage of time. The desired degree of stability depends on the length of time which elapses between the production of the gasoline and its use in an automobile or airplane engine. Unstable gasolines may deposit certain quantities of a semi-solid substance known as "gum," which will plug the fuel lines and the carburetor and thus interfere with the free flow of fuel to the engine cylinders. It is, therefore, highly important that the quantity of gum present in the gasoline be kept as low as possible.

Gasoline must not be corrosive to the equipment, and its sulfur content should be low. If much sulfur is present, the combustion gases may corrode the engine, particularly in cold weather when the water vapors formed in combustion condense on the cooler parts of the engine and increase the corrosive properties of the sulfurous combustion gases. The maximum limit for the quantity of sulfur which may be tolerated in a gasoline varies for different climates and for different engines, because the corrosive action depends not only on the outside temperature conditions, but also on the type of materials employed in constructing various parts of the engine.

A number of other tests are also often included in gasoline specifications. These tests may refer to the color or odor, to the quantities of unsaturated hydrocarbons present, to the so-called "doctor test," and to a number of other properties. Not all of them are, however, of established practical value. For instance, color requirements have been repeatedly demonstrated to be superfluous because the color of gasoline has no relation to its performance. Meeting unsaturation tests such as acid-heat or bromine number, recently developed for aviation gasolines, is of the same questionable value, particularly because in some instances the degree of refining required to pass them may have an unfavorable effect on some of the important properties. This happens because by far the larger proportion of unsaturated hydrocarbons found in gasolines is quite stable, and their presence may be even desirable because of their good antiknock characteristics. Rigid acid-heat, or bromine tests preclude their incorporation in high-grade gasoline.

As was already mentioned, the severity of the above requirements varies with the type of gasoline. The most exacting specifications have been developed for gasoline employed in airplane engines, because failure of these engines during flight may result in a catastrophe. Aviation gasolines also differ from regular motor gasolines in having a lower and narrower boiling range to insure the best possible performance. However, both aviation and motor gasolines are subdivided into a number of grades in order to satisfy a variety of customers, some of whom are more interested in price than in quality of the product they buy.

In order to meet the demand for the various gasolines, the refiner resorts to blending of numerous materials which he has on hand and which boil within the gasoline range. Such materials may arise from a number of sources and may be produced directly from the crude or obtained in the course of its processing. These materials may include straight-run gasoline, cracked gasoline, natural gasoline, and various synthetic materials which have recently come into considerable prominence. As the refinery operations are quite involved, it is almost impossible to discuss production of gasoline without describing simultaneously the manufacture of the synthetic type of materials which are obtained from crude oil by processes other than straight distillation.

Distillation of Crude Oil

When the crude oil is received by the refinery, it is distilled in order to obtain a preliminary separation into various portions, or fractions, of different boiling points. The gasoline thus recovered is referred to as "straight-run" gasoline. Distillation is done in stills which have recently been developed to a high degree of perfection. A modern pipe still, shown schematically in Figure 3, consists of a furnace, a fractionating tower and condensers. The crude is pumped under pressure through pipe coils located in the furnace and heated by flame or by hot combustion gases. The flow of crude through the coils is very fast in order to avoid as far as possible its decomposition at the high temperatures prevailing in the furnace. After leaving the furnace, the

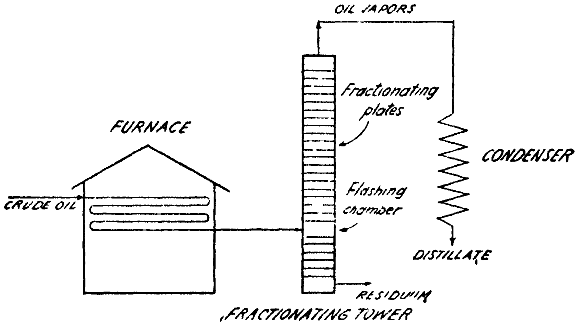


FIGURE 3. How crude oil is fractionated.

hot crude is injected into a flashing chamber located within the fractionating tower. The flashing chamber is represented by an empty space between the fractionating plates. As the pressure in the flashing chamber is considerably less than in the pipe coils, most of the crude vaporizes, or flashes, into the free space. The resulting vapors ascend the fractionating tower by condensing and re-evaporating at each successive fractionating plate, as was described in connection with the fractionation of natural gasoline. The unevaporated portions of the crude flow toward the still bottom in a direction opposite to that of the ascending vapors; on their way they encounter a number of fractionating plates which serve to strip them from the light fractions they may still contain. To facilitate stripping, steam may be passed through the tower, and the bottom of the still may be equipped with a reboiler, *i.e.*, with heating coils which supply additional heat to the oil bottoms before they leave the system. The presence of steam insures evaporation of light petroleum fractions at temperatures lower than those which would be required in its absence, and thus prevents undue overheating of the oil. The number of fractionating plates in a tower may vary within wide limits. Usually about twenty or thirty plates are located above the flashing chamber, although for some special purposes, when fractions having boiling points very close together must be prepared, the number may be raised to fifty or sixty. Such conditions are encountered, for instance, in the preparation of iso-pentane from natural gasoline described in the previous chapter. The number of fractionating plates below the flashing chamber is seldom above six.

Vapors leaving the top of the fractionating tower are liquefied by passing them through condensers. Condensers must have a large cooling surface in order to obtain the desired condensation of vapors into liquid. The liquid from the bottom of the fractionating tower, frequently referred to as *residuum*, is withdrawn from the still in a continuous manner, thus completing separation of the oil charge into a light and heavy fraction, or "overhead" and "bottoms" respectively.

The actual design of commercial stills is, however, considerably more complicated than the foregoing simplified description. Separation of the oil bled into the fractionating tower into more than two fractions is often accomplished. This is done by withdrawing from the tower the liquids condensed on the intermediate plates.

The liquid is usually withdrawn into a separate vessel attached to the fractionating tower, where it is heated by means of coils to eliminate as completely as possible the low-boiling components before the fraction is actually removed from the still. Vapors arising from this reboiling operation are returned to the appropriate places within the main fractionating column so as to interfere as little as possible with the preparation of other fractions.

Considerable attention is now being given to the conservation of fuel to insure maximum operating economy. This is done by employing a large number of heat exchangers. In these, the oil to be heated is passed in the opposite direction to the oil to be cooled. The two oil streams are separated from each other by metal walls permitting a good transfer of heat between the two streams. Such improvements in still design have resulted in enormous savings in the cost of fuel required to distill the crude. Thus in 1940 the average consumption of fuel per barrel of crude oil distilled was approximately half that in 1925.

Pipe stills are a relatively recent development. Before they were adopted by the petroleum industry, distillations were conducted in the so-called shell stills which were of simple construction, but consumed much fuel and required a considerably longer time to bring the oil to the distillation temperature than is necessary with pipe stills. However, shell stills are used when the quantities of materials handled are small and when fuel economy is of secondary importance.

The construction of shell stills is very simple. They consist of a large steel vessel which is charged with the oil to be distilled. The fire is started under the still, and as the oil begins to boil the fractions of increasingly higher boiling ranges are collected by passing vapors through fractionating towers and condensers into the receivers. By comparing the two types of stills it may be observed that the pipe still operates continuously while operation of the shell still is intermittent. For the same reason the products obtained from the pipe still are of a uniform boiling range, whereas those obtained from the shell still are not. But a shell still can also be operated continuously. Thus the fresh feed may be introduced while withdrawing an equivalent volume of bottoms. If several shell stills are interconnected, forming a "still battery," the bottoms from one still may serve as the feed to the next still of the series. With this arrangement each still produces a continuous stream of a uniform product, although separation of light and heavier fractions is usually less satisfactory than in a pipe still. The fuel consumption is high because the system of heat interchangers cannot be as elaborate as in a pipe still. Shell still batteries were widely used during the early stages of pipe still development, because they permitted a relatively efficient utilization of obsolete equipment and thus avoided considerable cash outlays.

As has been mentioned, the oil is brought to distillation temperature by applying heat directly to the metal tubes or still shells containing the oil. Gas, oil or coal may be employed as the sources of heat, depending on the cost of these commodities in different localities. This direct application of heat presents some objections, however, because of the possibility of locally overheating the oil above safe limits. Consequently, processes were developed wherein the heat is transferred to the oil in an indirect manner, eliminating the danger of overheating. In such processes an auxiliary heat-stable substance, sometimes referred to as a "thermophore," is heated directly with the flame; the hot gases are then circulated through heat exchangers where the heat is given off to the oil. The auxiliary heating medium thus circulates in a completely enclosed space and its mechanical losses due to leakage are reduced to a minimum. Commercial processes of this type are exemplified by the

Mercury Process, employing mercury, and by the Dowtherm Process, employing an organic material (diphenyl oxide) as thermophore. Mixtures of sodium and potassium nitrates and nitrites are also used in some commercial processes. Obviously the nature of the heating medium has no relation to the quality of the distilled products, because the heating medium and the oil are never brought into direct contact. The choice between the individual thermophores is thus one of the economies, provided their physical and chemical characteristics are satisfactory for the type of operation contemplated at the refinery. However, properly designed pipe stills usually eliminate the necessity of employing thermophores in most of the refinery installations. In some instances the oil is heated by means of steam, employing suitable heat exchangers. If steam is used in this manner it may be also regarded as a thermophore.

Separation of light fractions from the crude oil by distillation is relatively simple because the required temperatures are below those at which the oil begins to decompose. Complications arise in distilling the high-boiling fractions which require high temperature for their vaporization. In general, when the crude oil is reworked into various types of fuel, decomposition due to high temperatures prevailing in the stills is of little importance, provided formation of carbon deposits and consequent plugging of the pipes is avoided. However, in the preparation of lubricating oils, overheating may impair the quality of the resulting products or their physical characteristics.

If overheating of the oil must be avoided, distillation is usually conducted in two steps. The lightest fractions are first separated from the heavier ones by distilling the crude under atmospheric pressure in an "atmospheric" still. The bottoms from this distillation are transferred to a second still, the so-called "vacuum" still, for further distillation. Here distillation is carried out under vacuum and in the presence of large quantities of steam, to reduce the distillation temperature to the lowest possible minimum and thus eliminate the hazard of decomposing the oil. In this type of distillation, residuum from the atmospheric still is frequently referred to as "long residuum," and that from the vacuum still as "short residuum."

In distilling the crude oil for the recovery of light products and fuel oils, the refiner obtains the straight-run gasoline fractions, kerosene, and gas oil. These products are enumerated in the order of the progressive increase in their boiling point. Residuum is withdrawn from the bottom of the fractionating tower and used as fuel or reworked into asphalt, provided the crude is suitable for this purpose. In distilling the crude oil for the recovery of lubricating-oil fractions, the refiner obtains straight-run gasoline and kerosene from the atmospheric tower and a number of lubricating-oil fractions from the vacuum tower. A small quantity of gas oil boiling between kerosene and the lightest of the lubricating-oil fractions may be also recovered. The number and physical characteristics of the lubricating-oil fractions depend on the type of finished products desired.

For this description it may be assumed that the fractions or "cuts" are collected in a certain definite order and that there is no overlap in the boiling ranges of the manufactured products. This, however, is not always the case, because a number of refinery products contain common fractions boiling within the same temperature ranges. The tabulation on page 76 and its graphical representation in Figure 4 give the approximate distillation ranges of a few of the well known petroleum materials illustrating the existing overlaps.

In preparing products of different boiling ranges the refiner has to adjust the width of the

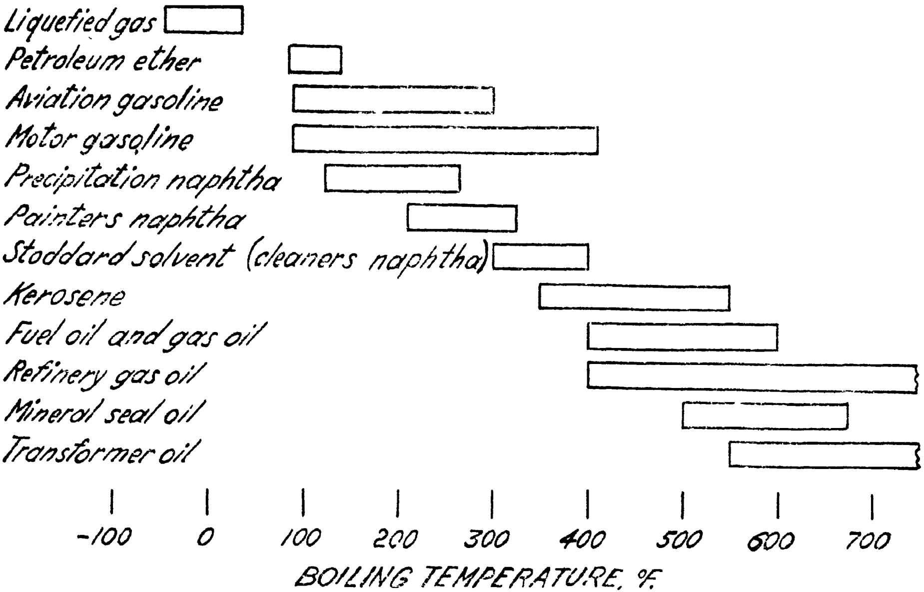


FIGURE 4. Distillation range of crude oil components. Note the extent to which they overlap.

Substance	Approximate Boiling Range (°F.)
Liquefied gas	−48 to +34
Petroleum ether	+86 to 140
Aviation gasoline	90 to 300
Motor gasoline	90 to 410
Precipitation naphtha	122 to 266
Painters' naphtha	210 to 325
Stoddard solvent (Cleaners' naphtha)	300 to 400
Kerosene	350 to 550
Fuel oil (gas oil)	400 to 600
Refinery gas oil	400 to 750+
Mineral seal oil	500 to 675
Transformer oil	550 to 750+

fractions in order to secure the desired materials. Sometimes a portion of kerosene may be included in gas oil. If the refinery is interested in preparing aviation gasoline, the motor gasoline cut may be resolved into aviation gasoline, and cleaners' (Stoddard) solvent without resorting to secondary distillation. However, if small quantities of narrow-boiling materials are required, they are usually obtained by redistilling broader fractions in small shell stills, which in this instance may be more economical because the loss involved in bringing a continuous still to uniform operating conditions might be prohibitive.

The discussion shows that considerable skill is required in planning and timing the various plant operations. Highly trained technical personnel is needed to tackle problems of a scientific nature which the refinery has to meet. For this reason some of the advanced petroleum companies choose their plant personnel from the research and development department staff in order to keep the refinery always abreast of modern developments.

Chapter 6

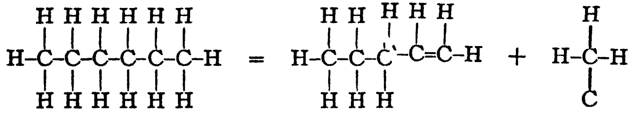
Cracking

What is Meant by Cracking?

Plant operations mentioned in the previous chapter described the refinery processes employed to separate straight-run gasoline and other materials from other crude-oil fractions. However, about one-half of the gasoline sold to the public is derived not from straight-run distillation but from transformation of heavy crude-oil fractions into lighter ones. Transformations of this type are accomplished by means of the so-called cracking processes.

What happens during cracking is essentially this: at high temperatures substances consisting of molecules containing many atoms decompose into substances consisting of molecules containing fewer atoms. In other words, a large, complicated molecule is broken down by application of heat into two or more simple ones. This decomposition results in lowering the boiling point and in changing a number of other properties of the original materials. The more drastic are the cracking conditions, the smaller are the molecules and the lower is the boiling range of the cracked products. At extremely high temperatures all hydrocarbons decompose into their elements, carbon and hydrogen.

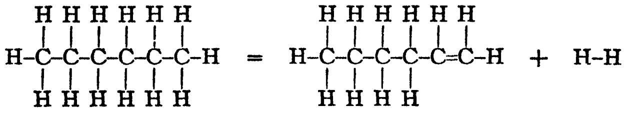
A hydrocarbon molecule can be decomposed in a variety of ways. Some of these reactions may be visualized by considering a few of the many theoretically possible splittings of a molecule of a saturated hydrocarbon which are shown below. Hexane, a saturated hydrocarbon containing six-carbon atoms and fourteen hydrogen atoms, may be used for illustrative purposes. One such splitting may yield an unsaturated hydrocarbon and a gas (methane):



$$C_6H_{14} \qquad C_5H_{10} \qquad CH_4$$

Hexane *Pentene* *Methane*

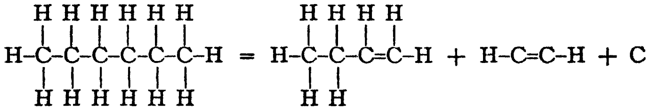
Another splitting may yield an unsaturated hydrocarbon and hydrogen:



$$C_6H_{14} = C_6H_{12} + H_2$$

Hexane *Hexene* *Hydrogen*

Still another splitting may result theoretically in the formation of two unsaturated hydrocarbons and carbon:



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H = H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}{-}H + H{-}C{=}C{-}H + C}$$

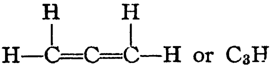
$$C_6H_{14} = C_3H_8 + C_2H_4 + C$$

Hexane *Propylene* *Ethylene*

Not all the above reactions actually occur in the course of cracking. For instance, carbon is never formed from hexane directly but is produced in the course of secondary reactions involving complicated chemical transformations. However, in the present discussion this fact has been neglected for simplicity.

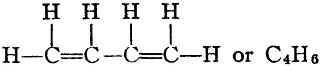
From the few examples shown it may be seen that gases, liquids and solids are formed in the cracking processes. Of these products gasoline is the desirable material while gas and coke may be regarded as the unavoidable by-products.

Actual reactions involved in cracking are considerably more complicated than those shown above. Some highly unsaturated hydrocarbons may be formed, that is, hydrocarbons containing two or more double bonds in the molecule. These hydrocarbons are usually referred to as diolefins. The simplest members of this hydrocarbon series are allene and butadiene:



$H-\overset{H}{\overset{|}{C}}=C=\overset{H}{\overset{|}{C}}-H$ or C_3H

Allene



$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H$ or C_4H_6

Butadiene

The light unsaturated hydrocarbon molecules produced by decomposition of the heavier ones may combine with other molecules, forming new substances which are relatively stable under conditions of cracking. These newly formed substances may decompose in their turn, depending on the severity of the cracking conditions to which they are exposed. The complexity of such innumerable reactions prevents a detailed analysis of cracking phenomena except in a very general manner.

THERMAL AND CATALYTIC CRACKING PROCESSES

Two major types of cracking processes are now in commercial use: the *thermal* cracking processes and the *catalytic* cracking processes. In the thermal cracking processes decomposition of the heavy oil fractions is accomplished by high temperature treatment without attempting to influence the course of the reactions by conditions other than temperature, pressure and time. In the catalytic processes, which are now coming into prominence, the course of the reactions is also controlled by the presence of catalysts, which are substances which are capable of influencing the direction and rate of the reactions without taking an active part in them. A small quantity of catalyst is thus theoretically capable of transforming an infinite quantity of material from one type into another without losing its activity. These two general types of cracking processes are discussed separately.

The thermal cracking processes may be subdivided into two groups depending on whether or not sufficient pressure is employed to keep the oil in the cracking unit in liquid form, or phase. The liquid-phase processes employ high temperatures and high pressures; the vapor-phase processes use even higher temperatures but low pressures. However, this differentiation is to a certain extent artificial, because numerous investigations have shown that the temperatures employed in liquid-phase cracking are higher than those which permit existence of the majority of hydrocarbons as liquids. For this reason, in most of the so-called liquid-phase processes the oil should be considered as being in the state of a highly compressed vapor and not of a true liquid. Nevertheless, the original division between the liquid- and vapor-phase processes is still retained by refiners for its convenience.

