DEVELOPMENT OF HIGH DENSITY - HIGH STRENGTH - ISOTROPIC GRAPHITE FROM MESOCARBON MICROBEADS

THESIS

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By

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TO MY PARENTS

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CERTIFICATE

This is to certify that the thesis entitled "DEVELOPMENT OF HIGH DENSITY - HIGH STRENGTH - ISOTROPIC GRAPHITE FROM MESOCARBON MICROBEADS" and submitted by Ms. NAMRATA PUNJABI, ID No. 90 PZYF 004, for award of Ph.D Degree of the Institute, embodies original work done by her under my supervision.

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PREFACE

This thesis describes the work carried out by the author on the development of high density - high strength - isotropic graphite from mesocarbon microbeads. The products made from this specialty graphite find extensive applications in mechanical, metallurgical, nuclear, aerospace, semiconductor and other industries. Although, there are basically three methods to produce this graphite, the method involving use of mesocarbon microbeads has been adopted in the present investigations because of its excellent performance in the practical tests. The proposed research work was aimed to study the scientific and technological aspects of the production of this graphite.

Heat-treatment of coal tar pitches results in the formation of liquid crystalline phase known as mesophase. The mesophase spherules can be separated out of the heat-treated pitch using a suitable solvent and are called `mesocarbon microbeads (MCMB)'. These MCMB are excellent precursors for the production of binderless high density - isotropic graphite. In the recent years, considerable interest has been taken in this type of graphite, but not much has been published regarding its developmental aspects.

With this objective in mind, various studies relating to development of this fascinating graphite material were conducted, the results of which have been compiled in the present thesis in the following sequence.

CHAPTER - I

This chapter gives a brief introduction to the Carbon Science and Technology. This includes general background of the subject and an up-to-date comprehensive review. This chapter clearly brings out the scope and objectives of the present investigations.

CHAPTER - II

This chapter deals with the experimentation, i.e. design and fabrication of the experimental set-ups, and procedures used in the preparation of isotropic graphite. The methodologies used for the preparation and characterisation of coal tar pitches, mesophase powders and mesocarbon microbeads have also been described in the present chapter. The method used for moulding the mesocarbon microbeads to get a product (plate) and the procedures involved in carbonisation and graphitisation of the MCMB-based plates are also discussed. The procedures employed for the determination of various characteristics of carbon plates are also described in this chapter.

CHAPTER - III

This chapter is entirely focussed on the study of mesophase formation in coal tar pitches and the development of monolithic carbons from the self-sintering mesocarbon microbeads. The suitability of a solvent for extraction of mesophase pitches and the effect of QI content in the precursor coal tar pitch on the characteristucs of the resulting MCMB-based graphite have been

studied in detail. These studies are of paramount importance in finding the process conditions for a particular precursor pitch which may result in high yield of mesocarbon microbeads, thereby helping in the cost-effectiveness of the process.

CHAPTER - IV

This chapter deals with the sintering behavior of mesocarbon microbeads-based products. An extensive study of the changes in the various properties of the product with the heat-treatment temperature (ranging between 350°C and 2700°C) has been carried out and discussed in detail in this chapter.

CHAPTER - V

This chapter has been devoted to the studies on the optimisation of the critical process steps such as extraction of mesophase pitch and calcination of MCMB. Though, the properties of the specialty graphite depend greatly on the conditions of extraction and calcination, no information is available in the published literature regarding these aspects. Therefore, the effect of type of tar oil (in respect of its boiling range) used in the extraction of mesophase pitch on the characteristics of the resulting carbons has also been studied. Further, the conditions for calcination of MCMB have been optimised by studying the effect of temperature, time and atmosphere (inert/vacuum) of calcination on the characteristic of the resulting high density - high strength - isotropic graphite. Finally, high density - high strength

isotropic graphite of high quality was produced using the processing conditions optimised under the present investigations.

CONCLUSIONS

The important conclusions drawn from the present invesigations are reported in this chapter.

CONTENTS

CHAPTER - I

BRIEF INTRODUCTION OF CARBON SCIENCE AND TECHNOLOGY

1.1 INTRODUCTION

Carbon and graphite products, in one form or the other, form indispensable components of almost all major industries, and thus they act as the backbone of the industrialisation of a country. Graphite electrodes for the steel industry, carbon anodes and cathodes for the aluminium industry, carbon lining for the electrolytic cell in the production of caustic soda, calcium carbide etc., carbon brushes for the electric motors and generators, carbon granules for the telephone receiver set, carbon crucibles for the melting of metals and alloys, carbon seals and bearings for mechanical applications, nose-cones and nozzle inserts for missiles and rockets, leading edges and brake pads for military and advanced civilian aircrafts, and graphite for nuclear reactors are some of the examples showing vast applications of carbon and graphite. Recently, there has been an increased interest in this material, than ever before, and as a result, several newer carbon products such as pyrolytic graphite, glassy carbon, carbon fibers and carbon fibers based composites and high density-isotropic graphite have come into existence. These products are further widening the scope of the applications of this wonderful material, carbon.

1.2 THE ELEMENT `CARBON'

The element carbon has an atomic weight of 12.011 and an atomic number of 6. The electronic ground state $2s^2\ 2p^2$ is almost unknown because of the energetic advantage of involving all the four outer orbital electrons in bonding between carbon atoms

themselves, or with other atoms. Carbon displays catenation (bonding to itself) to a unique degree which results in structure of chains, rings, and networks. In most chemical compounds, carbon is tetravalent because of the transition of one electron from the 2s orbital to the 2p orbital, resulting in the excited state configuration $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$. These s and p orbitals in the outer shell undergo hybridization to give hybrid orbitals. In diamond, one s and three p orbitals hybridize to give four sp^3 hybridized orbitals, resulting in a tetrahedral structure with a bond angle of 109.28°. In graphite, one s and two p orbitals hybridize to give three sp^2 hybridized orbitals, resulting in a planar triangular structure with a bond angle of 120°.

1.2.1 STRUCTURE OF DIAMOND

The diamond crystal has a face-centered-cubic structure with an interatomic distance of 154 pm. Each atom is covalently bonded to four other carbon atoms in the form of a regular tetrahedron (1). The three dimensional isotropic structure accounts for the extreme hardness of diamond. Diamond is stable and chemically inert at moderate temperatures. However, at temperatures above 1500°C in the absence of air, it is transformed into graphite (2). Diamond can be synthesized from graphite at a pressure of about 85 KBars and a temperature of about 1600°C (3).

1.2.2 STRUCTURE OF IDEAL GRAPHITE

The structure of ideal graphite was first proposed by Hull (4) in 1917 and later confirmed by Bernal (5) in 1924. It consists of

parallel plane layers of carbon atoms covalently bonded in a regular open-centered hexagonal array. The layers are bonded together by weak Van der Waal's forces at a separation of 335.4 pm in a (AB AB AB .. ..) stacking sequence, as shown in Fig.1.1, in such a way that atoms in alternate planes align with each other. Within each layer, C-C distance is 141.5 pm. The three sp^2 hybridized orbitals of each carbon atom form bonds with adjacent carbon atoms and the fourth electron in the p orbital gives conjugated bonding. This results in delocalization of the π electrons throughout the layer structure.

A less frequently occurring structure is rhomboid with ABC ABC --- stacking arrangement in which the atoms of every fourth layer align with each other (6,7). This rhombohedral form, which occurs only in conjunction with hexagonal form, is less stable, and converts to the hexagonal form irreversibly at 2100°C (8). The bond energy between planes is 17 KJ $mole^{-1}$ and within planes is 477 KJ $mole^{-1}$. Graphite sublimes at a temperature of 3640 ± 25°K at atmospheric pressure. However, it may be made to melt under a pressure of 125 ± 15 atmosphere at a temperature of 4020 ± 50°K (9,13). This temperature of about 4000°K has been moved to about 5000°K in recent years (14) by way of more accurate measurements.

1.2.3 STRUCTURE OF FULLERENES

Fullerenes represent the third allotropic form of the element Carbon, referring to a new class of discrete molecules. C_{60} molecule was first reported by Kroto et al. in 1985 in the mass

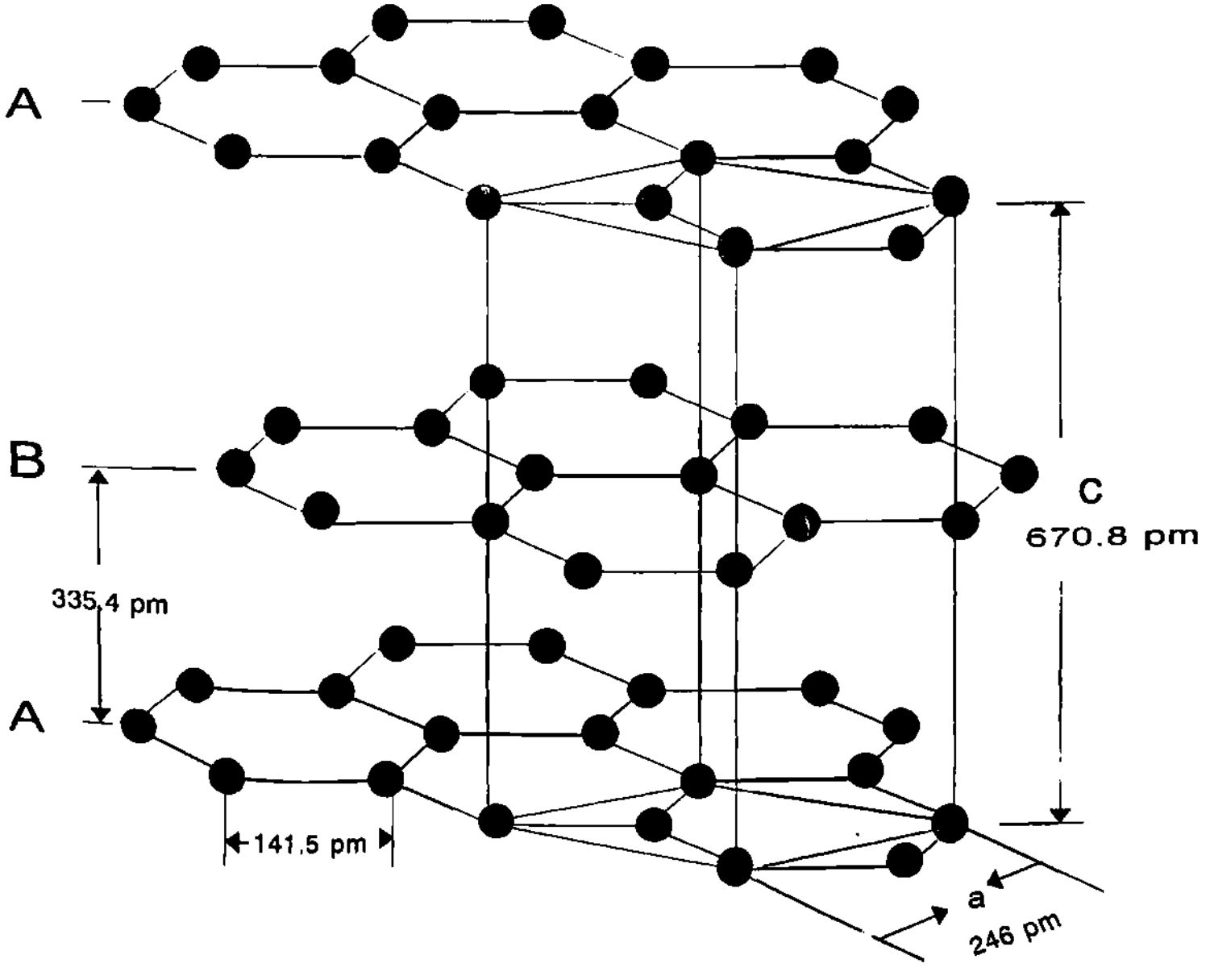


Fig 1.1 Structure of the ideal graphite crystal.

spectrum of laser-ablated graphite (15). Five years later, in 1990, W. Kratschmer et al. reported evidences for the presence of C_{60} in a sample of carbon dust prepared from vaporised graphite (16) and they were able to isolate macroscopic quantities of C_{60} and C_{70} (17). Fullerenes can be considered as networks of pentagons and hexagons. Such molecules invariably have twelve pentagons in order to close into a spheroid although the number of hexagons varies widely. Examples of fullerenes are C_{60} and C_{70} molecules. The C_{60} molecule contains 20 hexagons. It is the roundest of all fullerene molecules. Its stability can be explained by the molecular structure having perfect symmetry of a soccerball.

1.2.4 ELECTRICAL AND THERMAL PROPERTIES OF GRAPHITE SINGLE CRYSTAL

Since there is pronounced difference in bonding within the layers of carbon atoms and that between the layers, the thermal and electrical properties of graphite are highly anisotropic (18,19). Along the layer planes, at the room temperature, resistivity is about 4×10^{-5} Ohm cm (20), whereas across the layer planes, resistivity values vary from around 1 Ohm cm (21) to 4×10^{-3} Ohm cm (20). Thus, the anisotropic ratio of electrical resistivity is at least 100.

The room temperature values of thermal conductivity of the graphite crystal have been measured to be around 400 and 80 W/m°K, respectively, in the direction parallel and perpendicular to the layer planes (19). The anisotropic ratio of thermal conductivity is, therefore, 5.

1.3 MANUFACTURE OF CONVENTIONAL CARBONS

As the graphite-liquid-gas triple point of the element carbon is close to 4020°K at a pressure of 125 atmosphere, the process of melting and casting normally used with metals is inapplicable to carbon. Consequently, the bulk of carbon and graphite products are manufactured by a process analogous to the powder metallurgy. The conventional carbon products are therefore, generally manufactured by kneading a carbonaceous filler material such as petroleum coke, pitch coke, metallurgical coke, anthracite coal, carbon black or natural graphite with a carbonaceous binder material, for example, coal tar pitch. The mixture after being moulded or extruded into a product of desired shape and size is carbonized in an inert or non-oxidising atmosphere to a temperature of 1000°C or higher. Products in this form are widely used. However, for many applications, such a carbon product is further heat-treated to a temperature of about 2700°C (Fig 1.2) to convert it into a so called `graphite' product. The various technological aspects in the manufacture of carbon and graphite products have been described in details by Mantell, Liggett and others (22-25).

1.3.1 TERMINOLOGY IN CARBON AND GRAPHITE INDUSTRY

As is the case in many other industries, the `carbon and graphite' industry also has a language of its own. The terms `carbon', `amorphous carbon', `baked carbon' or `manufactured carbon' are used by the industry to mean products made from the mixtures of suitable carbonaceous filler and binder materials, which have

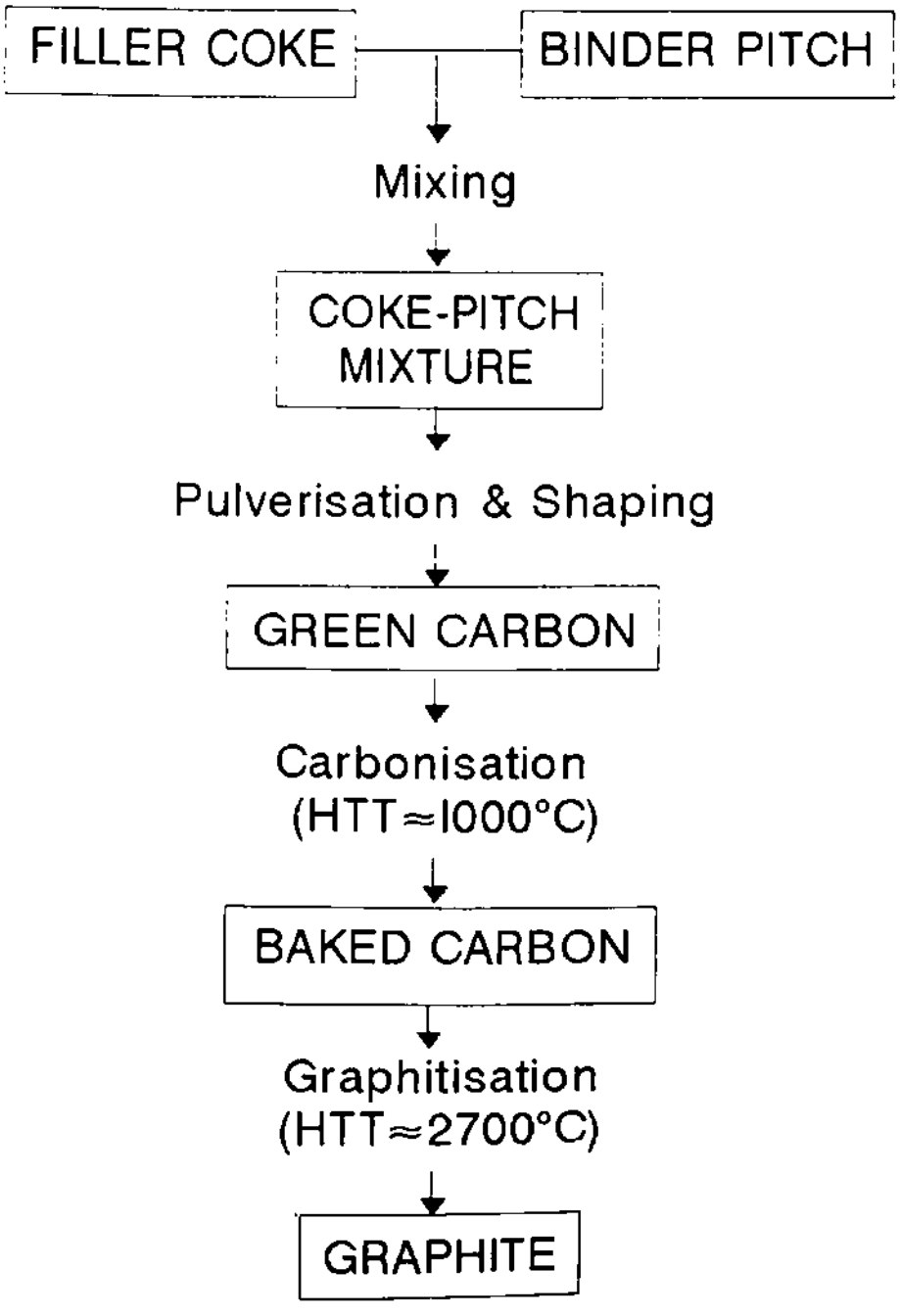


Fig.1.2 Block diagram for the manufacture of conventional graphite products

been baked to a temperature of 900-1800°C. The term `green carbon' refers to the formed carbonaceous product prior to the baking operation. The terms `graphite', `electrographite', `synthetic graphite' or `industrial graphite' refer to a product obtained from the heat-treatment of the baked carbon to a temperature of 2400°C or higher.

However, the International Committee on Characterization and Nomenclature of Carbon has reviewed the scope of the terms `carbon' and `graphite' (26). According to this committee, the term `carbon' refers to the materials possessing an atomic C H ratio of at least 10 and the term `graphite' refers to such carbons which have acquired the near-ideal structure of graphite. The term `carbon' thus comprises all types of cokes and electrographite, all types of polycrystalline carbons and graphites, all types of activated carbons, all types of carbon blacks and all natural graphites etc. among the common varieties. Special varieties of carbon have increased in number in recent years and include pyrolytic graphite, graphite foils and felts, all types of carbon fibers, glass-like carbon as well as high density - isotropic graphite.

1.3.2 PHYSICAL STRUCTURE OF CARBON PRODUCTS

Carbons are composed of a large number of group of graphite-like layers (crystallites) together with a certain proportion of non-organized carbon (27). The graphite-like layers in a group, though held parallel, lack the stacking order because of their finite size. The average crystallite size in carbons varies

widely, all the way from a low value of 1 nm for some carbon blacks and activated carbons to a value as high as 1 cm for some special synthetic graphites.

1.3.3 ELECTRICAL AND THERMAL PROPERTIES OF CARBON PRODUCTS

Typical room-temperature values of electrical resistivity and thermal conductivity parallel to the extrusion direction in baked carbon products (with total porosity of about 25 %) are 5×10^{-3} Ohm cm and 4 W/m°K, respectively. Upon graphitisation at about 2600°C, a carbon product of similar porosity has typical electrical resistivity of 7×10^{-4} Ohm cm and 9×10^{-4} Ohm cm in directions parallel and perpendicular respectively, to the direction of extrusion. The anisotropy of electrical resistivity is thus only 1.3 compared to at least 100 in single graphite crystal. The comparable graphitised carbon products have typical thermal conductivity of 230 and 140 W/m°K in parallel and perpendicular directions, respectively. The anisotropy of thermal conductivity is 1.6 compared to 5 for a single crystal. The decrease in anisotropy in properties of carbon products compared to graphite single crystals has been attributed primarily to the resistance to electron and heat flow by the binder carbon bridges between the filler particles (28).

The properties of carbon materials can be altered or tailor-made by changing various production conditions such as raw materials, size of blended particles, method of forming and conditions of baking and graphitisation so as to make them acceptable to broad range of use in analytical, mechanical, electronics, aerospace, nuclear and other industries.

1.4 HIGH DENSITY - HIGH STRENGTH - ISOTROPIC GRAPHITE (HD-HS-IG)

High density - high strength - isotropic graphite is a term, basically given to a type of high purity graphite, which possesses a bulk density of more than 1.8 g cm^{-3}, bending strength of more than 600 kg cm^{-2}, anisotropic ratio of 0.9-1.1, besides a homogeneous and fine structure.

1.5 IMPORTANT PRECURSORS USED IN THE PRODUCTION OF HD - HS - IG

Some of the important raw materials used in the production of high density - high strength - isotropic graphite are discussed below :

1.5.1 PITCHES

Pitches are carbonaceous materials derived from organic precursors such as coal tar, petroleum tar, synthetic compounds like PVC, acenaphthalene etc., by relatively low temperature processes, e.g. distillation at temperatures below 700°K. Most pitches melt on heating to give an isotropic fluid. As heating is continued above 660°K, alignment of lamellar molecules occurs leading to the formation of nematic discotic liquid crystalline phase called `mesophase'. Two principal types of pitches used for the fabrication of carbon materials are coal tar pitch and petroleum pitch.

1.5.1.1 COAL TAR PITCH

Coal tar pitch is obtained as the residue in the distillation of coal tar, a by-product in the coking of bituminous coals to produce metallurgical coke. Coal tar pitches are complex mixtures of aromatic and heterocyclic compounds. Many compounds are substituted, the methyl group being the most prevalent. The compounds that have been isolated contain from 3 to 6 aromatic rings and boil in the range of 340-550°C. Coal tar pitch thus consists predominantly of the elements carbon and hydrogen with small amounts of nitrogen, oxygen and sulphur (29,30).

1.5.1.2 PETROLEUM PITCH

Petroleum pitch is the residue from heat-treatment and distillation of petroleum fractions. It is often obtained from catalytic crackers' bottoms, i.e., the heavy residue from a catalytic cracking process, from steam cracker tar, a by-product of steam cracking of naphtha or gas oils to produce ethylene, or from any residue obtained from crude oil distillation or refining. Pitch can be produced from these feedstocks by many different processes including thermal treatment, vacuum or steam stripping, oxidation, simple distillation or a combination of these (31). These pitches consist of a complex mixture of numerous predominantly aromatic and alkyl substituted aromatic hydrocarbons. In general, petroleum pitches are less aromatic than coal tar pitches. However, the chemical and physical characteristics are dependent on the process and the conditions used, especially the process temperature and heat-treatment time.

1.5.1.3 MESOPHASE FORMATION IN PITCHES

The development of mesophase spherules during carbonization of coal tar and petroleum pitches as well as in various model organic compounds was first reported by Brooks and Taylor (32,33). Since then numerous contributions have appeared on this subject, which have been very well reviewed by several authors (34-38). As already mentioned, pitches are complex mixtures of a large number of predominantly aromatic hydrocarbons, their alkyl and hydroxyl derivatives and the corresponding hetrocylic compounds. Since the average molecular weight of the compounds in the pitches is generally 400-600, there is no interaction between the molecules, and as a result, these pitches are isotropic in nature (39). However, when such pitches are heated in an inert atmosphere at 350-450°C, dehydrogenative condensation of the molecules takes place resulting in the formation of large planar condensed molecules and consequently small liquid crystalline spheres start forming in the pitch as a result of high surface tension. Within a mesophase spherule, the constituent lamellar molecules lie parallel to the equatorial plane, as indicated by electron diffraction (33). Optical microscopy indicates that the layers become orientated towards the poles of the spherules and that they approach the surface of the spherules at right angles, as shown in Fig.1.3.

If heating is continued, these spherules grow in size and after about 50% volume concentration (40) they start coalescing to form bigger spherules or masses. These spherules or masses, in turn, come closer and coalesce to form domains or mosaic of

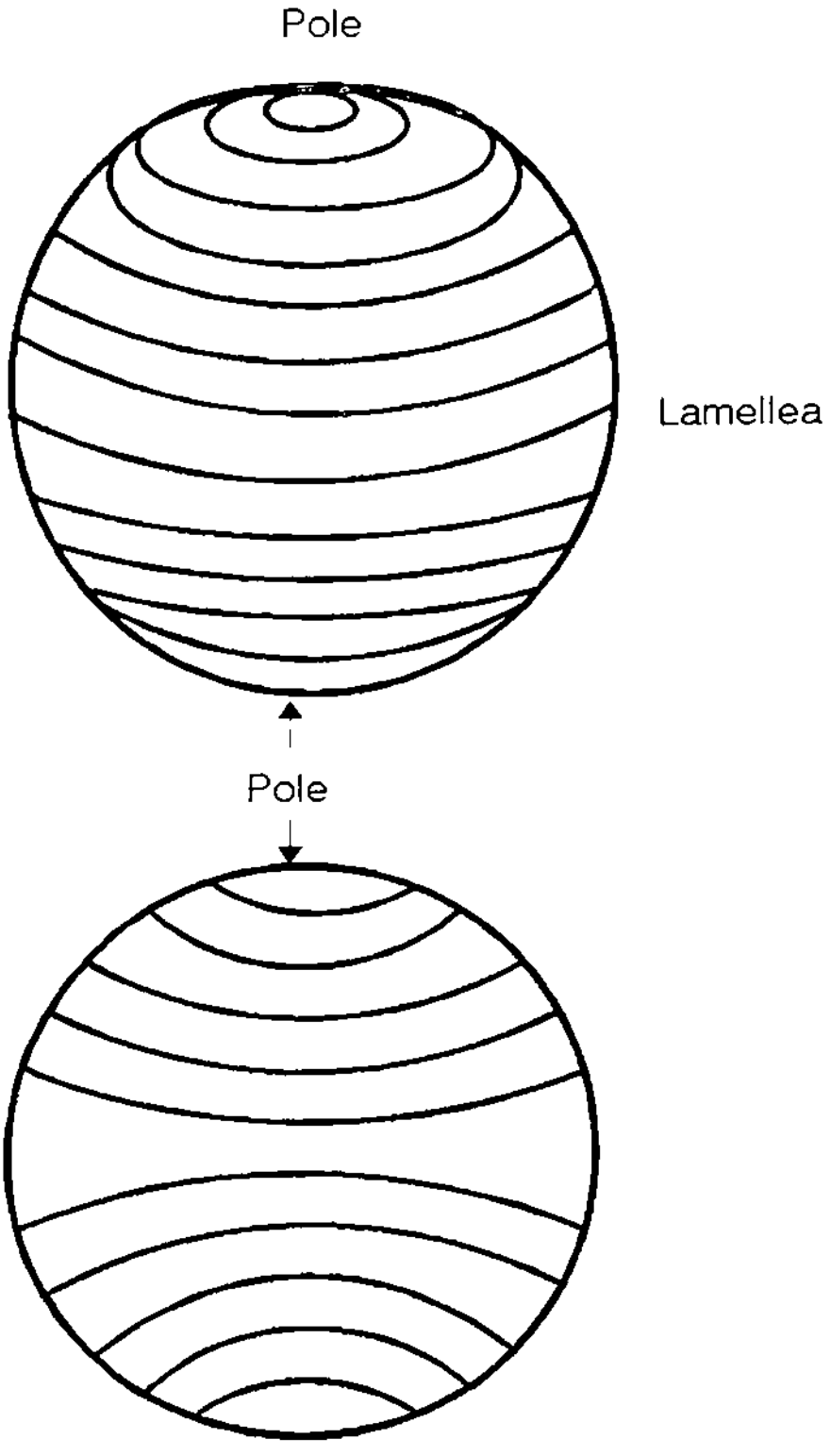


FIG 1.3 Structure of a mesophase sphere.

graphite-like parallel layers of planar condensed molecules which constitute the mesophase.

Bhatia et al. reported on the formation of these mesophase spherules in different fractions of a coal tar pitch and their mixtures (41). The condition for a good mesophase formation depends to a large extent on the viscosity of the system. It has been observed from the viscosity behavior of a coal tar pitch, its fractions such as toluene solubles and insolubles and their defined mixtures as well as a petroleum pitch, toluene insoluble fraction of coal tar pitch does not reach the necessary minimum viscosity during heat treatment as reached by other systems such as pitch itself, toluene soluble fraction.

It has been known for some time that the solid contents of the precursor pitch should be low if the coke produced is to be highly graphitisable (42). This is because the solid impurities such as quinoline insolubles reside over the surface of mesophase spherules and thus hinder their coalescence and subsequent growth. Thus, the size of the mesophase spherules is much lower in a pitch containing quinoline insoluble particles than in its quinoline soluble fraction. In other words, structure of the final coke is predetermined already in the state of growth and coalescence of mesophase.

1.5.2. COKES

Coke is a highly carbonaceous product of pyrolysis of organic materials, at least parts of which have passed through a liquid or liquid - crystalline state during the carbonization process.

Most coke materials are graphitisable carbons. Their microstructure is a mixture of optical texture of various sizes, from the optically isotropic to domain and flow anisotropy. Only short range order associated with non - graphitic carbons, usually exists at the crystallographic level. Various types of cokes are green coke, calcined coke, petroleum coke, metallurgical coke, delayed coke, needle coke and coal-derived pitch coke.