Liquid-Phase Cracking

Liquid-phase processes operate at temperatures of 850° F. to 950° F. and at pressures ranging from 1000 to 1500 pounds per square inch or even higher. The oil, usually the gas-oil fraction, is passed through a furnace, where it is heated to the desired temperature and for a sufficient length of time to obtain the desired degree of cracking. As shown in Figure 5, the cracked mixture is pumped to fractionating towers in order to distill off the gasoline produced. However, such a simplified system would not be commercially possible because of many technical complications arising in the course of cracking operations. Some explanation is, therefore, re-

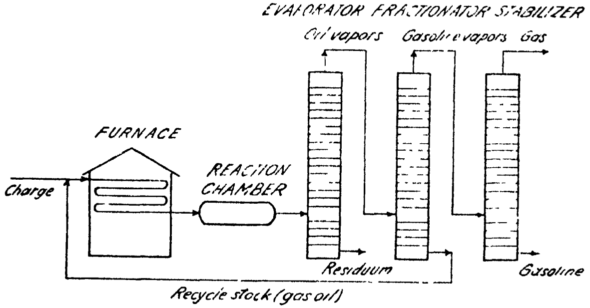


FIGURE 5. Diagram of liquid-phase cracking process.

quired in order to present the cracking problems from the point of view of the refiner and of the designer of cracking equipment.

As has been mentioned, three major variables are involved in cracking operations: temperature, time and pressure. Within certain limits the effects of temperature and time are interchangeable, *i.e.*, approximately the same results may be obtained by operating at higher temperatures and shorter cracking times as by operating at lower temperatures and longer cracking times. In order to make the best use of the time factor, many cracking processes, such as the Cross, Holmes-Manley, Dubbs, or Tube and Tank, employ so-called reaction chambers. These are sometimes also referred to as soaking chambers, cracking chambers, or reactors, depending on the local nomenclature. The hot oil passes into the reaction chamber, which is well insulated to keep the oil in the chamber at the highest possible temperature. During this time the cracking reactions continue to progress, resulting in an increased gasoline yield. From the reaction chamber the oil passes into fractionating towers to remove the gasoline. If the reaction chamber is omitted—and this is done in the more recently developed processes of Winkler-Koch, Donnelly, and others—a similar effect is obtained by raising the furnace temperature or by increasing the time the oil is kept in the furnace. However, under these conditions a much closer control of cracking operations is required because of the rapidity of cracking reactions at high temperatures.

Pressure is also an important factor. For units having equal volumes of cracking space and operating at equal temperatures, the time of cracking, and consequently the gasoline yield, is greater for units operating at high pressures. The solubility of heavy carbonaceous materials in the oil is greater at higher than at lower pressures, which is helpful in reducing the quantity of carbon deposits in the cracking units.

Depending on the severity of cracking, the charge stock may be decomposed into gas, gasoline, gas oil, which is usually referred to as cycle or recycle stock, and heavy liquid residuum, or into gas, gasoline and solid coke. If residuum is formed, the process is classified as a residuum cracking process; if coke is formed instead of residuum, the process is classified as a nonresiduum cracking process.

In the residuum process the cracked oil from the furnace or cracking chamber enters the fractionating tower, frequently called the evaporator. In this tower a very heavy but still liquid residuum separates at the bottom and is drained from the system. The remaining cracked products pass as vapors to a second tower, or fractionator. Here the gasoline separates from the gas oil or cycle stock, which is also withdrawn from the bottom. The gasoline finally passes into a third fractionating tower, or stabilizer, where gasoline is separated from the light hydrocarbon gases.

Residuum from the first fractionating tower is usually used as fuel. This cracked residuum is often unstable and forms sediment on standing. If residuum is not properly treated or blended with other oil fractions, difficulties may arise from plugging of burners which are employed for its combustion.

Recycling. Gas oil withdrawn from the bottom of the second fractionating tower may be used as light fuel oil or for some other purposes. When it is used as fuel oil, some treatment may be required to improve its stability, that is, to prevent formation of sediment during storage. Very frequently, however, it is returned to the charging stock entering the cracking unit to accomplish its further decomposition into gasoline and residuum. If this is done, the process is said to involve recycling. The question naturally arises why the charging stock is not cracked directly into gas, gasoline, and residuum without formation of an intermediate gas oil or recycle fraction. This is not done because it involves excessive coke formation and consequent plugging of the unit with carbonaceous deposits, which requires frequent cleaning of the equipment. Excessive amount of cracking should, therefore, never be attempted in one-pass operation, *i.e.*, without recycling. Similar considerations are involved in establishing the proper demarkation line between recycle stock and residuum. If very heavy residuum is returned to the cracking system, excessive coke deposits are formed in the unit, but if a large proportion of light fractions is included in the residuum, the yield of gasoline per unit volume of charge diminishes.

The cracked gas oil is more stable to heat than the original charge stock from which the gas oil is obtained. This is to be expected because the thermally less stable hydrocarbons boiling within the gas oil range decompose during cracking. For this reason the recycle stock should be more difficult to crack than the fresh feed. In order to avoid separate cracking of recycle stock in a different cracking unit, a compromise is reached in recycle cracking operations by adjusting the severity of cracking conditions somewhere between the most favorable ones for the fresh feed and for the recycle stock. However, the operation may be improved by cracking the recycle stock separately from the virgin stock if this is economically feasible. This is done in the so-called selective cracking processes, where the gas oil from the fractionator is not mixed with the virgin stock but is passed through a separate set of coils often located in the same furnace. The two streams of cracked products emerging from the two coils are united before they enter the fractionating system. In the past the same effect was obtained by segregating the gas oil from once-through operation and then rerunning it separately through the cracking unit after a sufficient quantity of it had accumulated to warrant separate processing.

In the above discussion recycle stock was shown to be thermally more stable than virgin stock. This does not imply, however, stability toward oxidation, but only stability toward high-temperature decomposition in the absence of air or oxygen. Actually the recycle stock is much less resistant to oxidation than the virgin stock, which explains the necessity of treating it if high storage stability and freedom from sediment formation are important.

If fresh feed and recycle stock are cracked independently but blended before they enter the fractionating equipment, the temperature of the recycle stock is reduced by the injection of the fresh feed cracked at a lower temperature. This quenching is advantageous because it serves to utilize very efficiently the extra heat present in the recycle stock for additional cracking of the fresh feed and facilitates control of the cracking operations. Quenching was first used in the Donnelly cracking process.

Coke Formation. The non-residuum cracking processes require some modification in the design of the equipment as compared to the residuum processes because of the necessity of eliminating solid coke from the system. In these processes the oil passes from the cracking coils into coke settlers or coking chambers. In the coke chambers the coke settles out and only the liquid is allowed to enter the fractionating equipment. All liquid products heavier than gasoline are returned to the cracking zone in order to accomplish their complete conversion into gas, gasoline and coke. Settling of coke before the oil reaches the coke settler is prevented by maintaining high oil velocities in the cracking coils and pipes leading to the settler. High oil velocities are important, however, in all types of cracking units to avoid local overheating and coke deposition.

Comparing the non-residuum processes with the previously described residuum processes, it may be noted that the coke settler may be regarded as a modification of the reaction chamber. However, coke is deliberately deposited in the coke settler, whereas its deposition in the reaction chamber is undesirable, though not entirely avoidable.

The size of the coke settlers is larger than that of reaction chambers in order to insure more room for coke deposits, *i.e.*, to provide for longer operating times. When the coke settler fills up, the oil stream is diverted into another settler to insure continuity of the cracking operation. The coke is removed from the settlers mechanically.

So far it has been implied that cracking is conducted for the sole purpose of preparing gasoline. However, gas oil also finds a considerable market, and the ratio between the gasoline and the gas oil produced by a refinery depends to a great extent on the current demand for these products. If gas oil is an important refinery item, a delayed coking process may be installed.

The delayed coking processes were developed for cracking residual stocks to a maximum yield of gas oil. Although some 20-25 per cent of gasoline is produced together with the gas oil, this gasoline may be regarded as a by-product.

Two types of delayed coking processes are available, the Knowles and the Diwoky.

The Knowles Delayed Coking Process is a batch process. The oil is charged to a shell still and the distillate passed to a fractionating tower where gasoline and gas oil are separated from the residuum. Residuum is returned to the still for further cracking. The temperature in the still is gradually raised until all the charge is converted into gas oil and gasoline. Firing of the still is then discontinued and the accumulated coke is removed from the still mechanically.

The Diwoky Delayed Coking Process is continuous and may be compared with the non-residuum cracking process. The charge is heated by passing it through a pipe still. Gasoline and gas oil are separated in a fractionating tower from the residuum, which is recycled. Coke deposits are removed periodically from the alternate coking chambers without interfering with the continuous operation of the unit.

Viscosity Breaking. Another important application of cracking is in viscosity breaking or "vis-breaking" of residuum. Residuum from straight-run distillation of crude oil easily congeals at ordinary temperatures and its viscosity is high, making it unsuitable for use in burners. Viscosity may be lowered or "broken," that is, the residuum may be rendered more fluid, by cracking at relatively low temperatures. Some gasoline, normally from five to ten per cent of the charge, is obtained as a by-product from this operation. Viscosity breaking may be also achieved by injecting residuum into the hot-cracked products resulting from normal cracking operations at the point where these products leave the cracking furnace. The quantity of heat supplied in this manner to the residuum is sufficient to obtain the desired degree of cracking. This method of breaking viscosity of the residuum is usually referred to as the "injection flow" method.

In operating an oil refinery, conservation of heat is a very important problem. The difference between profit and loss may be often traced to the difference in the quantity of fuel burned. No efforts are, therefore, spared by the refiner to reduce fuel consumption to the lowest possible minimum. The reduction in fuel consumption is obtained by employing elaborate heat-exchange systems which may interconnect several refinery units. The purpose of these is to utilize the heat from outgoing products to warm the incoming materials to processing temperature; in this way little heat is lost from the system. Such units may also have other equipment in common, for instance, fractionating towers or furnaces. Thus straight-run distillation, cracking, viscosity breaking and a number of other operations may be combined in this manner. Such complicated installations are known as "combination units." The combination units have the weakness that the failure of one of their component parts may result in the shut-down of the whole system. However, their practical value has been well established by refinery experience.

Vapor-Phase Cracking

The vapor-phase cracking processes employ temperatures from 1050° F. to 1200° F. or even higher, and pressures of 50 to 150 pounds per square inch. Under exceptional conditions pressures of 500 pounds per square inch appear commercially feasible provided suitable alloy steels are used in constructing the units. Kerosene or light gas oil are used as charging stocks to permit their complete vaporization within the unit. The vapor-phase processes include Gyro, DeFlorez, Pratt, True Vapor Phase (Knox), and others. The cracked vapors are passed from the furnace directly to the fractionating columns. Because of the very high temperatures used, the oil is cracked rapidly and the reaction time is measured not by minutes, as in liquid-phase cracking, but by seconds. An extremely careful control of the entire cracking operation is therefore imperative. Quenching of cracked vapors is often resorted to. Light distillates (Gyro Process) or heavy oil fractions (Pratt Process) may be employed for this purpose. In some of the vapor-phase processes high temperatures are reached by mixing the oil vapors with hot inert gases (True Vapor Phase Process). Vapor-phase processes have been devised wherein heat is supplied internally, *i.e.*, a controlled amount of air is injected into the oil vapors to effect their partial combustion and thus raise the temperature of the remaining oil vapors to the desired level (Dubrovai Process). Although the vapor-phase processes are more difficult to operate than the liquid-phase they yield gasoline of high-antiknock quality. However, vapor-phase gasolines are usually less stable than liquid-phase gasolines and require considerable care in finishing them to marketable products.

Catalytic Cracking

The catalytic cracking processes came into prominence with the rapid commercial development of the Houdry units. In the Houdry process the charge stock is passed through the furnace into a tar separator where the incompletely vaporized heavy materials are separated from the vapors. A simplified diagram of the process is shown in Figure 6. From the tar separator the oil vapors enter the catalytic chamber which is filled either with a clay or with a synthetic catalyst prepared in the form of pellets. From the catalytic chamber the vapors are conducted into the fractionating equipment.

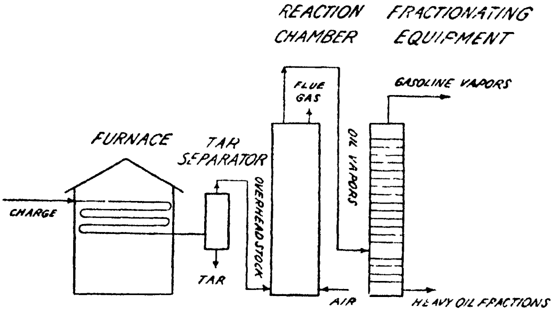


FIGURE 6. The Houdry catalytic cracking process.

Although theoretically the catalyst should last indefinitely, certain quantities of carbon formed and deposited on the catalyst during cracking must be removed at frequent intervals. These carbon deposits contaminate the surface of the catalyst, which is the active portion, and prevent contact between it and the oil vapors. In commercial units the catalyst is regenerated after every ten to sixty minutes of operation, depending on the nature of charging stock, operating conditions and design of the cracking unit. Regeneration is accomplished by blowing air through the catalyst bed and thus burning off the carbon. Continuous operation of the plant is insured by employing several, usually three, catalytic chambers in parallel. While one of the chambers is employed for cracking the oil vapors, the two others are in various stages of regeneration.

The burning off of carbon deposits is accompanied by evolution of large quantities of heat. During the cracking operation some heat is, on the contrary, absorbed by the oil. A careful temperature control during both the regeneration and cracking cycles is therefore necessary to obtain satisfactory performance of the unit and to protect the catalyst from overheating. The temperature control is effected by circulating molten salt through a series of tubes located inside the catalytic cracking chambers. This arrangement permits preservation of high catalyst activity over a considerable time.

The Houdry process yields gasoline of exceptionally high antiknock quality and stability. The presence of a catalyst modifies the course of the cracking reactions preventing formation of unstable, unsaturated hydrocarbons and favor-ing formation of stable, saturated hydrocarbons of the type which is most desirable in motor fuels.

Recently a continuous catalytic cracking process known as the TCC (Thermofor Catalytic Cracking) process was developed by the Socony-Vacuum Oil Co., Inc. A granular catalyst is passed through the system in the opposite direction to the flow of oil vapors. The spent catalyst is continuously withdrawn and burned free from carbon in contact with air. The regenerated catalyst is then returned to the system.

In the "fluid" catalytic cracking process developed by the Standard Oil Development Company (N. J.) oil vapors are contacted with a very finely divided catalyst. The spent catalyst is separated from the oil vapors, regenerated by burning, and returned to the system. The so-called Suspensoid Process of the Imperial Oil Co., Ltd., a subsidiary of the Standard Oil Co. (N. J.), consists in injecting small quantities of clay into the feed to the thermal cracking units to improve the yield and quality of product.

A catalytic process employing aluminum chloride as a catalyst has been tried on a commercial scale for a number of years. The charging stock is mixed with relatively small proportions of powdered anhydrous aluminum chloride and heated under atmospheric pressure to effect cracking. The gasoline obtained is very stable, but the consumption of aluminum chloride is relatively high, thus adding to the cost of the process.

Cracking in the presence of very large quantities of steam, known as "aquolization," yields good gasoline, of a somewhat different type from that obtained by normal thermal cracking. However, the tremendous quantities of steam required make the operation expensive.

Cracking processes may be also applied to naphtha, which consists almost exclusively of gasoline fractions. When naphtha is used as a charging stock the process is known as "re-forming." Re-forming of naphtha is done primarily to improve the antiknocking quality of the gasoline. Re-forming differs somewhat from cracking because of the use of somewhat higher temperatures and of the absence of recycling. High temperatures are required because of the greater thermal stability of naphtha at elevated temperatures as compared to that of the heavier petroleum products. Recycling is omitted because carbon formation is small. Catalytic re-forming processes are also in existence.

The Houdry Reforming Process employs a catalyst similar to that developed for the corresponding cracking process. The Kellogg process also uses a catalyst, but the design of equipment is different from that of the Houdry process because of the absence of the salt circulating system. The Phillips Company Catalytic Reforming Process uses bauxite (aluminum ore) as a catalyst.

Chapter 7

Hydrogenation and Aviation Gasolines

The Hydrogenation Process

Formation of carbon and unsaturated hydrocarbons cannot be avoided in normal cracking operations. However, if cracking is carried out in the presence of hydrogen, the excess carbon unites with hydrogen, forming hydrocarbons of the saturated type, thus increasing the yield of light distillates. Petroleum hydrogenation processes were developed by the Standard Oil Company (N. J.) in collaboration with the I. G. Farbenindustrie A.-G.

The hydrogenation process equivalent to cracking is known under the name of "hydrocracking" (hydro (gen) cracking). The charging stock with the necessary amount of hydrogen is fed at about 850-950° F. and at approximately 3000 pounds per square inch pressure into a reaction chamber containing a suitable catalyst. Under these conditions formation of carbon or unsaturated hydrocarbons is practically eliminated because enough hydrogen is available to form saturated products. The nature and quality of these products are regulated by the nature of the charge stock and conditions of hydrogenation. The process may be applied not only to the manufacture of gasoline but also to that of other petroleum products, such as lubricating oils. In many of their characteristics these hydrogenated products are similar to, or better than, those obtained directly from crude oil.

A certain parallel exists between catalytic cracking and hydrogenation which explains some similarity in the quality of the products resulting from the two operations. In catalytic cracking deficient hydrogen is supplied to the gasoline fractions by the remainder of the crude, whereas in hydrogenation it is supplied from an outside source. In both instances catalysts direct the cracking reactions toward formation of saturated hydrocarbons.

The necessity of supplying hydrogen considerably increases the cost of the hydrogenation processes and hinders their development, while the supply of crude is still plentiful. Hydrogen for this purpose is usually obtained by decomposing methane at high temperatures into hydrogen and carbon. This is the cheapest way to manufacture hydrogen in large quantities. Other processes for its manufacture are also available, such as the Schultze Process, where hydrogen is obtained from water gas and iron ore, or the electrolytic process for producing both hydrogen and oxygen by decomposing water; but they are able to compete with the methane process only in small installations.

Hydrogenation may be employed in re-forming operations, for improving the antiknock and other properties of naphtha or gasoline. This modification of the hydrogenation process is known as "hydroforming" (hydro(gen re)-forming).

A very mild degree of hydrogenation is sometimes sufficient for improving the quality of petroleum products obtained from sources other than hydrogenation. This involves principally the conversion of unsaturated hydrocarbons into saturated ones. Such mild hydrogenation is known as "hydrofining" (hydro(gen re)fining).

Aviation Gasoline

Wartime demands on the aviation industry have placed on the shoulders of the refiner the heavy burden of producing extra grades of gasoline having exceptional antiknock properties and oxidation stability. Until recently aviation fuels were prepared from a few selected crudes which yielded on distillation straight-run gasolines of about 80 octane number. The octane number of gasolines obtained from a vast majority of crudes is considerably below this figure. However, at the present time even the standard grades of motor gasoline sold to automobile owners have an octane number of 80 or more, while the premium grades surpass the 90 mark. The value of high-octane gasolines may be better understood from the following comparisons. The change from a 70-octane to an 85-octane gasoline permits a 30 per cent increase in compression ratio, with the corresponding increase of 23 per cent in the horse-power output and in a 13 per cent improvement in fuel economy. With a 95-octane gasoline the compression ratio may be raised by 65 per cent, resulting in a 40 per cent increase in horse-power and a 25 per cent improvement in fuel economy as compared to 70-octane gasoline. For these reasons the aviation industry is demanding gasolines of 100-octane or even better. Such gasolines should, therefore, equal or surpass in performance pure iso-octane, generally considered as a hydrocarbon possessing exceptional antiknock properties as compared to other pure chemical compounds.

In order to meet these exacting specifications petroleum refiners have started the manufacture of products resembling chemicals and are gradually encroaching on the domain of synthetic organic chemistry. Production of such chemicals has now become one of the specialized branches of petroleum industry.

Blending Agents

Chemicals proposed as gasoline blending agents include not only hydrocarbons but also substances which in addition to hydrogen and carbon may contain some oxygen. They may be divided into those manufactured on a commercial scale and those which cannot yet be obtained in large quantities at a reasonable cost, but which may be available in the future after completion of the development work now in progress. The commercially available materials include iso-octane and neo-hexane. Materials of possible future interest include triptane and a few other hydrocarbons.

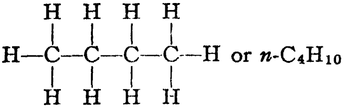
Substances containing hydrogen, carbon and oxygen and recommended for gasoline blends are represented by isopropyl ether. However, such blends, although possessing good antiknock quality, are less satisfactory than those containing hydrocarbon materials only, because in addition to some undesirable features, they develop less heat on combustion, *i.e.*, more fuel is required for covering equal distances.

Polymerization

Iso-octane which, as was already mentioned is a chemical misnomer, was the first hydrocarbon synthesized and used commercially in gasoline blends. The processes employed for its manufacture may be divided into two main groups. The earlier polymerization processes involve a two-step operation: polymerization of selected unsaturated hydrocarbons followed by hydrogenation. Polymerization is the chemical combination of a number of small molecules to form large molecules. The more recent alkylation processes form iso-octane in one step and do not require hydrogenation.

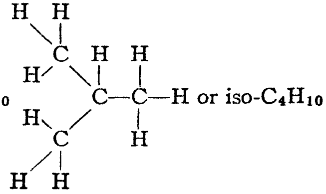
In the polymerization processes the unsaturated hydrocarbons occurring in refinery cracking gases and containing four carbon and eight hydrogen atoms are employed as basic materials for further synthesis. These unsaturated hydrocarbons are known as butenes. The chemical formulas of the three known butenes are shown below in comparison with those of the two saturated hydrocarbons having the same number of carbon atoms but containing no double bonds:

Butanes (saturated hydrocarbons)



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \text{ or } n\text{-}C_4H_{10}$$

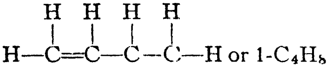
Normal butane



or iso-C_4H_{10}

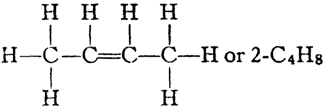
Iso-butane

Butenes (unsaturated hydrocarbons)



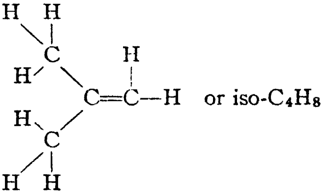
$$H-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}-\overset{H}{C}-H \text{ or } 1\text{-}C_4H_8$$

1-Butene



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-H \text{ or } 2\text{-}C_4H_8$$

2-Butene



or iso-C_4H_8

Iso-butene

In the presence of suitable catalysts and by employing proper temperature and pressures the butenes are easily polymerized, that is, several molecules of butene unite to form a heavier molecule. The desired product is the one obtained by interaction of two molecules of isobutene which results in the formation of isooctene (also a misnomer):

$$\underset{\textit{Iso-butene}}{\text{iso-}C_4H_8} + \underset{\textit{Iso-butene}}{\text{iso-}C_4H_8} = \underset{\textit{Iso-octene}}{\text{iso-}C_8H_{16}}$$

In commercial operations a number of side reactions cannot be avoided. Besides iso-octene, heavier substances are formed which contain three or more molecules of iso-butene. In addition, similar polymerization products are obtained because they are always present in the stock charged to the polymerization units.

Iso-butene polymerizes at a faster rate than other butenes, and the iso-butene polymers may be obtained in a fairly pure state if yield is of secondary importance. However, polymers of other butenes have also relatively high antiknock properties and may be included in the final product without greatly lowering its quality but considerably improving the yield. In commercial operations an economic balance is, therefore, established between yield and quality of product.

All butanes and butenes are gases at ordinary temperatures. They may be liquefied if they are cooled at atmospheric pressure to a temperature not much below the freezing point of water. They may be also liquefied if slight pressure is applied at somewhat higher temperatures. Because the boiling points of individual butanes and butenes are very close to one another, they cannot be conveniently isolated by distillation, and the refinery uses their mixtures and not the individual hydrocarbons as the charge to the iso-octane plants. This mixture is known as the butane-butene fraction, or as the "BB cut."

The BB-fraction is passed at suitable temperatures and pressures through a catalyst to bring about polymerization of the unsaturated hydrocarbons. Several catalysts have been developed for this purpose. The Shell Oil Company and the Standard Oil Company (N. J.) employ warm and hot sulfuric acid respectively, the Universal Oil Products Company uses phosphoric acid, the Polymerization Process Corporation (Polyco Process) resorts to copper phosphate, and the Houdry Corporation utilizes a modified clay-type catalyst. As was already mentioned, the desirable products of the reaction are the so-called di-polymers, *i.e.*, polymers formed from two unsaturated molecules of butene. Formation of higher polymers should be avoided because they boil above the aviation gasoline range. Of the higher polymers, the tri-polymers—polymers produced by the union of three butene molecules—may be employed in motor gasoline; but heavier polymers do not find even this application.

After the BB-fraction is polymerized, the resulting products are fractionated. The butanes and the unreacted butenes are separated from the polymers, and the di-polymers or the "iso-octene," sometimes called "co-dimer," are separated from the heavier polymers. The heavier polymers, or "polymers" in refinery nomenclature, are distilled to obtain the tri-polymers or "trimers" which are used in motor gasoline blends. The polymers boiling above the gasoline range are used as fuel.

Iso-octene, also a chemical misnomer, is similar in chemical structure to iso-octane, except that it lacks two hydrogen atoms in the molecule. The two hydrogen atoms required for converting it into iso-octane are supplied by hydrogenation. Hydrogenation of iso-octene in the presence of suitable catalysts proceeds without difficulty under relatively mild conditions of temperature and pressure. Hydrogenated iso-octene is commercial iso-octane approaching rather closely pure iso-octane in its antiknock and other physical and chemical characteristics.

Alkylation

In the alkylation process marketed by the M. W. Kellogg Company, iso-octane is known as "alkylate" and is obtained in a one-step operation. This is done by uniting an unsaturated molecule of butene and a saturated molecule of isobutane to form a saturated molecule of iso-octane in the presence of sulfuric acid as a catalyst:

$$C_4H_8 + C_4H_{10} = C_8H_{18}$$

Butene · *Iso-butane* *Iso-octane* (*alkylate*)

It may be noted that iso-butane and not normal butane has been shown as taking part in the reaction. This is because of the chemical reactivity of iso-butane and relative inertness of normal butane which may be considered as taking no part in the alkylation process. A similar alkylation process employing hydrogen fluoride as a catalyst instead of sulfuric acid has been recently developed by the Universal Oil Products Company and is now on the market.

Neohexane is obtained by uniting ethylene with iso-butane. Commercial units are operated at about 950°F. and 4800 pounds per square inch pressure. No catalyst is necessary for promoting the reaction. As an unsaturated hydrocarbon (ethylene) is united directly with a saturated hydrocarbon (iso-butane) the reaction may be classified as an alkylation reaction:

$$C_2H_4 + C_4H_{10} = C_6H_{14}$$

Ethylene *Iso-butane* *Neohexane*

The process is licensed by the Polymerization Process Corporation (Polyco).

A number of other similar processes involving the manufacture of high antiknock hydrocarbons are now in various stages of development. These processes are more or less similar to the ones previously described. The main differences are in the nature of the charge materials and in the type of the resulting products. It may be expected, therefore, that new synthetic hydrocarbons of high antiknock properties will appear on the market in not a far distant future.

Tetraethyl Lead as Antiknock Agent

Improvement in the antiknock characteristics of motor fuels may be secured not only by employing synthetic hydrocarbons in the gasoline blends but also by adding very small quantities of certain chemicals which are capable of suppressing detonation in the engine. Of these chemicals tetraethyl lead is the most important.

Tetraethyl lead is sold by the Ethyl Gasoline Corporation in the form of Ethyl Fluid which contains, in addition to tetraethyl lead, some chlorine and bromine compounds and usually a red dye. The presence of these chlorine and bromine compounds is necessary to improve the volatility of lead and to prevent formation of engine deposits. The dye is used to forewarn the public that highly poisonous tetraethyl lead is blended with the gasoline. According to the specifications, the maximum quantity of tetraethyl lead in motor gasolines must not exceed three cubic centimeters per gallon (or 0.08% by volume). In exceptional cases, such as in preparing certain grades of aviation gasolines, this quantity may be raised to four or even six cubic centimeters per gallon. The use of tetraethyl lead in very large amounts is of little benefit because its efficiency in improving the antiknock properties of gasoline is not proportional to the quantity added, but falls off rapidly as the quantity increases. Moreover, if concentration of tetraethyl lead in the gasoline is high, formation of lead deposits may have an unfavorable effect on the overall operation of the engine. The high cost of tetraethyl lead is an additional factor inducing the refiner to economize on its consumption. In the "leaded" gasolines sold to the public the quantity of tetraethyl lead very seldom approaches the upper legal limit of three cubic centimeters, and is frequently below one cubic centimeter.

Nickel carbonyl has been tried for a number of years, particularly in Germany, as a possible substitute for tetraethyl lead. However, difficulties in handling it in engines resulted in the final abandonment of such attempts. Tetraethyl lead should therefore be regarded as the only practical compound of this type in existence.

The synthetic hydrocarbon materials described above are blended before they are used in the engine. This is done not only for economic reasons, but also for meeting specifications other than antiknock properties, such as boiling range and volatility. Iso-octane is blended with the lower-boiling hydrocarbon materials which may comprise iso-pentane, selected fractions of catalytically cracked gasolines, and similar substances. The choice of the blending materials depends on their availability at the various refineries. The resulting blends are mixed with tetraethyl lead which allows their antiknock properties to approach those of pure iso-octane. The more rigid the octane number requirements, the larger is the proportion of the expensive ingredients and, consequently, the higher the cost of the finished fuel.

Consumption of high-grade aviation gasolines is now considerable on account of the war and tremendous exports abroad. The quantities required by warplanes are enormous. For instance, an airplane equipped with two 1000-horsepower engines will consume as much as 1100 pounds of gasoline per hour of flight. Our country is well ahead of all others in manufacturing high-grade aviation gasolines and the existing shortage is due primarily to the present state of emergency.

The polymerization and alkylation processes are described in this chapter with particular reference to the manufacture of high-grade aviation fuels. For this reason the importance of properly selecting the charging stocks and of properly controlling the progress of the reactions has been stressed. The processes involving such careful control are frequently referred to as "selective" polymerization or alkylation processes. However, similar processes may be applied to any charge stock provided it contains suitable gaseous hydrocarbons which might be converted into liquids boiling within the gasoline range. In the "non-selective" processes of this type, the hydrogenation step is omitted because the resulting polymer gasoline is sufficiently stable for use in motor gasolines, and its octane rating is not much improved by expensive hydrogenation. Although the antiknock properties of polymer gasoline are considerably lower than those of iso-octane, the product is much cheaper to manufacture. The yield from a given volume of hydrocarbon gases is greater than the yield of iso-octane, because many more hydrocarbons are allowed to take part in the reaction. The plant operations are usually controlled with the primary purpose of obtaining the maximum yield of liquid hydrocarbons rather than the maximum octane rating. Up to the present time the polymerization processes were almost exclusively applied to the conversion of refinery mixtures of gaseous hydrocarbons of unsaturated type into liquids. The non-selective catalytic alkylation processes have been little used commercially, but thermal processes are available which promote polymerization and alkylation reactions by employing suitable temperatures and pressures.

Gas Conversion Processes

Both selective and non-selective processes for manufacturing gasoline from petroleum gases require the presence of reactive unsaturated hydrocarbons in the charge stock. If the quantity of these hydrocarbons is small, it may be increased by cracking the saturated hydrocarbons. The newly formed unsaturated hydrocarbons supply additional quantities of polymerizable materials and increase the yield of liquid products. Processes were, therefore, developed which simultaneously crack and polymerize the hydrocarbon gases under suitable conditions of temperature and pressure. These processes employ no catalysts and are known as gas conversion processes.

The simplest of these, known as the Unitary Gas Conversion Process, cracks and polymerizes hydrocarbons in one step. The gases are heated to 950-1100° F. under a pressure of 800-3000 pounds per square inch, depending on the nature of the charge. The one-step operation does not permit the use of the temperature and pressure required to insure optimum conditions both for cracking and poylmerization reactions. These considerations led to the development of more complicated multiple-coil polymerization processes involving two- or three-stage operations and permitting better control of the individual reactions than is possible with the single-coil process. The two- and three-stage processes were developed by the Pure Oil Company and Alco Products, Inc.

In the two-stage process the gases are first cracked at 1100-1300° F. and low pressure to convert saturated hydrocarbons into unsaturated ones. The cracked products are retreated at 900-1000° F. and 600-800 pounds per square inch pressure in order to effect polymerization. If the gases charged to the unit contain large quantities of unsaturated hydrocarbons and relatively small quantities of saturated hydrocarbons, the first step of the process may be omitted.

In the three-stage process the unsaturated hydrocarbons originally present in refinery gases are polymerized in the first stage. The unreacted saturated hydrocarbons are cracked in the second stage to produce new quantities of unsaturated hydrocarbons, which are then poylmerized in the third stage of the process. Temperatures and pressures are adjusted for each individual stage to insure the most economical operation.

Gas conversion processes may be conducted in connection with reforming operations. In such combinations gases containing unsaturated hydrocarbons are mixed with the charge stock entering the furnace (Gas Reversion Process) or preheated separately and then injected into one of the middle coils of the cracking furnace (Polyform Process).

Isomerization

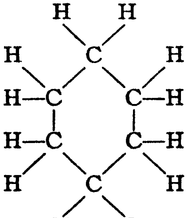
Previous discussions showed that iso-butane is one of the important hydrocarbons for the preparation of synthetic fuels, and methods are now available for manufacturing it on a commercial scale from the much less reactive normal butane. These methods involve the use of catalysts to effect rearrangements within the butane molecule. Aluminum chloride is suitable for this purpose. As normal butane and iso-butane contain the same number of carbon and hydrogen atoms, the reaction does not require an outside supply of other materials. Substances such as these are called isomers, and the processes relating to the conversion of one isomer into another are referred to as "isomerization processes." Several such processes are now in existence. The one developed by the Shell Oil Company converts normal butane into iso-butane. The Universal Oil Products Company Process may be also used for converting normal pentanes and hexanes into corresponding isomers, thus improving the antiknock properties of fuels. The Indiana isomerization process achieves the same effect by charging a light straight-run naphtha obtained from natural gasoline. The product containing isomers is often referred to as "isomate."

Aromatization

Recently considerable attention has been devoted to the manufacture of aromatic (ring-structure) hydrocarbons from petroleums. Aromatic hydrocarbons have excellent antiknock characteristics and are, therefore, desirable gasoline constituents. Some oil companies are, or were, marketing gasolines containing benzene bought from the coal tar industry. In addition the use of toluene (or toluol) in the explosives industry for the preparation of TNT (trinitrotoluol) creates a big demand for this commodity in time of war, which cannot be met by the regular sources of production. During the last World War the petroleum industry was supplying some of the toluene obtained by very heavy cracking of selected crude-oil fractions. At the present time a number of methods have been developed which permit manufacture of toluol from petroleum, although at a somewhat greater expense than that at which it can be produced by the coal-tar industry. Plants of this type are, therefore, economically warranted only when the market price for toluene exceeds a certain minimum.

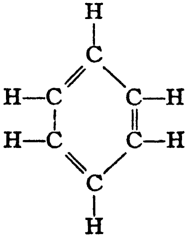
Enrichment of gasoline fractions of the crude with aromatic hydrocarbons is accomplished by the so-called "aromatization" processes. These processes are briefly as follows. The simplest method for preparing aromatic hydrocarbons from petroleum is very drastic cracking. At high temperatures the cracking reactions progress toward formation of aromatic hydrocarbons. Vapor-phase cracking processes which involve the use of high temperatures always yield products rich in aromatics and are, therefore, particularly suitable for this purpose. The selected oil fraction, usually kerosene, is very heavily cracked to obtain the maximum possible yield of aromatic hydrocarbons. The resulting product is fractionally distilled to prepare pure aromatics.

Another type of aromatization process involves dehydrogenation. Certain crude-oil fractions may contain relatively large proportions of naphthenic hydrocarbons, like cyclohexane or methyl-cyclohexane, which differ from the corresponding aromatic hydrocarbons only by the number of hydrogen atoms attached to the carbon atoms. If this surplus of hydrogen is removed, cyclohexane and methyl cyclohexane are converted into benzene and toluene respectively.



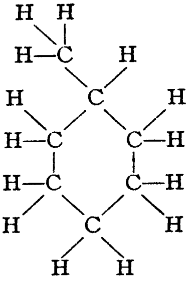
or C_6H_{12}

Cyclohexane (*saturated*)



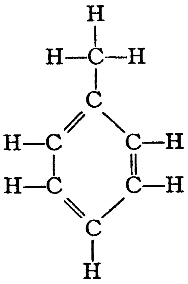
or C_6H_6

Benzene (*unsaturated*)



or $C_6H_{11} . CH_3$

Methylcyclohexane
(saturated)



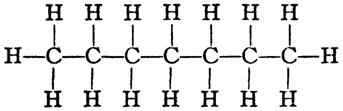
or $C_6H_5 . CH_3$

Toluene
(unsaturated)

In the dehydrogenation processes the charge is passed through a catalyst capable of removing hydrogen, and the product of the reaction is fractionally distilled to isolate the desired aromatic hydrocarbons.

Cyclization

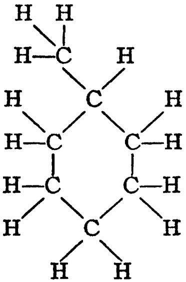
Other reactions suitable for the manufacture of aromatic hydrocarbons involve *cyclization.* Straight-chain (aliphatic) hydrocarbons are capable under certain conditions of temperature and pressure, particularly in the presence of catalysts, to rearrange their carbon atoms into the ring structure characteristic of aromatic hydrocarbons. The processes employing these reactions are referred to as cyclization processes. As the number of hydrogen atoms in the straight-chain hydrocarbons, especially in the saturated ones, is greater than in the aromatic (ring structure) hydrocarbons, cyclization and dehydrogenation processes must be combined to yield the desired product. Such transformations of the hydrocarbons may be best visualized from the diagram



$$\begin{array}{ccccccccccccccccc} & & H & & H & & H & & H & & H & & H & & H & & \\ & & \mid & & \mid & & \mid & & \mid & & \mid & & \mid & & \mid & & \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & H \\ & & \mid & & \mid & & \mid & & \mid & & \mid & & \mid & & \mid & & \\ & & H & & H & & H & & H & & H & & H & & H & & \end{array}$$

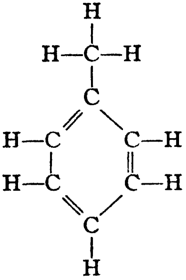
or C_7H_{18} *normal heptane*

Straight-chain
(saturated)



or $C_6H_{11}.CH_3$ *Methylcyclohexane*

(Cyclization
saturated)



or $C_6H_5 . CH_3$ *Toluene*

(dehydrogenation unsaturated)

on page 122 referring to the conversion of normal heptane into toluene.