1.5.3 CARBON BLACKS

Carbon blacks are industrially manufactured colloidal carbon materials in the form of spheres and their fused aggregates with sizes between 10 to 1000 μm. The structural order found in carbon blacks varies with the method of preparation, but, in general, there is alignment of the carbon layers parallel to the surface of the sphere (43).

1.6 CHRONOLOGICAL DEVELOPMENTS IN THE PRODUCTION OF HD - HS - IG

High density - high strength - isotropic graphite is, in fact, a recent addition to the family of existing carbon products. The main development work on this graphite seems to have been initiated by the Japanese workers (44-49), the overview of which has been presented by Oya in 1989 (50). Honda and Yamada (44) were the first to separate the mesophase spherules formed in a coal tar pitch by thermal treatment and called them `mesocarbon microbeads (MCMB)', which were then used by them (45) in the production of binderless high density - high strength - isotropic

graphite. Since then, considerable interest has been shown in this type of carbon because of its potential applications as electrodes for electric discharge machines and as material for electrical brushes and contacts, trolley wheels, hot pressing dies, casting moulds, mechanical seals, crucibles and nuclear reactors etc.

T. Hoshikawa et al. (46,47), in 1982, reported the production of large sized isotropic graphite of density 1.78 g cm^{-3} by employing cold isostatic pressing and slow and uniform baking rate. Nakagawa et al. (48), in 1985, reported the development of an industrial process for the production of mesocarbon microbeads by thermal treatment of coal tar pitches, capable of resulting in high density isotropic graphite (1.67 g cm^{-3} at 1000°C), using only the conventional pressing. Then in 1988, Fukuda et al. (49) produced graphite blocks of high density (upto 1.9 g cm^{-3}), excellent bending strength (upto 1000 kg cm^{-2}), and anisotropic ratio of 1.01, using mesophase carbon spherules developed in a coal tar pitch by thermal treatment. It has been further reported that the MCMB-based high density graphite has shown excellent performance in the practical tests (50).

Bhatia et al. (51), in 1989 reported some preliminary developmental work wherein they obtained a density of 1.65 g cm^{-3} and bending strength of 668 kg cm^{-2} of the carbonised plates. Later, in 1989, Fujimoto K. et al. (52) reported the development of high density (≈1.95 g cm^{-3}), high hardness (Shore hardness = 80-100) but machinable graphites, using a mixture of coal tar pitch with needle coke or carbon black, partially carbonized to temperatures upto 475°C. Rand (53), in 1990, reported bending

strength of 120 MPa and bulk density of 1.9 g cm^{-3} in sintered carbon produced from commercially available mesophase microbeads and ground bulk mesophase powders (without mentioning the supplier). Takekawa et al. (54), in 1990, produced high density (1.9 g cm^{-3}) isotropic carbon (HDIC) from randomly oriented mesophase powder (ROMS), produced by heat-treatment of pitch followed by melt pulverisation and oxidation. Using the same ROMS Kato et al. (55), in 1991, reported density of 2.0 g cm^{-3} and strength of 1300 kg cm^{-2} with Shore hardness of 80 in HDIC (anisotropic ratio = 1.01) moulded by cold isostatic press.

Nagayama et al. (56), in 1991, reported the development of graphitised KMFC compacts having density of 1.9 g cm^{-3} and strength of 1000 kg cm^{-2}. In the same year, Rand and Stirling (57) produced sintered carbons from mesophase powders with bulk density of 1.87 g cm^{-3} and flexural strength of 118 MPa at HTT of 2200°C. In 1994, Huttinger and coworkers (58,59) reported high density of 1.95 g cm^{-3} and flexural strength of 160 MPa in isotropic carbon produced from commercially available mesophase powders produced by thermal process from coal tar or coal tar pitches (the details about the raw materials from which the mesophase powders were produced and about the production conditions were not available). Further, they also reported high density of 1.88 g cm^{-3} and high strength of 150 MPa in isotropic carbons based on mesophase powder obtained by extraction of a catalytically produced mesophase pitch with tetrahydrofuran. Mochida et al. (60) in 1994, produced carbon discs of bulk density 1.88 cm^{-3} and compressive strength of 29 tf/cm^{-2} (HTT=1573°K) from self-adhesive carbon grains oxidatively prepared from

naphthalene derived mesophase pitch.

Recently, in 1995, Braun and Huttinger (61) produced sintered carbon from catalytically produced mesophase and obtained a high strength of 180 MPa in graphitised carbons. Again in 1995, Rand and Ting (62) used commercially available mesocarbon microbeads (called `KMFC' powder) to produce fine - grained carbons possessing a bulk density of 1.92 g cm^{-3} at the HTT of 2000°C. Further, Fujiura et al. (63), also in 1995, produced binderless isotropic graphite from catalytically produced mesophase pitch derived from pure naphthalene. This graphite made using very fine grains with an average size of 2.4 μm showed bending strength of 100 MPa and bulk density of 2.04 g cm^{-3}.

It is thus apparent from the above that a lot of interest is being taken in the development of this specialty graphite.

1.7 DEVELOPMENTAL ASPECTS OF HD - HS - IG

In the conventional manufacturing of graphite, as explained in section 1.3, the shaping is mainly done by extrusion or by moulding (using a conventional press), in which the alignment of particles takes place resulting in significant anisotropy in the product. However, in certain applications, like in aerospace or nuclear field, isotropy of the material is very critical. Therefore, in order to produce high density - high strength - isotropic graphite, one has to proceed in a manner which imparts isotropy, homogeneity, fine texture, high density, high strength and high purity in the product. The principal techniques involved in the development work of this graphite (discussed in Section 1.5) to achieve these properties are briefly explained below.

1.7.1 ISOTROPY, HOMOGENEITY AND FINE TEXTURE

There are two ways to have isotropy in the product. One way is to use the finely-ground filler coke as well as coke-binder mixture. The needle coke used in the conventional graphite manufacture employing extrusion or simple moulding tends to impart anisotropy in the product. However, fine grinding of the needle coke and that of the coke-binder mixture, followed by the isostatic pressing, is able to result in the isotropy, homogeneity and fine structure of the product.

The recent way is to use the spherical particles such as mesocarbon microbeads (mesophase spherules). These mesophase spherules, as explained in section 1.3, though possessing an anisotropic structure, lead to an isotropic product because of their random placement due to sphericity during their compaction to form the product (Fig.1.4). A product made from mesocarbon microbeads (average size $<\approx 10\mu m$) is automatically found to have homogeneity and fine texture.

1.7.2 HIGH DENSITY AND HIGH STRENGTH

High density in a graphite can be achieved by using a high density filler coke or by using a semi-coke filler exhibiting large shrinkage with a small weight loss during the baking process. It is possible to produce such semi-cokes by heating to a suitable temperature a coal tar pitch, as such, or a filler material like needle coke or carbon black soaked in an excess amount of a binder pitch. It may also be mentioned here, that in the conventional method involving use of coke-binder mixture, it may be neces-

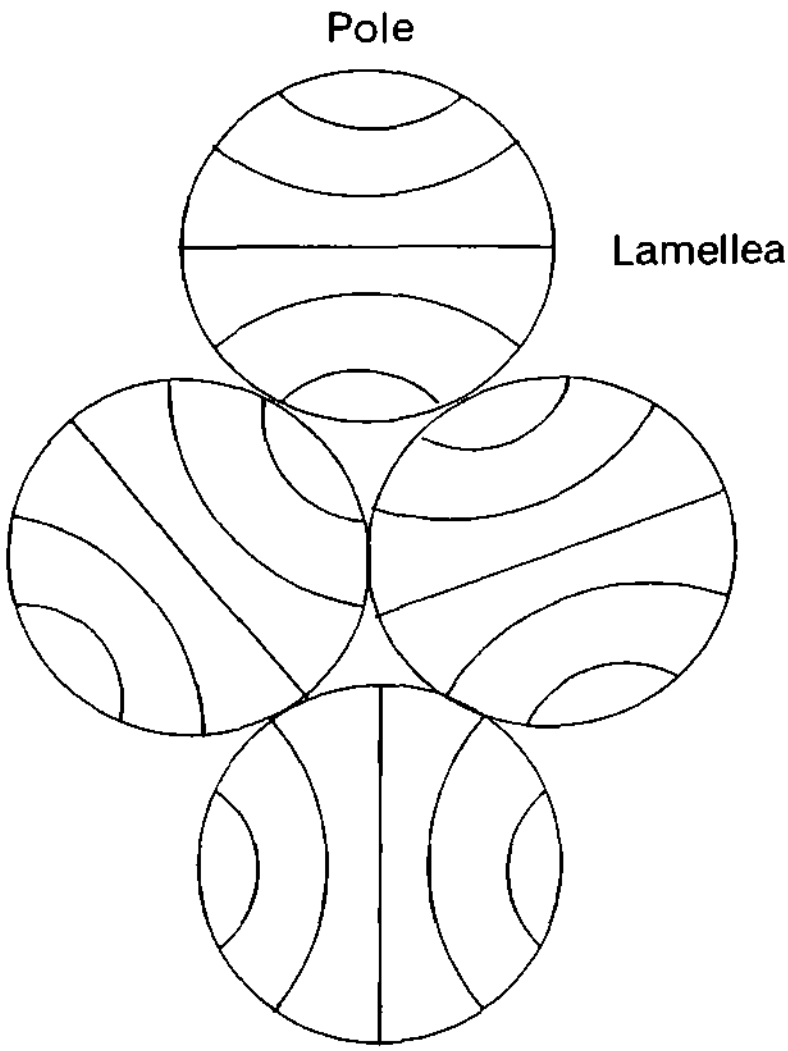


Fig.1.4 Arrangement of mesocarbon microbeads during moulding.

sary to use pitch impregnation or chemical vapour deposition to improve the density of the product. A high density product obtained in this manner is automatically found to be associated with a high strength.

1.7.3 HIGH PURITY

High purity is a critical parameter for certain applications of the isotropic graphite. To achieve this, it is necessary to use high purity raw materials. However, the material like coke and pitch invariably contain some unavoidable amounts of impurities. Therefore, heat-treatment of the product to about 3000°C lowers the impurity level to a few hundred ppm, which can be further lowered to below 10 ppm by further heating the product in an atmosphere of a halogen gas.

1.8 MANUFACTURING TECHNIQUES OF HD - HS - IG

It has been observed during developments in the production of high density isotropic graphite (discussed in Section 1.5) that there are essentially three methods of manufacturing the high density - high strength - isotropic graphite as briefly described below :

1.8.1 HD - HS - IG FROM FILLER COKE AND BINDER PITCH MIXTURE (METHOD `A' - CONVENTIONAL METHOD)

This method of producing the high density - high strength - isotropic graphite is quite similar to the commercial method of pro-

ducing the conventional graphite as can be seen from Fig.1.5. In this method, the coke filler such as petroleum coke or needle coke is kneaded with the pitch binder, such as coal tar pitch, to obtain a mixture, which is isostatically pressed and then carbonised to around 1000°C, followed by repeated cycles of impregnation and recarbonisation. The product is finally graphitised to around 2700°C to obtain the high-density isotropic graphite.

1.8.2 HD - HS - IG FROM GREEN COKE (METHOD `B')

Fig.1.6 shows the block diagram for the production of high density - high strength - isotropic graphite from green coke. As seen in this figure, the precursor pitch is heat-treated to convert it into a semicoke - like material, called the `green coke', which possesses self-sinterability. This green coke is pulverized into a fine powder, moulded by isostatic pressing and then heat-treated, baked and graphitised to result in the high density - high strength - isotropic graphite.

1.8.3 HD - HS - IG FROM MESOCARBON MICROBEADS (METHOD `C')

Fig 1.7 shows the block diagram for the production of high density - high strength - isotropic graphite from mesocarbon microbeads (carbon spherules). In this method, a suitable coal tar pitch is heated at 400-500°C in an inert atmosphere to form mesophase spherules which are then separated out of the heat-treated pitch by solvent extraction using a suitable solvent. These carbon spherules obtained as solvent insolubles (mesocarbon microbeads) are calcined at a suitable temperature and then

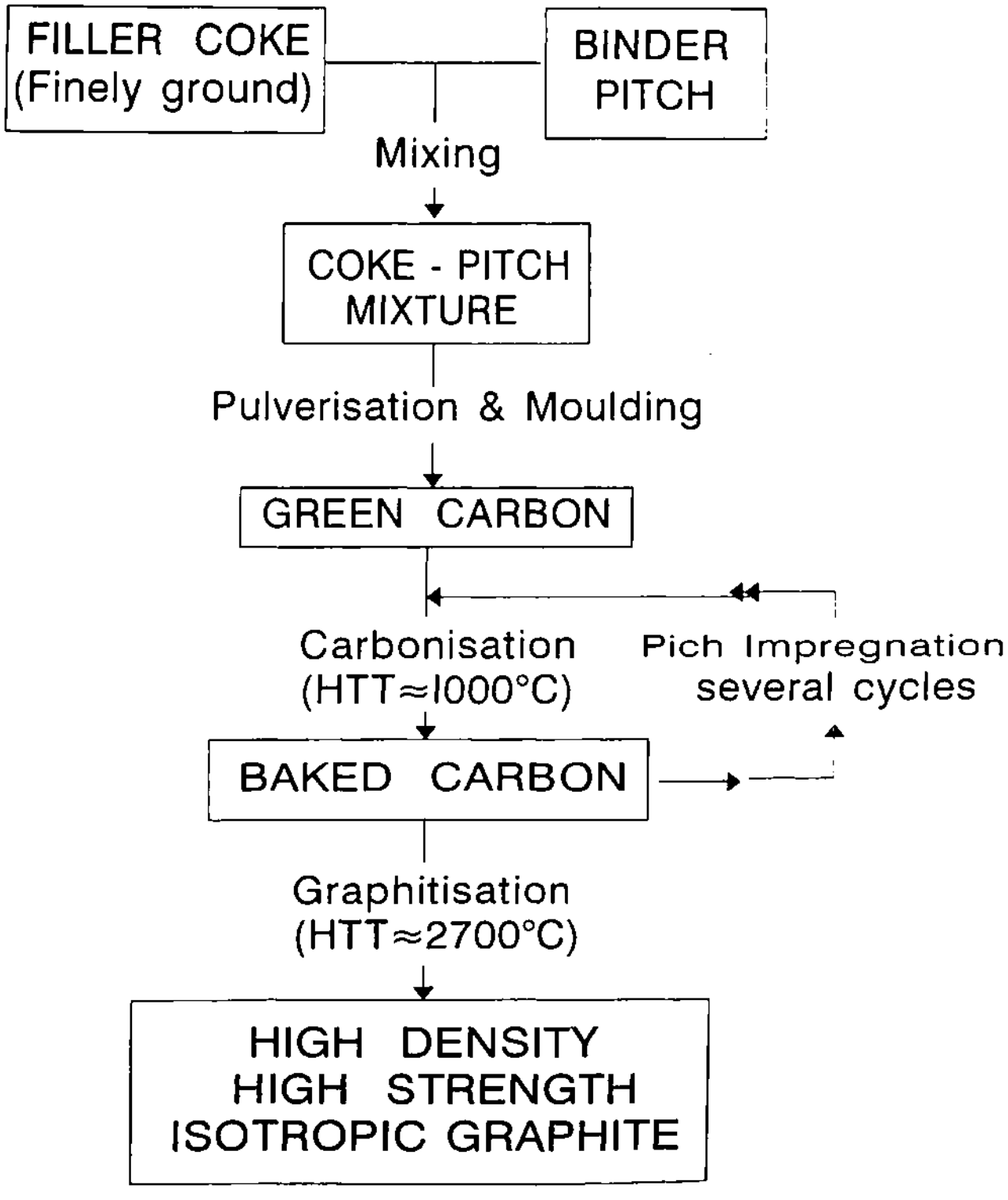


Fig.1.5 Block diagram for the production of high density-high strength-isotropic graphite from filler coke and binder pitch mixture (Method A)

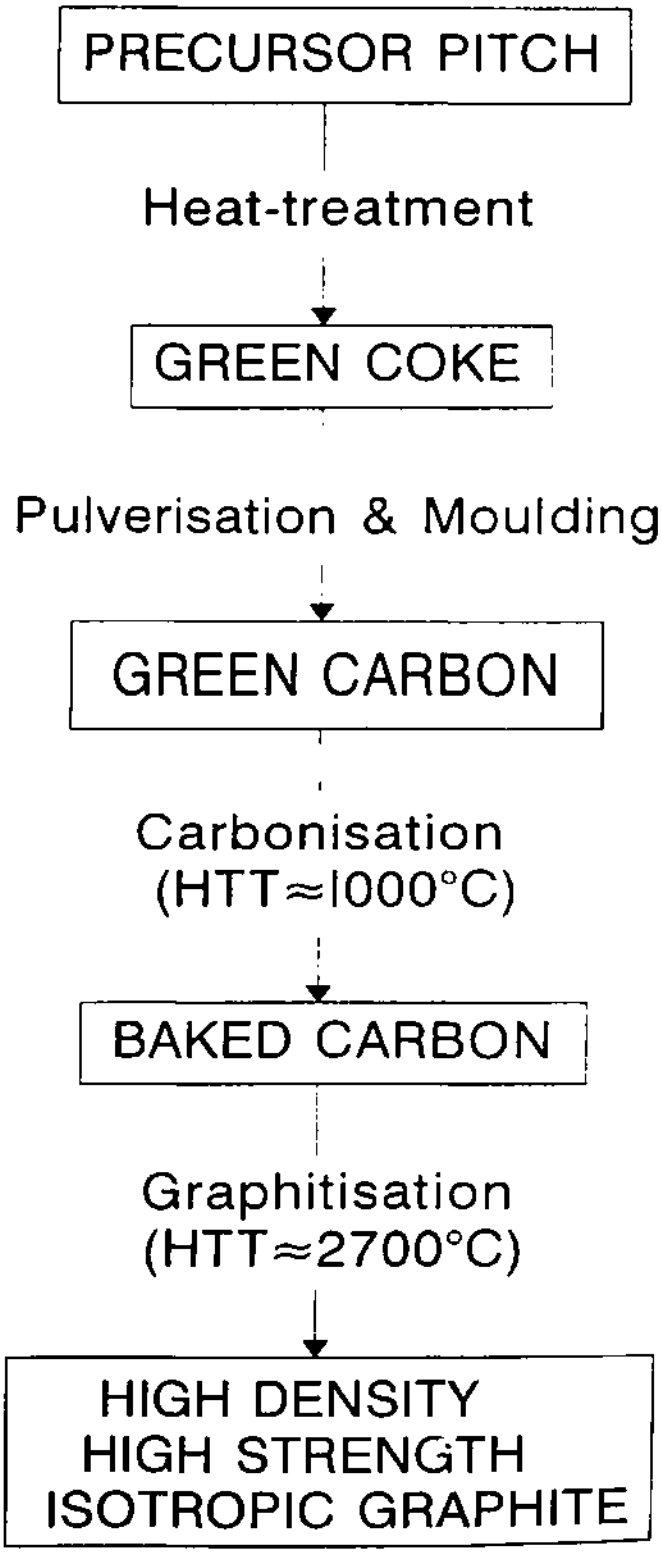


Fig.1.6 Block diagram for the production of high density-high strength-isotropic graphite by green coke method (Method `B')

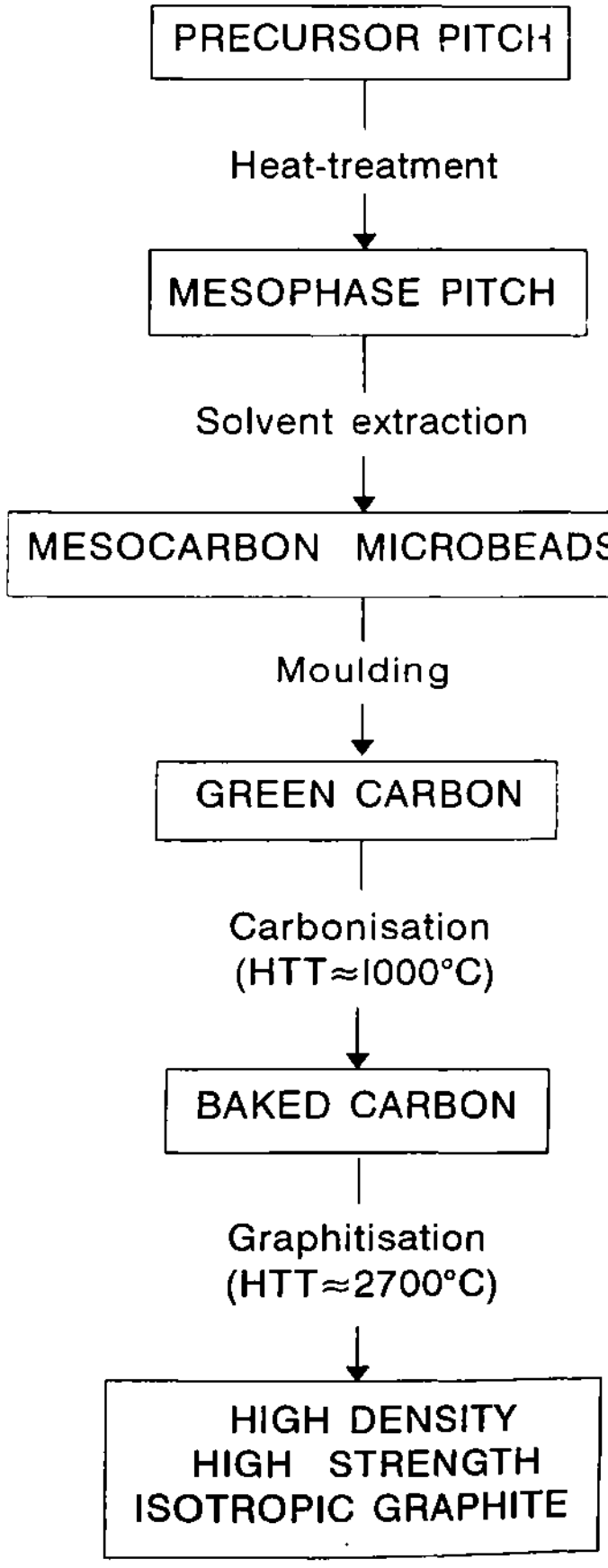


Fig.1.7 Block diagram for the production of high density-high strength-isotropic graphite from mesocarbon microbeads (method `C')

moulded into a product, which is carbonised and finally graphitised to obtain the high density - high strength - isotropic graphite.

The typical range of properties of the high density - high strength - isotropic graphite produced by these three methods are given in Table 1.1. It is seen from this table that isotropic graphite with wide range of properties are obtained from the three different methods mentioned above.

Among the three methods, it may be mentioned that the product obtained by method `A' does not possess high density with fine isotropic texture which are critical for a number of applications which will be mentioned in the next sub-section. This is because large amounts of volatiles such as methane, hydrogen, carbon dioxide and carbon monooxide etc. are evolved from the binder during baking which make the product porous. As a result, this product has low density and inferior mechanical properties. These inferior characteristics of the product can only be improved by repeated cycles of impregnation of the product with an impregnating-grade coal tar pitch and recarbonisation. This method is thus cumbersome, time-consuming and expensive. Moreover, in this method, the density of the product cannot be improved beyond a maximum value of 1.8 g cm^{-3} because of the limitations of the impregnation process.

In the method `B', the preparation of the green coke having an optimum amount (around 10%) of the binding components (volatile matter) is a critical step, since a slight excess of the binding components in the green coke will result in the swelling of the product during baking, and a slight deficiency of

TABLE 1.1

A COMPARISON OF THE PROPERTIES OF HIGH DENSITY - ISOTROPIC GRAPHITES PRODUCED BY THE THREE METHODS

S.No.	PROPERTY	METHOD`A' (FILLER+BINDER)	METHOD`B' (GREEN COKE)	METHOD`C' (MCMB)
1.	Bulk density (g cm^{-3})	1.77-1.82	1.90-2.00	1.90-2.0
2.	Open porosity (%)	15-20	8-14	8-14
3.	Bending strength (Kg cm^{-2})	250-400	600-1000	600-1000
4.	Elect. resistivity (mOhm cm)	1.1-1.6	1.5-3.0	1.5-3.0
5.	Shore hardness	40-50	75-100	75-100
6.	Thermal expan. coeff. (10^{-6} $°C^{-1}$)	3.0-8.0	5-7	5-7
7.	Degree of anisotropy	1.1-1.2	1.05-1.10	1.01-1.05
8.	Ash content (%)	0.2 (Max.)	0.05 (Max.)	0.05 (Max.)

the binding components will result in an improper binding of the green coke particles, leading to a weak and low-density product. Moreover, because of the invariably high value of the shape factor (ratio of longest dimension of a particles to its thickness) of the green coke particles, a high degree of compaction cannot be achieved, resulting again in a lower value of the density of the product.

The product obtained by the method `C' seems to be more expensive than those made by the other two methods because of low yield of mesophase spherules obtained from the heat-treated parent pitch. However, the product obtained by the method`C' has the highest degree of isotropy even if conventional press is used. Further, the products made from method `C' have shown excellent performance in practical applications.

1.9 APPLICATIONS OF HD - HS - IG

High density - high strength - isotropic graphite is a versatile material having widely ranging applications. Seals, bearings, packings and carbon blades represent some of its applications in the mechanical field. Here, its high lubricity, high workability and high thermostability are exploited. Metallurgical applications of this graphite include hot-pressing dies, dies for continuous casting of metals and alloys and crucibles. These applications make use of low wettability, high thermal stability and high workability of this graphite. High thermal conductivity of this specialty graphite is exploited in its use as jigs.

Electrodes of the electrical discharge machines represent an old and important application of this graphite, where it is counted superior to copper (the other common material in use for the purpose) because of its dense, fine and homogeneous structure and high workability to be machined into a complex and fine shape. Crucibles, susceptors, heaters are its main applications in the semiconductor field which make use of its high purity as one of the critical requirements.

Nuclear graphite is also a promising application of this high density isotropic graphite which exploits its high purity, high thermal and electrical conductivity and high degree of isotropy. Here, anisotropic thermal expansion causes serious stress in the nuclear furnace.

Besides above applications, this graphite is also used to form rocket nozzles, electrical brushes and contacts, trolley wheels and so on. In fact, more and more applications of this material are being explored. A relation between applications and properties of this graphite is shown in Table 1.2.

1.10 SCOPE OF THE PRESENT INVESTIGATIONS

As has been mentioned in the earlier sections, high density - high strength - isotropic graphite is a recent development and refers to a high quality isotropic graphite. The products made from this specialty graphite find extensive applications in mechanical, metallurgical, nuclear, aerospace, semiconductor and other industries. Though, there are basically three methods to produce this graphite as already mentioned in Section 1.8, the

TABLE 1.2

RELATION BETWEEN APPLICATIONS AND PROPERTIES OF THE HIGH DENSITY - HIGH STRENGTH - ISOTROPIC GRAPHITE

PROPERTY	ELECTRIC DISCHARGE MACHINE	MECHANICAL FIELD	SEMICONDUCTOR FIELD	METALLURGICAL FIELD	NUCLEAR FIELD
High lubricity		**		*	
High workability	**	**		**	
High thermostability	**	*	**	**	
High purity			**	*	**
Low thermal expansion	*	*		*	*
High elect. conductivity	**		*		**
High thermal conductivity	*	*	**	**	**
High chemical resistance	*	*	*	*	*
Low wettability to metals	**	*	**	**	
Isotropic structure	**		**	*	**

**: Very important *: Important

present investigations have been confined to the method `C', i.e., the method involving the use of mesocarbon microbeads. In fact, a lot of interest is being taken in this MCMB-based fine-textured isotropic graphite because of its excellent performance of in the practical tests. However, a search of the literature reveals that the processing technology is a closely guarded secret. In view of this, the present investigations have been conducted to understand the scientific and technological aspects of the processing of this specialty graphite from coal tar pitch.

It may be recollected that the first step in the present process of production of high density - high strength - isotropic graphite is the heat-treatment of a coal tar pitch to generate mesophase in it. Though, mesophase formation in coal tar pitches has been paid a great deal of attention by various authors as revealed from the published literature, little is reported regarding the size and content of mesophase developed in the coal tar pitches as a result of different heat-treatment conditions. Such studies are of paramount importance in finding out the process conditions of a particular precursor pitch which may result in high yield of the mesophase spherules (microbeads), thereby helping in reducing the cost of this MCMB-based high density graphite. Thus, to optimise the characteristics of the precursor pitch, particularly its QI-content, the dependence of characteristics of the monolithic carbons on the quinoline insoluble contents of the several precursor pitches has been studied in detail.

Further, with a view to investigate the sintering behaviour of a MCMB-based product, an extensive study of the chang-

es in the various properties of the product with the heat-treatment temperature (ranging between 350°C and 2700°C) has been carried out.

Another important step in the present process is the extraction of mesophase pitch, followed by calcination of the mesocarbon microbeads. Though, the properties of this specialty graphite depend greatly on the conditions of extraction and calcination, no information is available in the published literature regarding these aspects. Therefore, the effect of type of tar oil (in respect of its boiling range) used in the extraction of a mesophase pitch on the characteristics of the resulting carbons has also been studied. Further, the conditions of calcination of MCMB have been optimised by studying the effect of temperature, time and atmosphere (inert/vacuum) of calcination on the characteristic of the resulting high density - high strength - isotropic graphite. Finally, a high quality high density - high strength - isotropic graphite was produced using the processing conditions optimised under the present investigations.

CHAPTER - II

EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

The present investigations involved the development of several processing facilities such as mesophase formation apparatus, solvent extraction assembly, compression moulding dies, electrically heated muffle furnaces etc. The use of some specialised instruments and machines was also made during the present investigations.