Hydrogen is obtained as a by-product. The above reactions take place simultaneously and the recently developed cyclization processes are thus capable of converting straight-chain saturated or unsaturated hydrocarbons into ring-structure (aromatic) compounds, provided they contain the necessary number of carbon atoms in the molecule.

Toluene from Petroleum

For the manufacture of toluene the napthenic and unsaturated or saturated straight-chain hydrocarbon containing seven carbon atoms and having at least six carbon atoms in the ring or in the chain are suitable raw materials. The boiling points of petroleum fractions used as charge stocks are, therefore, adjusted so as to include all the above hydrocarbons, but as little as possible of the others in order to reduce the complexity of the product. This requires preparation of fractions whose boiling points are very close together by careful fractionation of the charge stock. The nature of the charge stock is of much importance because similar boiling-point fractions from different crudes vary in their content of the hydrocarbons most suitable for manufacturing toluene. High-temperature cracking of hydrocarbon gases is the basis of another process for producing toluene on a commercial scale.

Appreciable quantities of toluene are found in certain crude oils. If such crudes are available, the recovery of toluene is reduced to careful fractionation or extraction with solvents. The latter methods are also used in conjunction with the aromatization processes if the recovery of toluene or other aromatic hydrocarbons in the pure state is attempted.

Chapter 8

Chemical Treatment of Light Petroleum Products

Purposes of Chemical Refining

Distillates used for preparing commercial gasoline are almost always treated with chemicals before they are released to the market. This treatment is necessary in order to meet various specifications and to improve the quality of products. Treating before blending is frequently more economical than treating after blending, because the individual gasoline components may require different types and degrees of refining. The consumption of reagents is lowered because the impurities are removed from more concentrated solutions, and the size of the treating equipment is reduced because smaller volumes are handled.

Straight-run distillates are the easiest to refine because their composition is simpler than that of cracked distillates, which contain a large number of additional compounds not present in the crude but formed in the course of cracking. A simple wash with caustic (sodium hydroxide) solution is often sufficient to meet the required specifications. Such a wash will remove from distillates the objectionable hydrogen sulfide and thus improve their stability and odor. However, considerable complications are experienced in treating cracked gasolines, which must be freed from a number of objectionable impurities. Many treating procedures have been developed for this purpose and are in current use. The proper selection of these procedures and the sequence of their application to the gasoline or other petroleum products depends on the nature of stock, market specifications, available equipment and other variables peculiar to the individual plants.

Chemical refining is not capable of improving all the properties of gasoline, but is restricted to the following major points:

1. Decrease in the tendency of oils to oxidize and elimination of gum-forming constituents.
2. Improvement of color and odor.
3. Elimination of corrosive substances.
4. Reduction of sulfur content.
5. Reduction in the content of undesirable types of unsaturated hydrocarbons.
6. Elimination or transformation of certain substances which prevent gasoline from passing specifications such as the doctor test.

Chemical treatment is unable to correct the distillation range or other properties of gasoline which depend not on the impurities present but on the quality and variety of hydrocarbons of which the main body of the gasoline is composed. Such corrections can be made only by proper selection of the crude and by its physical or thermal treatment prior to chemical refining.

Chemical treatment of gasoline cannot be applied at random, but should be carefully worked out in order to make it economical and avoid the danger of impairing some of the desirable properties by undertreating or overtreating. For instance, removal of substantial quantities of unsaturated hydrocarbons may lower the octane number of a gasoline. However, simultaneous removal of sulfur compounds may result in an improved lead susceptibility, *i.e.*, increase in the octane number per unit quantity of tetraethyl lead added. Treating losses must be also considered, in addition to the cost of chemicals, labor and equipment. All these various influences should be carefully balanced before selecting the proper treating methods for the individual refinery products.

Methods of Chemical Treatment

The oil may be treated in either the liquid or the vapor phase, which permits classification of the treating methods into liquid phase and vapor phase methods respectively. Combination of these two types of methods may be also employed.

The most common reagents used in treating gasoline are sulfuric acid, caustic soda (sodium hydroxide), special types of "active" clays, and a number of others, the most important of which are described below.

Treatment with sulfuric acid is the oldest method, and is still used by many refineries. Gasoline is agitated with acid, the resulting sludge removed, and the gasoline neutralized by washing with a solution of caustic soda. This is necessary because, as a prerequisite to their stability, petroleum oils should never be left in the acid state. The neutralized gasoline is washed with water to remove the last traces of caustic and is frequently redistilled or "re-run" to eliminate the undesirable high-boiling constitutents formed in the course of acid refining.

This treatment is usually carried out at normal temperatures. Gasoline and acid are mechanically agitated for a certain length of time to make sure that they are thoroughly mixed. However, in treating some gasolines the time of contact should be reduced to the lowest possible minimum. This is accomplished in some processes, like those of Sharples and DeLaval, by employing very efficient mixing devices in connection with the centrifuges for quick separation of the sludge. Low-temperature treatment is beneficial for certain types of gasolines, particularly those containing large quantities of sulfur compounds. The Stratcold Acid Treating Process has been developed to meet the needs of refiners who are confronted with such problems.

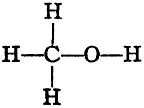
Instead of caustic solutions, special types of active clays may be used for neutralizing the acid-treated gasoline. Clay treatment usually improves the color of oils to a greater extent than do caustic solutions. However, washing with caustic soda may be resorted to after acid and clay treatment to keep the color from changing in storage.

Vapor-phase refining involves contacting oil vapors emerging from the still with various chemicals. These chemicals may include clay (Gray Process), clay-naphtha slurry (R. K. Stratford Process), catalysts (Houdry Treating Process), solutions of zinc chloride or other substances (Lachman Process), zinc compounds and chlorine (Howard Process), and others. Treatment of gasoline at elevated temperatures, but under sufficient pressure to keep it liquid, forms the basis of a number of other processes employing clay (Osterstrom Process), zinc catalyst and hydrogen chloride (Universal Oil Products Company Treating Process), and other refining agents.

The foregoing treating methods improve color, odor, oxidation and color stability, and gum content of gasoline. Some of them, such as Houdry, Howard, sulfuric acid or the Universal Oil Products Company processes, may be also effective in reducing the sulfur content. In general, the quantity of detrimental compounds present in the raw gasoline is small, and sufficient improvement in its properties may be obtained by a relatively mild treatment intended to remove only the most unstable unsaturated hydrocarbons, namely the diolefins.

"Sweetening" Processes

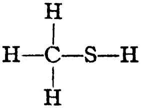
One of the usual requirements of the finished gasoline is that it be "sweet," or negative to the doctor test. The test requires that no discoloration occur on mixing gasoline with the "doctor solution," that is, a solution of caustic soda containing lead oxide (litharge), in the presence of elemental sulfur. A "positive" doctor test shows



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}O{-}H}$$

or CH_3OH

Methyl alcohol



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}S{-}H}$$

or CH_3SH

Methyl mercaptan

the presence of mercaptans, which are sulfur compounds similar to alcohols.

Mercaptans are considered to be objectionable on account of their offensive odor, which is similar to that of the skunk. Under certain conditions they may be corrosive and have an unfavorable effect on the lead susceptibility of gasolines. Gasolines containing mercaptans or some other sulfur compounds frequently require more tetraethyl lead to raise their octane numbers to a predetermined level than similar gasolines that are free from them.

With the possible exception of the Houdry, Howard and hydrofining processes, none of those already described is capable of yielding a "doctor sweet" gasoline. A large variety of special sweetening processes have been developed, however, to accomplish this purpose. These may be classified into two groups: those converting mercaptans into other types of sulfur compounds, the disulfides, which remain in the gasoline but which are negative to the doctor test; and those removing the mercaptans, thereby reducing the total sulfur content of the gasoline. Some occupy an intermediate position, removing a portion of the mercaptans and transforming the remainder into the gasoline-soluble disulfides. As the disulfides sometimes have an unfavorable effect on color stability and lead susceptibility, removal of mercaptans is preferable to changing them into disulfides.

The oldest sweetening method is doctor treatment which parallels the laboratory doctor test. Gasoline is agitated with the doctor solution either before or after the addition of elemental sulfur. Sulfur may be added in powdered form or in gasoline solution. Gasoline is separated from the mixture by settling. Although some sulfur is added to the oil, the total sulfur content of the gasoline remains unchanged because the added sulfur precipitates at the end of the reaction in the form of lead sulfide, and is removed from the system. The spent doctor solution is regenerated by blowing air through it.

Several other sweetening methods have recently been developed. Some of these offer certain advantages over doctor treatment which may appeal to the taste of individual refiners. These new processes include the modified doctor procedure employing lead sulfide and air (Stratco Lead Sulfide Sweetening Process), oxygen and dry copper chloride slurry (Perco Process), hypochlorite solutions, and a few others. The hypochlorite is extensively used for sweetening natural gasolines containing mercaptans.

The simplest method for reducing the mercaptan content is by washing gasoline with caustic solution. However, mercaptan removal is seldom complete because the higher mercaptans are only slightly soluble in caustic. Gasoline may be completely freed from mercaptans with solutions of caustic in alcohols. A process of this type employing methyl alcohol has been recently developed by the Universal Oil Products and the Atlantic Refining Companies. The Shell Development Company has also developed a process, known as the Solutizer Process, which involves washing the gasoline with caustic solution containing certain organic compounds capable of increasing the solubility of the mercaptans in it. The spent solutions are continually regenerated by heating and blowing with steam.

Mercaptans usually represent only a small portion of the sulfur compounds, and if a substantial reduction in the sulfur content is required, the gasoline is often treated with sulfuric acid. Aluminum chloride has been recommended for the same purpose, but the treating costs are high. Some years ago the Frasch Process, in which gasoline vapors are passed over copper oxide, was used for reducing the sulfur content of certain gasolines, but the process has been abandoned in favor of other methods. In general, the problems of sulfur removal from gasolines

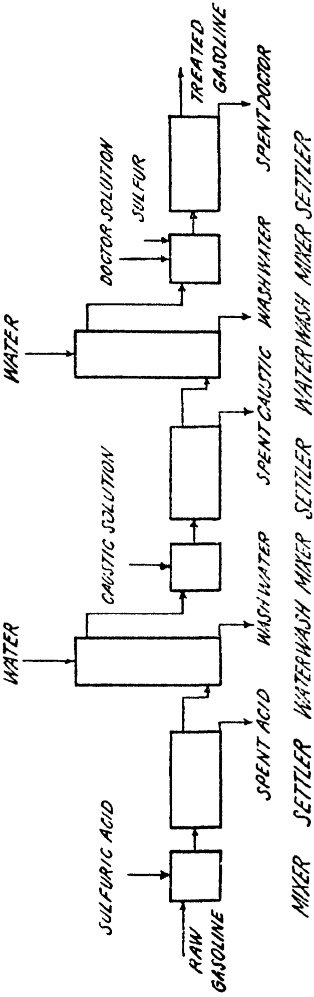


FIGURE 7. Diagram of gasoline refining process.

of high sulfur content is very complicated and cannot be considered as solved. The existing methods are expensive and involve high treating losses. In some instances these losses are unavoidable, because the molecules containing sulfur also contain appreciable quantities of hydrogen and carbon. Under such circumstances the losses can be reduced only by devising methods for removing the sulfur atoms from the molecules without completely shattering their structure. However, methods of this type are not yet known.

Gasoline is almost always treated with chemicals in a continuous system. A conventional treating system of this type is shown diagrammatically in Figure 7.

Inhibitors

The chemical methods thus far described are of the so-called "subtractive" type because they involve separation of impurities from the main body of the oil. However, methods have recently been developed which permit improvement of the gasoline without removing the impurities, but by neutralizing their undesirable effects by the addition of chemicals. These chemicals are called inhibitors, protective agents or stabilizers. A number of inhibitors have been developed during the last few years which protect gasoline and other petroleum products from oxidation and deterioration, such as from excessive gum formation or discoloration in storage. The use of inhibitors permits the refiner to reduce the severity of chemical treatment and to conserve in the gasoline those components which are of benefit to the motorist. For instance, a large proportion of the unsaturated hydrocarbons possessing good antiknock qualities may be left in the gasoline without making it liable to oxidize. Thermally cracked gasolines which were previously treated with large quantities of sulfuric acid may be often satisfactorily finished by passing them in vapor form through a bed of clay, washing with caustic solution, and adding inhibitor. The resulting product has a higher octane number than a drastically refined one and is at least equal to it in oxidation stability. The manufacturing cost is at the same time considerably reduced.

The use of inhibitors requires a careful study of refinery problems. Their effectiveness varies with the type of gasoline and with the conditions of service. The presence of excessive amounts of inhibitor may be as detrimental as their deficiency. The same inhibitor may protect the gasoline under a certain set of conditions, but have a harmful effect if the conditions are changed. For these reasons the use of accelerated tests for evaluating the efficiency of inhibitors is not necessarily a direct indication of their actual commercial value. Furthermore, inhibitors are not universal in their action. One inhibitor may be effective for reducing the gum content but at the same time have an adverse effect on color stability. Thus two or more inhibitors may be required to improve the overall performance of gasoline or other refinery products. Chemical treatment should be also adjusted to improve the response of the gasoline to inhibitors. If two or more inhibitors are used, a study should be made to ascertain that they do not interact chemically. This is the type of problem that is constantly confronting those in charge of refinery operations.

Kerosene

Kerosene also requires chemical treatment. However, the problems involved in its refining are somewhat different from those connected with gasoline. In addition to general stability requirements, kerosene must burn without smoke and have no damaging effect on a lamp wick. This necessitates elimination of aromatic and other unsaturated hydrocarbons and sulfur compounds. The antiknock characteristics of kerosene are of no value to the customer because kerosene is not used as motor fuel. The above shows that, while the purpose of refining gasoline is to preserve as far as possible the aromatic and other unsaturated hydrocarbons, refining of kerosene is directed toward completely eliminating them. Drastic refining of kerosene is thus desirable, particularly if kerosene is obtained from crudes which contain considerable quantities of aromatic hydrocarbons.

Kerosene is frequently refined with sulfuric acid, but if the quantity of acid required is excessive, the solvent method is employed. This method, which is applied to kerosene as well as to some other petroleum products, involves the use of liquid sulfur dioxide, and is often referred to as the Edeleanu Process.

Kerosene is mixed with liquid sulfur dioxide in a pressure system to avoid the loss of reagent, which is a gas at ordinary temperatures. The mixture is cooled to about −10°F. or lower, to obtain separation into two layers. The lower layer, or the extract, consists of aromatic hydrocarbons dissolved in the liquid sulfur dioxide; the upper layer, or raffinate, consists of sulfur dioxide dissolved in the remaining hydrocarbons. The efficiency of separation is improved by per-

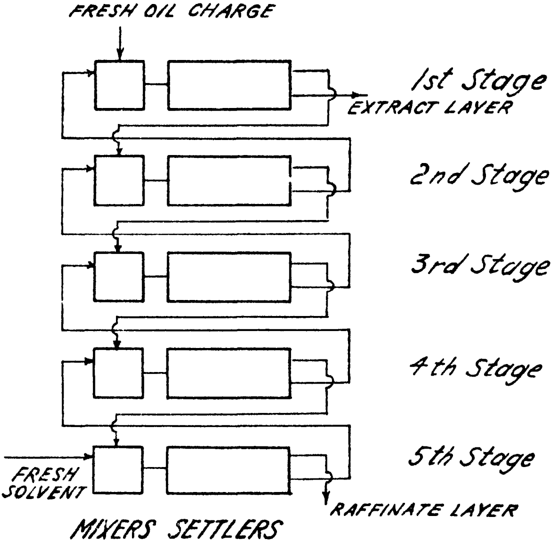


FIGURE 8. Solvent refining of kerosene.

mitting the liquid sulfur dioxide to contact the oil in a countercurrent manner. The fresh oil is thus first contacted with the solvent which contains a substantial amount of aromatic hydrocarbons, while the oil leaving the sytem is contacted with the fresh solvent having the greatest solvent action on aromatics. The treating unit thus consists of several mixers and settlers depending on the number of stages required to obtain the desired degree of separation. A diagrammatic representation of a five-stage solvent refining unit is shown in Figure 8. Sulfur dioxide is removed from the two layers by distillation and then returned to the extraction system.

The description of the method shows that none of the oil is lost to the refiner. The raffinate is used for manufacturing kerosene, and the extract containing the aromatic hydrocarbons is utilized for manufacturing industrial solvents, or for similar purposes. The lighter portions of the extract may be added to gasoline to improve its antiknock qualities. In sulfuric acid refining the hydrocarbons forming the extract layer cannot be recovered.

Recently sulfur dioxide has been applied for improving the antiknock qualities of gasolines. In this modification of the process the extract and not the raffinate phase contains the desired product, because the aromatic hydrocarbons are the most valuable gasoline constituents. Unfortunately the use of this treating method is not applicable to all gasoline stocks because, in addition to the aromatic hydrocarbons, liquid sulfur dioxide dissolves large quantities of sulfur compounds which cannot be easily separated from the aromatics. If the quantity of sulfur compounds is excessive, the resulting gasoline is very difficult to refine to specification standards.

Refining of other light distillates, such as various solvents, safety fuels, and numerous specialties follows the same general lines as have been described in connection with refining gasoline and kerosene. The choice of treating procedures and of their sequence is determined after a careful study of specific requirements of the finished products. Each product has its own specifications, which are too numerous to permit their discussion in this brief review of petroleum refining methods.

Diesel Fuels

Requirements of diesel fuels are quite different from those of gasolines. Their boiling range is relatively high, but their antiknock properties must be exactly the opposite to those of gasoline. This is due to the inherent differences in the design of the engines in which they are used. The ignition qualities of diesel fuels are expressed in cetane or cetene numbers, which range from 0 to 100. The numbers refer to mixtures of cetane or cetene with methyl naphthalene, and are in this respect similar to octane numbers. The higher cetane and cetene numbers correspond to low octane numbers, and low cetane and cetene numbers correspond to high octane numbers. Types of hydrocarbons which are most desirable in diesel fuels are therefore least desirable in gasoline.

The cetane number of diesel fuels may be improved by addition of certain chemicals, such as amyl nitrate or organic peroxides. These chemicals are not used commercially because straight-run petroleum products are generally satisfactory for the present design of diesel engines. Furthermore, the use of these additional agents often involves an explosion hazard to the refinery. The effect of these agents on the ignition quality of fuels is the reverse of that of tetraethyl lead.

Originally it was expected that diesel fuels could be manufactured cheaper than gasoline. However, the requirements of good diesel fuels are becoming stricter; and with further development in diesel engine design it may be expected that the problems connected with the two types of engine fuels will become equally complex.

Fuel Oils

Two common types of fuel oils are generally recognized by the refineries; light distillate fuel oils employed in domestic burners or similar equipment; and heavy, or the so-called bunker fuel oils, which represent residual petroleum products. The distillate oils are prepared with greater care than the residual oils because of differences in burner requirements and in conditions of service. Fuel oils must meet certain viscosity specifications and must not form sediment during storage. Additional tests may be included in the specifications, depending on the type of service for which they are intended. Due to their cheapness the fuel oils cannot be extensively refined, although they may receive an occasional acid treatment or a caustic wash.

Chapter 9

Chemical Treatment of Lubricating Oils

Requirements of Lubricating Oils

Lubricating oils include a very large number of liquid petroleum products which have been developed for lubricating various types of machinery. Practically all moving mechanisms must be lubricated to keep them in operation. The adaptability of petroleum oils to this service is one of the important factors in speeding up the progress of our civilization and in permitting us to enjoy our present everyday comfort.

Petroleum oils are employed for lubricating all types of machinery, from the delicate mechanisms of watches to rough devices like pulleys. Because of such diversified applications, a large variety of lubricants must be manufactured by refineries. However, some of these are consumed in very small quantities, and may therefore be regarded as specialities rather than as major petroleum products. This discussion refers only to the most important classes of lubricating oils, particularly to those used in internal combustion engines.

Lubricating oils must meet a number of different requirements. To insure good lubrication they must flow freely toward the rubbing surfaces. The free flow is determined by the fluidity of the oil and by its tendency to "freeze," or congeal, at service temperatures. Instead of measuring fluidity or ease of flow, petroleum chemists measure the opposite property, viscosity, or resistance to flow. The higher the viscosity of the oil in numerical units, the poorer is its fluidity. However, viscosity changes with temperature. Oils are more fluid (less viscous) at higher than at lower temperatures. Oils from different crudes vary in this respect; that is, two oils may have the same viscosity at one temperature and a different viscosity at another. To determine accurately the lubricating properties of an oil, the actual operating temperature prevailing in the engine should be known; but for convenience the viscosity is measured at some standard temperature, usually 100, 130 or 210° F. The change of viscosity with temperature is for similar reasons an important property of certain types of lubricants.

Experience has revealed that among the natural products Pennsylvania oils show the least change in viscosity with temperature, and Coastal oils the greatest change. Consequently, the Pennsylvania oils were arbitrarily assigned a numerical value of 100 and the Coastal oils a numerical value of 0. By employing this system, oils prepared from other types of crudes may be assigned a numerical value indicating their relative position with respect to the two standard crudes. This numerical value is referred to as the *viscosity index* of the oil. High viscosity index is important for oils which are used for lubricating engines operating under variable temperature conditions, such as are encountered during the warm-up period of a motor. The viscosity index has little if any importance for oils employed for lubricating engines which operate at a constant temperature or within narrow temperature limits.

The freezing point of the oil is measured by means of the so-called pour test—a laboratory test showing the temperature at which the oil stops flowing under exactly specified experimental conditions. The test is arbitrary, and a slight change in its technique with respect to size of vessel, volume of sample, rate of cooling and similar variables may have a very marked effect on the pour-point determinations. The cloud point of the oil is often determined together with the pour point; this indicates the temperature at which the oil begins to cloud because of partial solidification of some of its component parts, for example, high-melting point waxes.

The oil should also have an important property known, for lack of a better name as "oiliness." This means the ability to form a tenacious oil film around metal surfaces. Oiliness is important in products which must lubricate rubbing surfaces having small clearances from which the oil may be squeezed out by excessive pressures. Such conditions exist in some special types of machinery, and in automobile engines during the break-in period. Special break-in oils possessing high oiliness are often used in new engines for this reason. The importance of such oils disappears after proper clearances are established.

The oil must not be corrosive and should have no adverse effect on the metals from which the engine is made. The need for this requirement is self-evident.

Stability of oils, that is, their tendency to remain in their original condition, affects the frequency at which the oil must be changed. Present oils are very stable in service, assuming that they are manufactured by reputable companies. However, stability of an oil is not sufficient to guarantee its satisfactory performance in an engine, because the oil may accumulate abrasive materials in the form of dirt from the road or small metal particles chipped from the moving parts of the motor. Frequent oil changes are therefore desirable, particularly because oil is cheap and engine repairs expensive.

On evaporation, lubricating oils should leave as little carbonaceous residue as possible. This property is determined in the laboratory by means of special tests. In the United States the "carbon residue" test is widely used, while in Great Britain the "coke number" test is employed. The lower the carbon residue or the coke number of an oil, the better it is believed to be in service. However, these tests fail to indicate the type of carbon deposits and are therefore inconclusive. Fluffy carbon is easily removed through the engine exhaust, but hard carbon may remain in the engine and impair its performance. Therefore, an oil possessing a low carbon residue may not be superior in service to one with a high carbon residue.

A number of complicated laboratory oxidation tests have been developed to predict the rate of deterioration of oils in service. To save time, these tests are conducted under conditions far more severe than those of actual service; at high temperatures, in contact with air or oxygen, and in the presence or absence of metals. These are called "accelerated" tests. Unfortunately such tests do not necessarily indicate the actual performance of oils in engines because they no more than approximate conditions of actual service. Therefore, an oil which satisfactorily passes the laboratory tests may be sometimes inferior to an oil which does not pass them. Large oil concerns spent enormous amounts of money in developing oils of the best possible characteristics by testing them both in laboratory engines and on the road. For these reasons, the brand of oil is the only true guide for the customer in selecting the best product for his needs.

The oil must meet a number of other specifications, such as flash and fire points, color and various other tests, depending on the use for which it is intended. Flash and fire points refer to temperatures at which the oil flashes or ignites under a certain set of experimental conditions. They are supposed to indicate safety from fire hazard and, to a certain extent, the rate of oil consumption, because the light fractions are the first to evaporate in an engine. However, in actual service a certain amount of oil must always be consumed to insure good lubrication. If oil consumption is reduced below a reasonable minimum, lubrication is inadequate and the wear of the engine is rapid. The motorist trying to effect such economies is penalized by heavy repair bills.

The color and fluorescence of an oil are properties which are still required by the trade though they have no relation whatever to its performance. Color is determined by permitting the light to pass through an oil layer of definite thickness and by comparing the color of the transmitted light with some standard color. Fluorescence, "bloom," or cast, refers to the appearance of the oil in the light reflected from its surface. The deceitful nature of such tests may be illustrated by the following example. An oil having good fluorescence will conceal all the dirt which it may accumulate in service, while an oil having poor fluorescence will expose all particles of carbon or other materials which it may carry in suspension, because the first oil reflects while the second oil transmits most of the light through its body. For this reason a highly fluorescent oil may be unfit for use and still appear satisfactory to the eye, whereas the non-fluorescent oil will look black, although its degree of deterioration may be negligible. Moreover, fluorescence is often due to the presence in the oil of substances which are likely to form carbon in engines and which are themselves harmful.

Constituents of Lubricating Oils

In preparing lubricating oils, a refiner assumes that the raw stock contains four major constituents: wax, asphalt, undesirable oily substances, which are responsible for poor stability and low viscosity index, and desirable fractions forming the body of a high-grade product. They are referred to in the following discussion as wax, asphalt, low viscosity index, and high viscosity index constituents respectively.

Wax is a well known substance which is solid at room temperatures. Solutions of wax in oil solidify on cooling, thus interfering with the free flow of oil. The larger the percentage of wax, the higher the congealing temperature, or pour point, of the oil.

Asphalt contributes to the carbonization of oils in service and to their instability. It does not volatilize, but cracks on heating to elevated temperatures, forming carbon. The carbon residue or coke number of oils containing asphalt is therefore high.

The low viscosity index constituents have an unfavorable effect on the viscosity index of the oil. Moreover, they often represent substances unstable in service. For these reasons they should be removed in the course of refining.

From the above discussion it may appear that wax, asphalt, low viscosity index and high viscosity index constituents are distinct components of unrefined oils. However, this is incorrect. The oil consists of an infinite number of substances, the properties of which vary imperceptibly from oil to wax or from oil to asphalt. No definite demarkation line can be drawn between them. Although the presence of wax or asphalt is definitely undesirable in the finished products, the presence of compounds intermediate between oil and wax or oil and asphalt may be beneficial. This shows that in developing an oil the refiner is obliged to investigate a very large number of experimental products which may be prepared from a number of raw stocks by varying the degree of refining. Over-refining may often be as harmful as under-refining.

Refining of Lubricating Oils

The old method of refining lubricating oils consisted in agitating the raw stock with sulfuric acid, usually by air blowing, settling out the sludge and neutralizing the oil either with caustic solution or with clay. The oils neutralized with caustic are sometimes also finished with clay. Acid treatment and neutralization with caustic are carried out at temperatures sufficiently high to permit good mixing and settling of the acid sludge or spent caustic solution. However, the treating temperature must not be excessive because this may impair the quality of the oil. Difficulties are frequently encountered in obtaining complete settling of the acid sludge and in preventing formation of emulsions when the acid oil is washed with caustic. Numerous precautions must be taken in carrying out the treatment in order to avoid possible complications. In treating viscous stocks, dilution with naphtha is sometimes resorted to in order to facilitate separation of the spent reagents. Naphtha is then removed from the oil by distillation; this should be done with considerable care because of the danger of harming the finished products by exposure to high temperature. In some instances the acid-treated oils are neutralized with ammonia instead of caustic to avoid emulsification.

In recent years new continuous processes have been developed by the Sharples Speciality and DeLaval Separator Companies for treating lubricating oils with sulfuric acid. The oil is agitated mechanically with the acid and the mixture passed in a continuous stream to a centrifuge where the sludge is separated from the oil by rapid rotation. The centrifugal force causes the heavier material (sludge) to separate from the lighter (oil). Although these processes are theoretically superior to the old batch process involving agitation with air, their value to the individual refineries must be carefully studied in relation to the individual plant problems, because the product obtained by mechanical agitation is not necessarily identical with that obtained by agitation with air.

Clay treatment of acid oil is sometimes substituted for neutralization with caustic solution. This is helpful in eliminating the possibility of forming emulsions and in improving the color of the product. A treatment known as the Clay Contact Process involves mixing the acid oil with finely divided clay, heating the mixture by passing it through a furnace, and filtering out the clay. The temperature to which the mixture is heated depends on the nature of the stock, and is higher for the more viscous than for the less viscous oils. Similar treatment is sometimes applied to light petroleum distillates such as gasoline or kerosene. However, these light distillates are treated at ordinary temperatures well below the boiling point of water. For these reasons, contact clays used for treating light distillates must be dry; but those employed for treating lubricating oils should preferably contain some moisture. The moisture evaporates on heating the oil-clay mixture and protects it from atmospheric oxidation by maintaining a film of steam on its surface. A few refineries even employ a clay-water slurry for treating lubricating oil stocks. This may have advantages in preserving efficiencies of certain clays which may deteriorate on exposure to air.

The oils neutralized with caustic, and sometimes even those contacted with fine clays, are frequently given an additional percolation treatment through coarse clay. Percolation through clay may be also applied to certain raw stocks. Pennsylvania oils, for instance, are practically never refined with sulfuric acid, but are finished directly with clay, or refined with solvents and then percolated through clay. The oil or its solution in naphtha is charged to large filters or percolators containing the coarse clay. The filters are cylindrical in shape and may contain as much as 30 or 60 tons of clay. The oil is permitted to flow downward through the clay, although some plants percolate it upward, employing the so-called anti-gravity filtration method. If the oil is percolated in solution, naphtha is distilled from the finished product, and all necessary precautions are taken to avoid overheating. Percolation through clay is generally done at temperatures below the boiling point of water, and for this reason the clay must be dry.

Sometimes the oils are treated with clay directly in the crude oil stills. The contact clay is mixed with the raw oil charge, and residuum containing spent clay is continually withdrawn from the bottom of the still and passed to the filters. This modification of the contact method of clay treatment is known as the Filtrol Fractionation Process.

At some, though very few, refineries the oil is treated by heating with anhydrous aluminum chloride. The resulting sludge is separated from the treated oil by settling. This treatment is usually done in combination with some of the other treating methods described in this chapter.

Dewaxing

The processes thus far discussed are suitable for the removal of various undesirable substances from the oil, with the exception of wax. Removal of wax is accomplished separately by the so-called dewaxing processes. Some of these are suitable for removing wax from distillate stocks, and others for removing it from residual stocks; the recently developed processes are applicable to all types of stocks.

Two types of waxes are found in crude oils: paraffin wax and petrolatum. Paraffin wax has a crystalline structure and is associated with light distillates. Petrolatum, sometimes referred to as amorphous wax, has a micro-crystalline structure and is associated with the residuum. The older dewaxing methods, some of which are still in existence, differed in their applicability depending on the type of wax to be removed. In preparing lubricating oils the refiner was, therefore, obliged to distill the crude in such a way that lubricating-oil fractions containing crystalline wax were obtained in the distillate, while the fractions containing amorphous wax were obtained as residuum. If sharp separation could not be secured, an intermediate "slop cut" containing both types of waxes was collected and disposed of as fuel because it could not be dewaxed by the conventional methods.

The distillate stocks were and still are dewaxed by filter-pressing. The stock is chilled and the separated wax, known as slack wax, is removed by low-temperature filtration. The pour test of the resulting oil is determined by the chilling temperature. Viscous distillates are diluted with naphtha to reduce their viscosity and the naphtha is then distilled off, with the usual precautions to protect the oil from overheating.

Residual stocks were dewaxed either by cold settling or by centrifuging. Cold settling, now practically obsolete, involved settling the oil in tanks at low temperatures. Originally this was done during the winter months. The oil was then poured from the petrolatum which settled out at the bottom of the tank. In the centrifuging process, which is now also to a great extent obsolete, the oil is diluted with naphtha, chilled and centrifuged in order to separate the petrolatum.

Modern Refining Methods

A few years ago new refining methods were developed, and these are now rapidly replacing the older ones. The new methods employ solvents and involve deasphalting, dewaxing and strictly solvent refining processes, depending on whether they are capable of separating asphalt, wax, or low viscosity index constituents respectively. Conventional sulfuric acid treatment removed from the oil the asphaltic and low viscosity index constituents, but much less efficiently than the solvent methods; besides, these constituents were extracted in the form of sludge, from which they could not be recovered without undergoing chemical changes. However, in refining certain oils, particularly those requiring only a light treat, sulfuric acid can still be efficiently utilized, and occasionally yields better products and at a lower cost than the solvent methods.

Deasphalting

The deasphalting processes include propane deasphalting and distillation. In propane deasphalting the oil is mixed with liquefied propane under pressure. Asphaltic substances settle from the oil which is poured off. The process is continuous, and propane is applied to the oil in a counter-current manner to reduce oil losses and to insure sharp separation. When the oils are deasphalted by distillation, the residual stocks are charged into special stills, such as are employed in the Coubrough Process, and were developed for obtaining the maximum possible quantity of oil as overhead. High vacuum and steam are used to facilitate this operation. The asphalt is obtained as the residue. From this description of the process it may be seen that the distillate stocks never contain asphalt unless some of the still bottoms appear in the overhead fractions because of mechanical carry-over.

Solvent Dewaxing

The new dewaxing processes include the use of filter-aids and of solvents other than naphtha. The advantage of these processes over the older ones lies in their ability to dewax the oil irrespective of the kind of wax present. They are also more economical because they usually require less chilling and are capable of securing a better separation of oil from wax, thus reducing oil losses.

The Weir process, which was used until recently by some oil companies, involves mixing clay with the oil in naphtha solution. The mixture is chilled and filtered. Filtration of petrolatum is made possible without clogging the filters because petrolatum deposits on clay, forming a rigid wax cake.

Processes using solvents other than naphtha may employ filters or centrifuges for separating the wax from the oil. Those using filters include the Propane Process and the Benzol-Ketone Process, also known as the Benzol-Acetone Process. Recently the Methyl-Butyl Ketone Process came into prominence. In their general aspects all these are quite similar. They resemble filter-pressing of waxy oils in naphtha solution which has been previously described. The oil is mixed with the solvent, chilled and filtered. The rate of chilling can be very rapid, whereas with naphtha it must be slow in order to insure formation of relatively large crystals of wax. The solvent is separated from the oil or wax by distillation, and returned to the system. Precautions are taken to minimize the solvent losses as far as possible by employing a closed circulating system. This is very important, because solvents are quite expensive. In the propane process, cooling of the oil is achieved by evaporating some of the propane under reduced pressure from the oil-propane solution. This method of chilling is known as self-refrigeration. In some instances small quantities of filter-aids may be added to the oil solutions to modify the shape and size of the wax crystals and thus improve the filtering rates.

In the centrifuging processes (Bari-Sol and Separator-Nobel Dewaxing Processes) the solvents consist of chlorinated hydrocarbons or their blends with benzene. New types of centrifuges are equipped with scrapers which make them adaptable to the removal of solid wax cakes such as are formed by the crystalline wax. Conventional centrifuges have no scrapers and can be employed only for discharging petrolatum which has a certain degree of fluidity.

Centrifuging with solvents is often done in two steps. Oil containing wax is diluted with the solvent, chilled and centrifuged. The separated wax is mixed with an additional quantity of solvent and recentrifuged to recover the oil held by the wax. The solvent recovered from centrifuging the wax is employed for diluting the fresh oil charge in order to reduce distillation expenses. Two-stage centrifuging of the above type might be also employed, using naphtha for the dewaxing solvent (Sharples Dewaxing Process).

The Union Oil Company of California has recently developed a process for precipitating wax particles from the chilled oil solutions by electrical precipitation methods. These methods are similar in principle to those described in connection with the resolution of oil-field emulsions.

Solvent Refining

The solvent processes for removing the low viscosity index constituents resemble those described in connection with the Edeleanu Process for refining kerosene. Liquid sulfur dioxide cannot be employed, however, on most of the lubricating oil stocks because of its lack of solvent power. Other solvents or combinations of solvents were therefore developed. The single-solvent processes are represented by the Phenol, the Furfural, the Chlorex, and the Nitrobenzene Processes. The only mixed-solvent process is the liquid sulfur dioxide-benzol process employed in this country by the Union Oil Company of California. With the exception of sulfur dioxide the other solvents enumerated above are liquids at ordinary temperatures and atmospheric pressure. The individual solvents vary from one another as regards their selectivity and solvent power, but these differences tend to disappear if the conditions of extraction are properly adjusted, namely, the extraction temperature, quantity of solvent, and number of extraction stages. In choosing the most desirable solvent for an individual refinery, the above variables must be studied with relation to the stocks to be treated. In addition, the solvent should be non-corrosive, relatively cheap, and easily separated from the oil by distillation. The quantity of heat required to vaporize the solvent should not be excessive in order to have a low fuel cost.

The design of conventional extraction units which may consist of four to eight extraction stages has been discussed in connection with the Edeleanu process for refining kerosene. In some installations packed towers are employed wherein the solvent is allowed to gravitate toward the bottom of the tower against the rising stream of oil. The use of towers is possible only with the distillate stocks, which do not precipitate asphaltic bodies that may clog the tower.