The general procedure for the preparation of isotropic graphite is briefly described in Section 2.2. The methodologies used for the preparation of coal tar pitch and mesophase powders have been described in Sections 2.3 and 2.4, respectively. The method used for moulding the mesocarbon microbeads to get a product (plate) is described in Section 2.5. The procedures involved in carbonisation and graphitisation of MCMB-based plates are discussed in Sections 2.6 and 2.7, respectively.

The procedures used for characterisation of various pitch materials with respect to their softening point, quinoline and toluene insoluble contents, coking value, ash content, specific gravity, elemental analysis (C,H,N contents) etc. have been described in Section 2.8. The procedures employed for the determination of various characteristics of carbon plates, namely, weight loss, linear and volume shrinkages, apparent density, specific gravity, kerosene density, open porosity, electrical resistivity, bending strength, Young's modulus, Shore hardness, elemental analysis and microstructure (optical and scanning electron microscopy) have been described in Section 2.9 of this chapter.

2.2 PREPARATION OF ISOTROPIC GRAPHITE

The general procedure for the preparation of high density - high strength - isotropic carbon is briefly described as follows. The precursor coal tar pitch is heat-treated to around 420-430°C to generate mesophase spherules in it. The resulting heat-treated pitch is subjected to solvent extraction to obtain mesocarbon microbeads (MCMB) as insolubles. These MCMB are then compacted by hot-pressing using a moulding die into a green artifact which is carbonised to around 1000°C and finally graphitised to about 2700°C in an inert atmosphere to get the high density - high strength - isotropic graphite. The essential steps mentioned above in making this isotropic graphite are summarised in the form of a block diagram shown in Fig.2.1.

2.3 PREPARATION OF COAL TAR PITCHES

The coal tar pitches used in different studies were prepared by vacuum distillation of a suitable coal tar, using pitch processing assembly fabricated at the Glass Technology Unit of the NPL, as shown in Fig 2.2. The coal tar pitch is obtained as a residue in the distillation of coal tar, a by product in the distillation of bituminuous coal to produce metallurgical coke.

2.4 PREPARATION OF MESOCARBON MICROBEADS

The coal tar pitches are heat-treated to temperatures of 420-430°C in an inert atmosphere to produce mesophase spherules in them. The assembly used for the mesophase formation is similar

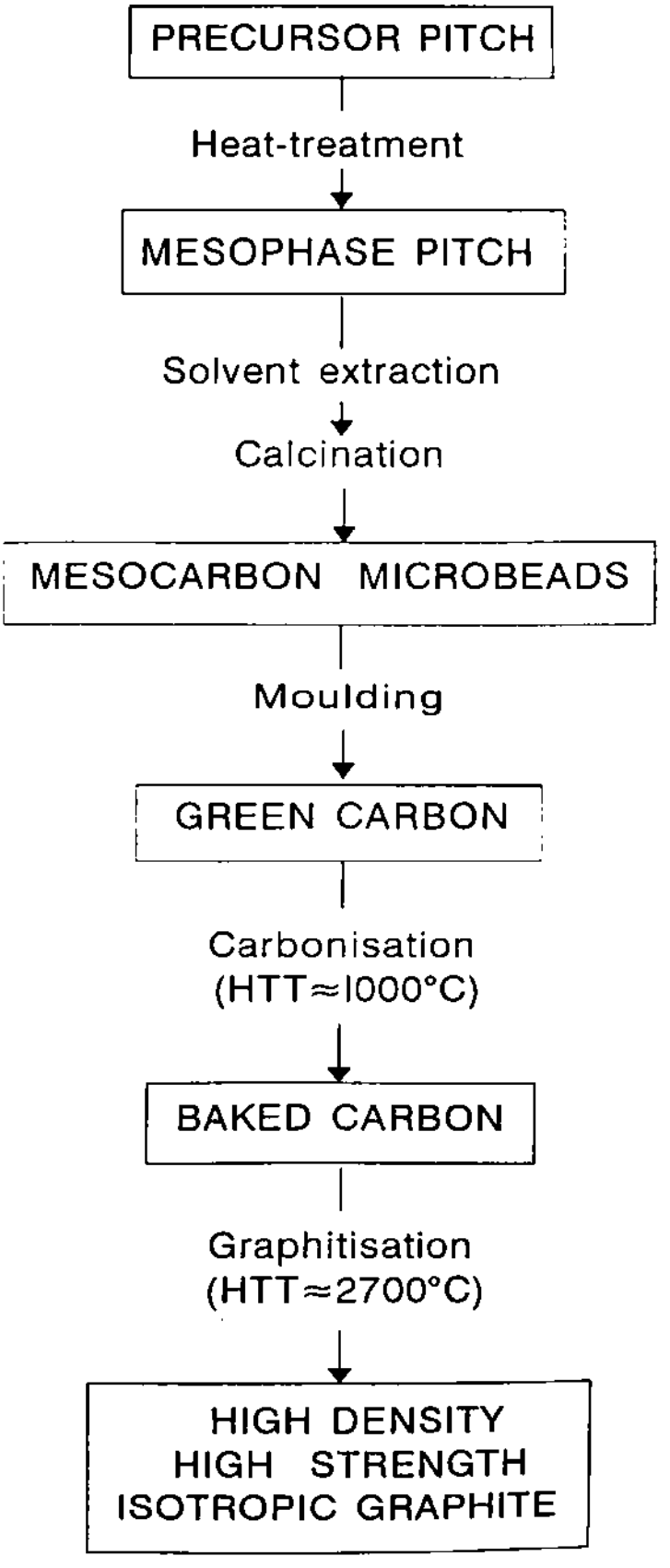


Fig.2.1 Block diagram for the development of high density-high strength-isotropic graphite from mesocarbon microbeads.

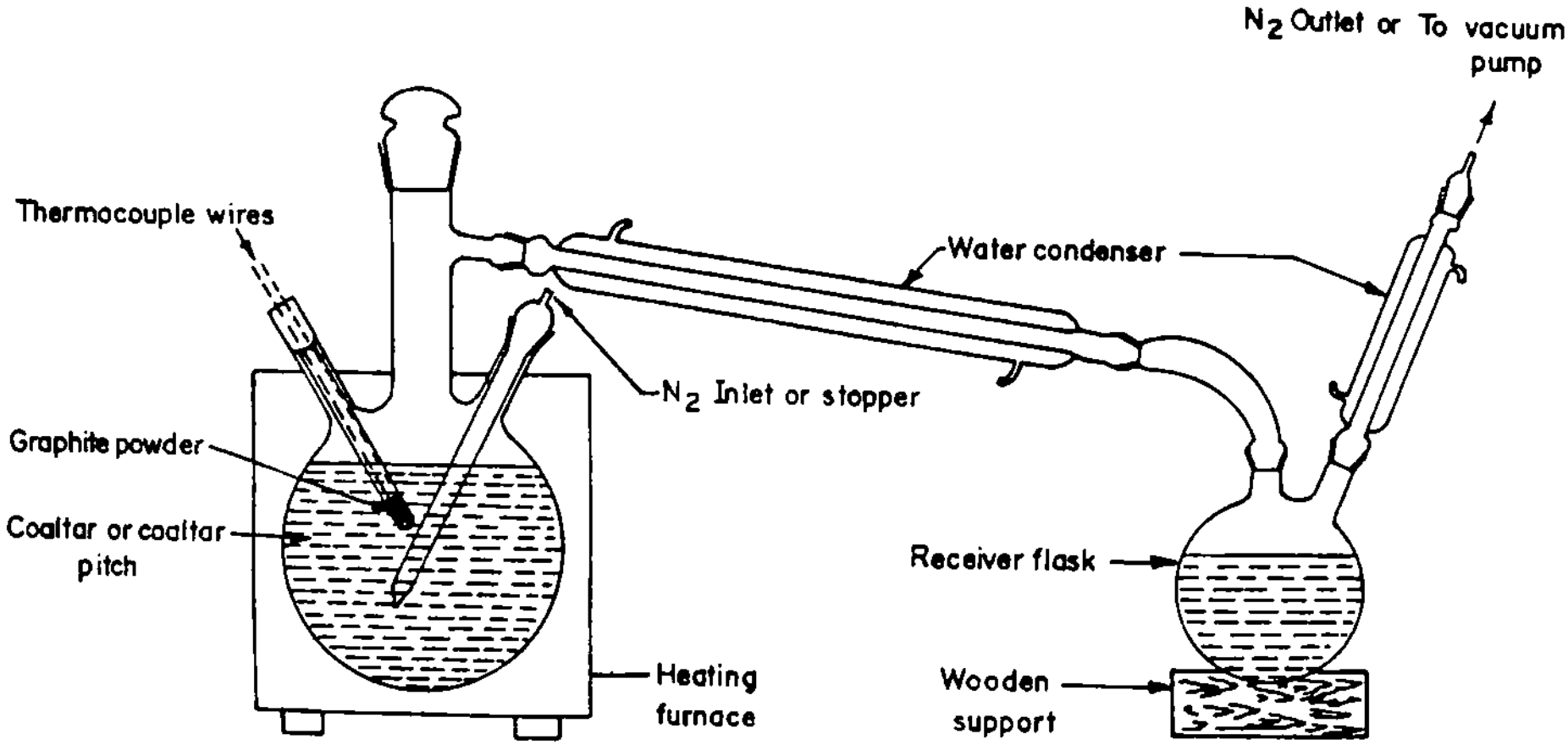


Fig 2.2 Pitch processing assembly used for the preparation of coal tar pitches and mesophase pitches.

to the one shown in Fig.2.2. The mesophase containing pitch, i.e. heat-treated pitch, is subjected to solvent extraction using a suitable tar oil and the mesophase spherules along with some binding components are obtained as the tar oil insolubles. These insolubles are washed with toluene and then dried at about 110°C. For small batches of mesophase powder, washing with toluene is effective in removing the entrapped tar oil. However, for large batches, toluene washed tar oil insolubles are further subjected to calcination at a temperature in the range of 200-350°C in inert atmosphere/partial vacuum. The mesophase powder, so prepared are called "mesocarbon microbeads (MCMB)".

2.5 MOULDING OF MESOCARBON MICROBEADS (MESOPHASE POWDERS)

About six grams of the mesophase powder is hot-pressed into plates of size 60mm x 20mm x 4mm using chrome steel dies kept between heated plates of a conventional compression moulding machine. The moulding temperature used ranges from 100-120°C and the pressure applied is around 1000 kg cm^{-2}.

2.6 CARBONISATION OF GREEN CARBONS

The green carbon plates are packed in a graphite boat using graphite powder as the packing material. The boat is then loaded in a quartz tube having a provision for maintaining an inert atmosphere of ultra high purity nitrogen. The quartz tube containing the green carbons is then placed inside the muffle of a Kanthal-wound muffle furnace, which is heated to around 1000°C

at the rate of 10°C/h, maintaining nitrogen atmosphere inside the quartz tube. The quartz tube is maintained at the final temperature for half an hour and then cooled to room temperature at the rate of 30°C/h upto 700°C followed by 60°C/h upto room temperature.

2.7 GRAPHITISATION OF BAKED CARBONS

The baked carbons (heated to around 1000°C) are kept in a graphite boat and then graphitisied, i.e. heat-treated to 2700°C in a graphite tube furnace in an atmosphere of high purity argon gas with a rate of heating of 500°C/h. The furnace is then cooled to room temperature to obtain the graphitised carbons.

2.8 CHARACTERISATION OF PITCHES

As mentioned in section 2.1 of this chapter, pitches are characterised w.r.t. a number of parameters, the procedures involved in which are described in the following sub-sections.

2.8.1 DETERMINATION OF SOFTENING POINT

Softening point of the coal tar pitch has been measured by Ring and Ball method, in accordance with ASTM-D-2398 specifications which covers softening point range of 30-200°C. The softening point is defined as the temperature at which a disc of the sample held within a horizontal ring is forced downward a distance of 2.54 cm under the specific weight of a steel ball as the sample is heated at a prescribed rate in a water or glycerin bath.

A portion of the sample is heated until it has become sufficiently liquid to pour, the temperature to be raised by no more than 75°C above the anticipated softening point. The sample is poured into two rings preheated to the pouring temperature. While being filled, the rings should rest on an amalgamated brass plate. After cooling to room temperature, the excess material is trimmed off with a heated spatula or knife. Should it be necessary to repeat the process, a fresh sample and clean rings are mandatory. Centering guides are used to place the balls on the specimen, and the assembly is placed in a bath filled with distilled water or glycerin, to a depth of not less than 10 cm and not more than 10.6 cm.

The temperature is raised at 5±0.5°C/min. The temperature observed at the instant the sample surrounding the ball touches the bottom plate is recorded. The bottom plate is placed 2.54 cm below the ring holder. If the difference between the values obtained for two specimens exceeds 1°C, the test is repeated.

2.8.2 DETERMINATION OF COKING VALUE (CV)

Coking value indicates the coke forming properties of a pitch. A sample of the pitch is vaporised and pyrolysed for a specific time at a specified temperature in an equipment that limits the oxygen supply.

A dried pitch sample (1-2 g) is weighed in a quartz crucible and placed in a quartz glass reaction vessel having a provision for flowing of high purity nitrogen gas. The quartz assembly is then placed in an electrical muffle furnace, the tempera-

ture of which is gradually raised to 950°C at a rate of 200°C/h and maintained at 950°C for 30 minutes and cooled to room temperature. The crucible is then cooled to room temperature and again weighed to get weight of the coke. From these observations, coking value is calculated as the residue percent weight of the sample taken.

2.8.3 DETERMINATION OF ASH CONTENT

A representative portion of the dry sample is reduced to minus 30 mesh. 10g of the prepared sample is weighed out in an ignited crucible (porcelain, silica, or platinum) on an analytical balance. The crucible is then carefully heated in an electrical muffle furnace to 950°C for 30 minutes. When all the carbon has been combusted, the crucible is cooled and weighed again. The ignition at 950°C is repeated until constant weight is obtained. From these observations, the ash content is calculated as the residue percent weight of the sample taken.

2.8.4 DETERMINATION OF QUINOLINE INSOLUBLE CONTENT (QI)

Quinoline insoluble component represents very high molecular weight aromatic compounds as well as the solid impurities. To determine quinoline insoluble content of a pitch, the sample is crushed to -30 BS mesh. About 1 g of this powder is digested with 30 ml of distilled quinoline at 70°C for half an hour. The mixture is then rapidly filtered with suction in a Grade-4 sintered glass crucible. The residue is washed with small portions of toluene and acetone successively and the crucible is dried at

110°C in a drying oven. After cooling, it is weighed to get the quinoline insolubles content.

2.8.5 DETERMINATION OF TOLUENE INSOLUBLE CONTENT (TI)

The toluene insoluble content of a coal tar pitch is a measure of the resin present in the pitch. To determine the toluene insoluble content of a pitch, the sample is crushed to -30 BS mesh, 1 g of sample is weighed and is digested with 30 ml of toluene at 90°C for half an hour. Then it is rapidly filtered with suction in a Grade-4 sintered glass crucible and subsequently washed with small portions of acetone. The crucible is dried at 110°C in a drying oven. After cooling, it is weighed to get the toluene insoluble content.

2.8.6 DETERMINATION OF SPECIFIC GRAVITY (SG)

A pitch sample weighing about 5-10 g is suspended by a thin synthetic fiber from the frame of a mono-pan balance and its weight in air (W), as well as in distilled water (w), at room temperature are determined. The specific gravity is calculated as

$$S.G. = \text{Weight in air/loss in weight in distilled water}$$
$$= W/(W-w)$$

2.8.7 ELEMENTAL ANALYSIS

Elemental analysis is carried out using `CARLO ERBA' Elemental Analyzer, Model 1106. Carbon, nitrogen, hydrogen, sulphur and oxygen can be estimated within an accuracy of +0.2 %. The organ-

ic samples are weighed into tiny tin containers by the CAHN 29 automatic electro-balance and dropped at preset times into the CHN analyzer.

The analytical technique involves instantaneous pyrolysis of the samples in a stream of helium enriched with oxygen. Flash combustion takes place primed by oxidation of containers. Quantitative combustion is then achieved by passing the gases over Cr_2O_3. In this process C is converted into CO_2, N to N_2 and H to H_2O. The mixture of combustion is passed through a reduction reactor filled with copper at 650°C, to remove the excess oxygen, then through a chromatographic column heated at about 100°C. The individual components are measured in the order of N_2, CO_2, H_2O by a thermal conductivity detector. The detector signal is fed to a potentiometric recorder, an integrator with digital print-out or a data processor. The instrument is calibrated using standard compounds.

2.8.8 THERMOGRAVIMETRIC ANALYSIS

The Thermo-Gravimetric Analysis (TGA) of a coal tar pitch or mesocarbon microbeads was carried out using the Mettler TA 3000 Thermal Analyser. In TGA, the weight of the sample is continuously monitored and plotted while it is heated in a furnace under controlled conditions and a themogram is obtained. TG 50 themobalance of the Mettler TA-3000 system was used for thermogravimetric analysis. About 5 mg of the sample is taken in a ceramic crucible and the crucible is kept in the balance pan enclosed in the furnace and weight of the sample is continuously measured and recorded by the microprocessor to give a themogram.

2.9 CHARACTERISATION OF HEAT - TREATED SAMPLES

Characterisation of monolithic carbons heat-treated to around 1000°C and 2700°C was done with respect to weight loss, linear and volume shrinkages, apparent density, specific gravity, kerosene density, electrical resistivity, bending strength, Young's modulus, Shore hardness, and elemental analysis as per the procedures described in the following sub-sections. For determination of most of the above mentioned characteristics, an average of the values of ten to fifteen samples was taken.

2.9.1 DETERMINATION OF WEIGHT LOSS

The weight loss in a green carbon product during the heat-treatment is obtained by the following expression:

Weight loss (%) = [w/W] x 100

where, W = weight of the green carbon product

and w = loss in weight of the green carbon upon heat-treatment

2.9.2 DETERMINATION OF LINEAR SHRINKAGE

The linear shrinkage occuring in a green carbon product during the heat-treatment is determined knowing the length of the product in the green and heat-treated states. It is given by the expression:

Linear shrinkage (%) = (l/L) x 100

where, L = length of the green carbon product

l = reduction in length of the product after heat-treatment

2.9.3 DETERMINATION OF VOLUME SHRINKAGE

The volume shrinkage occurring in a green carbon product during the heat-treatment is determined knowing the volume of the product in the green and heat-treated states. It is given by the expression:

Volume shrinkage (%) = (v/V) x 100

where, V = volume of the green carbon product

v = reduction in the volume of product after heat-treatment

2.9.4 DETERMINATION OF APPARENT DENSITY

The apparent density of the carbon and graphite products is calculated from the measurements of their mass and dimensions.

2.9.5 DETERMINATION OF SPECIFIC GRAVITY

The specific gravity is a convenient parameter indicating the apparent density of carbons of irregular shapes. The procedure used for determining specific gravity of the carbon samples is similar to the one used for characterisation of pitches as described in Section 2.8.6.

2.9.6 DETERMINATION OF KEROSENE DENSITY

An oven dried specific gravity bottle is weighed and filled with pure distilled water and then weighed. This procedure is repeated with the kerosene oil. The ratio of the weight of kerosene oil to the weight of distilled water multiplied by the density of distilled water at room temperature gives the density of kerosene oil used. An oven dried sample of the carbon material in the powder form (-200 B.S.mesh) is introduced into a weighed specific gravity bottle, which is then weighed again. The bottle is then partially filled with kerosene oil such that the sample dips well into the oil. The unstoppered bottle is then placed in a vacuum desiccator and evacuation is started with the help of a vacuum pump and is continued until no air bubbles are observed in the bottle. The remaining space in then filled with kerosene oil upto the full capacity and then weighed. The kerosene density of the material is then calculated by the following expression:

Kerosene density = $(W/w) \times \delta$

where, W = weight of the sample

w = weight of kerosene oil displaced by the sample

and δ = density of kerosene oil

2.9.7 DETERMINATION OF OPEN POROSITY

The open porosity in a carbon sample is obtained by the following expression:

Open porosity (%) = $(1 - A.D./K.D.) \times 100$

where, A.D. = apparent density

K.D. = kerosene density

2.9.8 DETERMINATION OF ELECTRICAL RESISTIVITY

The electrical resistivity of a test-specimen is determined by passing a suitable current across the cross-section of the specimen placed between two thick copper or brass plates and measuring the potential drop across a known distance along the length of the specimen with the help of a microvoltmeter using two probes.

The electrical resistivity is obtained from the following equation:

$$r = (V \times A) / (I \times l)$$

where, r = electrical resistivity of the test-specimen

V = potential drop across the probe pins

A = area of cross-section of the test specimen

I = magnitude of direct current

l = distance between the probe pins

2.9.9 DETERMINATION OF BENDING STRENGTH

Instron Universal Testing Machine, Model 1122, was used to determine the bending strength of carbon plates. The test specimen is kept on two knife edges to hold the specimen tightly. A slowly increasing load is then applied at a cross head speed of 0.5 mm/min on the specimen through the middle knife edge till the specimen breaks. Stresses so developed in the test are measured with the help of a load cell and recorded on a chart. Vertical movement of the chart corresponds to the deflection in the specimen. Thus, a load versus deflection plot is obtained. The bending strength of the test-specimen is calculated as follows:

Bending strength = (3 P_{max} S) / (2 b t^2)

where, Pmax = maximum load arrived by the test specimen

S = Span length (30 mm)

b = width of the test-specimen

t = thickness of the test-specimen

2.9.10 DETERMINATION OF YOUNG'S MODULUS

The Young's modulus is determined from the load versus deflection plot as obtained in the bending strength measurement of carbon plates on the Instron Universal Testing Machine, Model 1122. The Young's modulus is calculated from the following expression :

Young's modulus = [S^3 / (4 b t^3)] x p/d

where, S = span length

b = width of the test-specimen

t = thickness of the test-specimen

p/d = slope of initial straight line portion of load-deflection curve

2.9.11 DETERMINATION OF SHORE HARDNESS

In the present investigations, the hardness was measured using a Shore's scleroscope (made by Coats Machine Tools Co., Ltd., London) which is shown in Fig.2.5. The method of measurement is based on the dynamic rebound of a diamond-tipped hammer falling from a fixed height on the polished surface of the specimen. The rebound height of the hammer gives a measure of the hardness of the specimen. For the measurement of hardness the specimen surface may be polished with a medium grit emery paper.

2.9.12 THERMOMECHANICAL ANALYSIS

The thermo-mechanical analysis of the carbon products have been carried out using Mettler TMA 40. In thermo-mechanical analysis, changes in the length of test specimen with temperature are continuously monitored and elongation in the test specimen with temperature is plotted.

For this purpose, about 5mm of the test-specimen is fixed on the TMA measuring probe and the base, which is then inserted in the furnace and heated to the desired temperatures. Changes of the order of +0.1 μm in the length of the test-specimen can be detected by this method.

To determine anisotropy ratio of the product, coefficient of thermal expansion in directions ⁞⁞ and ⊥ to moulding directions is determined. Ratio of the two coefficients gives anisotropy ratio of the product.

2.9.13 SCANNING ELECTRON MICROSCOPY

JEOL Scanning Electron Microscopy, Model JSM 35 CF, is used to examine the surface texture of carbon samples. The samples are fixed on the sample holder with the help of a silver paste, which acts as an adhesive as well as a conducting material. Gold/ silver coating is done on the specimen for making it conducting. Specimens are scanned at different angles using various magnifications.

2.9.14 OPTICAL MICROSCOPY

The optical microscopic examination of carbon samples was done on

a Litz Metalloplan Optical Microscope. The first stage in the microscopic examination of anisotropic constituents in heat-treated pitches is the preparation of the sample which is done in the following manner.

The test material is taken in a cylindrical plastic capsule (approx. 20 mm diameter and 15 mm height), and a freshly prepared epoxy or polyester resin is poured over the material such that it just covers the specimen. After the resin has partially set, more of it is poured to fill the capsule completely and allowed to stand at room temperature till it is completely set. The mounted specimen is then removed from the plastic capsule and its surface is first ground manually on a silicon carbide water-proof cloth with grit size varying successively from 200 to 800, using tap water as a lubricant. Subsequently, the mounted specimen is polished on a lapping machine using alumina powders of size varying from 1 micron down to 0.05 micron, and is then washed with tap water to remove off any sticking alumina particles using an ultrasonic cleaner containing water. The sample is then dried in air to make it ready for the microscopic examination. The anisotropic mesophase is observed under crossed polarisers.

2.9.15 X-RAY DIFFRACTOMETRY

Semen D-500 X-ray diffractometer with Cu K_α (wavelength= 1.54 Å) radiation as source has been used to record the diffractograms of carbons using powder technique. The crystallite parameters, L_a and L_c, of the material have been determined using the Scherrer equation :

Crystallite parameter = $(k \cdot \lambda) / (\beta \cdot \cos \theta)$

Where, λ = wavelength of radiation used = 1.5418 Å

θ = scattering angle

k = 0.9-1.84

β = Half maximum intensity width

CHAPTER - III

EFFECT OF HEAT-TREATMENT CONDITIONS ON MESOPHASE FORMATION IN COAL TAR PITCHES AND DEVELOPMENT OF MONOLITHIC CARBONS THEREFROM

3.1 INTRODUCTION

It has been already introduced in Chapter-I that suitable heat-treatment of coal tar pitches results in the formation of liquid crystalline spherules known as mesophase spherules. These mesophase spherules generated in a coal tar pitch can be separated out of the heat-treated pitch using a suitable tar based solvent and are called `mesocarbon microbeads (MCMB)'. These MCMB are excellent precursors for the production of binderless high density - isotropic graphite. In the recent years, considerable interest has been taken in this type of graphite, but not much is published regarding its developmental aspects. Some work in this direction has been reported by Bhatia et al. (64-66).

In the present investigations, efforts have been made to study the effect of heat-treatment conditions on the mesophase formation in different coal tar pitches. This study has been described in Section 3.2. Next attempt has been made towards the development of high density - high strength - isotropic carbon. For this purpose, a mesophase pitch based on a coal tar pitch precursor (containing only 0.5% Q1) was subjected to solvent extraction using quinoline, toluene and tar oil as solvents. The different insolubles, so obtained, after processing were characterised with respect to various parameters according to the procedures given in Section 2.8 and then hot-moulded into rectangular plates of 60mm x 20mm x 4mm size using conventional hydraulic press and finally carbonised to a temperature of 950°C in an atmosphere of high purity nitrogen. The results of this study are discussed in Section 3.3.

Further, with an idea of economising the process, an attempt has been made to develop isotropic carbon from coal tar pitches containing some primary quinoline insolubles. For this purpose, three coal tar pitches containing different amounts of primary quinoline insolubles were subjected to heat-treatments in inert atmosphere to generate mesophase spherules with mean size of about 5 μm. The mesophase pitches, so obtained, were subjected to extraction with a tar oil to obtain mesocarbon microbeads, which, after characterisation, were hot-moulded into rectangular plates of 60mm x 20mm x 4mm size using conventional hydraulic press and then carbonised to temperatures of 950°C in an atmosphere of high purity nitrogen. Some plates were also graphitised to 2700°C in an atmosphere of argon. All these plates were then characterised with respect to the usual parameters mentioned in Section 2.9. The details of this study along with the results obtained are discussed in Section 3.4. Further, a comparision of the characteristics of monolithic carbons from different coal tar pitch precursors, varying in their content of quinoline insolubles was made and has been discussed in Section 3.5. The important conclusions drawn after carrying out these studies have been given in Section 3.6.

3.2 EFFECT OF HEAT-TREATMENT CONDITIONS ON MESOPHASE FORMATION IN DIFFERENT COAL TAR PITCHES

Quinoline insolubles (QI) are an integral part of the coal tar pitches, and are often described as carbon black like particles. It is also reported that primary QI, or additives like carbon

black or silica gel, retard the growth and coalescence of mesophase [67-72] resulting in a coke with more fine and isotropic carbon.

It has been noted that no systematic study on the development of mesophase (by heat-treatment) in coal tar pitches having different QI contents has been reported. In view of this, an attempt has been made in the present investigations to study the effect of heat-treatment conditions on mesophase formation in different coal tar pitches. For this purpose, four kilograms of coal tar of characteristics shown in Table 3.1 was taken in a 5 litre distillation flask and distilled at 290°C under a reduced pressure of 12 cm Hg. The pitch so obtained was designated as CTP-1. This pitch CTP-1 was tested w.r.t. various characterisation parameters following the procedures described in Section 2.8 and the values obtained are given in Table 3.2.

To get a QI free coal tar pitch, one part of CTP-1 and seven parts of light creosote oil were mixed and heated to 120°C in 3-litre-3-neck flask and the mixture was then filtered under suction using Buchner funnel fitted with Whatman filter paper no.44. The insoluble matter (obtained on filter paper) was rejected and the filtrate was subjected to distillation in the pitch processing assembly to distill out creosote oil and obtain the pitch (as residue). This pitch was designated as CTP-3. The coal tar pitches CTP-1 and CTP-3 were hot-mixed in equal proportions (1:1) to get another coal tar pitch which was designated as CTP-2.

Both the pitches CTP-2 and CTP-3 were characterised with respect to various parameters, and their values obtained are also

TABLE 3.1

CHARACTERISTICS OF COAL TAR

S.No.	CHARACTERISTICS	VALUE
1.	Ash content	0.16 %
2.	Quinoline insolubles	4.2 %
3.	Toluene insolubles	15.4 %
4.	Beta-resins	11.2 %
5.	Coking value	39.9 %
6.	Elemental analysis : Carbon Hydrogen Atomic C/H Ratio	 91.0 % 5.0 % 1.53

summarised in Table 3.2. In the present study, each of the above three coal tar pitches were heated in inert atmosphere to a temperature of 420°C at a rate of 150°C/h for different periods of time, ranging from 1-7 h resulting in overall 10 experiments (1-10) of mesophase formation. The heat-treated (mesophase) pitches were characterised with respect to a number of parameters and the results are given in Table 3.3. The anisotropic mesophase spherules were observed in the polished specimens of the mesophase pitches mounted in resin blocks, using a cross-polarised light optical microscope. The optical micrographs of the heat-treated pitches (Expts. 1-10) are shown in Figs.3.1-3.3. The size (diameter) of the mesophase spherules was determined from these micrographs by counting 500-1000 points for each experiment of heat-treatment. The mean size of the mesophase spherules formed in the three coal tar pitches as a function of the soaking time is plotted in Fig.3.4.