The solvent processes thus far described are capable of removing from the oil only one of the three undesirable constituents, either asphalt, or wax, or the low viscosity index components. The crude oil stock must therefore be subjected to several solvent refining operations before it becomes a marketable product. However, processes are known which are capable of combining several of these refining steps into one. The best example of this is the Duo-Sol process, which has attained considerable prominence among refiners. This involves the use of two solvents: propane and Selecto, representing mixture of cresylic acids and phenol. The oil is dissolved in propane

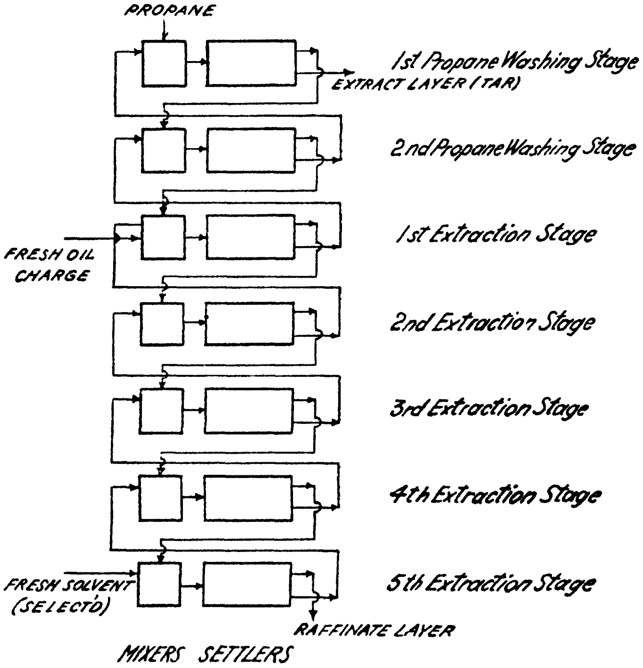


FIGURE 9. The Duo-Sol solvent refining process.

and contacted counter-currently with Selecto in the manner shown diagrammatically in Figure 9. In this process propane acts as the deasphalting agent and Selecto as the solvent for the low viscosity index constituents. However, when the two solvents are applied simultaneously, their combined effect on the oil is greater than might be expected from the results obtained by applying them separately.

Deasphalting and dewaxing processes may be combined. Thus it is possible to deasphalt the oil with propane at high temperatures and then dewax it by readjusting the quantity of propane in the mixture and by lowering the temperature. The product, which is still in propane solution, may be finally contacted with Selecto. A process of this type is now in operation at one of the plants of the Shell Oil Company.

Solvent-refined oils are usually percolated through clay before they are released to the market.

Lubricating oils in propane solution may be treated with sulfuric acid or clay. The resulting products are somewhat different from those obtained by treating them in naphtha solution because the deasphalting properties of propane enhance the action of other refining agents.

Additives

Application of additives was formerly restricted to the light petroleum distillates but was soon extended to lubricating oils. The general principles governing the use of additives have been discussed in connection with gasoline. However, the diversified requirements of high-grade lubricating oils permit utilization of additives on a considerably wider scale than is the case with light distillates.

The additives used in lubricating oils may be classified into numerous groups which include pour-point depressants, viscosity index improvers, oiliness carriers, oxidation and corrosion inhibitors, fluorescent agents and others. Some of these additives affect only one of the oil properties, while others are considerably more diversified in their action. For instance, the same additive may exhibit properties of a viscosity index improver and of a pour-point depressant; another may protect the oil from oxidation, act as a corrosion inhibitor, and have some detergent properties, that is, it would keep the engine free from heavy deposits.

As their name implies, pour-point depressants lower the pour-point of oils which contain wax. However, partial dewaxing of the oil is almost always necessary to obtain good commercial results. The ability of the pour-point depressants to lower the pour-point depends on their effect on the structure of the separated wax crystals. In the presence of these depressants wax crystallizes in small particles which remain suspended and do not interfere with the free flow of oil at low temperatures. In general, the presence of wax does not interfere with proper lubrication, and even improves some of the properties of the oil, such as viscosity index. Santopour and Paraflow are the two best known pour-point depressants in commercial use.

Viscosity index improvers are added to the oil to raise the viscosity index. They are usually very viscous liquids which are practically solids at room temperatures. Paratone is one of the commercial additives of this type. However, the use of viscosity index improvers is by no means general because of certain limitations which are explained in detail in more extensive treatises on oil refining.

Oiliness carriers form a relatively important group of additives, particularly in the preparation of special grades of lubricants. They have no value in lubricating engines having reasonable clearances between the moving parts and operating at low bearing pressures. However, when the clearances are small and the pressures high, the oil may be squeezed from the bearings, establishing direct metal-to-metal contacts. This results in excessive wear of the engine and raises the bearing temperature. To overcome this undesirable phenomenon certain substances are employed which tend to stick to the metal and thus maintain the oil film. Oiliness carriers are selected from a large variety of chemical compounds and are usually mildly acidic, or contain chlorine and similar corrosive agents. The nature and concentration of these additives must be, therefore, very carefully selected in order to avoid engine corrosion. The so-called "germ-processed" oils are representative of lubricants containing such additives. However, for automobile engines the use of oiliness agents is warranted only during the "break-in" period; new cars delivered from the factories are supplied with so-called "break-in oils," *i.e.*, oils containing oiliness agents. After the car has been in service for several hundred miles the necessary clearances are established and the use of such oils becomes unnecessary.

If pressure between the rubbing surfaces exceeds certain limits, a condition is reached when the oil film cannot be maintained even with the aid of oiliness carriers. So-called "high-pressure lubricants" are then employed. These lubricants contain corrosive compounds which act as metal polishes by attaching themselves to the protruding parts of the metal and smoothing the surfaces. The nature and quantity of corrosive compounds added to the oil vary widely, depending on the type of machinery and service.

Inhibitors are also employed to retard oxidation of oil by the oxygen of the air. In general, the oxidation products are of two types: asphalt-like materials forming sludge, and acidic substances which remain dissolved in the oil. Highly refined lubricating oils usually form acids, whereas poorly refined oils form sludge. If the oil is properly refined, the quantity of sludge deposited under normal conditions of service is small, but acid formation may be considerable. Acids may attack bearings, particularly if they are made of the new types of alloys developed with the primary purpose of sustaining high pressures and permitting high speeds rather than of resisting corrosion. To protect these bearings a special line of corrosion inhibitors has been developed. Reasons for protective action of corrosion inhibitors is not well clarified, but it appears that this may be due to chemical reaction between the metal and the inhibitor, resulting in formation of a corrosion-resistant film on the metal surface. True oxidation inhibitors should have no effect on the metal. Phosphorus compounds and organic derivatives of certain metals are representative of substances belonging to the class of corrosion inhibitors. They are sold under various trade names, such as Santolube or Paranox.

Sludge formed in the engine may settle out or remain suspended in the oil. Certain addition agents, which are said to possess detergent properties, are capable of keeping sludge in suspension and thus insure a clean engine and prevent formation of sludge deposits. The suspended sludge is easily removed from the engine when the oil is drained. These addition agents are mostly organic compounds of various metals.

In order to improve the appearance of oils lacking fluorescence certain dyes are sometimes employed. These dyes are carefully selected because only a few of them are capable of withstanding engine temperatures without decomposition.

Chapter 10

Wax, Asphalt, and Greases

Production of Waxes

Petroleum waxes find numerous applications in industry for manufacturing candles, waterproofing, preparation of polishes and for other uses originally developed for vegetable and animal waxes. Petroleum waxes may be used as such or after compounding with various ingredients depending on trade requirements. Two types of waxes are found in petroleum: paraffin wax, associated with distillate stocks, and petrolatum, associated with residual stocks. In dewaxing operations wax is obtained admixed with considerable quantities of oil, from which it must be separated before it is ready for sale. Because of inherent differences between paraffin wax and petrolatum various procedures are employed for deoiling them.

Paraffin wax from the dewaxing operations is obtained in the form of "slack wax." To separate oil from the slack wax, sweating or solvent-pressing may be employed. Sweating is conducted in large pans located in specially designed rooms or "sweaters," which are shown diagrammatically in Figure 10. Sweating pans contain screens fastened to the sides of the pans a few inches from the bottom and serve to support the wax cake. Rows of pipes carrying cold or hot water for controlling the temperature of the wax cake are located at close intervals above the screens. Provisions are also made for regulating the temperature of the air inside the sweaters. Sweating pans are charged with water up to the screen level, and molten wax is pumped on top to form a layer about six inches thick. Wax is solidified by circulating cold water through the pipes. Water is drawn from the bottom of the pans, leaving the wax cakes suspended on the screens. The tem-

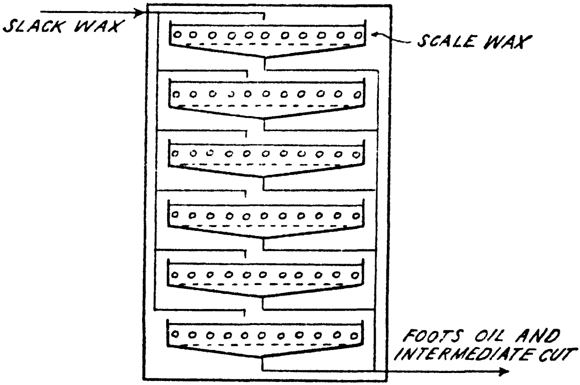


FIGURE 10. How paraffin wax is obtained.

perature of the wax cake is gradually raised at the rate of 1-2° F. per hour by circulating warm water through the pipes and by adjusting the air temperature. When the wax begins to melt, oil and the low-melting point waxes are liquefied, leaving on the screen the higher-melting-point waxes. The liquefied fractions are continually drained from the sweating pans into special receptacles. The first portions form "foots oil" and are discarded from the system. The subsequent portions, known as "intermediate cut," contain both oil and wax and are collected. Sweating is continued until the wax cake, or "scale wax," remaining on the screens reaches the desired melting point. The "scale wax" is then melted and removed from the sweaters. Scale wax may be marketed directly, but higher grades require finishing by percolation through clay or bauxite. Occasionally an acid treat or caustic wash may precede filtering or sweating operations. The intermediate cut may be blended with fresh feed to improve the total wax recovery, or sweated separately for the production of low-melting-point waxes.

The sweating process is far from being ideal because the recovery of wax is incomplete and much of it is lost with the oil. However, it is cheap to operate and, as wax is not an expensive commodity, sweating is frequently more economical than the more modern processes insuring higher wax yields.

The modern processes for deoiling paraffin wax include solvent-pressing. Slack wax is thoroughly mixed with naphtha, or solvents chilled and passed through a filter press. The chilling temperature and the quantity of solvents employed determine the melting point, oil content and other properties of the recovered wax.

Deoiling of petrolatum, which is frequently referred to as "ceresin wax," "amorphous wax" or "micro-crystalline wax," cannot be accomplished by sweating or by filtering with naphtha, because the wax present in residual stocks does not form large crystals, but settles out as a slimy precipitate. However, the oil may be removed by centrifuging petrolatum with naphtha or with special solvents. Filtering may be also resorted to provided solvents of the type employed in the benzol-ketone dewaxing process are substituted for naphtha. From these solvents wax is precipitated in a filterable form. Melting point, oil content and other properties of wax are controlled by adjusting the filtering or centrifuging temperature, and the quantity and nature of the naphtha or other solvent used. The separated wax is usually finished by percolation through clay.

"Vaseline," or petroleum jelly, is a familiar petroleum product which is manufactured for pharmaceutical and technical uses. Two types are known: natural and artificial. The former is obtained as a residue from the distillation of certain crudes; the latter is prepared by blending selected fractions of wax with selected fractions of oils. Pharmaceutical jellies are subjected to a very thorough chemical refining, but those used for technical purposes are often sold in the unrefined state.

Asphalt

Asphalt is used for paving, water-proofing fibrous and porous materials, preparation of paints, and similar purposes. Natural asphalts were considered for many years as superior products, but now the petroleum industry is capable of supplying asphalts which are as good or better in many respects. Consumption of asphalt is rapidly increasing. In 1942 the bituminous improved state roads in the United States comprised slightly over 9,000 miles, which was less than four per cent of all the available roads; in 1940 there were 200,000 miles of such roads, or 40 per cent of the total.

Commercial asphalts vary widely in their properties depending on their application. Specifications for the different grades usually include softening point, ductility, penetration and other tests. Softening point is determined instead of melting point, because asphalt does not show an abrupt change between the solid and liquid state on heating. For the same reason tests developed for measuring the softening point are quite arbitrary, and the results obtained by different procedures for its determination are not necessarily in agreement. Penetration refers to the rate at which a needle pierces asphalt under standard conditions of testing; ductility refers to the ability of asphalt to stretch without breaking.

In oil refineries asphalt is obtained as residue from distilling asphalt-base crudes. Residues from mixed-base crudes contain both asphalt and wax, and are not suitable for further processing because the presence of wax has an unfavorable effect on the properties of the asphalt, from which it cannot be separated commercially. Only in a few isolated instances, such as for oiling landing fields for airplanes, may admixture of wax with asphalt be beneficial.

In the preparation of high-grade asphalts selection of crude oil is of considerable importance. Not every refinery handling asphalt-base crudes can make good asphalts and, moreover, considerable caution is necessary in processing them. The oily constituents are separated from asphalt by distillation, but overheating must be avoided. If asphaltic residues are exposed to extreme temperatures, they may crack, forming coke and low-boiling materials, the presence of which has an unfavorable effect on the properties of asphalt.

Asphaltic residues from crude distillation are transferred into stills of special design and blown with steam or air at temperatures not exceeding 600° F. to avoid cracking. Steam assists in distilling off the oil which was not removed from the asphalt in the course of crude distillation. Removal of oil has relatively little effect on the softening point of the asphalt, but improves its penetration and ductility. Air-blowing results in chemical reactions which change the nature of the molecules composing asphalt. These molecules contain carbon and some hydrogen. The larger the proportion of carbon, the higher the melting point of the asphalt. In air-blowing some, but not all, of the hydrogen is burned off and the resulting molecules contain less hydrogen atoms than those which were present before air-blowing. By combining steam and air blowing it is thus possible to obtain products of different specifications by employing the same starting material. Attempts have been made to prepare asphalts by introducing sulfur before blowing with air or steam. However, these attempts are still in the experimental rather than in the commercial state of development.

Road oils are related to asphalt and are employed for covering dusty road surfaces with a minimum expenditure of labor. They differ from asphalt in that their oil content must be relatively high to insure proper fluidity.

Recently "colorless" asphalts have found some industrial applications. These are of a relatively light color, but by no means colorless as might be inferred from their name. They are employed in mixtures with various pigments, and the light color is important because the color of the asphalt should not interfere with the color of the pigment. Colorless asphalts may be obtained by treating crude asphalts with chemicals, such as with sulfuric acid in the presence of propane. This treatment removes the darkest-colored bodies from the asphalt; but as these also have the highest softening points, the softening point of colorless asphalts is relatively low.

Greases

Greases form an important class of lubricants and are used for a large variety of technical purposes; the result is an almost infinite number of formulas employed in their manufacture. In general, greases may be defined as solutions of soaps, *i.e.*, products formed by blending the salts of metals and organic acids with oils, although in some isolated instances products sold under the name of greases may be free from soaps but represent mixtures of mineral oils with graphite, talc, asbestos, waxes, rosin, fats or pitch. The demarkation line between greases and other petroleum products is not sharp, because some of the lubricating oils may contain soaps in the form of addition agents, although the resulting mixtures cannot be considered greases from the practical point of view. The soap content in mineral oils may thus vary from 60 to 0.25 per cent and the oil content from 99.75 to 40 per cent for products covered by the general definition of greases, but a mineral oil containing 0.25 per cent of soap will have none of the semi-solid or solid appearance of a grease.

Materials used in the manufacture of greases may include vegetable and animal oils, fats and waxes; inorganic basic substances like lime, sodium hydroxide and similar compounds of aluminum, lead, zinc, barium, magnesium or potassium; inorganic and organic fillers, like graphite, mica, asbestos, talc, animal hair and sawdust; as well as perfumed substances and dyes. Grease formulas usually represent closely guarded secrets by the manufacturers of these commodities; but recently considerable progress has been made in scientific studies which will lead eventually to a better understanding of grease-making processes and to the development of new and better products.

Greases are usually manufactured by the batch method; only in a very few instances are continuous processes employed. This is explained by the relatively small quantities of products made by the individual plants and by the difficulties encountered in securing raw materials of uniform quantity. Variations in the properties of raw materials may require certain adjustments during the manufacturing process which are difficult with a continuous system. For the same reasons grease-making has been considered for many years as an art rather than a science.

In preparing a grease careful attention is given to the time, temperature and degree of mixing and to the order in which the various ingredients are added to the grease kettle. These kettles may be open to air, but in the preparation of certain products closed chambers capable of withstanding considerable pressure are also used.

Greases which are sold on the market may be divided into several classes. Lime greases, represented by the so-called "cup greases," contain soaps of calcium. They are water-repellent and are excellent for lubricating mechanisms from which water cannot be eliminated. The "set greases" contain lime and rosin and find application in the lubrication of rough and slow-moving machinery. Sodium greases contain sodium soaps and are not water-repellent. They have a well developed "fiber" structure, and have other desirable characteristics which make them excellent lubricants if water is absent. Greases containing both lime and sodium soaps are also made. Aluminum-base greases contain aluminum oleate or aluminum stearate. Some of them have a rubber-like appearance. They are employed for lubricating special types of machinery, including certain parts of automobiles.

Lead greases contain lead oleate or similar lead compounds. They are widely used for lubricating transmission mechanisms in automobiles. They are often employed in combination with sulfur. Greases containing soaps of other metals than those mentioned above are also available but their consumption is small.

Greases containing no soaps are prepared by blending mineral oils with organic or inorganic fillers and other ingredients which are capable of forming paste-like products. Such ingredients may be also employed in combination with soaps.

Petroleum products used in grease manufacture may include lubricating oils, petrolatum, and even asphalt. Selection of the mineral oil is very important because the actual lubricating properties of a grease depend on the oil and not on the soap or other materials present.

Chapter 11

Waste Refinery Products

Sulfuric Acid Sludge

Disposal of waste products is an important refinery problem both from the economic point of view and for preventing pollution of air, soil and water. Formerly the spent chemical reagents were discarded without considering their harmful effect on plant and animal life. Sulfuric acid and caustic were discharged into streams or allowed to soak into the ground; gases like sulfur dioxide or hydrogen sulfide were freely vented into the air, and clouds of smoke emerged from the stacks, to settle on the neighboring country and in the lungs of the inhabitants. However, these unenviable conditions of industrial life have disappeared with the past. A modern refinery is forced to eliminate this practice not only on account of its nuisance but also because the wasted materials can often be converted into profit.

The refinery waste products may be of petroleum or other origin. They are represented by gases, liquids and solids requiring entirely different methods of disposal. The waste materials from non-petroleum sources are chemical reagents of which sulfuric acid, caustic and clay are the most important. They present problems of their own and are therefore discussed separately.

Spent sulfuric acid is one of the most difficult materials to dispose of both on account of its poisonous nature and the large quantities involved. However, the introduction of solvents has reduced the quantity of acid consumed in petroleum refining. In the past, sulfuric acid sludge from treating light petroleum distillates, such as gasoline and kerosene, was usually discharged into a convenient stream of water in the neighborhood, or allowed to seep into the ground. Occasionally this sludge was diluted with water or neutralized with spent caustic and the separated oil was skimmed off and used as fuel. The cheapness and availability of fresh acid offered no particular attraction for recovering the sludge. Sulfuric acid sludge from treating lubricating oils is more difficult to handle. It is a heavy, tarry material which quickly solidifies on standing because of chemical interaction between the substances of which the sludge is composed. It was usually discarded or burned under the refinery boilers.

During the last few decades several methods have been worked out for handling sulfuric acid sludges. One widely used process involves diluting them with water; for better separation of acid from oily constituents heat is applied. In some instances best results are obtained by employing pressure vessels which permit heating of the sludge above the boiling point of water. The recovered oil is poured from the acid layer and used as fuel. The acid layer, composed of dilute sulfuric acid with an admixture of organic materials, is concentrated by evaporating the water. In the Simonson-Mantius process this is done by vacuum distillation, whereas the Chemico process employs distillation under atmospheric pressure with air bubbling continuously through the acid. Use of vacuum or blowing with air is necessary to minimize foaming, due to evolution of gases. These gases consist principally of sulfur dioxide formed by decomposition of sulfuric acid by the organic substances present in the spent acid and not removed by dilution with water. The acid is seldom concentrated to more than 90-93 per cent strength, because at high concentrations the reaction between the acid and the dissolved organic substances becomes violent and results in the loss of large quantities of acid. However, acid of this strength is too weak for most refinery uses and is therefore fortified with fuming acid.