3.2.1 VARIATION OF QUINOLINE AND TOLUENE INSOLUBLE CONTENTS AND COKING YIELD WITH SOAKING TIME

The heat-treatment of coal tar pitches proceeds with the removal of relatively lower molecular weight components as well as with the polymerization and condensation reactions taking place between the various planar aromatic molecules present in these pitches. Such reactions also lead to increased contents of quinoline and toluene insolubles in the heat-treated (mesophase) pitches. Removal of the volatile components present in the precursor pitch as well as those generated during pyrolysis of pitch

TABLE 3.2

CHARACTERISTICS OF PRECURSOR COAL TAR PITCHES

S.No.	CHARACTERISTICS	CTP-1	CTP-2	CTP-3
1.	Softening point (°C)	81	79	77
2.	Quinoline insolubles (%)	6.5	3.3	0.5
3.	Toluene insolubles (%)	21.2	20.7	20.2
4.	Coking value (%)	48.6	48.0	47.7
5.	Specific gravity	1.28	1.27	1.27

results in a decreased volatile matter content or an increased coking value of the heat-treated (mesophase) pitch. It is thus clearly seen from Table 3.3 that in case of all the three pitches, different heat treatments invariably result in an increase in the quinoline and toluene insoluble contents, as well as an increase in the coking values of the resultant mesophase pitches.

3.2.2 VARIATION OF MEAN SIZE OF MESOPHASE SPHERULES WITH SOAKING TIME

It has already been mentioned that during the heat-treatment of coal tar pitches, polymerisation and condensation reactions take place between the constituent planar aromatic molecules present in these pitches. Such reactions would obviously lead to the formation and growth of mesophase spherules. This is what has been observed in the polished samples of these heat-treated pitches examined using the optical microscope, as shown in the optical micrographs given in Figs 3.1-3.3. It is clearly seen from these micrographs that in some cases, in addition to mesophase spheres, some non-spherical mesophase is also present. It has, in fact, been found that the size and concentration of mesophase in any heat-treated pitch increases as the soaking time of HTT (420°C) increases. Fig 3.1d, showing optical micrograph of mesophase formed by soaking CTP-1 (6.5% QI) at 420°C for 7h, reveals the presence of some non-spherical mesophase, probably due to incompletely coalescence of mesophase spheres. Whereas, Fig.3.3d shows that soaking time of only 3 h in case of CTP-3 (0.5% QI) leads to the formation of coalesced mass of mesophase in addition to

TABLE 3.3

CHARACTERISTICS OF THE HEAT-TREATED (MESOPHASE) PITCHES

Expt. No.	Precursor Pitch	Soaking Time (h) at 420°C	Quinoline Insolubles (%)	Toluene Insolubles (%)	Coking Value (%)
1.	CTP-1	2.0	28.8	57.5	72.0
2.	CTP-1	3.5	34.0	62.2	72.2
3.	CTP-1	5.0	39.0	67.0	72.7
4.	CTP-1	7.0	50.3	73.2	78.4
5.	CTP-2	2.0	24.5	49.0	64.0
6.	CTP-2	3.0	29.4	54.7	66.5
7.	CTP-2	5.0	32.1	56.3	69.0
8.	CTP-3	1.0	20.0	55.0	60.0
9.	CTP-3	1.5	22.4	55.8	66.0
10.	CTP-3	3.0	30.0	61.0	70.0

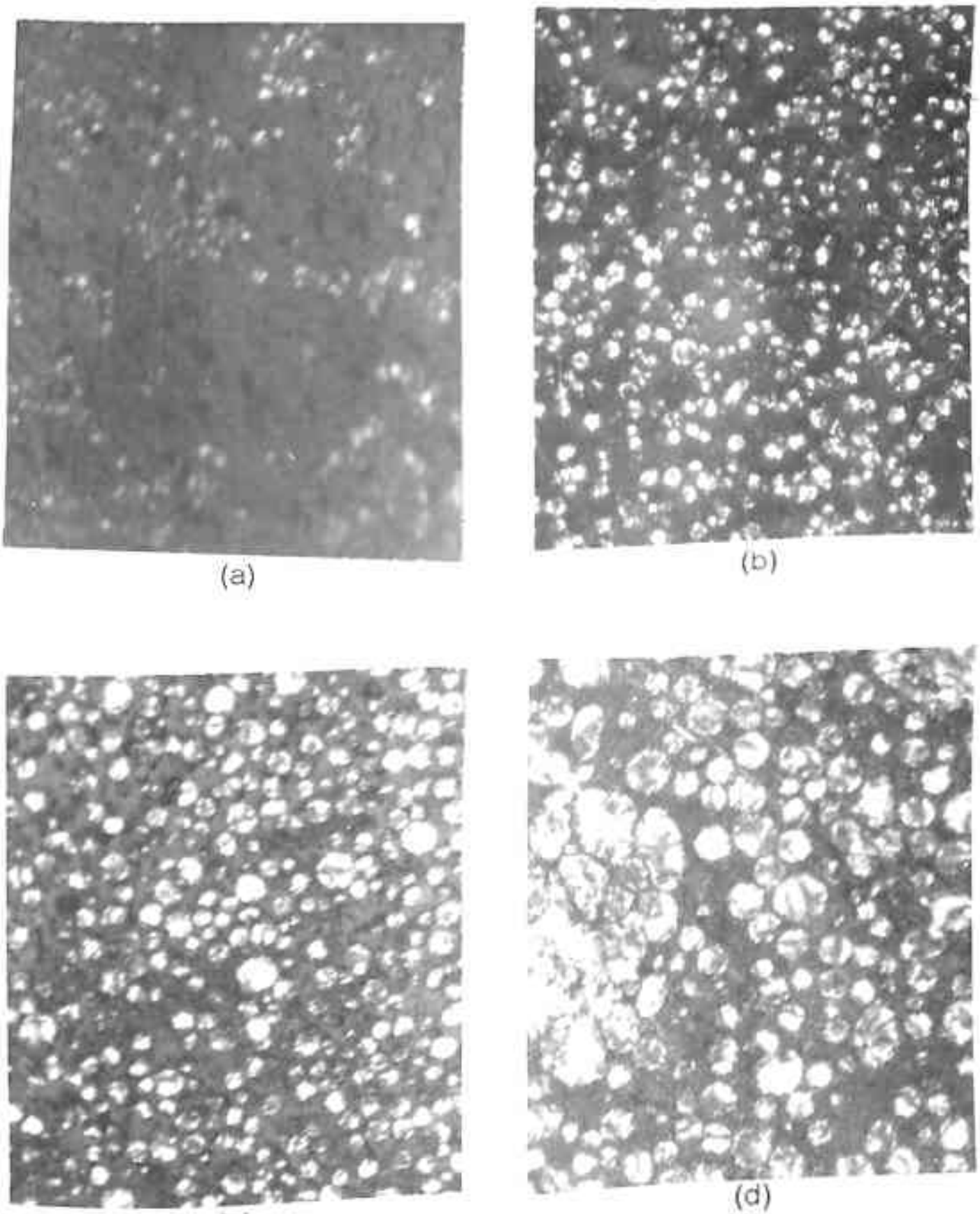
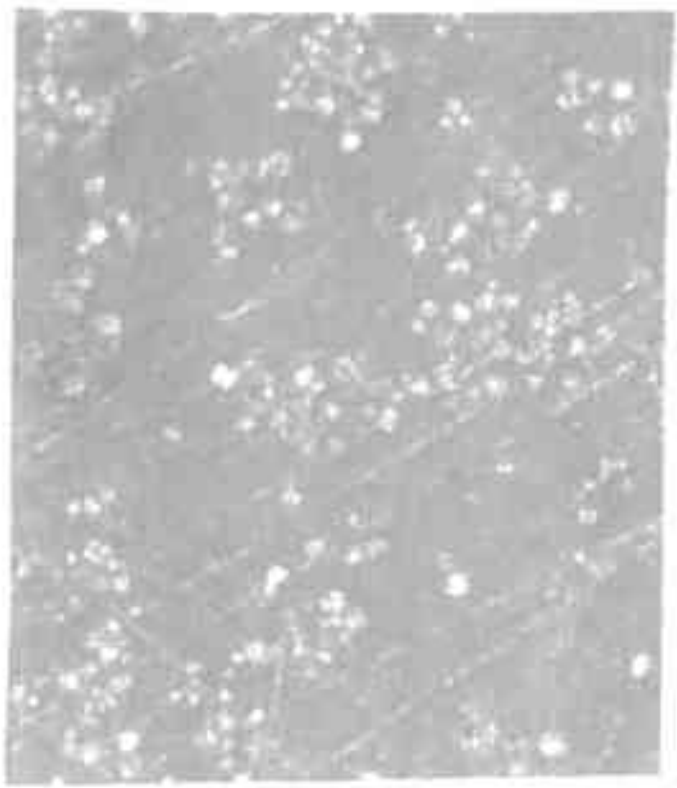
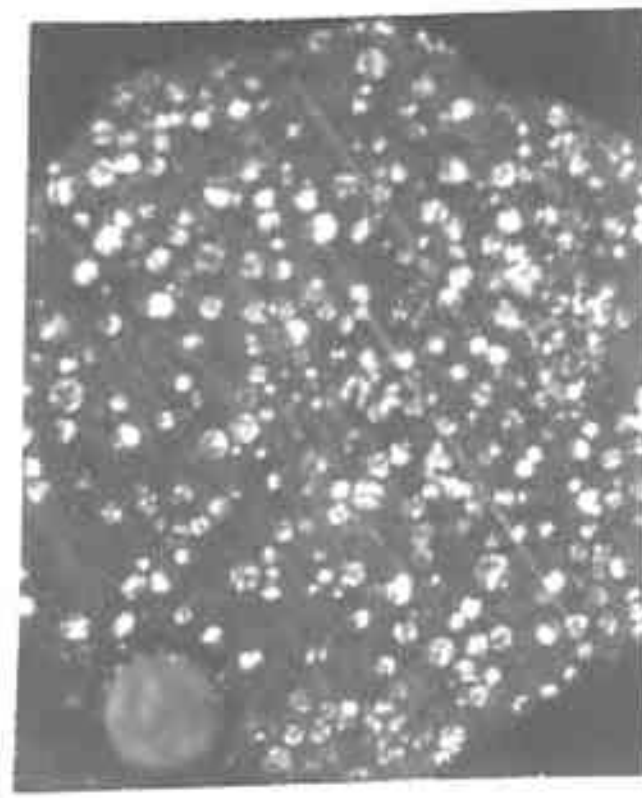


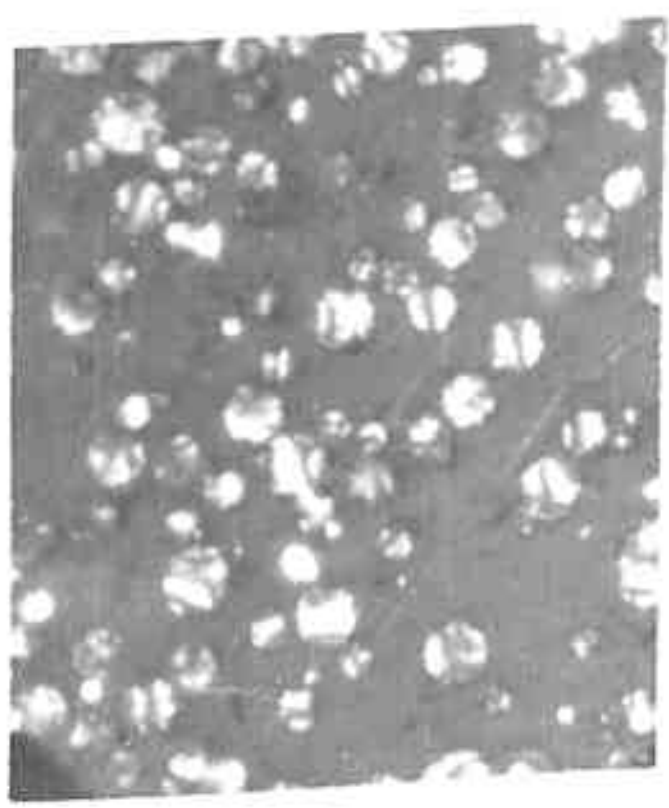
Fig 3.1 Optical micrographs of CTP-1 heat-treated at 420°C for (a) 2h, (b) 3.5h, (c) 5h and (d) 7h at a magnification of 400.



(a)

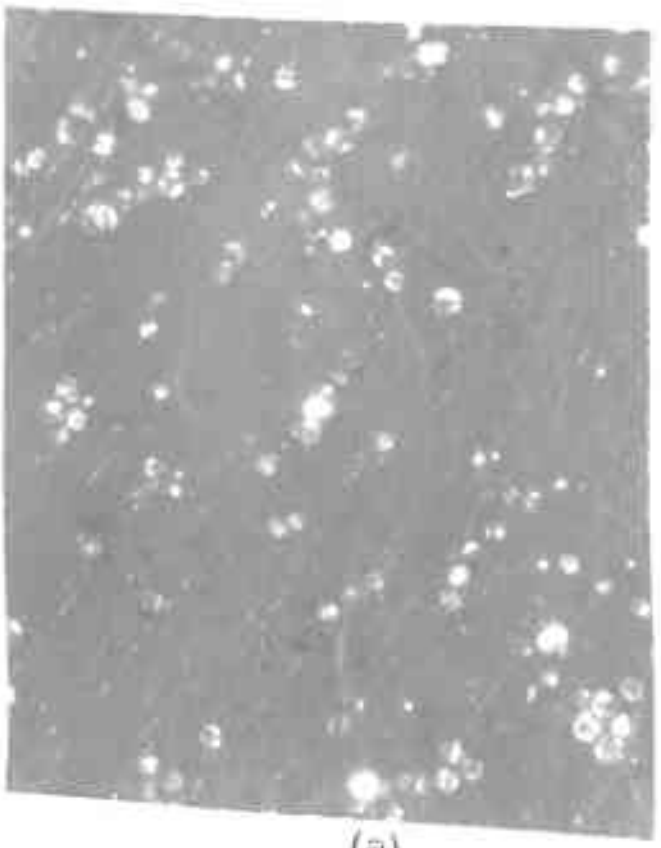


(b)

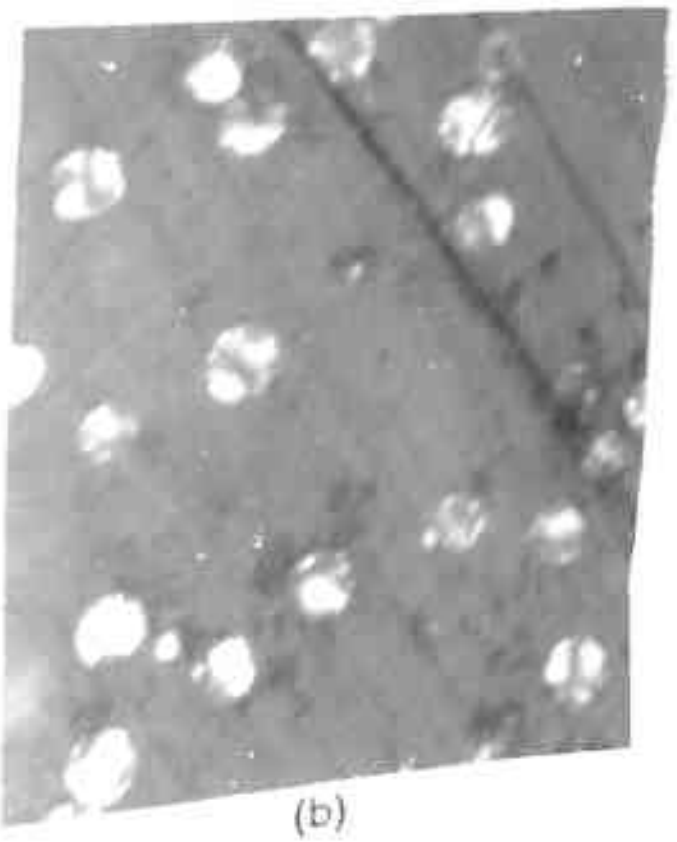


(c)

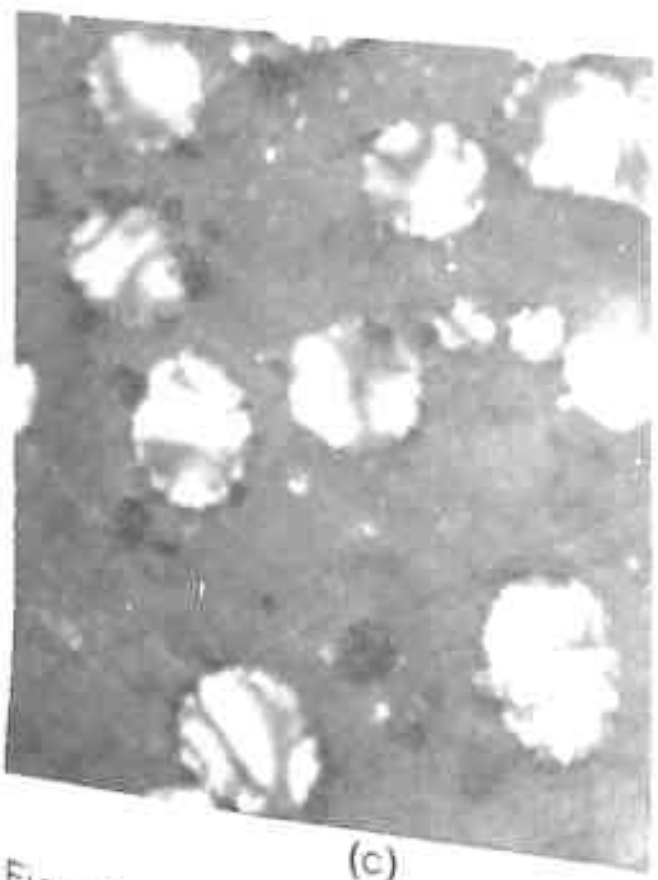
Fig 3.2 Optical micrographs of CTP-2 heat-treated at 420°C for (a) 2h, (b) 3h and (c) 5h at a magnification of 400.



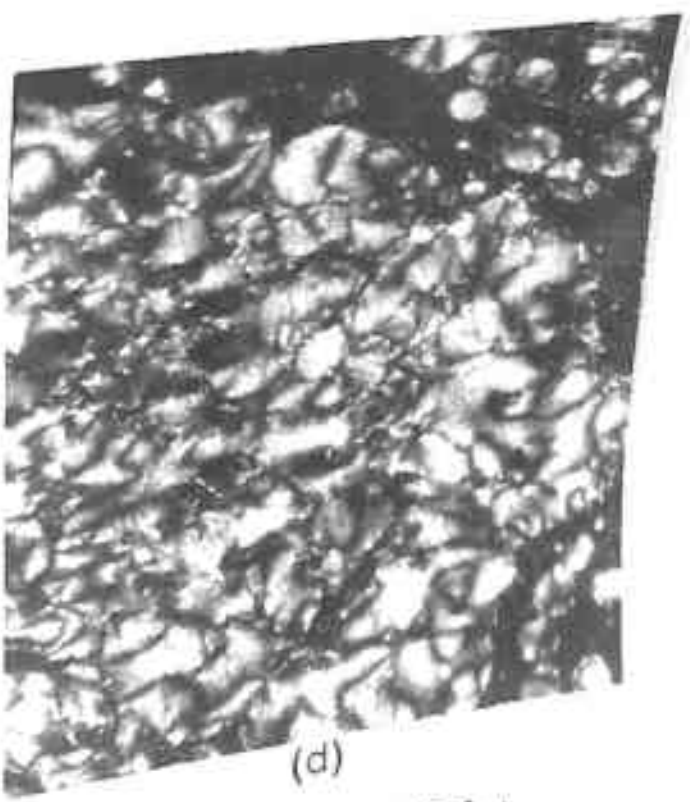
(a)



(b)



(c)



(d)

Fig 3.3 Optical micrographs of CTP-3 heat-treated at 420°C for (a) 1h, (b) 1 5h, (c & d) 3h, at a magnification of 400.

spherical mesophase. However, the increase in mesophase size (diameter) with soaking time is dependent upon the QI content in the precursor pitch. This is clearly seen from Fig.3.4 showing the curves of mean size of mesophase spherules versus soaking time at the HTT of 420°C for three coal tar pitches. It is interesting to note from Table 3.4 that whereas in the case of CTP-3, having a QI content of 0.5%, the mean size of the spherules rises as high as 24.2 μm for a heat-treatment period of 3h, it reaches a value of only 12.8 μm for CTP-1 having a QI content of 6.5%, even after 7h of the heat-treatment. For CTP-2, having a QI content of 3.3%, however, the mean size of the spherules is found to be 9.1 μm for a heat-treatment period of 5h. These observations can be attributed to the presence of primary-QI particles in the original pitches, which inhibit the coalescence and growth of mesophase spherules.

3.3 PREPARATION OF MONOLITHIC CARBON FROM MESOPHASE POWDERS

It is seen in the preceding subsection, that the in some cases of heat-treatment of coal tar pitches, in addition to mesophase spheres, some non-spherical mesophase is also formed, which is not desirable for producing high density - isotropic carbons. Thus for the purpose of development of monolithic carbon from mesophase spherules, the mesophase pitch obtained by heat-treatment of CTP-3 for 1.5 h (Expt.9 of study discussed in Section 3.2) was selected. Fig.3.5 shows the plots of differential (histogram) and cumulative frequencies of the mesophase spherules

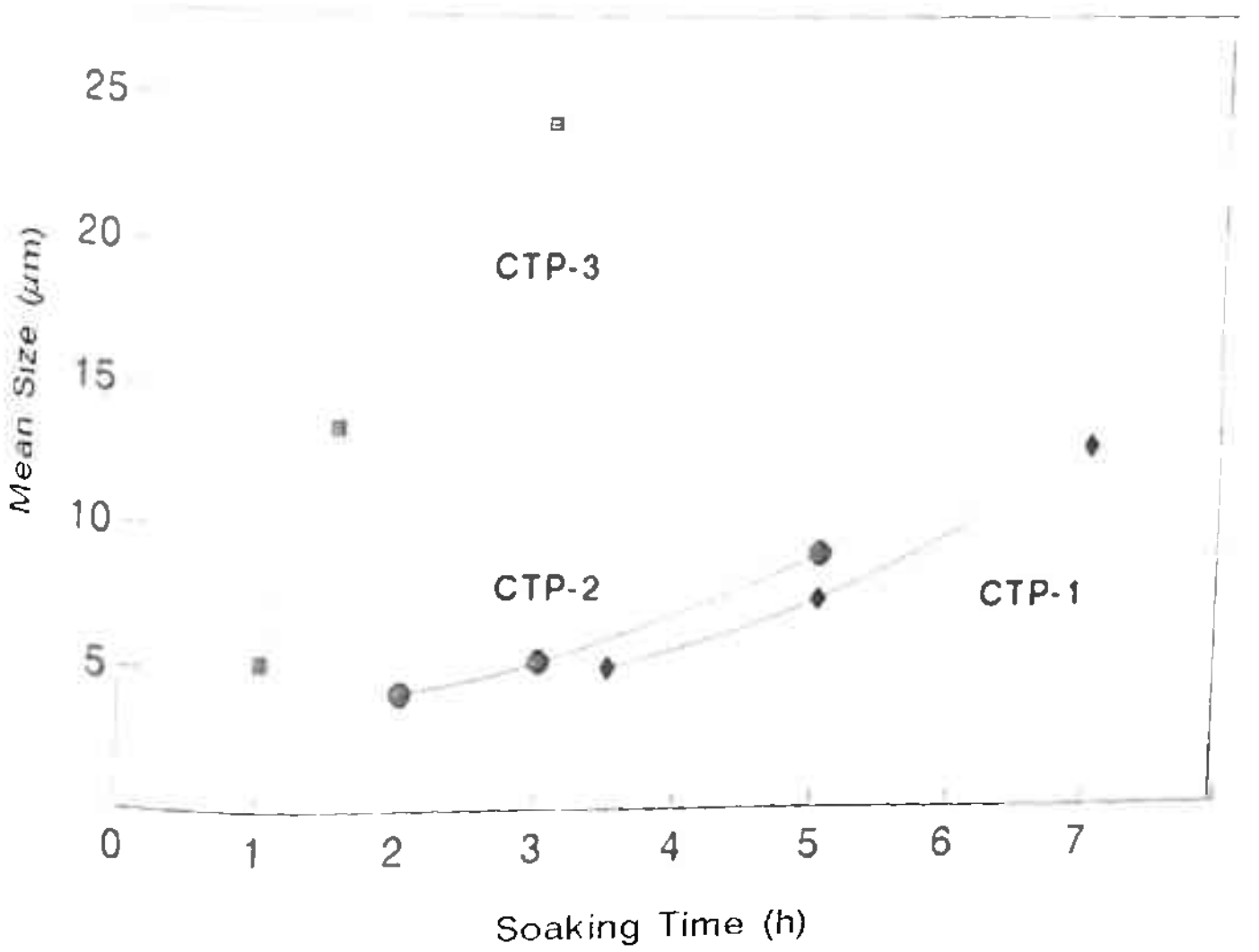


Fig 3.4 Mean size (dia) of the mesophase spherules formed in the three coal tar pitches as a function of soaking time at 420°C.

TABLE 3.4

SIZE OF MESOPHASE SPHERULES IN THE VARIOUS HEAT-TREATED (MESOPHASE) PITCHES

Expt. No.	Precursor Pitch	Soaking Time (h) at 420 C	Size of Mesophase Spherules		
			Predominant Range	Median	Mean
1.	CTP-1	2.0	--	--	--
2.	CTP-1	3.5	3.8- 7.5	5.0	5.1
3.	CTP-1	5.0	3.8-13.8	6.1	7.5
4.	CTP-1	7.0	6.3-21.3	10.8	12.8
5.	CTP-2	2.0	1.9- 6.9	3.6	4.2
6.	CTP-2	3.0	3.1- 8.1	4.6	5.3
7.	CTP-2	5.0	3.8-16.3	7.2	9.1
8.	CTP-3	1.0	1.9- 8.1	4.4	5.2
9.	CTP-3	1.5	6.3-21.3	12.3	13.5
10.	CTP-3	3.0	7.5-35.0	22.3	24.2

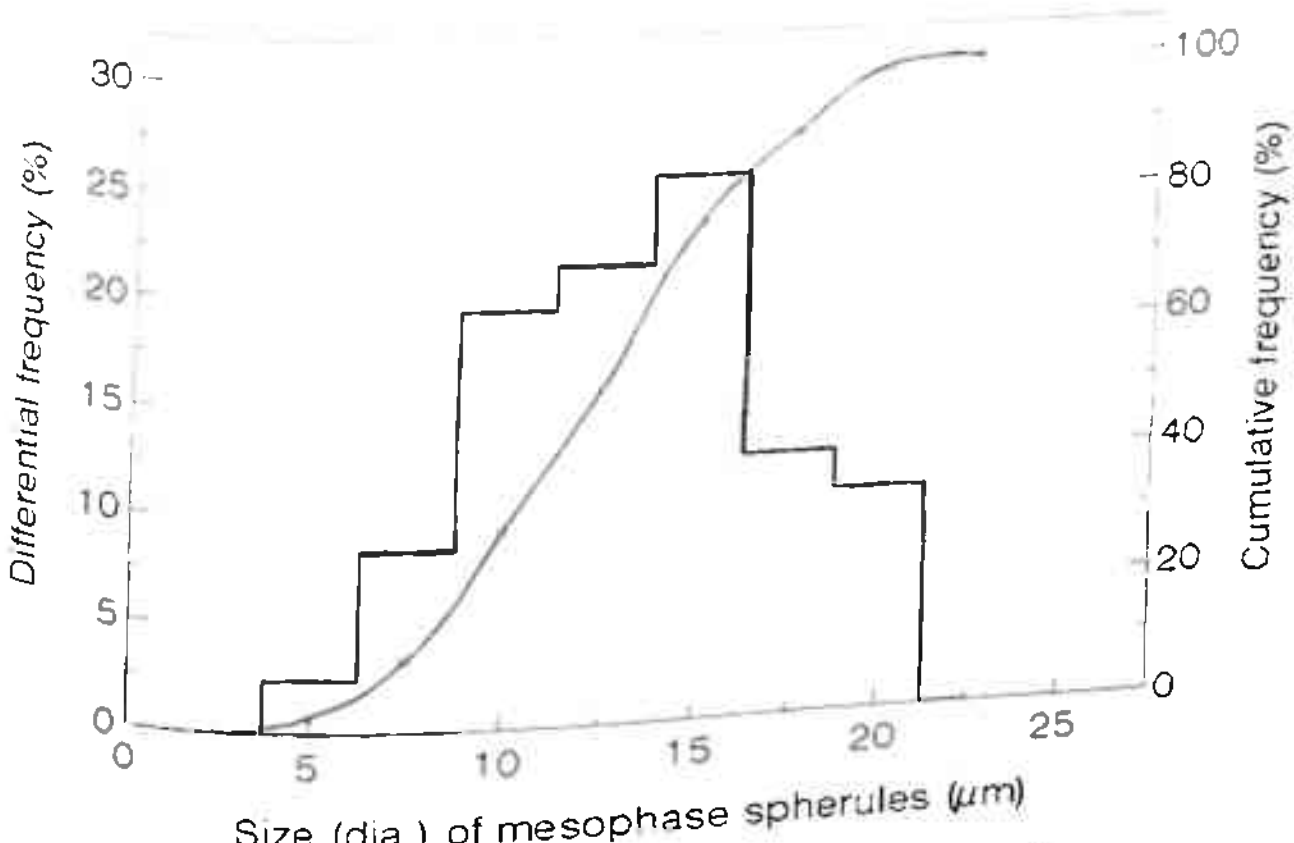


Fig 3.5 Differential (histogram) and cumulative frequencies of the mesophase spherules formed by heat-treatment of CTP-3 (QI=0.5%) at 420° C for 1.5 h, as a function of their size.

formed in this pitch versus their size. It is seen from this figure that the size of these spherules predominantly lies in the range of 6-21 μm with an average value of 13.5 μm. To separate mesophase spherules from the isotropic pitch matrix, the heat-treated (mesophase) pitch was extracted with different solvents, namely, quinoline, toluene and tar oil in separate lots. The mesophase pitch and solvents were taken in the ratio of 1:10. The quinoline insolubles were washed with toluene and then vacuum dried at 110°C. The resulting mesophase powder was called MP-QI. The toluene insolubles were also vacuum-dried at 110°C and the mesophase powder, so obtained, was named as MP-T. This mesophase powder MP-T was then calcined at 300 and 350°C, in parts, for a soaking period of 30 minutes each, in separate lots, and the resulting mesophase powders were named as MP-T1 and MP-T2, respectively. The third set of insolubles, i.e., tar oil insolubles were washed with toluene, and then vacuum-dried at 110°C to obtain another batch of mesophase powder named MP-TO.

All the batches of mesophase powders, after being classified (sieved through 400 B.S. mesh) were moulded into rectangular plates of 60 mm x 20 mm x 4 mm size using a conventional hydraulic press. The green plates, after characterisation, were carbonised to 950°C according to the procedure given in Section 2.6 and the resulting carbonised plates were characterised with respect to the various parameters described in Section 2.9.

3.3.1 MONOLITHIC CARBON FROM QUINOLINE INSOLUBLES

The mesophase powder obtained as quinoline insolubles (MP-Q) of

the mesophase pitch has a toluene insoluble content of 100% and volatile matter content of 6.2%, as seen from table 3.5. Thus there are no wetting and binding components present in this mesophase powder. As expected from these characteristics, an attempt to make a product from this powder could not be successful. Such mesophase powder is therefore, not suitable for the purpose of making a monolithic carbon. In other words, quinoline can not be used for the solvent extraction of a mesophase pitch to obtain the mesophase powder for the production of monolithic carbon.

3.3.2 MONOLITHIC CARBON FROM TOLUENE INSOLUBLES

Table 3.6 shows the characteristics of mesophase powder obtained as toluene insolubles, with and without calcination. It is seen from this table that the mesophase powder MP-T has a volatile matter of 13.2% with QI and TI contents of 42.9 and 99.2%, respectively. Further, the mesophase powders MP-T1 and MP-T2, obtained by calcination of MP-T at 300 and 350°C, respectively, contain volatile matter of 10.6 and 10.1%, quinoline insolubles of 55.3 and 70.0% and toluene insolubles of 99.4 and 99.5%, respectively.

The mesophase powder MP-T, which originally had a QI content of 42.9%, on calcination to 300 and 350°C undergoes polymerization and condensation reactions, thereby resulting in an increase in the QI content to 55.3 and 70.0% at the above-said temperatures, respectively. The calcination temperature is restricted to 350°C because the MP-T contains binder content of 56.3% which seems to be high enough to allow coalescence of mesophase

TABLE 3.5

CHARACTERISTICS OF MESOPHASE POWDER OBTAINED AS QUINOLINE INSOLUBLES

S.No.	Characteristics	MP-QI
1.	Quinoline insolubles	100 %
2.	Toluene insolubles	100 %
3.	Beta-resins content	0 %
4.	Volatile matter content	6.2 %

TABLE 3.6

CHARACTERISTICS OF MESOPHASE POWDER OBTAINED AS TOLUENE INSOLUBLES

S.No.	Characteristic	MP-T	MP-T1	MP-T2
1.	Calcination Temperature (°C)	--	300	350
	Time (min)	--	30	30
2	Quinoline insolubles (%)	42.9	55.3	70.0
3	Toluene insolubles (%)	99.2	99.4	99.5
4	Beta-resins content (%)	56.3	44.1	29.5
5	Volatile matter content (%)	13.2	10.6	10.1

spherules if heated above 350°C and might result in undesirable non spherical mesophase.

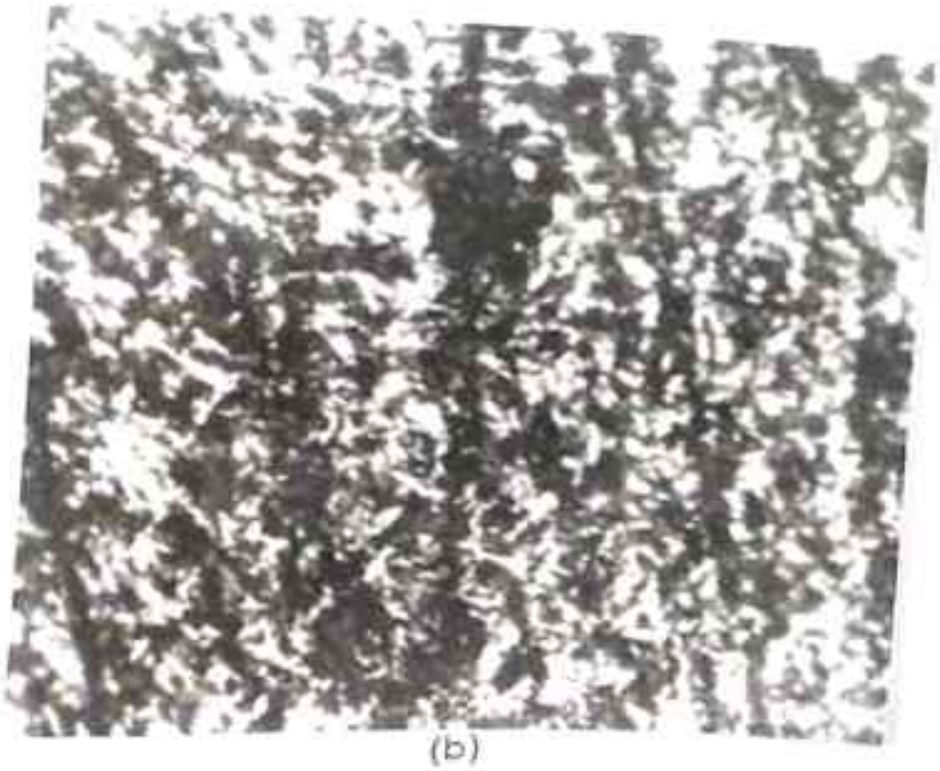
Compaction of all these three batches of mesophase powders gave good green plates but their carbonization resulted in fused carbon plates of little use. It is interesting to see that MP-T1 and MP-T2 contain volatile matter of only 10.6 and 10.1%, respectively, and one can expect to get good carbon products based on these powders as raw materials. But the swelling of the carbon plates suggests that the beta-resins (which act as the binding component) contents of 56.3, 44.1 and 29.5% in these mesophase powders are too high to yield good carbon products.

Further it is seen from the optical micrographs of MP-T, MP-T1 and MP-T2 based carbonised plates shown in Fig.3.6 that the optical texture of the plates changes from fine grained mosaic at green stage to granular flow at carbonised stage. This change in microstructure suggests that during carbonization, more of the polymerisation and condensation reactions take place which probably also lead to the fision of mesophase spheres. Thus, toluene is not suitable as a solvent for the extraction of mesophase spherules out of a mesophase pitch for the purpose of production of monolithic carbons.

3.3.3 MONOLITHIC CARBON FROM TAR OIL INSOLUBLES

Mesophase powder obtained as tar oil insolubles (MP-TO) of heat-treated pitch (yield=23%) contains a volatile matter of 9.8% with quinoline and toluene insoluble contents of 86.2 and 99.4%, respectively, as given in Table 3.7. The plates made from the tar

(a)



(b)

Fig 3.6 Optical micrographs of carbonised plates (HTT=950°C) based on
(a) Toluene insolubles cacined at 300°C
(b) Toluene insolubles calcined at 350°C
at magnification of $\frac{100}{71}$

TABLE 3.7

CHARACTERISTICS OF MESOPHASE POWDERS OBTAINED AS TAR OIL INSOLUBLES

S.No.	Characteristic	Value
1.	Yield	23.0 %
2.	Quinoline insolubles	86.2 %
3.	Toluene insolubles	99.4 %
4.	Beta-Resin content	13.2 %
5.	Volatile matter content	9.8 %

oil insoluble powder were subjected to heat-treated to 950°C. The characteristics of green and carbonised plates are given in Table 3.8. It is seen from this table that the green plates possessing an apparent density of 1.22 g cm^{-3} undergo a weight loss of 10.6% accompanied with a volume shrinkage of 32.0%, thereby resulting in an increase in the apparent density to 1.58 g cm^{-3} in the carbonised plates. These plates possess a bending strength of 52 MPa and a Shore hardness of 85. The coefficient of thermal expansion in the directions $\parallel$ and $\perp$ to the direction of moulding are found to be 7.2 and 7.1 x 10^{-6}°K^{-1} respectively. The anisotropy ratio, thus comes out to be 1.01, revealing isotropy in the product. Fig.3.7, showing the optical micrograph of the carbonised plate reveals that the product is homogeneous, fine-textured and isotropic.

The above results show that the extraction of a heat-treated pitch (containing mesophase spherules) with a tar oil yields a mesophase powder having sufficient amount of binding components, capable of resulting in isotropic carbons. It is may be noted that a very low QI content of 0.5% in the precursor coal tar pitch leads to mesophase spherules (mesocarbon microbeads) of large size due to ease of coalescence of the mesophase spherules in the presence of only few QI particles, besides resulting in a low yield of 23% of the mesocarbon microbeads.

Further, characteristics of the plates, particularly the bending strength and apparent density are also not very good. It appears that the mean size of 13.5 μm of microbeads is not suitable to result in high density - high strength - isotropic graphite. It may also be mentioned that in order to restrict the size

TABLE 3.8

CHARACTERISTICS OF THE CARBON PLATES HEAT-TREATED TO 950°C

S.No.	Characteristics	Value
1.	App. green density	1.22 g cm^{-3}
2.	App. baked density	1.58 g cm^{-3}
3.	Specific gravity	1.61
4.	Weight loss	10.6 %
5.	Volume shrinkage	32.0 %
6.	Linear shrinkage	12.2 %
7.	Bending strength	62 MPa
8.	Young's modulus	13 GPa
9.	Coeff. of thermal expansion ($x10^{-6} K^{-1}$)	7.2 (∥) 7.1 (⊥)
10.	Anisotropy ratio	1.01
11.	Shore hardness	85
12.	Electrical resistivity	9.2 mOhm cm
13.	Open porosity	9.0 %

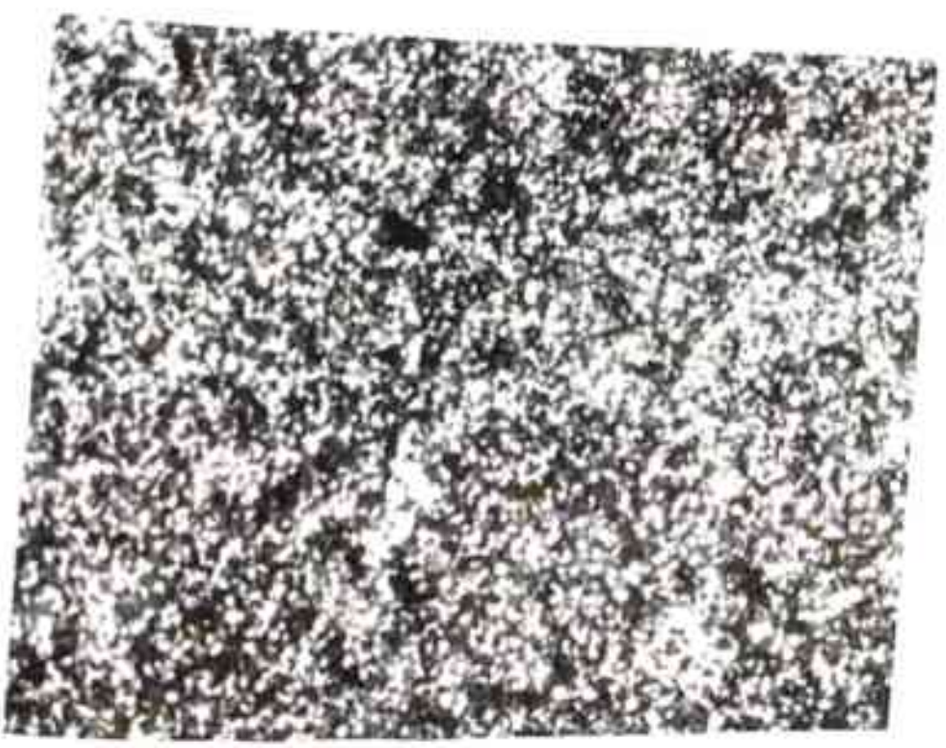


Fig 3.7 Optical micrograph of carbonised plates based on mesophase powder - TO at HTT of 950°C at a magnification of 100.

of mesophase spherules to a lesser value in this precursor pitch, the yield is going likely to be reduced significantly, thereby making the process economically unviable. Thus to use this procedure as an economic production process, the yield of microbeads as well as characteristics of the isotropic product need to be improved. The work was continued by using coal tar pitches containing some quinoline insolubles (3.3 - 9.2%) as described in the following section.

3.4 MONOLITHIC CARBONS FROM COAL TAR PITCH PRECURSORS HAVING DIFFERENT CONTENTS OF QUINOLINE INSOLUBLES (UPTO 9.2%)

In the preceding subsection, it has been shown that the mesophase powder obtained as the tar oil insolubles of the heat-treated pitch can be used for the production of isotropic graphite. However, the yield of the mesocarbon microbeads from the heat-treatment of a coal tar pitch containing QI of only 0.5% is very low (23%). Further, in the previous Section 3.2, it has been shown that the concentration of mesophase spherules of a given size range in the heat-treated pitch increases as the primary quinoline insoluble content in the precursor coal tar pitch increases. Thus, to get a better yield of mesocarbon microbeads of the same size range, an attempt was made towards the production of monolithic carbons from coal tar pitches containing comparatively higher contents of quinoline insolubles. For this purpose, three coal tar pitches containing 3.3, 6.5 and 9.2% of quinoline insolubles were selected and subjected to suitable heat-treat-

ments to generate mesophase spherules having a mean size of about 5 μm. It is important to mention here that in case of coal tar pitches having quinoline insolubles, the size of the spherical mesophase remains controlled and higher heat-treatments result only undesirable non-spherical mesophase as also discussed in Section 3.2.2. The heat-treated pitches were subjected to solvent extraction using a suitable tar oil to obtain the mesocarbon microbeads which were hot moulded into rectangular plates and carbonised to 950°C. The carbonised plates were then finally characterised w.r.t. various parameters, the results of which are discussed in the subsection below.

3.4.1 MONOLITHIC CARBONS FROM COAL TAR PITCH CONTAINING 3.3% OF QUINOLINE INSOLUBLES

The mesophase pitch obtained by heat-treatment at 420°C for 3 h of a coal tar pitch containing 3.3% of QI (Table 3.4, Expt.6 of Section 3.2) was selected for this purpose. Quinoline insolubles of the precursor pitch were separated and observed under scanning electron microscope (Fig.3.8). It is seen from the micrograph of the quinoline insolubles that these particles have essentially a spherical shape, with a size predominantly below 1 μm. The characteristics of this mesophase pitch along with those of the precursor coal tar pitch and the mesocarbon microbeads are summarised in Table 3.9. As can be seen from this Table this mesophase pitch was found to contain 40 wt.% of the mesophase spherules. The plots of differential (histogram) and cumulative frequencies of the mesophase spherules versus their size, shown

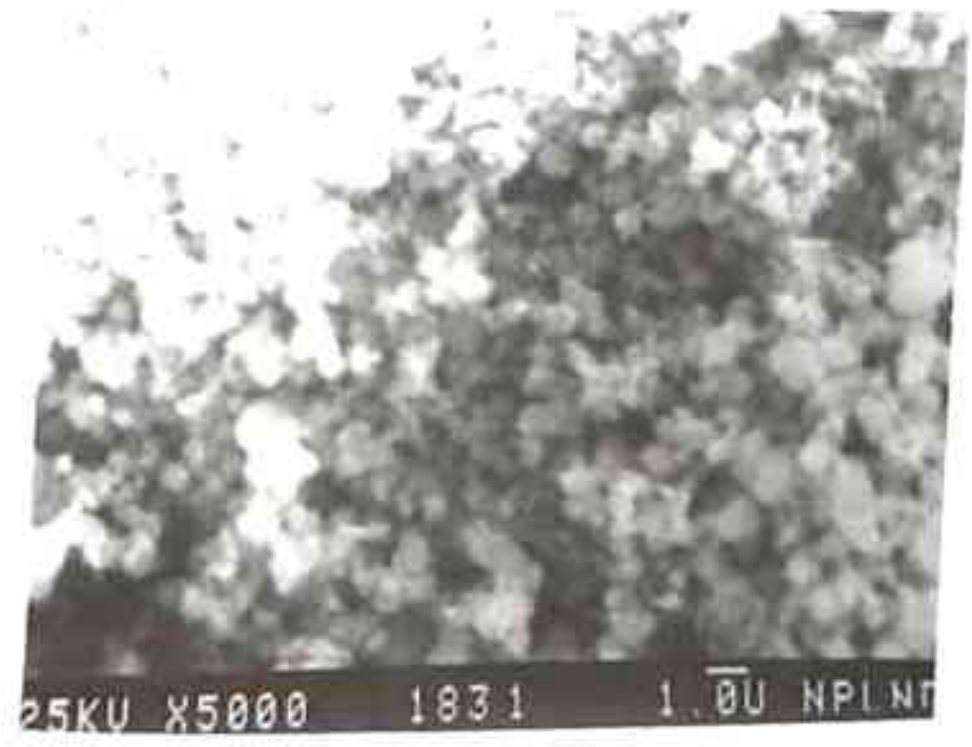


Fig 3.8 Scanning electron micrograph of quinoline insolubles separated from the precursor coal tar pitch (QI=3.3%)

TABLE 3.9

CHARACTERISTICS OF COAL TAR PITCH (QI=3.3%), MESOPHASE PITCH AND MESOCARBON MICROBEADS

S. No.	CHARACTERISTICS	COAL TAR PITCH	MESOPHASE PITCH	MESOCARBON MICROBEADS
1.	Softening point C	79	--	--
2.	Heat-treatment/ Extraction yield (%)	--	84.0	40.0
3.	Quinoline insolubles (%)	3.3	29.4	93.0
4.	Toluene insolubles (%)	20.7	54.7	96.0
5.	Beta-resins content (%)	17.4	25.3	3.0
6.	Coking yield (%)	48.0	66.5	89.0
7.	Size of mesophase spherules			
	Predominant range (μm)	--	3-8	3-8
	Mean (Average, μm)	--	5.3	5.3
8.	Carbon (C) content (%)	--	94.8	95.3
	Hydrogen (H) content (%)	--	3.52	3.02
	Atomic C/H ratio	--	2.26	2.65

in Fig.3.9, indicate that the size of the spherules predominantly lies in the range of about 3-8 μm. This is consistent with the SEM photograph of the MCMB shown in Fig.3.10.

Further, it is also seen from Table 3.9, that these microbeads have quinoline and toluene insoluble contents of 93 and 6%, respectively, and have a coking yield of 82% (heating rate = 00°C/h) as obtained using the thermo-gravimetric analyser. The GA curve is shown in Fig 3.11. However, this coking yield, as etermined by another test procedure (73) employing a heating ate of 200°C/h, is found to be 89%. This latter procedure gives le coking yield of the heat-treated pitch to be 66.5%, a value ignificantly lower compared to 89% obtained for the mesophase herules isolated from this heat-treated (mesophase) pitch. The gher coking yield of the MCMB compared to the heat-treated tch is in agreement with the higher atomic C/H ratio of 2.65 of ese MCMB, compared to a value of 2.26 for the heat-treated (mephase) pitch, as shown in Table 3.9.

The characteristics of MCMB-based carbon plates heateated to temperatures of 950 and 2700°C are given in Table 10. The green plates made from the microbeads show an apparent nsity of 1.25 g cm^{-3}, which increases to 1.66 g cm^{-3} on carnisation to 950°C, as is seen from Table 3.10. This increase in e apparent density on carbonisation of plates is due to an ormous volume shrinkage of 33.9% and a weight loss of only .7%, i.e. because of the dominance of volume shrinkage over ight loss. The carbonised plates (heat-treated to 950°C) have en found to have a high bending strength of 88 MPa and a Shore rdness of 95. On further heat-treatment from 950 to 2700°C, the

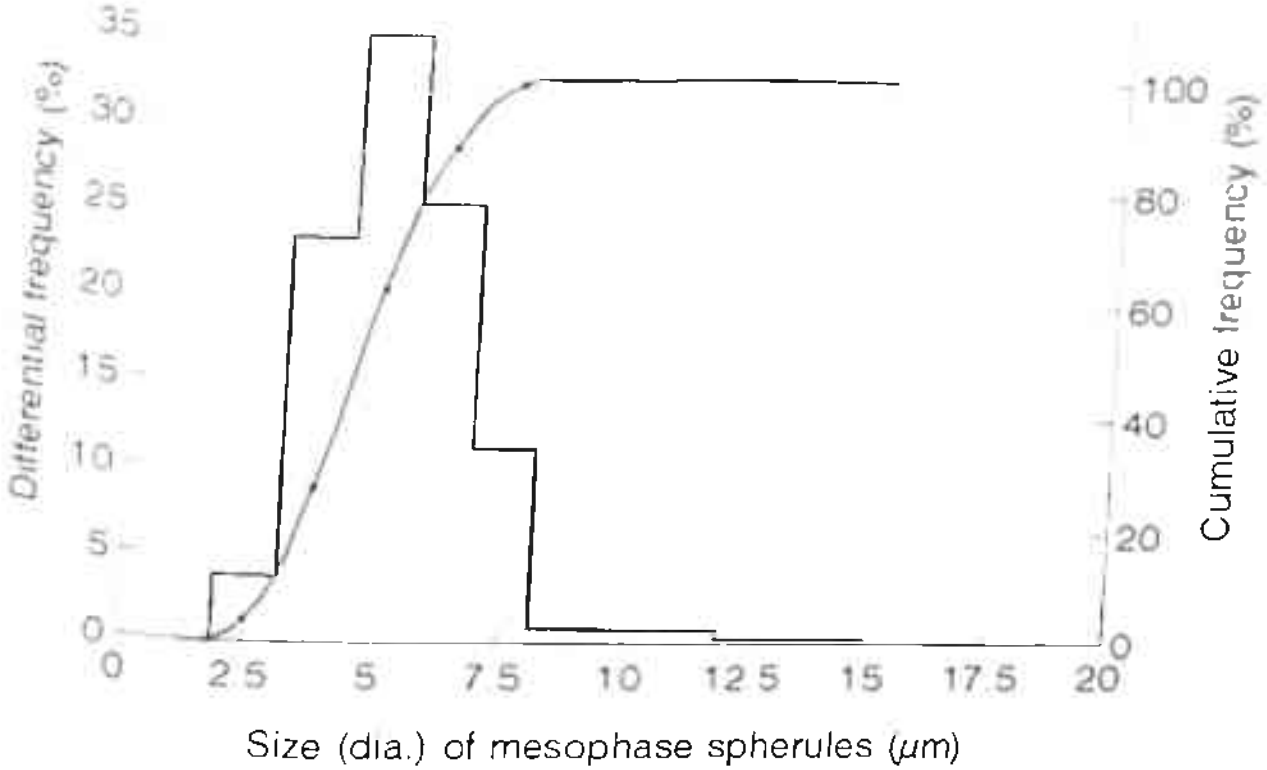


Fig. 3.9 Differential (histogram) and cumulative frequencies of the mesophase spherules formed by heat-treatment of coal tar pitch (QI=3.3%) at 420°C for 3 h, as a function of their size.

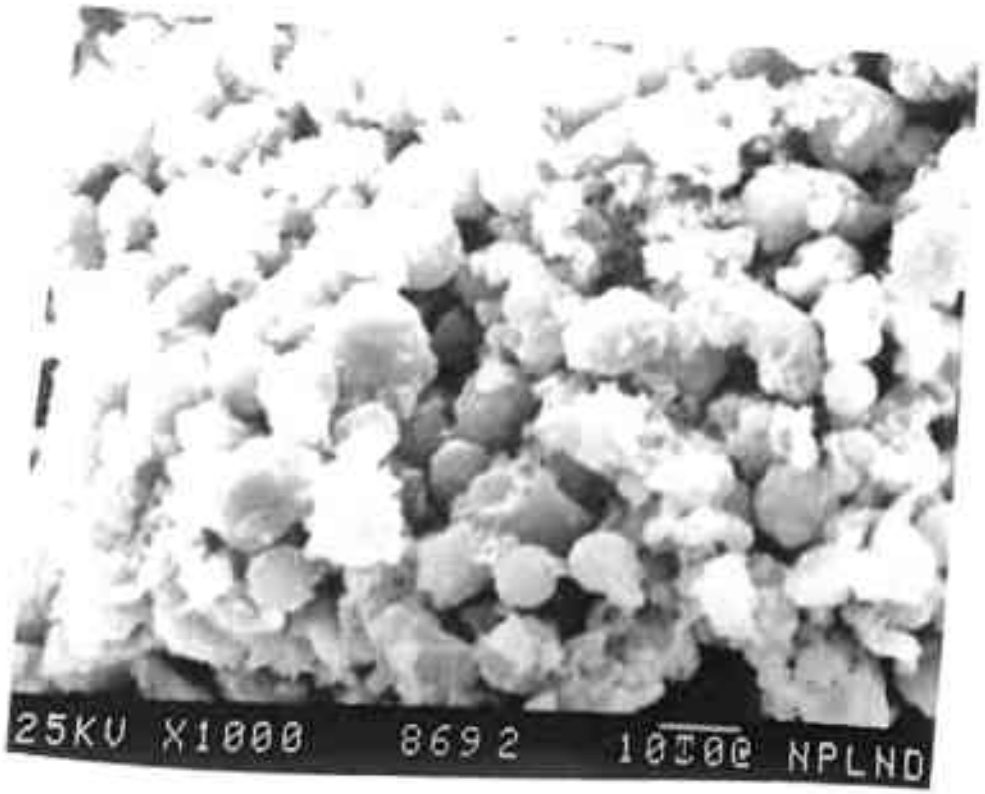


Fig 3.10 Scanning electron micrograph of mesocarbon microbeads separated from the heat-treated coal tar pitch (QI=3.3%).

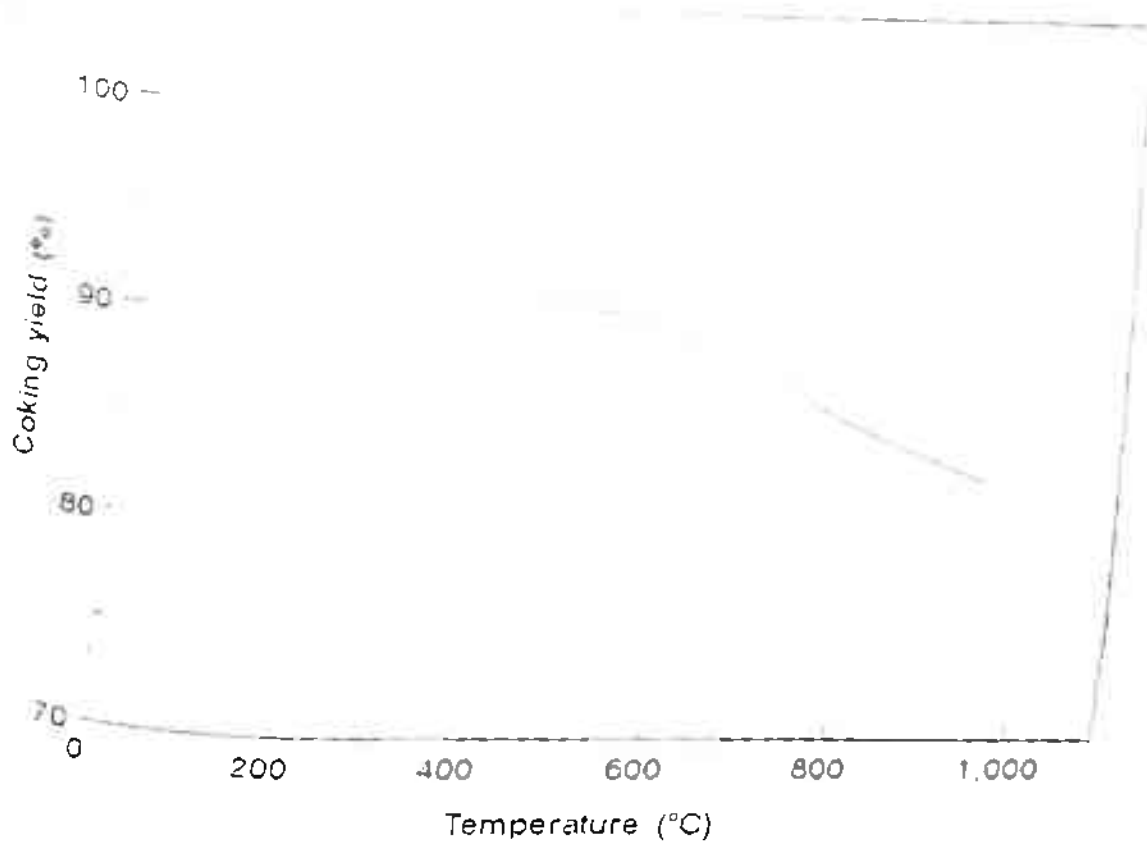


Fig 3.11 T G A curve of the mesocarbon microbeads

TABLE 3.10

CHARACTERISTICS OF CARBON PLATES (USING COAL TAR PITCH WITH 3.3% QI) HEAT-TREATED TO TEMPERATURES OF 950°C AND 2700°C

S. NO.	CHARACTERISTICS	VALUES AT HTT (°C) OF	
		950	2700
1.	Green apparent density (g cm^{-3})	1.25	1.25
2.	Apparent density (g cm^{-3})	1.66	1.85
3.	Specific gravity	1.68	1.86
4.	Weight loss (%)	13.7	20.5
5.	Volume shrinkage (%)	33.9	45.8
6.	Linear shrinkage (%)	12.7	18.6
7.	Bending strength (MPa)	88	68
8.	Young's modulus (GPa)	15.2	27.0
9.	Co. of thermal expansion ($x10^{-6}°K^{-1}$)		
	‖ to moulding direction	--	7.2
	⊥ to moulding direction	--	7.1
10.	Anisotropy ratio	--	1.01
11.	Scleroscopic hardness	95	70
12.	Electrical resistivity (mOhm cm)	6.7	2.7
13.	Open porosity (%)	7.9	14.5
14.	Crystallites parameters		
	i) d_{002} (pm)	351	336
	ii) L_c (nm)	1.59	15.8

plates show a cumulative weight loss of 20.5%, accompanied by cumulative volume and linear shrinkages, of 45.8 and 18.6%, respectively. The apparent density, in turn, increases from 1.66 g cm^{-3} at the HTT of 950° C to a value of 1.85 g cm^{-3} at 2700°C. This may again be attributed to continuing dominance of volume shrinkage over weight loss upto HTT of 2700°C.