Recently the Heckenbleikner Sludge Contact Process was introduced. Sulfuric acid sludge from the agitators is charged into special vessels where it is heated to effect its complete decomposition into sulfur dioxide. Some coke is also formed. Sulfur dioxide is mixed with air and passed through a catalytic chamber, where it is converted into sulfur trioxide. Sulfur trioxide is diluted with water to form acid of any desired strength. Although this process is quite simple, relatively large installations are required to make it economical.

Burning of the oil separated from sulfuric acid sludge is very common. This oil contains various organic compounds of sulfuric acid, but it may be burned either directly or after diluting with refinery fuel oils. Furnaces used for this purpose should be equipped with acid-resistant bricks, and stack temperatures maintained at a relatively high level to prevent deterioration of equipment from the combined effect of moisture and sulfur dioxide. In some instances the solid sludge obtained in refining lubricating oils is burned by spreading it over a bed of coal.

Spent sulfuric acid may be used for manufacturing certain chemicals. For instance, the Shell

Oil Company reacts the spent acid with ammonia to form ammonium sulfate, a well known fertilizer.

Caustic Solutions

Spent caustic solutions may be partially or completely neutralized with spent sulfuric acid, diluted with water and then discarded. The spent solution still containing some unutilized sodium hydroxide is often employed for treating refinery stocks requiring a less concentrated solution. Processes for regenerating spent caustic by blowing with air or steam are available. Such blowing removes the weak acidic substances from the spent caustic solution, which is then ready for reuse. Acidic substances present in the spent caustic solution are sometimes recovered and utilized in soap manufacture, as gasoline inhibitors and for other purposes. These substances may be also displaced from the caustic solution by treating it with carbon dioxide, *i.e.*, with flue gases. Addition of carbon dioxide may be made in steps so as to recover substances of progressively higher acidity.

Clays

The finely divided clays employed in contact filtration are usually discarded because no satisfactory methods are available for restoring their original decolorizing efficiency. Although this might be done to a considerable extent by employing solvents, such as mixtures of acetone and benzene, the cost of processing is quite high. Recently, however, the Sinclair Refining Company developed a process of this type which they use commercially. Partial restoration of efficiency is of little benefit because the total expense involved in treating oils with low efficiency clays is usually higher than the savings effected.

The coarse clays employed in percolation filtration are regenerated by burning. Conventional burning equipment employed at the refineries is not very well suited for this purpose because few precautions are taken for protecting the clay from exposure to excessive burning temperatures. Overheating causes it to form solid chunks, and also removes that portion of water which contributes to the efficiency of the clay. This loss in efficiency necessitates discarding the clay after it is reburned from 5 to 15 times, depending on the nature of oil stocks and the design of the burning equipment. Recently, a new Thermofor Kiln has been developed, however, which is capable of regenerating clays without an excessive loss in efficiency. The

Thermofor Kiln is also well adapted to carbonizing clays, *i.e.*, burning spent clays in the presence of limited quantities of air. In percolating certain stocks like those obtained by solvent refining, the efficiency of carbonized clays may be several times that of fresh clay. The Thermofor Kiln was developed by the Socony-Vacuum Oil Company and is now used by all their refineries.

Instead of employing conventional fullers' earth for oil percolation, some refineries, particularly those working with the Pennsylvania oils, use bauxite. Although bauxite is more expensive and less efficient than fullers' earth on a weight basis, it can be regenerated in the present refinery kilns without much loss in efficiency.

Clay discarded by the refineries may be still satisfactory for some other industrial applications. It may be used in the manufacture of building materials or as a filler. Considerable work has been done in the course of the last few years on the problem of utilizing spent clays, but up to the present time the progress in this direction has been relatively slow. Huge piles of discarded clay are therefore common around refineries.

WASTE REFINERY PRODUCTS

Doctor Solutions

Spent doctor solution containing lead sulfide is usually regenerated by air-blowing. Bayway Chemicals Recovery and other similar processes are available for this purpose. In general, regeneration of various refining agents is growing in importance and the success of many new processes frequently depends on the ability to regenerate spent chemicals successfully. Undesirable materials removed in the course of refining may be utilized for manufacturing by-products or as refinery fuel. Water used in processing oils is usually settled to recover the oil which may be carried in suspension.

Smoke nuisance is eliminated by properly controlling fuel combustion. This control is economically important because acute competition exists between the individual oil companies, and an excessive fuel bill will undermine refinery profits. Sulfur dioxide or other objectionable gases are dissipated into the atmosphere by means of high stacks. If this is not done, the refinery may be liable for damages inflicted by the fumes on the plant and animal life in the surrounding territory.

Chapter 12

Chemicals from Petroleum

Slow Progress of Petroleum Chemistry

Petroleum is a prolific source of hydrocarbon materials and for many years much work has been done by industrial and scientific laboratories to utilize it in the manufacture of various organic chemicals. However, many obstacles had to be overcome before the results of these efforts found commercial realization.

Wonderful achievements in the field of the chemistry of coal-tar products served as a great inducement to petroleum chemists in their ambitious studies. However, their work was handicapped by the presence of an endless variety of hydrocarbons in crude petroleum which had to be isolated before they could be used as starting materials for organic synthesis. These difficulties are not encountered with coal-tar, which contains large quantities of individual hydrocarbons such as benzene, toluene, xylene, naphthalene or anthracene which can be easily separated from one another by simple distillation. The immortal work of W. H. Perkin, the founder of the coal-tar chemistry, was made possible by the ease with which he was able to obtain large quantities of these hydrocarbons in a relatively pure state. For the same reasons the development of the chemistry of benzene (aromatic) hydrocarbons advanced infinitely faster than that of petroleum (aliphatic) hydrocarbons. Many new and important reactions involving the latter have only recently been discovered, and a number of errors and fallacies have been unearthed in the firmly established conceptions and theories which were based on insufficient experimental evidences or incorrect deductions.

Like the chemistry of coal-tar products, that of petroleum hydrocarbons began its development with the study of the low-boiling compounds which could be easily separated in large quantities by the improved methods of fractional distillation. The progress in these studies paralleled the discoveries of further possibilities of isolating new substances from petroleum in large quantities and at low cost. However, with the increase in boiling point, the variety of hydrocarbons present in petroleum increases at a very rapid rate, which places definite limitations both on the ease of their isolation and on the available quantities of the individual substances. For these reasons petroleum chemistry is to a great extent limited to the relatively few low-boiling hydrocarbons which are present in the crude or which are obtained by thermal decomposition of complex petroleum fractions.

Another factor contributing to the slow progress of the petroleum chemical industry is the organization of the marketing and distributing facilities of oil companies which are best suited for handling products in bulk quantities. New service branches and specially trained personnel had to be provided for dealing in synthetic materials. No immediate profit could be expected from such enterprises and much time was needed to pay off the initial investment. In addition, the income derived from selling chemicals was only a negligible addition to profits accruing from the sale of huge volumes of normal petroleum products. For these reasons, any real benefit to be realized from these new undertakings was postponed to the distant future.

Chemical companies were the first to use petroleum hydrocarbons as raw materials for synthesizing chemicals, that is, for making them artificially. These hydrocarbons were not necessarily obtained from petroleum sources. The petroleum industry has been able to supply them at a reasonable cost only in relatively recent times, because of complications involved in isolating them from crude oil. Chemical synthesis was frequently difficult and uneconomical as compared with the existing methods, which involved more expensive raw materials but presented fewer manufacturing problems. However, at the present time the manufacture of chemicals from petroleum is on a well established basis and has good possibilities for the future. A number of petroleum companies are actively engaged in supplying the market with chemicals and in developing new sources of income from their sale.

Because of their reactivity, the unsaturated petroleum hydrocarbons are best suited for the manufacture of chemicals. These hydrocarbons are obtained in large quantities in the course of cracking. However, many of the saturated hydrocarbons are also employed in this connection.

Methane

Methane, the only hydrocarbon possessing a single carbon atom in the molecule, is found in large quantities in the oil fields, but little has been done toward utilizing it in the manufacture of chemicals because of its saturated nature and relative inertness. It is widely used as fuel, as it forms by far the greatest part of natural gas.

Utilization of methane for manufacturing carbon black and hydrogen has already been described. By carefully controlled oxidation it may be converted into formaldehyde, which finds application in the preparation of synthetic resins, such as Bakelite, and as a disinfectant. Methane may be converted into acetylene by exposure to very high temperatures produced by an electric arc. Commercial plants of this type have been developed, but wide adoption of the process by the industry at large has been retarded by the high operating expense. Acetylene resulting from the process may be employed in welding, converted into benzene or acetic acid, and used for the preparation of a large number of other organic compounds. By interacting methane with chlorine, carbon tetrachloride, chloroform, methylene dichloride and methyl chloride are obtained, depending whether four, three, two or one of the hydrogen atoms in the methane molecule are replaced by chlorine. The individual reaction products are separated by distillation and may be employed for further synthesis. Recently methane has been successfully used for the preparation of nitromethane, which is used as a solvent. However, quantities of methane consumed by the above processes form a negligible fraction of those employed for fuel or lost by venting and burning in the air.

Ethane

Ethane may be utilized in the same ways as methane. On oxidation it can be converted into ethyl alcohol and on chlorination it yields a number of chlorinated compounds, like ethylene dichloride, which have good solvent properties. However, ethylene rather than ethane is attractive commercially, because of its unsaturated nature; it is used in preference to ethane for the manufacture of ethyl alcohol and ethylene dichloride. The latter is the starting point in making certain types of synthetic rubber. In the presence of water and chlorine, ethylene forms chlorhydrin which may be converted into ethylene glycol, the well known antifreeze sold under the trade name of "Prestone." Chlorhydrin may be also converted into ethylene oxide which is mixed with carbon dioxide and sold as a fumigant under the trade name of "Carbonozide." Ethylene glycol and other glycols react with ammonia, forming the industrially important ethanolamines. Dioxan and a number of other chemicals are likewise produced from ethylene glycol. Ethylene and a few other gaseous unsaturated hydrocarbons are used in artificial ripening of citrus fruits, for inducing growth of vegetables, and as anesthetics.

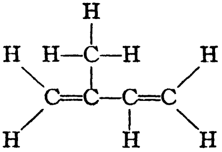
Propane

Propane, on oxidation or chlorination, yields the corresponding oxygen and chlorine derivatives. Commercially, however, propylene is employed in preference to propane. Isopropyl alcohol is formed by uniting propylene with water in the presence of sulfuric acid acting as a catalyst. Isopropyl alcohol can be converted by the same process into isopropyl ether, which has been proposed for improving antiknock properties of aviation fuels. Glycerin is obtained by treating propylene with chlorine and water. Acetone is manufactured from propylene by a recently developed process.

Butanes and Synthetic Rubbers

Butanes and butenes have also found commercial applications in the chemical industry besides their use in the manufacture of synthetic fuels. Methyl ethyl ketone, an important solvent employed in dewaxing petroleum oils and for other purposes, is prepared from one of the butenes. However, the present outstanding interest in these hydrocarbons is related to their use as raw materials in the manufacture of synthetic rubber.

The early attempts to manufacture synthetic rubber involved the use of isoprene as the starting raw material.



Isoprene

This method of attack was chosen since isoprene is obtained on decomposing rubber at high temperatures, thus indicating that it is the basic constituent of rubber. Recent developments have led to the abandonment of the attempts to use isoprene, as it has never been possible to produce this substance commercially at a reasonable cost.

Synthetic rubbers of present commercial importance may be divided into several groups. Neoprene rubbers are produced from butadiene which has one of its hydrogen atoms replaced by chlorine. The raw materials usually employed in their manufacture are coke, lime and hydrochloric acid. Buna rubbers, which are in many respects the best substitutes for natural rubber, are prepared by uniting butadiene with other substances, such as styrene or acrylonitrile. They are known under a variety of names, for example, Ameripol, Buna S, Buna N or Perbunan, Chemigum, Hycar, etc. The butadiene used in this process may be obtained from petroleum. Other classes of synthetic rubbers include Thiokol, made from ethylene, chlorine and sodium sulfide; Vistanex made from isobutene; vinyl rubbers, like Koroseal, made by polymerizing vinyl chloride; and the recently widely publicized Butyl rubber, a reaction product of butadiene and isobutene. It should be noted, however, that none of the synthetic rubbers is an exact overall substitute for natural rubber, although in some of their properties they may be superior to the natural product. For example, the abrasion resistance of the Buna rubbers is roughly equal to that of natural rubber. However, its adhesion to fabric is much less satisfactory.

Car Speed Miles per Hour	Relative Loss or Rubber for Equal Distance of Travel
25	100
30	106
35	120
40	136
50	200
60	430

It is worth noting at this point the pronounced effect of speed on the wearing qualities of tires, both natural and synthetic. This is shown by the approximate figures shown on the previous page.

In the summer the rate of wear is about twice that in the winter. The above shows that at 60 miles per hour in the summer time about 8.6 tires would be needed to cover the same distance which would wear out one tire in the winter time at a speed of 25 miles per hour.

Pentanes

Pentanes obtained by fractionating natural gasoline are chlorinated and converted into alcohols by hydrolysis, *i.e.*, by reacting with water which results in the exchange of the chlorine atom for the –OH group typical of alcohols. Hydrogen chloride is another product of the reaction. Mixtures of amyl alcohols or similar mixtures of butyl alcohols and their derivatives of the ether and ester types are used as solvents and are sold under the trade names of Pentasol, Pentacetate, "Cellosolve," "Cellosolve" Acetate, Butyl "Cellosolve," "Carbitol" and others.

Processes are also available for manufacturing derivatives of aromatic hydrocarbons, like benzene, using the unsaturated hydrocarbons obtained from cracked petroleum gases. By employing phenol instead of benzene, products are obtained which find application as germicides.

Other Chemicals

The foregoing discussion shows what a large number of organic chemicals may be prepared from petroleum. In addition to the substances mentioned in this and previous chapters, a large number of other compounds are obtained by further synthesis, although economic considerations may require the choice of other raw materials than petroleum, for reasons already explained.

Petroleum fractions containing hydrocarbons boiling above pentane are at the present time not suited for manufacturing pure chemicals because of the difficulties encountered in isolating the individual components. However, processes have been devised for converting such fractions by various chemical reactions into mixtures of unknown composition which find industrial applications. Polymerization of highly cracked petroleum distillates in the presence of aluminum, iron or zinc chlorides yields resinous substances of the quick-drying type suitable for the manufacture of paints and varnishes. Drying oils which may be used as substitutes for linseed oil are obtained by treating with clay the highly cracked distillates containing diolefins. Synthetic lubricating oils are prepared by polymerizing unsaturated gaseous hydrocarbons in the presence of aluminum chloride. Paratone, employed for improving the viscosity index of lubricating oils, is prepared from similar raw materials. Oxidation of kerosene yields satisfactory solvents for lacquers. Aldehol used for denaturing alcohol is obtained by a similar process. Oxidation of paraffin wax produces acids suitable for manufacturing soaps, while chlorination of wax yields oiliness agents and additives employed as high-pressure lubricants.

Besides hydrocarbons a number of other valuable compounds are found in crude oils, or may be obtained in the course of refining. Naphthenic acids are present in considerable quantities in certain crudes, particularly those of the Coastal type. They introduce certain complications in the refining operations due to corrosion of distillation equipment. Naphthenic acids are separated from the oil by washing with caustic solutions. They are used in the form of soaps of various metals as dryers for paints and lacquers, as emulsifying or demulsifying agents, in the manufacture of soaps, and for other purposes. Recovery of naphthenic acids and phenols from spent caustic solutions has been already described. Sulfonic acids are obtained as by-products from refining oils with sulfuric acid. Sulfonic acids soluble in the oil are usually referred to as "Mahogany Acids" and those soluble in water are known as "Green Acids." Mahogany acids are extracted from the oil with alcohol which is then removed by distillation. Sulfonic acids are used as emulsifying agents, detergents, or as important constituents of certain lubricants; they may be obtained by interaction of solvent extracts with sulfuric acid. The mercaptans present in cracked distillates and occasionally found in natural gas may be also utilized. Amyl mercaptan, a vile smelling substance, is employed for odorizing natural gas and is prepared from the chlorinated pentanes, while Alcotate and Calodorant, also used for odorizing natural gas as well as for denaturing alcohol, represent mercaptan-rich oils obtained from petroleum distillates.

Practically every large petroleum company is engaged in the manufacture of numerous specialties. These specialties are sold partly for profit and partly to accommodate customers for other petroleum products. These specialties include polishes, insecticides and a number of other products which contain materials of petroleum origin used as a base. For instance, the well known Bug-a-boo, Flit and similar fly sprays consist of a well refined kerosene fraction mixed with flower extracts, particularly those obtained from special varieties of pyrethrum, and which are poisonous to insects but not to human beings.

Glossary

Absorption Gasoline.—Gasoline extracted from natural gas by contacting the gas with the oil and distilling the mixture to recover gasoline dissolved by the oil.

Absorption Oil.—Oil used for dissolving gasoline vapors present in natural gas. See Absorption gasoline.

Accelerator.—A substance which increases the speed of a chemical reaction.

Acid Sludge.—Gummy acid material which separates from the oil after treating it with sulfuric acid.

Air Lift.—A method for lifting oil by pumping air at the bottom of the well and allowing the resulting mixture of oil and air to rise to the surface.

Aliphatic Hydrocarbons.—Hydrocarbons in which the major C atoms form a straight chain.

Alkylation.—Formation of complex saturated molecules by direct union of a saturated and an unsaturated molecule.

Aniline Point.—Temperature at which aniline and oil become completely miscible with each other under specified experimental conditions. This test serves as an indication of the content of aromatic hydrocarbons in the oil.

Anticline.—A fold or arch of rocks below the earth surface.

A.P.I. Gravity.—Arbitrary scale for measuring the density of oils which has been adopted by the

American Petroleum Institute. Its relation to specific gravity is as follows:

$$°\text{A.P.I.} = \frac{141.5}{\text{sp. gr. at } 60°/60°\text{F.}} - 131.5$$

Ash Content.—Solid material left on combustion of an oil sample and representing the contents of inorganic matter in the oil.

Asphalt.—Solid or semisolid mixture of hydrocarbons found in nature (natural asphalt) or manufactured by distillation, oxidation or other treatment of mineral oils (artificial asphalt).

Asphalt Base Crude.—Crude containing asphalt and practically no wax.

Asphalt Cement.—A specially prepared asphalt which can be used directly for building pavements.

Aviation Gasoline.—Light, high octane number gasoline used in airplanes.

Bailer.—Apparatus for removing mud, sand and water from a well which accumulate in drilling operations.

Barrel.—The 42 gallon barrel is generally used by the petroleum industry. However, 50 and 55 gallon barrels are occasionally employed.

Bauxite.—Naturally occurring aluminum oxide.

Bed.—The smallest division of subsurface layers.

Bitumen.—Mixture of solid or semisolid hydrocarbons.

Bloom.—See Fluorescence.

Blow-out.—A sudden violent escape of gas or air.

Blown Asphalt.—Asphalt produced by blowing air through residual oils.

Bottoms.—Residue left after oil distillation.

Bottom Settlings.—Sediment formed in storing crude petroleum and usually consisting of oil, water and inorganic matter.

Brightening.—Blowing lubricating oils with air at slightly elevated temperatures to remove traces of moisture which impart to the oil a cloudy or hazy appearance.