Further, the bending strength of the plates decreases from 88.2 to 68.3 MPa by further heat-treatment from 950 to 2700°C, which may be because of the corresponding increase in the open porosity from a value of 7.9 to 14.5%, resulting from the growth of crystallites by way of removal of disorganised matter between the crystallites and from an improvement in the alignment of the crystallites. The growth of crystallites during the heat-treatment from 950 to 2700°C is clear from the increase in the value of L_c from 1.59 to 15.8 nm and decrease in the value of d_{002} spacing from 351 to 336 pm, as is seen from Table 3.10.

The Shore hardness of the plates is found to have a similar pattern as the bending strength, and accordingly decreases from a value of 95 to 70 as the HTT increases from 950 to 2700°C. The coefficient of thermal expansion (CTE) in the direction ‖ to moulding is found to be 7.1 x 10^{-6} with an anisotropy ratio (wrt CTE) of 1.01 in the graphitised sample.

The electrical resistivity is seen to have a pronounced fall from 6.7 mOhm cm at the HTT of 950°C to a value of 2.7 mOhm cm at 2700°C, which is a usual phenomenon for all polycrystalline carbons, and corresponds to the growth of crystallites constituting these carbons. Finally, the microstructure of these MCMB based monolithic carbons (shown in Fig.3.12) in both carbonised

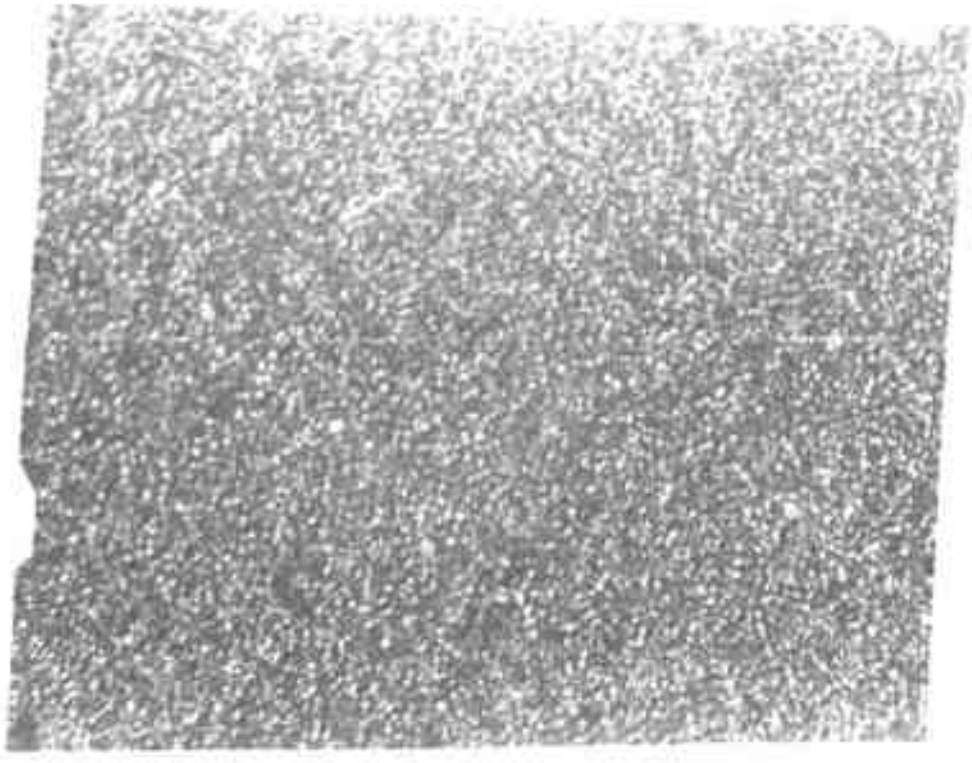


Fig 3.12 Optical micrograph of graphite plate (HTT=2700°C) based on coal tar pitch containing 3.3 % QI,at a magnification of 100.

(HTT=950°C) as well as graphitised (HTT = 2700°C) states, is found to be quite homogeneous with a fine isotropic texture.

3.4.2 MONOLITHIC CARBONS FROM COAL TAR PITCH CONTAINING 6.5% OF QUINOLINE INSOLUBLES

The mesophase pitch obtained by heat-treatment of a coal tar pitch containing 6.5% of primary quinoline insolubles at 420°C for 3.5 h (Expt.2 of Section 3.2) is found to contain mesophase spherules with mean size of about 5.1 μm. The plots of differential (histogram) and cumulative frequencies of the mesophase spherules formed in this pitch versus their size, shown in Fig.3.13, indicate the size of these spherules to be predominantly lying in the range of 3-8 μm.

Table 3.11 shows the characteristics of the precursor coal tar pitch (QI=6%), mesophase pitch and mesocarbon microbeads. Extraction of the heat-treated pitch with tar oil shows that it contains mesophase spherules to an extent of 47% by weight of it, as seen from Table 3.11. Further, it is also seen from this table that these microbeads have quinoline and toluene insoluble contents of 88.9 and 95.0%, respectively, with a coking value of 90.3% i.e. a volatile matter of 9.7%. The atomic C/H ratio of the microbeads is 2.68 as compared to a value of 2.26 for the heat-treated (mesophase) pitch.

The green plates made from the microbeads show an apparent density of 1.26 g cm^{-3}, which increases to 1.63 g cm^{-3} on carbonisation to 950°C, and further to 1.80 g cm^{-3} on graphitisation to 2700°C as is seen from Table 3.12. These plates undergo a

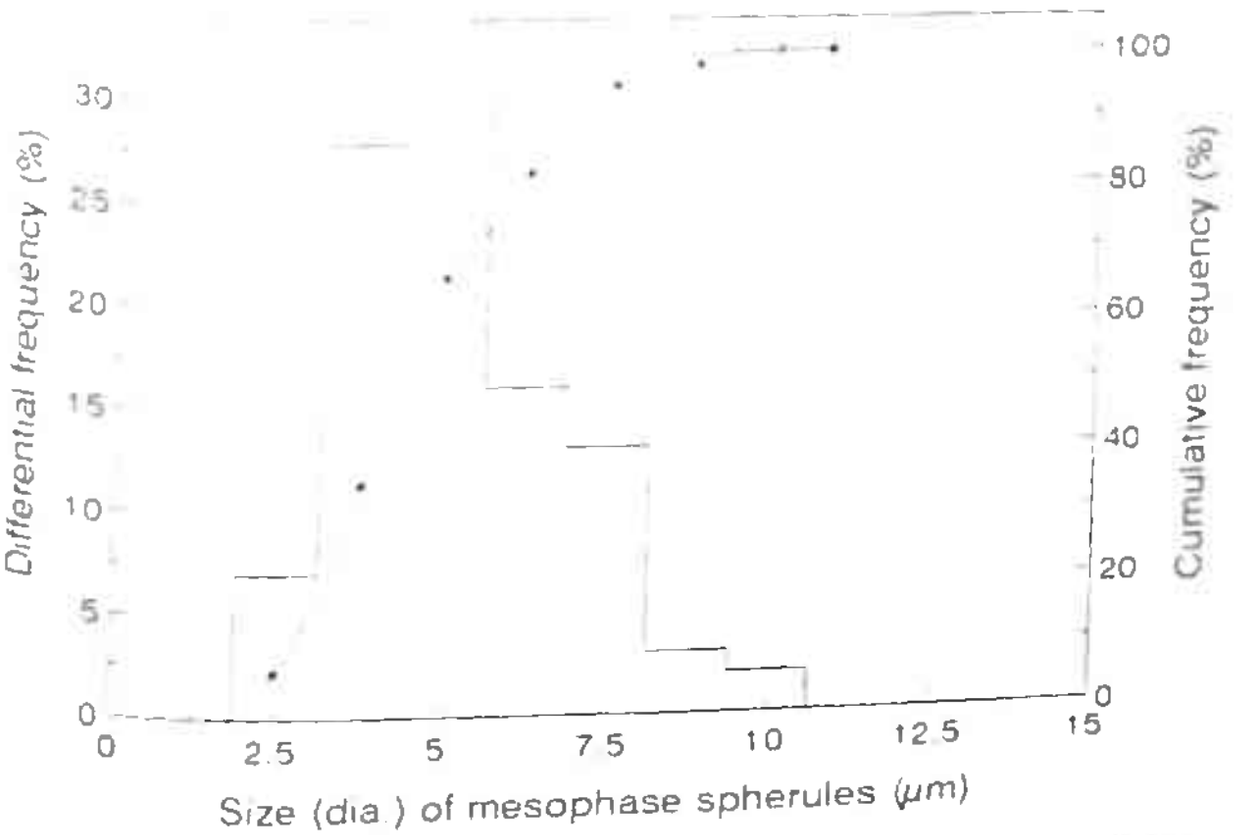


Fig.3.13 Differential (histogram) and cumulative frequencies of mesophase spherules formed in CTP-1 (QI=6.5%) by heat-treatment at 420°C for 3.5 h, as a function of their size.

TABLE 3.11

CHARACTERISTICS OF COAL TAR PITCH (QI=6.5%), MESOPHASE PITCH AND MESOCARBON MICROBEADS

S. No.	CHARACTERISTICS	COAL TAR PITCH	MESOPHASE PITCH	MESOCARBON MICROBEADS
1.	Softening point C	81	--	--
2.	Heat-treatment/ Extraction yield (%)	--	78.0	47.0
3.	Quinoline insolubles (%)	6.5	34.0	88.9
4.	Toluene insolubles (%)	21.2	62.2	95.0
5.	Beta-resins content (%)	14.7	28.2	6.1
6.	Coking yield (%)	48.6	72.2	90.3
7.	Specific gravity	1.28	1.31	--
8.	Size of mesophase spherules Predominant range (μm) Mean (Average, μm)	-- --	3-8 5.1	3-8 5.1
9.	Carbon (C) content (%) Hydrogen (H) content (%) Atomic C/H ratio	-- -- --	95.4 3.58 2.26	95.8 3.0 2.68

TABLE 3.12

CHARACTERISTICS OF CARBON PLATES (USING COAL TAR PITCH WITH 6.5% QI) HEAT-TREATED TO TEMPERATURES OF 950°C AND 2700°C

S. NO.	CHARACTERISTICS	VALUE AT HTT (°C) OF	
		950	2700
1.	App. green density (g cm^{-3})	1.26	1.26
2.	App. baked density (g cm^{-3})	1.63	1.80
3.	Specific gravity	1.65	1.82
4.	Weight loss (%)	11.8	18.1
5.	Volume shrinkage (%)	30.9	42.1
6.	Linear shrinkage (%)	10.3	16.2
7.	Bending strength (MPa)	73	55
8.	Young's modulus (GPa)	14.1	21.2
9.	Coeff. of thermal expansion ($\times 10^{-6} °K^{-1}$)	--	7.1
	$\perp$	--	6.9
10.	Anisotropy ratio	--	1.03
11.	Scleroscopic hardness	85	66
12.	Electrical resistivity (mOhm cm)	6.9	3.0
13.	Open porosity (%)	8.7	13.9

weight loss of 11.8% and 18.1% with a volume shrinkage of 30.9% and 42.1% during heat-treatment to 950 and 2700°C respectively leading to an increase in the apparent density of the plates. These plates have been found to possess a bending strength of 73 and 55 MPa and Shore hardness of 85 and 66 at heat-treatment temperature of 950 and 2700°C. The thermal expansion coefficient of graphitised samples $\perp$ to direction of moulding shows a value of 6.9×10^{-6} with an anisotropy ratio of 1.03. The optical micrographs of these plates, shown in Fig.3.14, reveal that these plates also possess homogeneous, isotropic and fine microstructure.

3.4.3 MONOLITHIC CARBONS FROM COAL TAR PITCH CONTAINING 9.2% OF QUINOLINE INSOLUBLES

In the previous Sections 3.4.1 and 3.4.2, it has been shown that mesophase pitches obtained by heat-treatment of coal tar pitches containing upto 6.5% primary quinoline insolubles have proved to be successful for the purpose of producing monolithic carbons. With a view to continue with the development of monolithic carbon from coal tar pitches containing (still high) primary quinoline insolubles, a coal tar pitch having QI content of 9.2% and possessing characteristics shown in Table 3.13 was subjected to heat-treatment at 420°C for 4 h to generate mesophase spheres in it. The plots of differential (histogram) and cumulative frequencies of the mesophase spherules formed in this pitch versus their size are plotted in Fig.3.15. It is seen that the size of these spherules predominantly lies in the range of 3-8 μm with a mean

Fig 3.14 Optical micrograph of graphite plate (HTT=2700°C) based on coal tar pitch containing 6.5 % QI, at a magnification of 100.

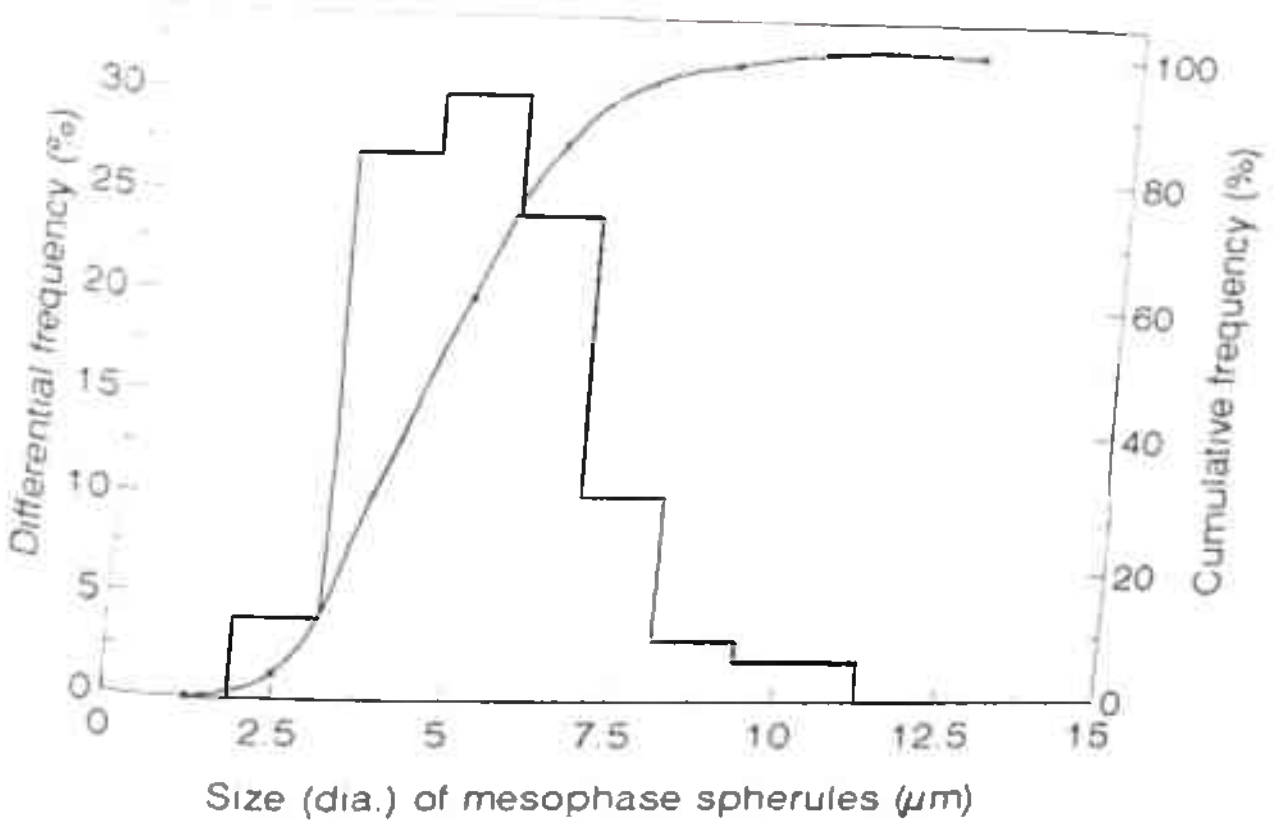


Fig 3.15 Differential (histogram) and cumulative frequencies of the mesophase spherules formed by heat-treatment of CTP (QI=9.2%) at 420°C for 4 h, as a function of their size.

TABLE 3.13

CHARACTERISTICS OF COAL TAR PITCH (QI=9.2%), MESOPHASE PITCH AND MESOCARBON MICROBEADS

S. No.	CHARACTERISTICS	COAL TAR PITCH	MESOPHASE PITCH	MESOCARBON MICROBEADS
1.	Softening point (C)	82	--	--
2.	Heat-treatment/ Extraction yield (%)	--	72.0	52.0
3.	Quinoline insolubles (%)	9.2	42.0	84.0
4.	Toluene insolubles (%)	26.4	69.0	98.0
5.	Beta-resins (%)	17.2	27.0	14.0
6.	Coking yield (%)	49.0	78.7	90.5
7.	Specific gravity	1.276	1.304	--
8.	Size of mesophase spherules Predominant range (μm) Mean (Average, μm)	-- --	3-8 5.3	3-8 5.3
9.	Carbon (C) content (%) Hydrogen (H) content (%) Atomic C/H ratio	-- -- --	94.8 3.52 2.26	95.3 3.02 2.65

size of about 5.3 μm. Extraction of the heat-treated pitch with tar oil shows that it contains mesophase spherules to an extent of abour 52% by weight of it, as can be seen from in Table 3.13. Further, it is also seen from this Table that these microbeads have quinoline and toluene insoluble contents of 84 and 98% respectively, with a volatile matter content of 9.5%. The atomic C/H ratio of the microbeads is 2.65 as compared to a value of 2.26 for the heat-treated (mesophase) pitch.

The green plates made from the microbeads have an apparent density of 1.27 g cm $^{-3}$ as seen in Table 3.14, which increases to a value of 1.60 and 1.78 g cm^{-3} due to a volume shrinkage of 29.7 and 40.8% with a weight loss of 11.0 and 17.5% at HTT of 950 and 2700°C respectively. These plates have been found to have a bending strength of 70 and 49 MPa and a Shore hardness of 84 and 60 at HTT of 950 and 2700°C respectively. The coefficient of thermal expansion of 2700°C treated samples in direction ‖ to that of moulding has a value of 7.3 x 10^{-6} with an anisotropy ratio of 1.04. The optical micrograph of these plates reveals homogeneity and fine texture as shown in Fig.3.16.

3.5 COMPARISON OF THE CHARACTERISTICS OF MONOLITHIC CARBONS FROM COAL TAR PITCHES HAVING DIFFERENT CONTENTS OF QUINOLINE INSOLUBLES

It has been shown in Sub-sections 3.3.3-3.4.3 that mesocarbon microbeads obtained from different precursor coal tar pitches (varying in their quinoline insoluble contents) are capable of resulting in good isotropic carbon and graphite products.

TABLE 3.14

CHARACTERISTICS OF CARBON PLATES (USING COAL TAR PITCH WITH 9.2% QI) HEAT-TREATED TO TEMPERATURES OF 950°C AND 2700°C

S. NO.	CHARACTERISTICS	VALUE AT HTT (°C) OF	
		950	2700
1.	App. green density (g cm^{-3})	1.27	1.27
2.	App. baked density (g cm^{-3})	1.60	1.78
3.	Specific gravity	1.62	1.80
4.	Weight loss (%)	11.4	17.5
5.	Volume shrinkage (%)	29.7	40.8
6.	Linear shrinkage (%)	10.1	16.1
7.	Bending strength (MPa)	70	49
8.	Young's modulus (GPa)	12.8	20.0
9.	Co. of thermal expansion ($x10^{-6}°K^{-1}$) ‖ to moulding direction ⊥ to moulding direction	-- --	7.3 7.0
10.	Anisotropy ratio	--	1.04
11.	Scleroscopic hardness	84	60
12.	Electrical resistivity (mOhm cm)	7.0	3.3
13.	Open porosity (%)	9.2	15.0

Fig 3.16 Optical micrograph of graphite plate (HTT=2700°C) based on coal tar pitch containing 9.2% QI, at a magnification of 100.

3.5.1 EFFECT OF QI CONTENT ON YIELD OF MCMB

A comparison of the yields of mesocarbon microbeads from coal tar pitches having QI contents from 0.5 to 9.2% by weight (Table 3.15) shows that the coal tar pitch containing 0.5% of QI results in only 23% (by wt.) of microbeads, that too with a mean size of about 13.5 μm, whereas the coal tar pitches containing 3.3%, 6.5% and 9.2% of QI lead to 40%, 47% and 52% of the mesocarbon microbeads with an average size of about 5 μm, respectively. Thus, the yield of the microbeads increases with the increase in the content of QI in the precursor pitch, the variation of which is shown in Fig 3.17. It is worth-noting here that initially a small increase in the QI content from 0.5% to 3.3% leads to a large increase in the yield of the MCMB (from a value of 23% to 40%). Thereafter, further increase in the QI content to 6.5% and 9.2% increases this yield to much less enhanced values of 47% and 52%, respectively.

Further, it may be noted that a very low QI content of 0.5% in the precursor coal tar pitch leads to mesophase spherules of large size due to ease of coalescence of the mesophase spherules in the presence of only few (0.5% by wt.) QI particles, besides resulting in a low yield of 23% of the mesocarbon microbeads. This high size of MCMB is not suitable for the production of fine grained - high density - high strength - isotropic graphite. It may be mentioned here that if the size of mesophase spherules is restricted to around 5 μm in 0.5% QI precursor pitch, the yield will be reduced significantly, which will have an adverse effect on the commercial viability of the process.

Heat-treatment conditions
Temperature (°C)
Time (h)
Yield (%)

2. Yield of MCMB (%)

3. Initial QI content in HT-pitch (%)

4. Initial QI content in MCMB (%)

5. Size of mesophase spherules
Predominant range (μm)
Mean (Average, μm)

6. Weight loss (%)

7. Volume shrinkage (%)

8. App. green density (g cm^{-3})

9. Density amplification factor

10. Expected baked density (g cm^{-3})

11. Actual baked density (g cm^{-3})

420 1.5 80	420 3 84	420 3.5 78	420 4 72
23	40	47	52
0.6	3.9	8.33	12.8
2.7	9.8	17.7	24.6
6-21 13.5	3-8 5.3	3-8 5.1	3-8 5.3
10.6	13.7	11.8	11.2
32.0	33.7	30.9	29.7
1.22	1.25	1.26	1.27
1.315	1.302	1.276	1.266
1.60	1.63	1.61	1.60
1.58	1.66	1.63	1.60

5
10
15
20
25
Actual content of MCMB (%)

It is interesting to note that in the present process, the quinoline insolubles in precursor coal tar pitch are retained in the mesophase pitch and finally in the mesocarbon microbeads. The content of quinoline insolubles, therefore, goes on increasing at each step of the process. Thus, a QI content of 0.5% in the precursor coal tar pitch amounts to a value of 2.7% in the mesophase powder resulting from it, as seen from Table 3.15. In other words, such a mesophase powder actually contains 2.7% of the initial quinoline insolubles and rest of it i.e. (97.3%) only constitutes the mesocarbon microbeads. Likewise, the QI contents of 3.3%, 6.5% and 9.2% in the precursor coal tar pitch lead to a significant increase in the content of the same to values of 9.9%, 17.7% and 24.6%, respectively, in the resulting mesophase powders, which thus actually contain only 90.2%, 82.3% and 75.4% of the mesocarbon microbeads.

3.5.2 EFFECT OF QI CONTENT ON GREEN DENSITY OF PLATES

Regarding the characteristics of the plates made from the precursor coal tar pitches having 0.5%, 3.3%, 6.5% and 9.5% of QI, it is seen from Fig.3.18 that the apparent green density of the plates shows a nominal increase with the increase in the QI content of the precursor pitch and attains values of 1.22, 1.25, 1.26 and 1.27 g cm^{-3} for precursor pitches having QI contents of 0.5%, 3.3%, 6.5% and 9.2%, respectively. The initial increase may be attributed to filling of the space between the mesocarbon microbeads by the very fine (~1 μm) QI particles, and the subsequent increase to the displacement of the mesocarbon microbeads by the QI particles, which are relatively denser than the microbeads.

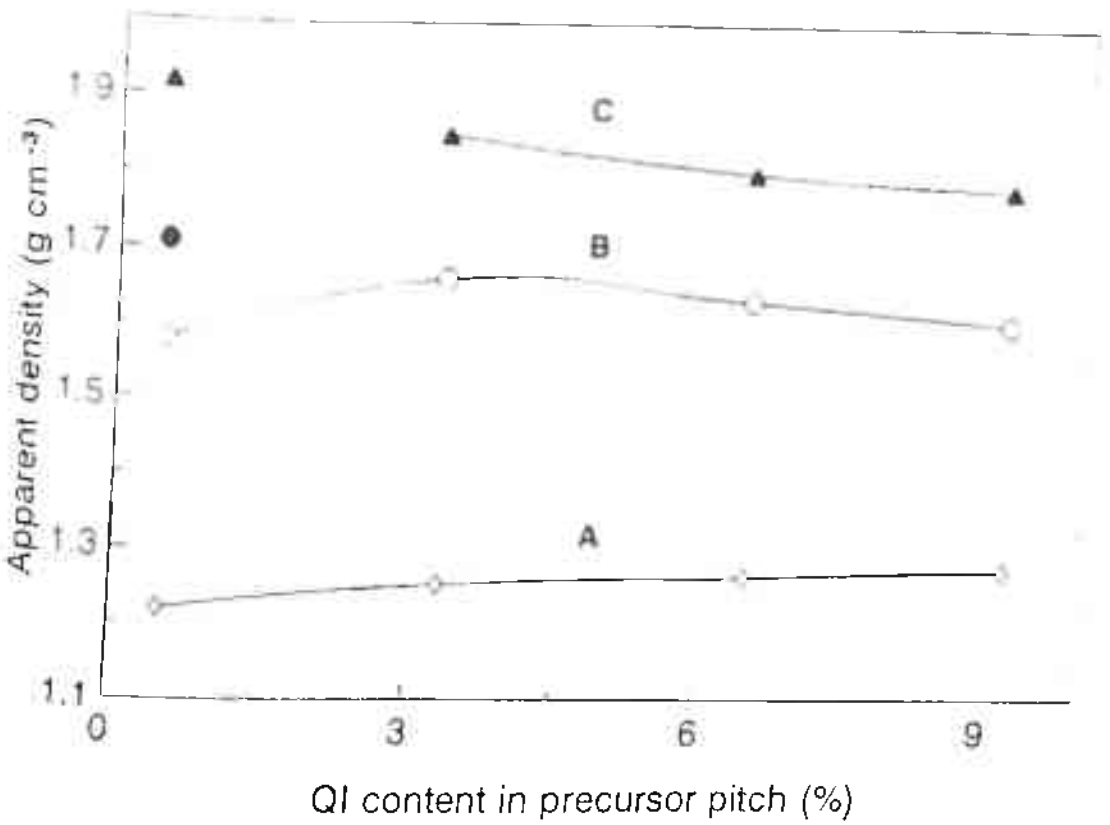


Fig 3.18 Variation of apparent density of MCMB-based plates at green stage (A), HTT of 950°C (B), and HTT of 2700°C (C) with QI content in precursor coal tar pitch.

3.5.3 EFFECT OF QI CONTENT ON WEIGHT LOSS AND VOLUME SHRINKAGE

Further, it is seen from Table 3.15, that the weight loss first increases significantly from a value of 10.6% to 13.7%, as the QI content in the precursor pitch increases from 0.5% to 3.3%, and thereafter it decreases relatively slowly to values of 11.8% and 11.2% at QI contents of 6.5% and 9.2% respectively. The significantly lower value of weight loss obtained in the case of 0.5% QI pitch compared to 3.3% QI pitch may be attributed to substantial- ly higher value of the mean size of 13.5 μm of the MCMB in the former case compared to a value of 5.3 in the latter case. The continuous decrease in the weight loss in the cases of 6.5% and 9.2% QI pitches, may be due to a continuous decrease in the actu- al contents of MCMB in the mesophase powders to values of 82.3% and 75.4%, respectively, in these cases, compared to the case of 13.1% QI pitch where this value is 90.2%. This is because in a mesophase powder, it is mainly the MCMB which undergo a weight loss, the weight loss suffered by the initial QI particles being only 3-5%(73). The volume shrinkage, in turn, is found to exhibit a pattern essentially similar to that of the weight loss. This is quite understandable as the volume shrinkage is associated with the weight loss, meaning that the higher the weight loss, the higher is the volume shrinkage.

3.5.4 EFFECT OF QI CONTENT ON APPARENT BAKED DENSITY

The apparent baked density of the plates is seen (from Fig. 3.18) to first increase from a value of 1.58 g cm^{-3} to 1.66 g cm^{-3} as

the QI content in the precursor pitch increases from 0.5% to 3.3%, and then decrease nominally to values of 1.63 g cm^{-3} and 1.60 g cm^{-3} for precursor pitches with QI contents of 6.5% and 9.2%, respectively.

The variations in the apparent baked density can be easily explained by the overall effect of green density, weight loss and volume shrinkage in the respective cases. For easy understanding of this overall effect, a term called 'density amplification factor (DAF)' referring to the ratio of fractional residual weight and fractional residual volume of a product on carbonisation, with respect to its weight and volume in the green stage is introduced here. Mathematically, one can write, Density amplification factor = (1-Wt.loss (%)/100) / (1-Vol.shrinkage (%)/100). The expected baked density then simply works out to be the product of green density and the density amplification factor. Based on these considerations, it is seen from Table 3.15 that the expected value of baked density first increases from 1.60 to 1.63 g cm^{-3} as the QI content increases from 0.5% to 3.3%, after which it decreases nominally to values of 1.61 and 1.60 g cm^{-3} for QI values of 6.5% and 9.2% in the precursor pitch respectively. Table 3.15 shows that the observed values of the baked density are in close agreement with these expected values. Further, it may be noted that if the curve of baked density vs. QI content for pitches is extrapolated with QI content of 3.3%, 6.5% and 9.2%, one gets a value of about 1.72 g cm^{-3} as the baked denisty of plates referring to a mean size of MCMB of about 5 μm for 0.5% QI pitch.

3.5.5 EFFECT OF QI CONTENT ON APPARENT GRAPHITISED DENSITY

The apparent graphitised density of the plates shows the same trend as the baked density with values of 1.85, 1.80 and 1.78 g cm^{-3} at a HTT of 2700°C for precursor coal tar pitches having QI content of 3.3%, 6.5% and 9.2%, respectively. This is quite understandable as, generally, the higher the baked density, the higher is the graphitised density, or the vice versa. It is interesting to note here that if the curve of graphitised density vs. QI content is extrapolated, one can expect a graphitised density of around 1.92 g cm^{-3} for the 0.5% QI precursor pitch. Thus, from the above discussion one can see that all other factors remaining same, the higher content of QI particles in the precursor pitch the lower is the apparent density of the resulting carbon or graphite plates.

3.5.6 EFFECT OF QI CONTENT ON BENDING STRENGTH

As seen from Fig 3.19 the bending strength of the plates heat-treated to 950°C, attains values of 62, 88, 73 and 65 MPa in cases of precursor coal tar pitches having respectively 0.5%, 3.3%, 6.5% and 9.2% of QI content. Here, the sudden increase in the strength from 62 MPa to 88 MPa as the QI content increases from 0.5% to 3.3% (amounting to a an effective increase from 2.7% to 9.8% in the corresponding MCMB) is basically due to the decrease in the size of the MCMB from a value of 13.5 μm to 5.1 μm, since generally, all other factors remaining same, the lower the size of the particles, the higher is the strength. Thereafter, the continuous decrease in the strength as the QI content in

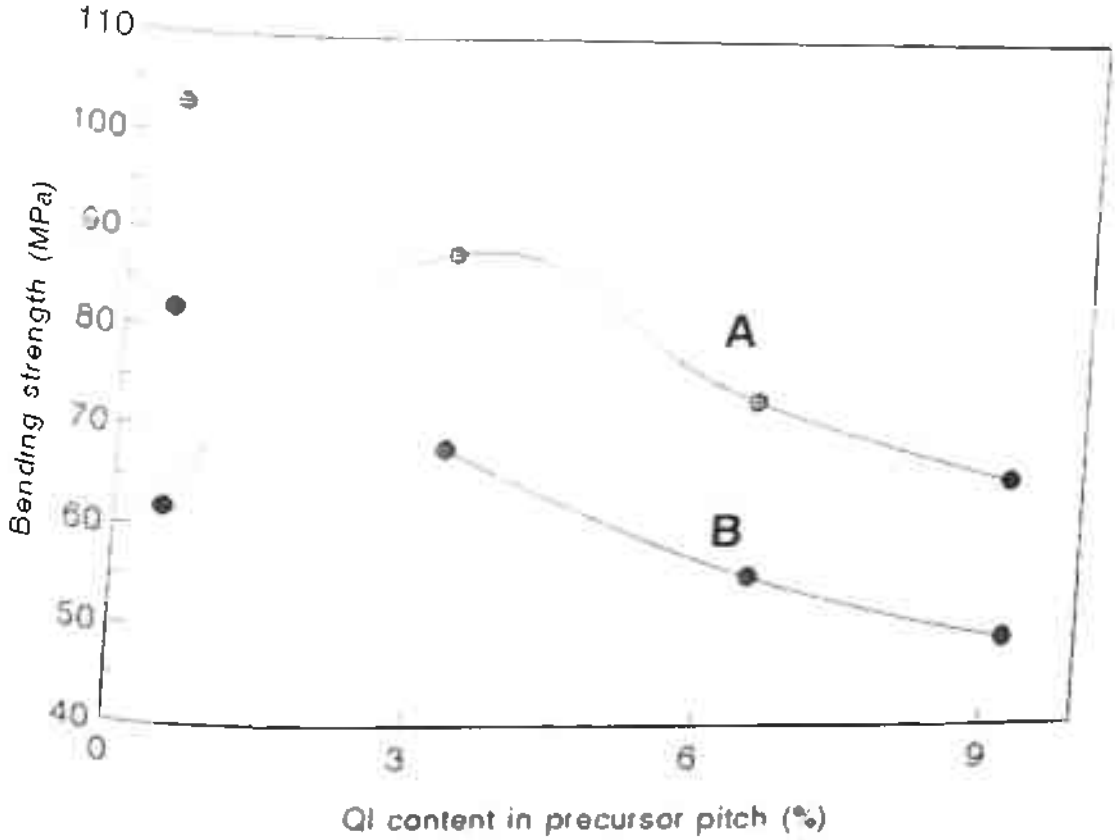


Fig 3.19 Variation of bending strength of MCMB-based plates at HTT of 950°C (A) and 2700°C (B), with QI content in precursor coal tar pitch.

creases further to values of 6.5% and 9.2% may be attributed to a continuous increase in the effective concentration of initial quinoline insolubles in the corresponding mesophase powder to values of 17.7% and 24.6%, which act as inert particles having no adhesive property of their own (and thus not contributing to the binding of the product).

It is interesting to note here that except in the case of 0.5% QI pitch, where the mean size of the MCMB is about 13.5 μm, in all other cases, the mean size is around 5 μm. So if the curve of bending strength vs. QI content is extrapolated, a strength of about 103 MPa is obtained for the 0.5% QI pitch which will refer to a particle size of around 5 μm, the same as in case of other pitches having 3.3%, 6.5% and 9.2% of QI. Thus, it is seen that the higher the content of QI in the precursor coal tar pitch, the lower is the strength of the baked product.

Further, it is also seen from Fig.3.19 that on graphitisation to 2700°C, the strength of the plates falls to values of 68, 55 and 49 MPa for pitch precursors having 3.3%, 6.5% and 9.2% of QI, respectively, from the values of 88, 73 and 65 MPa at HTT of 950°C. The extrapolation of the curve of bending strength (at 2700°C) vs. QI content gives a value of around 86 MPa for the 0.5% QI precursor pitch, resulting from the initially extrapolated value of 103 MPa at a HTT of 950°C. Thus, in all the cases of precursor pitches, there is a fall in the strength of the plates on graphitisation, compared to carbonisation. This is a general phenomenon and refers to an increase in the porosity of the plates on graphitisation by way of growth of the crystallites at the expanse of the disorganised matter between them as well as

by fusion, which results in an improvement in their orientation. Further, it may be noted that the strength of the graphitised plates also, like the carbonised plates, decreases as the QI-content in the precursor pitch increases, the reasons for which remain the same as for carbonised plates.

It may be noted from the results of carbonised as well as graphitised plates, discussed above, that the presence of QI particles in a precursor pitch causes a fall in the strength of the product. However, their presence in the precursor pitch results in an increase in the yield of the MCMB of smaller (desired) size. Therefore, giving due consideration to yield of the MCMB and strength of the resulting product, a QI content of around 3.3% in the precursor pitch appears to be optimum. In other words, from techno-economical considerations, it may be concluded that a coal tar pitch containing around 3% of quinoline insolubles can act as a good precursor for the production of high density - high strength - isotropic graphite.

3.6 CONCLUSIONS

(i) The heat-treatment of a coal tar pitch results in increased values of the quinoline and toluene insoluble contents, as well as the coking value of the resultant heat-treated or mesophase pitch, compared to those of the original (starting) pitch.

(ii) The size and concentration of mesophase in any heat-treated pitch increases as the soaking time at a particular heat-treatment temperature (420°C) increases. However, the increase in the mesophase size with heat-treatment temperature is dependent

upon the QI content in the precursor pitch, which is useful to control the size of mesophase spherules to a desired value.

(iii) As a solvent, toluene and quinoline are not suitable whereas tar oil is suitable as a solvent for the extraction of a mesophase pitch. The extraction of a mesophase pitch with a tar oil yields a mesophase powder (also called "mesocarbon microbeads, MCMB") suitable for producing dense and strong monolithic carbons.

(iv) The increase in the QI content of the precursor pitch results in an increase in the yield of the mesocarbon microbeads as well as the weight percent of inert QI matter in the MCMB.

(v) The MCMB-based carbons reveal microscopic homogeneity and isotropic texture as well as macroscopic isotropy in both carbonised and graphitised states.

(vi) The presence of very low QI (0.5%) in the precursor coal tar pitch, gives a low yield of 23% of the MCMB, that too with relatively higher mean size of 13.5 μm. This low yield makes the process economically unviable. A small increase in the content of QI particles to about 3% leads to a significant increase in the yield of MCMB (40%) of the desired size (about 5 μm). The presence of QI in excess of 3% in the precursor pitch, while slightly improving the yield of MCMB of similar size causes an appreciable fall in the density and strength of the product at both 950°C and 2700°C. Therefore, from techno-economical consideration, it may be concluded that a coal tar pitch containing around 3% of quinoline insolubles can act as a good precursor for the production of high density - high strength - isotropic graphite.

CHAPTER - IV

EFFECT OF SINTERING TEMPERATURE ON THE CHARACTERISTICS OF CARBONS BASED ON MESOCARBON MICROBEADS

4.1 INTRODUCTION

It has been already established in previous chapters that meso-phase spherules (mesocarbon microbeads, MCMB) require no external binder, for the production of fine grained isotropic graphite. Though considerable interest is being taken in the above mentioned MCMB-based fine textured isotropic graphite because of its excellent performance in the practical tests, only little is reported in the literature regarding its developmental aspects (56,74). In the present chapter this developmental work was extended to study the effect of heat-treatment (sintering) temperature on the changes in the physical properties and the microstructure of the carbon plates made from the MCMB (mesophase spherules), generated in a low-QI precursor coal tar pitch by a suitable heat-treatment and separated out of the heat-treated pitch using a suitable tar based solvent (75,76). This chapter gives a detailed account of the study and the results and conclusions obtained therefrom.

4.2 SINTERING BEHAVIOUR OF MCMB - BASED PLATES

To study the sintering behaviour of MCMB-based plates, a coal tar pitch having 2.5% of primary QI and other characteristics shown in Table 4.1, was selected as precursor pitch. The pitch was then heat-treated at 420°C for 2.5 h to generate the mesophase spherules in it. A polished specimen of the heat-treated pitch was examined under an optical microscope and the micrograph obtained is shown in Fig 4.1. The differential and cumulative frequencies of mesophase spherules as a function of their size

are plotted in Fig. 4.2. The heat-treated pitch was extracted with a tar oil, having a boiling range of 170-270°C, to separate the anisotropic mesophase spherules out of the heat-treated pitch. These mesophase spherules were also calcined at 350°C and examined on the scanning electron microscope and the micrograph obtained is shown in Fig.4.3. The mesophase pitch and the mesocarbon microbeads, both, were tested with respect to a number of parameters, using the characterization techniques described in Section 2.8. The various characteristics, so obtained, are discussed in Section 4.3.

The mesocarbon microbeads were hot-molded into rectangular plates of size 60mm X 20mm X 4mm under a pressure of 120 MPa using a conventional hydraulic press. The resulting green plates were carbonized in an atmosphere of high-purity nitrogen, at the rate of 10°C/h to different temperatures ranging between 350° and 1100°C, in steps of 150°C each, in different batches. Some of the plates heat-treated to 1100°C were further heated to higher temperatures of 1550 and 2700°C in two separate batches in a high-purity argon atmosphere. The plates, so obtained, were then characterized w.r.t. various parameters using the experimental techniques described in Section 2.9 of Chapter II. The results of characterization are discussed in various subsections of Section 4.4.

4.3 CHANGES IN THE PRECURSOR COAL TAR PITCH ON HEAT - TREATMENT

Table 4.1 shows the characteristics of the precursor coal tar pitch and the corresponding mesophase pitch. It is seen that the

TABLE 4.1

CHARACTERISTICS OF PRECURSOR COAL TAR PITCH AND MESOPHASE PITCH

S.No.	CHARACTERISTICS	COAL TAR PITCH	MESOPHASE PITCH
1.	Softening point	86	--
2.	Heat-treatment yield	--	80.0
3.	Quinoline insolubles	2.5	31.0
4.	Toluene insolubles	21.5	58.0
5.	Coking yield	46.8	67.0
6.	Atomic C/H ratio	--	2.06
7.	Size of mesophase spherules a) Predominant range (μm) b) Average (μm)	-- --	4-16 9.0

heat-treatment of the precursor coal tar pitch results in an increase in the quinoline and toluene insoluble contents as well as the coking value. This may be attributed to the removal of lower molecular weight components as well as to the polymerisation and condensation reactions taking place among the various molecular species in the pitch.

The quinoline and toluene insoluble contents and the coking value of the mesocarbon microbeads are seen to be considerably higher than those of the mesophase pitch, as seen from Table 4.1 and 4.2. This is quite obvious, since the MCMB represent the condensed (denser) component of the mesophase pitch. In addition, it is in agreement with the higher atomic C/H ratio (aromaticity) of 2.38 of the MCMB as compared to the 2.06 of the mesophase pitch. Fig.4.1. showing the optical micrograph of the heat-treated (mesophase) pitch reveals the mesophase to be in the form of spherules. The differential (histogram) and the cumulative frequency curves of these spherules (Fig.4.2) clearly show them to have a minimum size of 1.3 μm and a maximum size of 21.3 μm. The predominant range of the size of these spherules is seen to be 4-16 μm with an average of 9.0 μm. These very spherules on extraction out of the heat-treated pitch, i.e., the mesocarbon microbeads, are essentially spherical in shape, as observed in the scanning electron micrograph shown in Fig.4.3.

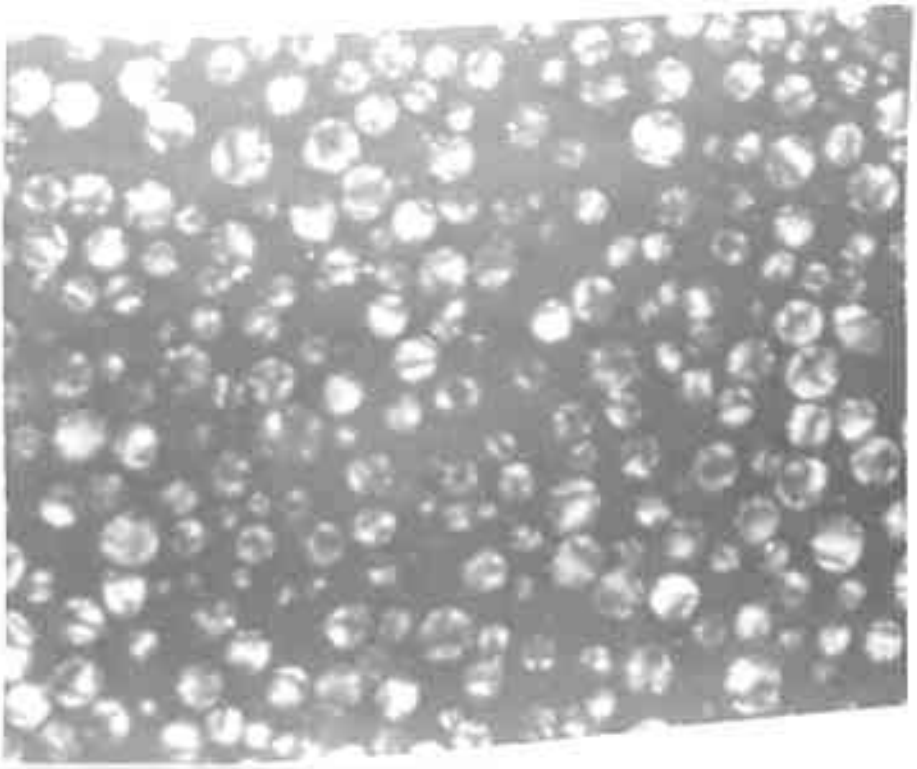
4.4 VARIATION OF THE CHARACTERISTICS OF MCMB - BASED PLATES WITH HEAT - TREATMENT TEMPERATURE

Having discussed in Section 4.3 about the changes that take place in the precursor coal tar pitch when it is heated to form meso-

TABLE 4.2

CHARACTERISTICS OF MESOCARBON MICROBEADS

S.No.	CHARACTERISTICS	VALUE
1.	Quinoline insolubles	92.6 %
2.	Toluene insolubles	99.7 %
3.	Beta resins content	7.1 %
4.	Volatile matter	10.9 %
5.	Extraction yield(%)	40.0 %
6.	Atomic C/H ratio	2.38
7.	Size of mesophase spherules a) Predominant range (μm) b) Average (μm)	 4-16 9.0



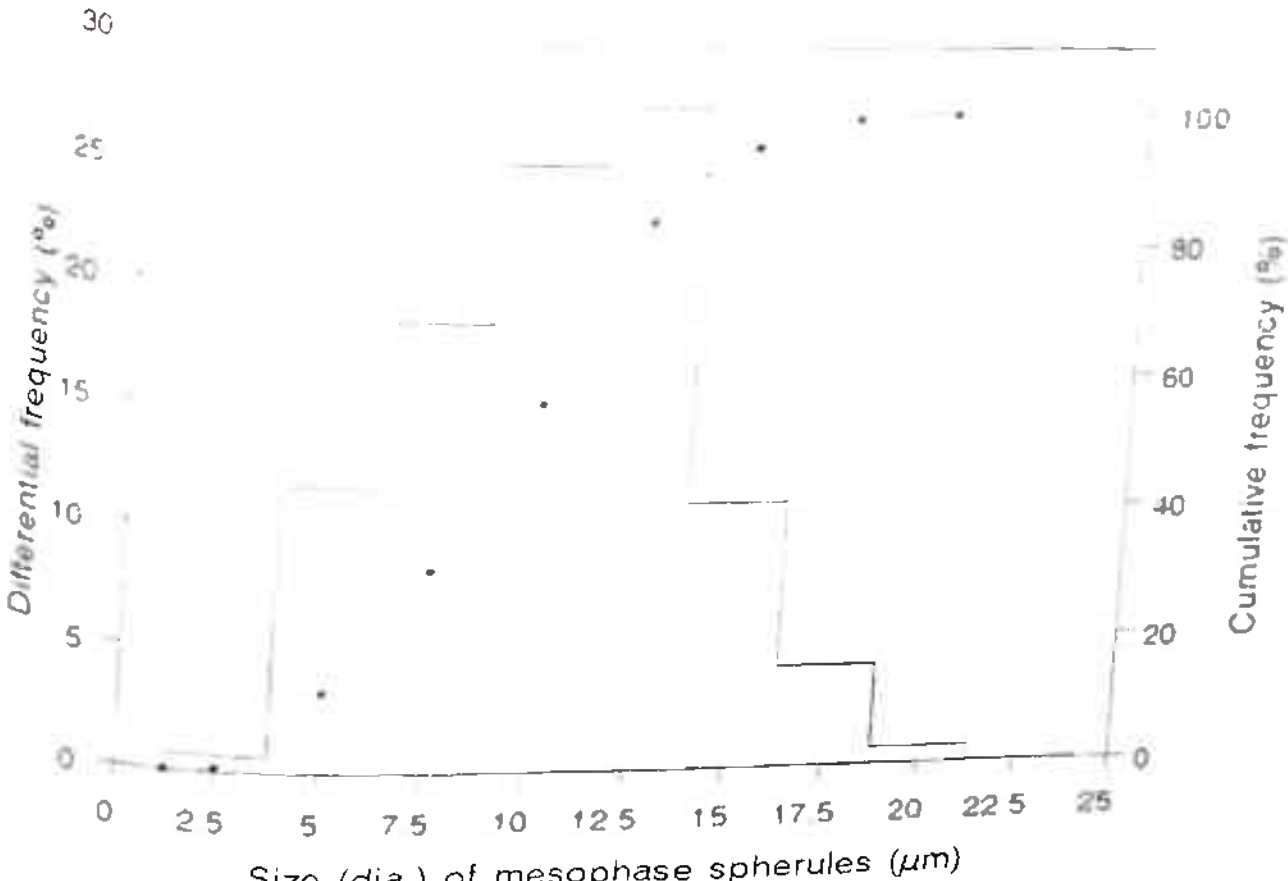


Fig 4.2 Differential (histogram) and cumulative frequencies of mesophase spherules formed in the precursor coal tar pitch with 2.5% QI by heat-treatment at 420°C for 2.5 h, as a function of their size

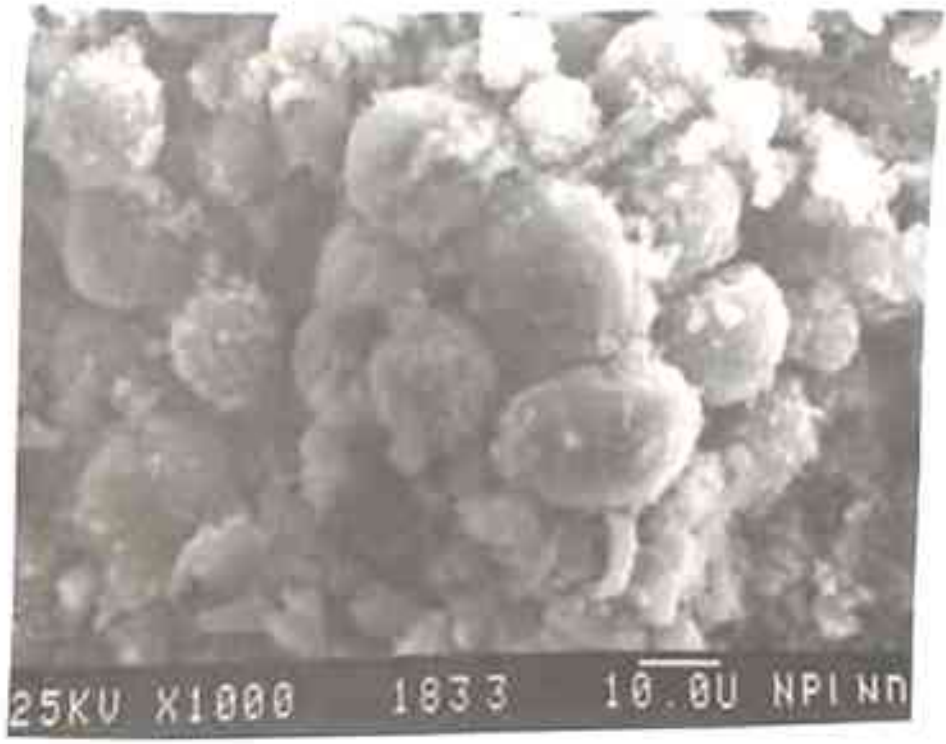


Fig 4.3 Scanning electron micrograph of mesocarbon microbeads separated from the heat-treated pitch.

phase spherules, the variations in the various characteristics of the carbons based on these mesophase spherules (mesocarbon microbeads) are discussed in this section.

4.4.1 VARIATION OF WEIGHT LOSS AND VOLUME AND LINEAR SHRINKAGES WITH HEAT - TREATMENT TEMPERATURE

Fig.4.4 shows the variation of weight loss and volume and linear shrinkages with heat-treatment temperature. It is seen that during the heat-treatment of the MCMB plates, the weight loss increases sharply from a value of 6.2% at 500°C to 11.8% at 1000°C, which corresponds to the evolution of various pyrolysis products. Above 1000°C, however, the rate of weight loss with the HTT decreases gradually and reaches a value of 15.3% at 2700°C. The volume shrinkage, in turn, shows a rapid increase from a value of 6.4% at 500°C to a value of about 32.4% as the HTT increase to 1000°C, beyond which, however, the increase is comparatively slow till the highest HTT of 2700°C, when the volume shrinkage attains a value of 45.0%. The linear shrinkage as expected shows an essentially parallel behavior with the volume shrinkage, with a value of 16.3% at heat-treatment temperature of 2700°C.

4.4.2 VARIATION OF APPARENT DENSITY, KEROSENE DENSITY AND OPEN POROSITY WITH HEAT - TREATMENT TEMPERATURE

Fig.4.5 shows the variation of apparent and kerosene densities and open porosity of plates with heat-treatment temperature. It is seen that the apparent density of the plates upto heat-treat-

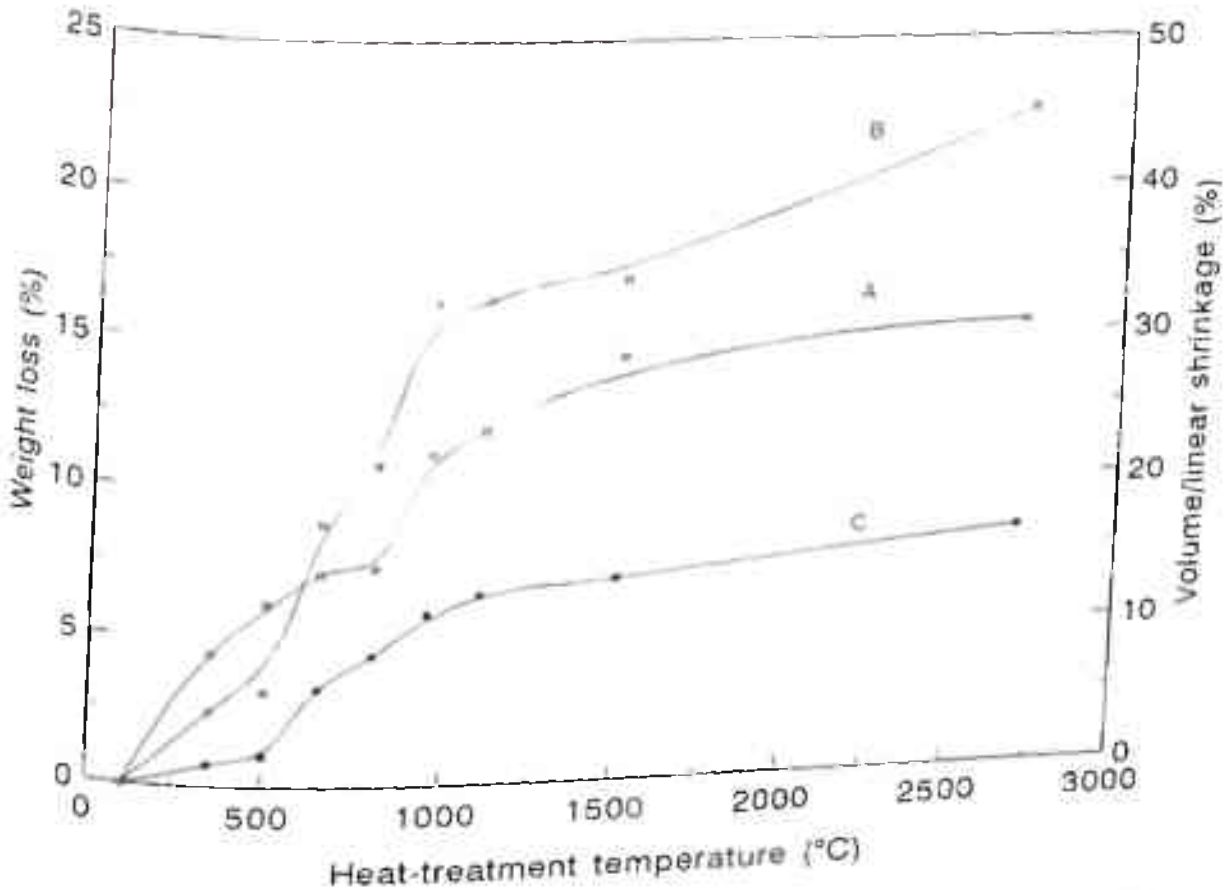


Fig.4.4 Variation of weight loss (A), volume shrinkage (B) and linear shrinkage (C) of MCMB-based plates with heat-treatment temperature

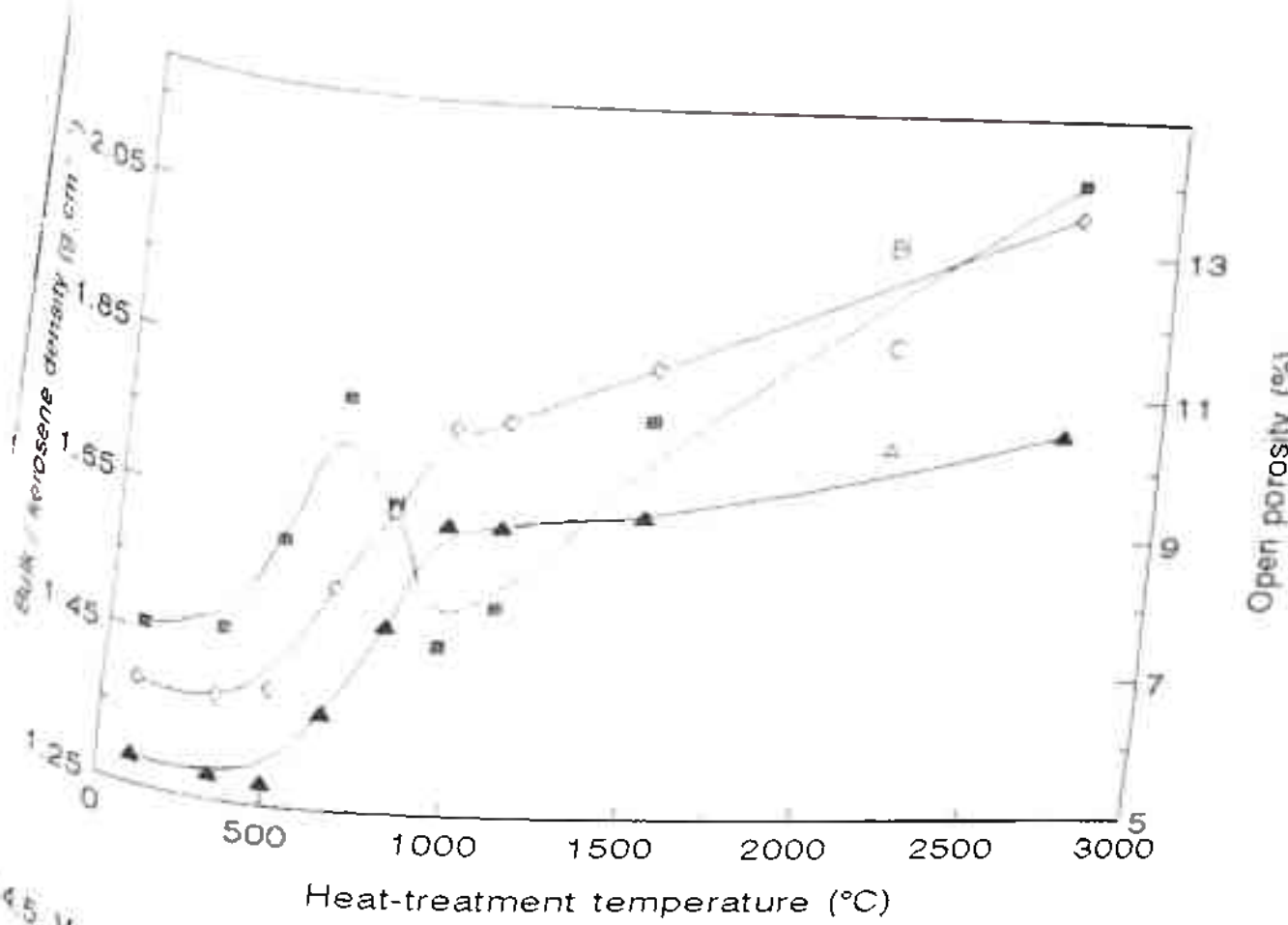


Fig. 4.5 Variation of bulk density (A), kerosene density (B), and open porosity (C) of MCMB-based plates with heat-treatment temperature.

ment temperature of 500°C remains almost same as in the green stage (1.29 g cm^{-3}), above which it increases and attains a value of about 1.64 g cm^{-3} at 1000°C and finally a value of 1.78 g cm^{-3} at 2700°C. As seen from Fig.4.4 and 4.5, the effects of weight loss and volume shrinkage nullify each other and result in the constant value of apparent density upto 500°C. However, above 500°C, the volume shrinkage dominates the weight loss and thus increases the density of the plates till the final HTT of 2700°C. Further, the kerosene density follows the same pattern as that of apparent density and is found to be always higher than the apparent density of the plates, which reflects the presence of some porosity in the plates at all stages of the heat-treatment.