Bright Stock.—A heavy viscous residual oil of a clear pale or red color. The term is sometimes applied to very viscous distillate stocks.

Brine.—Strong solution of salt in water.

Burning Oil.—Kerosene.

Burning Test.—Test for determining burning qualities of kerosene.

Burnt Oil.—A lubricating oil improperly treated with sulfuric acid which resulted in destruction of the pleasant color associated with the well refined oils.

Cable System.—System of drilling wells by a heavy string of tools suspended from a cable and consisting in breaking the ground by a series of blows produced by alternately lifting and dropping the tools.

Capping.—Controlling the flow of oil wells by employing strong valves attached to the casing.

Carbon Black.—A solid finely divided material consisting almost exclusively of carbon and produced by incomplete combustion of natural gas or oil.

Carbon Residue.—Residue left on heating and evaporating a lubricating oil under specified conditions.

Casing.—Steel or iron pipe for lining oil wells.

Casing Head.—A device at the top of the casing for separating gas from the oil and providing an access to the well for pumping, cleaning and other purposes.

Casinghead Gasoline.—Obsolete term for natural gasoline.

Catalysis.—A process employing a substance which promotes chemical reactions without itself undergoing chemical changes.

Centrifuge.—An apparatus effecting gravity separation by the application of a centrifugal force caused by rapid rotation.

Ceresin.—A substance prepared from ozokerite and resembling beeswax. The name is often applied to similar substances present in crude oil. See Petrolatum.

Clay.—A heterogeneous mixture of hydrated aluminum silicates containing impurities like iron, calcium, etc. Some of the clays have property of absorbing impurities from oils and are employed in oil refining.

Cleaners' Solvent.—A well refined petroleum fraction boiling between 300°F. and 400°F. and primarily intended for use in dry cleaning.

Cloud Test.—Temperature at which paraffin wax or other substances present in the oil begin to separate on chilling affecting the oil transparency.

Coking.—The process of distilling petroleum to dryness resulting in the decomposition of heavy hydrocarbons with resulting formation of coke in the still.

Cold Pressing.—Separating paraffin wax from distillate oils by chilling and filtering through a filter press.

Cold Settling.—Separation of petrolatum from oils by chilling, settling and decanting the petrolatum free material.

GLOSSARY

Cold Test.—Temperature at which wax or other materials congeal on chilling preventing the free flow of the oil under conditions of testing.

Color Stability.—Resistance of oil to discoloration under the influence of light, aging, etc.

Compounded Oil.—Mineral oils containing added vegetable or animal oils.

Conradson Carbon.—See Carbon residue.

Corrosion Test.—Test designed to indicate whether an oil is corrosive to metals and is usually conducted by immersing a copper strip in the oil under specified conditions of testing.

Cracking.—Decomposition of heavy petroleum products into lighter ones by application of heat.

Crude.—Unrefined petroleum.

Cut.—Fraction of oil obtained by distillation.

Cut-back Products.—Blends of heavy and light oils to bring the heavy oil to desired specifications.

Cutting Oil.—Oil for lubricating and cooling metal cutting tools and made by blending mineral oils with lard oil or similar oils (insoluble cutting oils) or with sulfonated products (soluble cutting oils).

Cylinder Oil.—Heavy oil for lubricating steam cylinders, frequently compounded. The use of the term is sometimes extended to very heavy residual stocks.

Dehydrator.—Apparatus for removing water from oil or gas.

Derrick.—Tower over an oil well for hoisting or lowering the boring tools.

Destructive Distillation.—See Cracking.

Detergent.—A cleansing agent.

Detonation.—Sharp explosion resulting in the characteristic noise in a motor produced by inferior grades of motor fuel.

Diatomaceous Earth.—Mineral composed of the siliceous skeletons of minute organisms (diatoms).

Diesel Engine Oil.—Oil used for lubricating Diesel engines.

Dip.—The angle at which a bed is inclined from the horizontal.

Distillate.—Product of distillation collected by passing vapors through a condenser. The name is sometimes applied to a petroleum fraction intermediate between gasoline and kerosene.

Doctor Test.—A test employed for determining the presence of certain sulfur compounds (mercaptans) in the gasoline.

Dome.—Cupola. An uplift in which the beds dip outward in all directions from a center. Oil and gas pools are frequently found under the domes.

Drilling.—Process of making an oil well. Two general methods of drilling are employed: cable or percussion system, and rotary system or boring.

Drive Pipe.—A pipe which is forced into a bored hole to shut off water or prevent caving.

Dry Distillation.—See Cracking.

Dry Gas.—Natural gas void of gasoline vapors.

Dry Hole.—A well containing no oil or gas.

Drying Oil.—Oil capable of absorbing oxygen from the air forming a relatively hard, tough and elastic film when exposed in thin layers to the atmosphere.

Dry Sand.—Nonproductive sand encountered in drilling.

Ductility.—The property of a substance to be drawn into threads or wires.

Edge Water.—Water that holds oil and gas in an oil field in place and which encroaches on a field after much of the oil and gas is recovered and the pressure is reduced.

Emulsifiable Oil.—An oil treated or compounded so as to form stable emulsions with water.

Emulsification Test.—A test showing the relative ease of emulsion formation between the oil sample and water under prescribed conditions.

Emulsion.—Dispersion of fine particles of one liquid in another liquid.

End Point.—The maximum temperature indicated on the thermometer in standard laboratory distillation tests (usually ASTM or Engler tests).

Engine Oil.—A light lubricating oil intended for the lubrication of the reciprocating parts of an engine or similar machinery.

Erosion.—Loosening or dissolving and removing earthy or rock materials from any part of the earth surface by natural weathering.

Evaporation Test.—A test for determining the completeness or rapidity of evaporation of volatile petroleum products.

Fault.—A break in the continuity of a bed.

Fire Point.—The lowest temperature at which a petroleum product forms vapors, under specified experimental conditions, at a rate sufficient to maintain continuous burning when ignited with a small flame.

Flash Point.—The lowest temperature at which a petroleum product forms sufficient vapors, under specified experimental conditions, which give a flash or slight explosion when ignited by a flame.

Floc Test.—A test applied to illuminating oils for detecting formation of substances rendered insoluble by heat.

Floridin.—Fuller's earth from Florida.

Flotation Oil.—Oil used for separating valuable minerals from finely ground rock by employing their relative ability to float in the liquid.

Flue.—A passage for air, gas or smoke.

Fluorescence.—Emission by illuminated substances of a light having a color different from their own.

Flux.—Oil blended with heavy petroleum products, like asphalt, for the purpose of softening them.

Foamite.—The trade name for a preparation used in extinguishing oil fires.

Fold.—A bend in a bed with steeply inclined sides.

Foots Oil.—Oil separated from the wax and containing a large proportion of low melting point waxes.

Fractionation.—Separation of mixtures into their components.

Fuel Oil.—Any petroleum product used for combustion. The term is often restricted to petroleum products heavier than gasoline and which may be either distillates (distillate fuel oils) or residua (bunker fuels). Some of the highest grade distillate fuel oils are used in Diesel engines and are often referred to as Diesel fuels.

Fuller's Earth.—A porous earth resembling clay but having adsorptive properties towards impurities present in the oil.

Gas Oil.—A petroleum distillate having a viscosity and boiling range intermediate between those of kerosene and lubricating oils.

Gasoline.—A light fraction obtained from the distillation or cracking of petroleum having a boiling range from 80°F. to 400°F. or 437°F. depending on specifications imposed and the use for which it is intended. Gasoline for aviation engines may have an end point as low as 300°F.

Gasser.—A gas producing well, especially an oil well producing much gas.

Geological Horizon.—Rocks belonging to the same geological age.

Gravity.—Ratio of the density of a substance to the density of an equal volume of water under certain standard conditions. Gravity of gases is usually referred to air and not water as the standard substance.

Grease.—Solution of soap in mineral oil.

Ground Water Level.—The level below the earth surface which is filled or saturated with water to unknown depth.

Gum.—Sticky semisolid deposits formed on deterioration of gasoline and other oils.

Gusher.—An oil well with a large natural flow.

Heat Test.—A test applied to oils for measuring their stability towards heat.

Horizon.—Geological strata formed at the same time.

Illuminating Oil.—Oil used for illuminating purposes, such as kerosene or mineral seal oil.

Induction Period.—Time interval under given conditions in which an oil does not absorb oxygen to form gum.

Infusorial Earth.—Material consisting chiefly of silicious skeletons of microscopic organisms.

Inhibitor.—A substance which arrests or prevents a chemical reaction.

Initial Boiling Point.—The temperature at which the first drop of distillate falls from the condenser into the receiver in a standard laboratory distillation procedure.

Insecticidal Oil.—Oil used for combating insects.

Insulating Oil.—Oil used in electrical installations to conduct away heat and provide electrical insulation.

Iodine Number.—Measure of iodine absorption by oil under standard conditions of test which serves as an indication of the quantity of unsaturated compounds present in the oil.

Isoclinal.—Dipping in the same direction.

Jar.—To drill by impact.

Kerosene.—Petroleum fraction boiling above gasoline and having a boiling range between 300°F. and 600°F. depending on specifications.

Kinematic Viscosity.—Ratio of absolute viscosity to density.

Knock.—See Detonation.

Lampblack.—See Carbon black.

Lamp Oil.—See Kerosene.

Lamp Burning Test.—Test consisting in burning an oil in a lamp under standard conditions.

Light Distillates.—Low boiling petroleum fractions including kerosene.

Layer.—A bed or stratum of rocks.

Liquid Gas.—Normally gaseous petroleum fractions liquefied by applying pressure and used for heating or illuminating purposes.

Log.—Detailed drilling record.

Long Residuum.—Residual oil from distillation which contains oil fractions carrying crystalline wax.

Lubricating Oil.—Oil used as a lubricant.

Machine Oil.—Oil used to lubricate the moving parts of machinery.

Mazout (Mazut or Masut).—See Residuum.

Medicinal Oil.—A very highly refined lubricating oil distillate for internal use.

Melting Point.—Temperature of melting.

Middle Oil Distillate.—Distillate collected between kerosene and lubricating oil fractions.

Mineral Seal Oil.—A distillate boiling above kerosene and used for lighthouse illumination.

Mixed Base Crude.—Crude petroleum containing both asphalt and wax.

Monoclinal.—Dipping only in one direction.

Motor Spirit.—Fuel suitable for burning in motors.

Mud.—Mixture of water, clay and other materials used in drilling wells.

Naphtha.—A generic term loosely applied to petroleum distillate boiling below kerosene.

Natural Asphalt.—A naturally occurring asphalt.

Natural Gas.—Mixture of gaseous hydrocarbons occurring in nature.

Natural Gasoline.—Light liquid product obtained by extracting gasoline vapors present in natural gas.

Neutralization Number.—Measure of acidity present in an oil.

Neutral Oil.—A generic term loosely applied to lubricating oil distillates of low or medium viscosity.

Nujol.—Medicinal oil manufactured by the Standard Oil Co. (N. J.).

Oil Flotation.—A process employing oil for concentrating ores. See Flotation oil.

Oil Pool.—An underground accumulation of oil that yields petroleum on drilling.

Open Hole.—The part of the well which is not protected by casing.

Organic Acidity.—Acidity due to the presence of organic acids.

Overhead.—Distillate.

Ozokerite (Ozocerite).—A naturally occurring wax.

Pale Oil.—A loose term applied to lubricating oils of relatively light color and viscosity.

Paraffin Base Crude.—Crude containing paraffin wax and practically no asphalt.

Paraffin Distillate.—Lubricating oil distillate containing paraffin wax.

Paraffin Wax.—A white waxy substance resembling spermacetti and associated with the petroleum distillates.

Penetration.—Measure of consistency of semisolid materials expressed as the distance travelled by a needle through the substance under specified conditions.

Petrolatum.—Soft petroleum material obtained from petroleum residua and consisting of soft amorphous wax and oil.

Petroleum Ether.—The lightest fractions distilled from petroleum and having an end point usually below 175°F.

Perfumery Oil.—A light, highly refined, colorless and odorless oil used in the manufacture of perfumes.

Pitch.—Solid material obtained from distillation of bituminous materials. The term is usually applied to residua obtained from coal tars and is not in good usage in petroleum terminology.

Polymerization.—Formation of complex molecules by direct union of unsaturated molecules.

Pour Point.—The lowest temperature at which an oil will pour or flow when chilled under specified conditions.

Pressed Distillate.—Oil obtained after removing wax by cold pressing.

Pressure Filter.—A filter through which the liquid to be filtered is forced under pressure.

Red Oil.—A term loosely applied to lubricating oils of relatively dark colors. The same term is also applied to commercial oleic acid.

Reducing.—Removal of light fractions by distillation.

Residuum.—The thick viscous residue left on distillation of crude oil.

Resins.—Substances of asphaltic nature and usually included in the asphalt but having properties intermediate between oil and asphalt.

Rig.—A derrick with accessory equipment.

Road Oil.—Oil suitable for dust proofing and hardening the road surface.

Rope Drilling.—Drilling with a bit attached to the end of a rope permitting both horizontal (twisting) and vertical (raising and dropping) movement of the bit.

Rotary System.—Drilling by rotating the bit.

Run Down Tanks.—Tanks for collecting products of distillation emerging from condensers.

Saponification Number.—A measure of combined acids present in an oil.

Saturated Oil.—An oil free of hydrocarbons and other materials capable of adding hydrogen to their molecules.

Saybolt Viscosity.—Number of seconds required for an oil to pass through Saybolt viscosimeter under standard conditions of test.

Scale Wax.—Paraffin wax obtained after the oil is removed by sweating and left as a scale on the pans.

Slack Wax.—Paraffin wax obtained after it is separated from oil but still containing large quantities of oil from which it may be freed by the sweating process.

Sludge.—Sediment obtained on treating an oil with a chemical agent and settling. The term is also applied to the sediment formed on deterioration of lubricating oils.

Sludge Acid.—Sulfuric acid and the impurities absorbed in the treatment of an oil with sulfuric acid.

Sludge Test.—Test intended to show the amount of material in an oil which can be absorbed by sulfuric acid under specified experimental conditions.

Soda Ash.—Sodium carbonate.

Solar Oil.—Gas oil from Coastal or Midcontinent crudes.

Solidification Point.—Temperature at which a substance changes from a solid to a liquid state.

Solidified Petroleum.—A light petroleum distillate "solidified" by addition of soaps. Another method involves impregnation of porous materials, preferably also combustible, like peat, with liquid petroleum products.

Soluble Oil.—See Emulsifiable oil.

Solvent Naphtha.—Term applied to coal tar and wood naphthas but occasionally also applied to petroleum products of high solvent power.

Sour Oil.—Oil treated with sulfuric acid but not neutralized with alkalies or adsorbents. The term is also applied to oils which contain mercaptans and do not pass the doctor test.

Specific Gravity.—See Gravity.

Spindle Oil.—Lightest lubricating oil fraction used for lubricating small high speed machinery working under a light load.

Spray Oil.—See Insecticidal Oil.

Spudding.—The initial step in drilling performed with a dull drilling tool for working in earth down to the rock.

Stoddard Solvent.—See Cleaners' solvent.

Stratum.—A layer or a bed, sheet, or thickness such as of rock or tissue.

Stripping.—The removal of light fractions from oil by distillation. The term frequently applied to removal of naphtha from stocks refined in naphtha solution with chemicals.

Sulfonic Acids.—Hydrocarbon derivatives of sulfuric acid usually produced in sulfuric acid treatment.

Sump-hole.—A small reservoir near the derrick for discharging bailings or drilling mud from the well.

Sun Test.—Test intended to show stability of the color of an oil on exposure to sunlight.

Sweating.—Separation of oil from paraffin wax by gradual application of heat.

Sweetening.—Rendering the oil negative to the doctor test.

Switch Oil.—Oil for insulating electric switches.

Syncline.—A fold in rocks in which the strata dip inward from both sides.

Tar.—A thick viscous liquid obtained by distillation of wood, coal, peat and other organic materials. The term is loosely applied to any sticky and very viscous or even solid or semisolid oil residue.

Thickened Oil.—Mineral oils thickened by dissolving in them small amounts of rubber, aluminum soaps, or similar materials in order to improve their lubricating properties for some specific purpose.

Thief.—A device for drawing samples from an oil well.

Topping.—Removal of volatile fractions by distillation.

Top Water.—Water which enters the well from a sand above the productive sand.

Transformer Oil.—Oil used in electrical transformers to conduct away heat and to provide electrical insulation.

Turbine Oil.—Oil used for lubricating turbines.

Underreamer.—An oil well tool for enlarging the hole.

Unsaturation.—Ability of certain chemical compounds to add other elements, such as hydrogen, chlorine, bromine, iodine, etc., without giving up hydrogen or some of their constituents.

Vaseline.—A yellowish, translucent, semisolid petroleum product representing a mixture of oil and low melting point waxes. Vaseline may be natural or artificial depending whether it is obtained directly from the crude oil or by blending its component parts.

Viscosity.—Measure of the resistance to flow of a liquid.

Viscosity, absolute.—Expression of viscosity in absolute units, *i.e.*, poises, which refer to the force in dynes required to move a surface of one sq. cm. past an equal parallel surface one cm. distant with a velocity of one cm. per second.

Viscosity, kinematic.—See Kinematic viscosity.

Walking Beam.—An oscillating beam or lever for transmitting reciprocating vertical motion to the drilling tools.

Water Acid.—The first small portion of sulfuric acid frequently applied to remove moisture from the oil before treating with additional quantities of acid.

Water Soluble Oil.—See Emulsifiable oil.

Wax.—Plastic, fusible and viscous or solid substance having a characteristic luster, insoluble in water but more or less soluble in a variety of organic solvents. Wax present in the crude oil belongs to two major varieties: paraffin wax and ceresin wax (petrolatum).

Weathering.—Exposure of oil to the atmosphere resulting in the loss of light fractions by evaporation.

Wet Gas.—Natural gas containing gasoline vapors.

White Oil.—A colorless and odorless viscous oil used in medicine, in the preparation of creams and ointments, and also as a substitute for edible oils.

Treatises on Petroleum

Abraham, H. Asphalt and Allied Substances. 4th Edition. 1515 p. (1938).

Bell, H. S. American Petroleum Refining. 2nd Edition. 621 p. (1930).

Brooks, B. T., Dunstan, A. E., Nash, A. W., and Tizard, H. T. The Science of Petroleum. 3192 p. (1938).

Ellis, C. The Chemistry of Petroleum Derivatives. 2749 p. (1934-9). Reinhold Publishing Corp.

Gurwitsch, L. Scientific Principles of Petroleum Technology. 2nd Edition. 556 p. (1932).

Kalichevsky, V. A. Modern Methods of Refining Lubricating Oils. 240 p. (1938). Reinhold Publishing Corp.

Kalichevsky, V. A., and Stagner, B. A. Chemical Refining of Petroleum. 2nd Edition. 550 p. (1942). Reinhold Publishing Corp.

Klemgard, E. N. Lubricating Greases: Their Manufacture and Use. 2nd Edition. 872 p. (1937). Reinhold Publishing Corp.

Nelson, W. L. Petroleum Refinery Engineering. 2nd Edition. 715 p. (1941).

Sachanen, A. N. Conversion of Petroleum. 413 p. (1940). Reinhold Publishing Corp.

Uren, L. C. Petroleum Production Engineering.
Vol. I. Oil Field Development. 2nd Edition. 531 p. (1934).
Vol. II. Oil Field Exploitation. 756 p. (1939).

Index

INDEX

INDEX

INDEX

INDEX

INDEX

INDEX

INDEX