It is further-more observed from Fig 4.5 that the open porosity increases from 7.2% in the green stage to 10.1% at the HTT of 650°C, beyond which it rapidly decreases to a value of 7.6% at 1000°C. Above 1000°C, however, once again the porosity starts increasing continuously and attains a maximum value of 14.0% at 2700°C. The increase in the open porosity upto 650°C, corresponds to the evolution of pyrolysis products resulting in the creation of pores, and the decrease (during 650-1000°C) may be due to the narrowing of these pores as a result of the dominating effect of the volume shrinkage over the weight loss. Finally, the continuous increase in the open porosity during the HTT range of 1000-2700°C may be attributed to an improvement in the alignment of the crystallites, as discussed below in Section 4.4.3, which takes place because of their growth at the cost of the disorganised matter between the crystallites.

4.4.3 VARIATION OF CRYSTALLITE PARAMETERS WITH HEAT - TREATMENT TEMPERATURE

The X-ray studies of the carbon plates show that both L_a and L_c increase from 1.57 and 1.59 nm at about 1000°C to 24.1 and 20.5 nm at 2700°C, respectively, as shown in Fig.4.6. This increase in the size of L_a and L_c results in a corresponding decrease in the d_{002} inter-layer spacing from a value of about 351 pm at 1000°C to 336.5 pm at 2700°C. These results can be attributed to an improvement in the alignment of the crystallites which takes place because of their growth at the cost of the disorganised matter between the crystallites, followed by their rearrangement and fusion.

4.4.4 VARIATION OF ATOMIC C/H RATIO WITH HEAT - TREATMENT TEMPERATURE

Fig.4.7 shows the variation of atomic C/H ratio of the carbons Plates with heat-treatment temperature. It is seen that just upon formation of the plates (moulding temperature = 110°C) the atomic C/H ratio is 2.4, which increases slowly to 2.45 and 2.63 approx. at temperatures of 350 and 500°C, respectively. This may be attributed mainly to the loss of volatile hydrocarbons. Beyond 500°C, however, this ratio increase rapidly and attains a value of about 3.7 at 650°C and 7.6 at 800°C, which may be due to the removal of relatively lower molecular weight components as well as to the dehydrogenative condensation reactions which occur between the various molecular species (76). Further, above

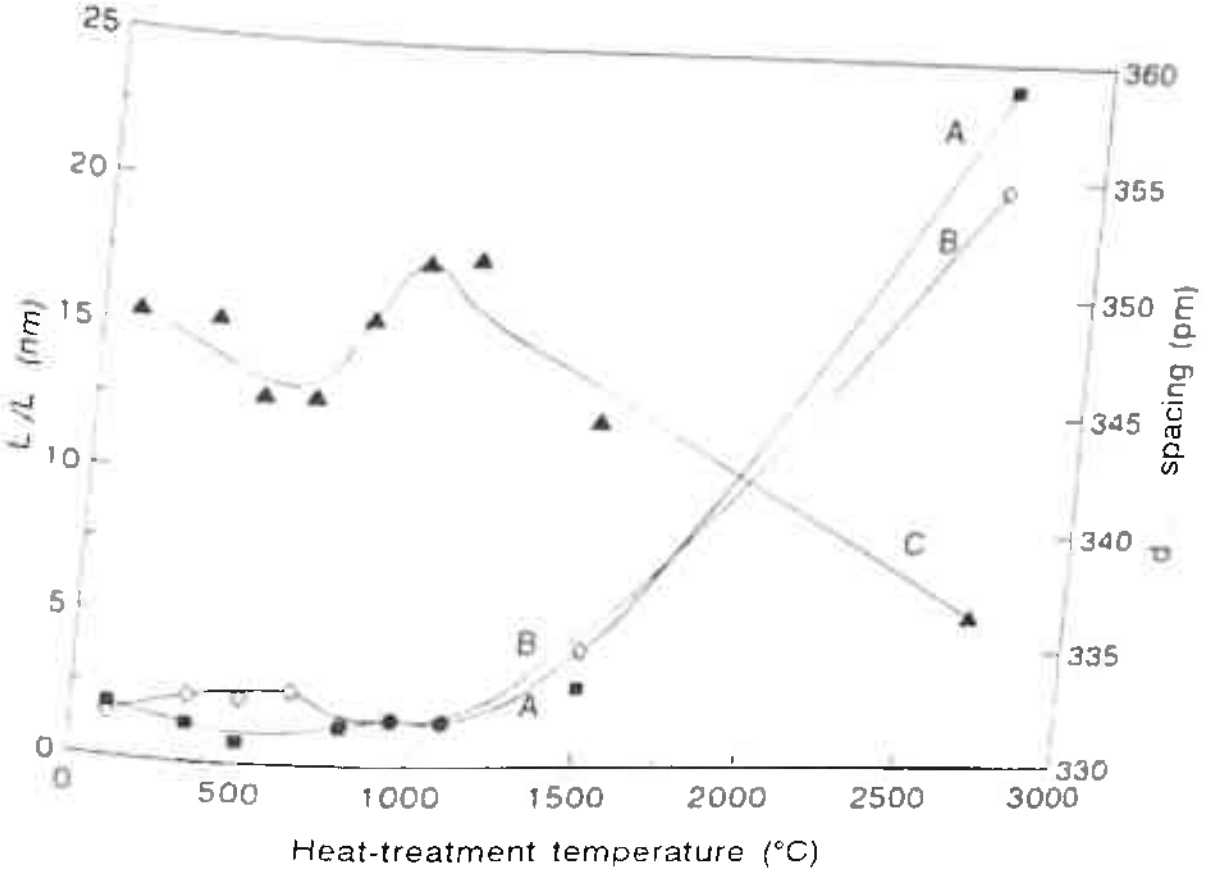


Fig 4 6 Variation of L_a (A), L_c (B) and d_{002} spacing (C) of crystallites in materials of MCMB-based plates with heat-treatment temperature.

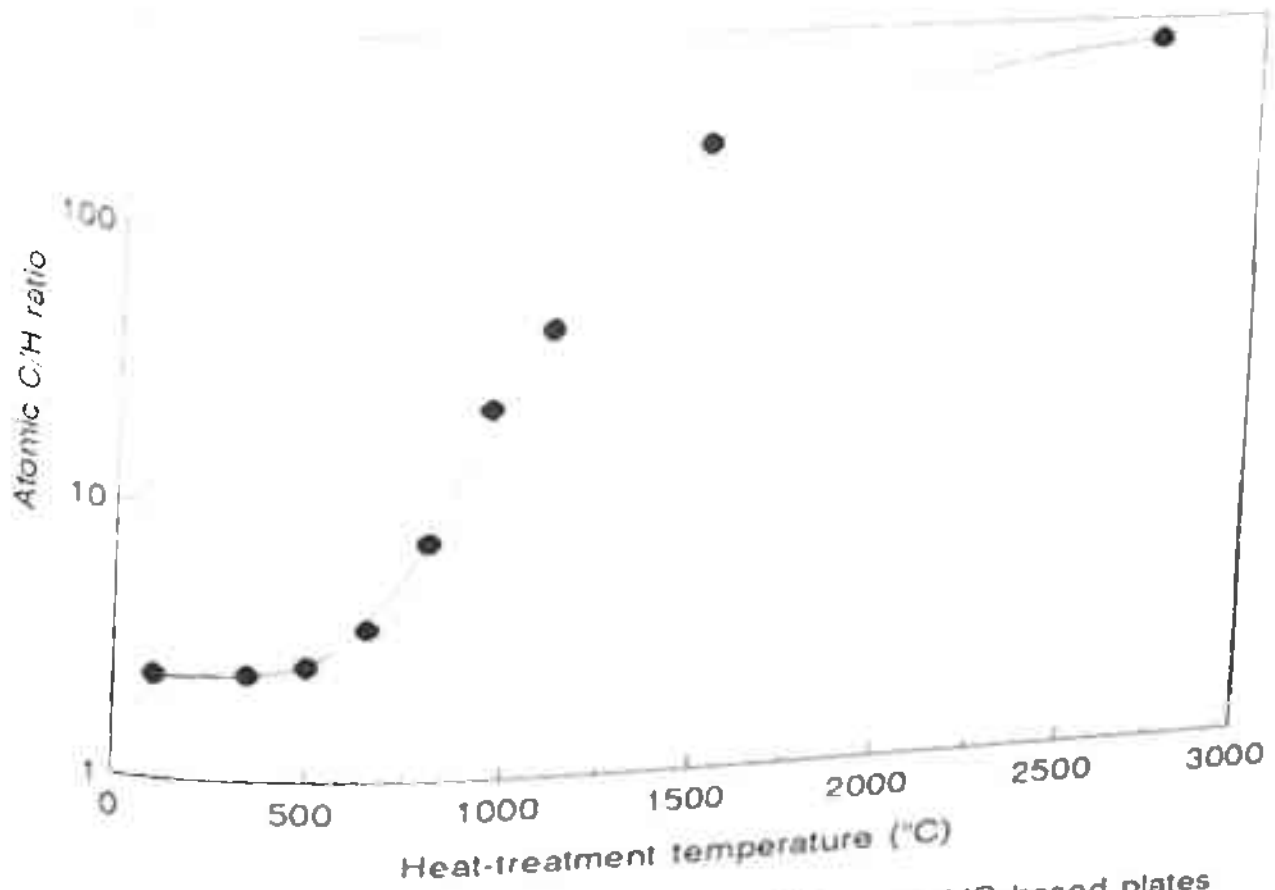


Fig.4.7 Variation of atomic C/H ratio of materials of MCMB-based plates with heat-treatment temperature.

800°C, the carbonisation proceeds more and more by dehydrogenative reactions leading to a sharp increase in the atomic C/H ratio to a value of 20 at 1000°C, and finally to a value of 417 at the heat-treatment temperature of 2700°C.

4.4.5 VARIATION OF BENDING STRENGTH AND YOUNG'S MODULUS WITH HEAT - TREATMENT TEMPERATURE

Regarding the variation in bending strength and Young's modulus of the carbons with heat-treatment temperature, it is seen from Fig.4.8 that during the heat-treatment from 500 to 1000°C, the bending strength of the plates goes on increasing almost linearly and reaches a maximum value of 71 MPa at about 1000°C. This may be attributed to both, a continuous increase in the apparent density of the plates as well as, in general, a continuous decrease in the open porosity during this HTT range. Beyond 1000°C, however, the bending strength shows a gradual fall right upto 2700°C, at which it attains a value of 50 MPa. This may be due to the corresponding increase in the open porosity during this HTT range. The Young's modulus, in turn, first decreases from a value of 18 GPa at 500°C to 10 GPa at 800°C, after which it increases continuously and attains a value of 29 GPa at 2700°C.

4.4.6 VARIATION OF SHORE HARDNESS WITH HEAT - TREATMENT TEMPERATURE

It is seen from Fig.4.9 that starting from a value of 93 at the HTT of 500°C, the Shore hardness of the plates increases gradually and attains a maximum value of 102 at the HTT of about

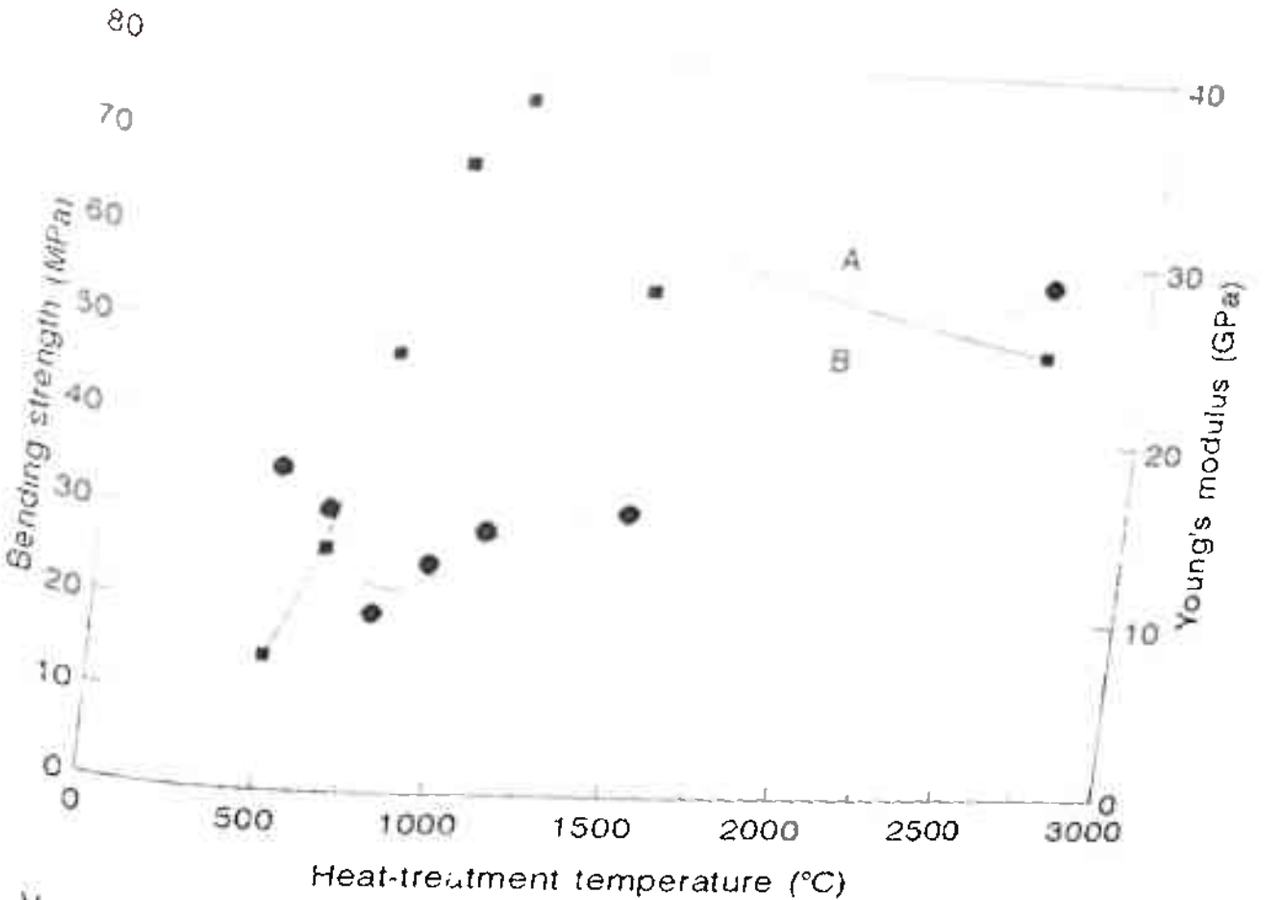


Fig 4.8 Variation of bending strength (A) and Young's modulus (B) of MCMB-based plates with heat-treatment temperature

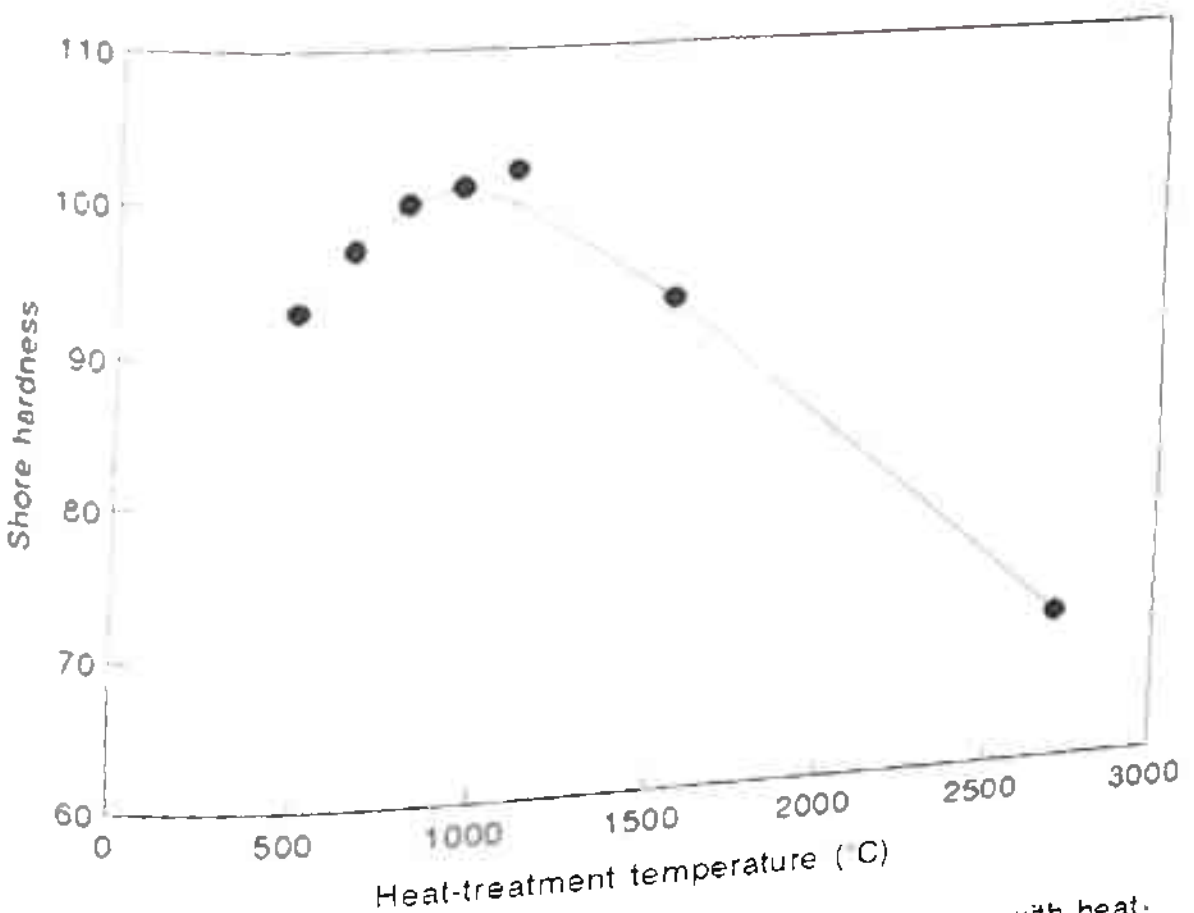


Fig.4.9 Variation of Shore hardness of MCMB-based plates with heat-treatment temperature.

1000°C, beyond which it decreases almost linearly, attaining a value of about 70 at the final HTT of 2700°C. It is interesting to note here that the variation of the Shore hardness follows a pattern similar to that of the bending strength.

4.4.7 VARIATION OF ELECTRICAL RESISTIVITY OF PLATES WITH HEAT-TREATMENT TEMPERATURE

Fig.4.10 shows the variation of electrical resistivity with heat-treatment temperature. It is clearly seen from this figure that the electrical resistivity of the plates undergoes a steep fall from 933 m Ohm cm to 30.6 m Ohm cm as the HTT is increased from 550 to 800°C. However, it decreases gradually to 7.1, 4.9 and 2.4 m Ohm cm at the heat-treatment temperatures of 950, 1550 and 2700°C. This is what is expected since the material is gradually getting converted from a polynuclear aromatic solid to graphite.

4.4.8 VARIATION OF MICROSTRUCTURE OF PLATES WITH HEAT-TREATMENT TEMPERATURE

Finally, as regards the microstructure of the MCMB-based plates, it is found that there is homogeneity and fine isotropic texture in the plates at all the stages of heat-treatment. However, this microstructure of the plates gets increasingly finer as the HTT increase. This is in complete agreement with the variations in the weight loss, volume shrinkage and open porosity of the plates with the HTT. It is expected that the homogeneity and the fine texture, both, would be considerably improved if the compaction of the mesocarbon microbeads is done using an isostatic press in

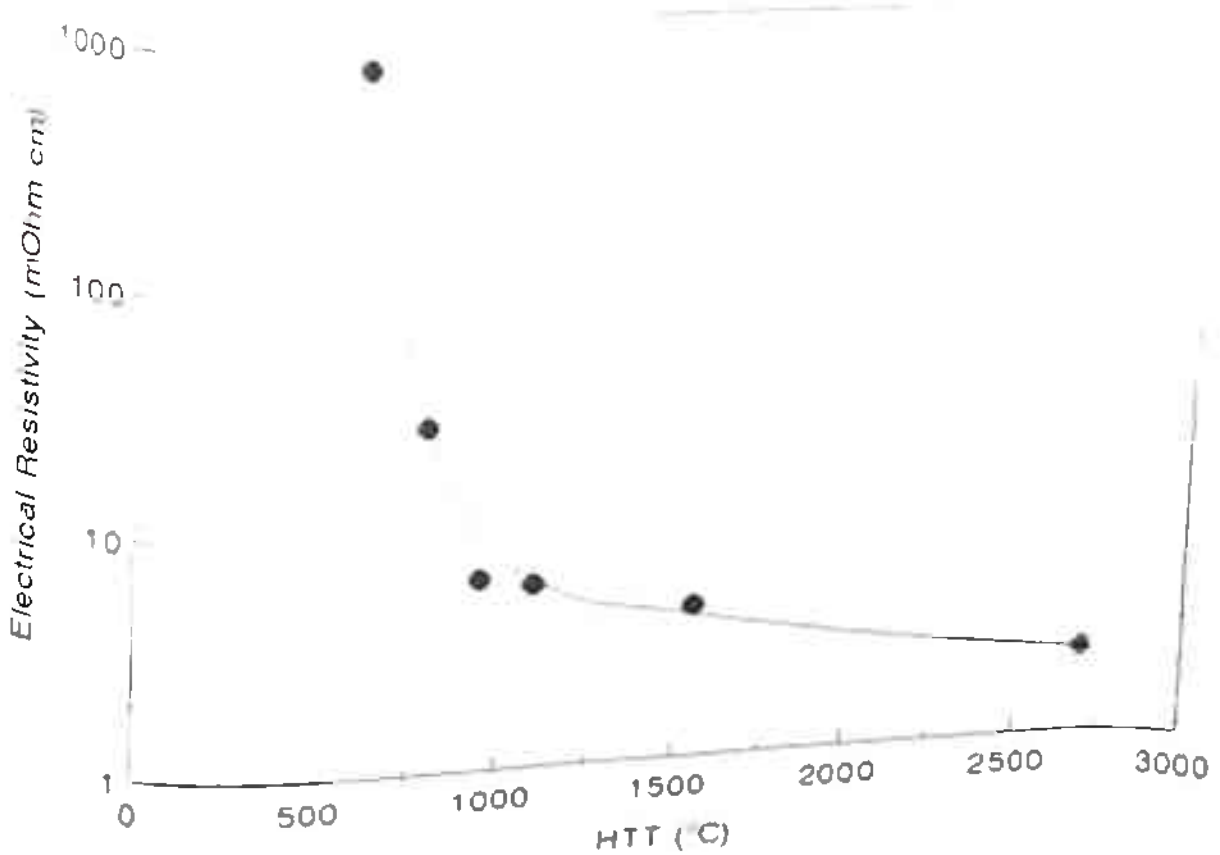


Fig.4.10 Variation of electrical resistivity of MCMB-based plates with heat treatment temperature.

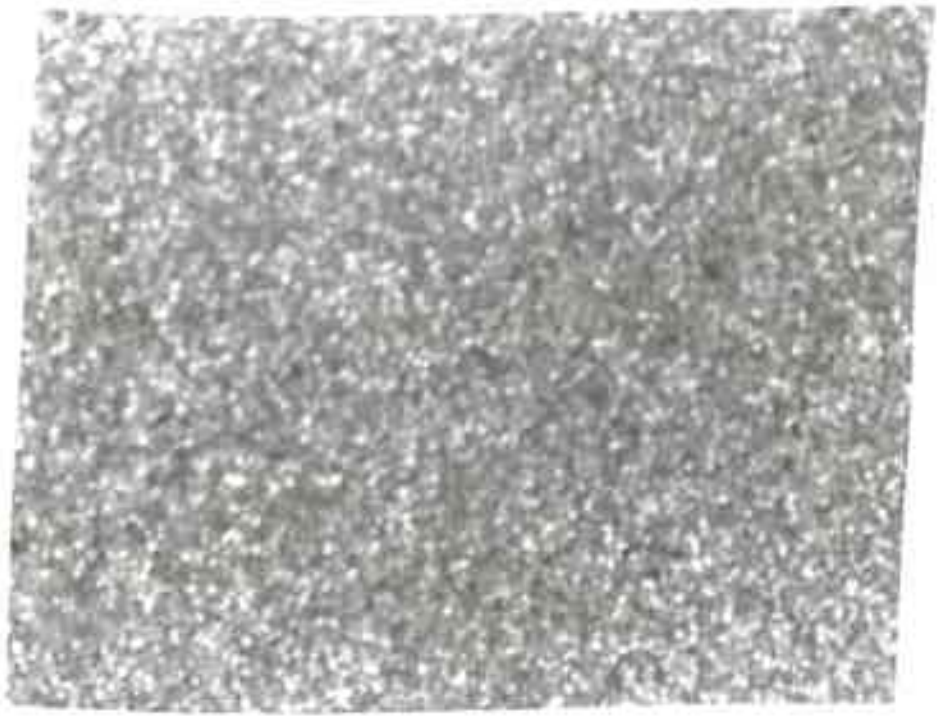


Fig 4.11 Optical micrograph of the MCMB-based plate heat-treated to 2700°C, at a magnification of 100.

place of the conventional (uni-directional) press employed in this study.

4.5 CONCLUSIONS

1. The plates heat-treated to 1000 and 2700°C exhibit apparent density of 1.64 and 1.78 g cm^{-3}, with weight loss of only 12.5 % and 15.3 % and enormous volume shrinkage of 32.4 % and 45.0 %, respectively.

2. The open porosity has a value of 7.6 % at the HTT of 1000°C which is close to its minimum value of 7.2 % in the green stage, and a maximum value of 14.0% at an HTT of 2700°C.

3. The atomic C/H ratio of the plates increases from an initial value of 2.4 in the green stage to 30 and 417 at the HTT of 1000 and 2700°C, respectively.

4. The bending strength is found to have a maximum value of 72 MPa at an HTT of about 1000°C, above which it decreases gradually to attain a value of 50 MPa at 2700°C.

5. The Shore hardness gradually increases from an initial high value of 93 at 500°C to attain a maximum value of 102 at 1000°C, beyond which it decreases almost linearly to a value of 70 at 2700°C.

6. The electrical resistivity undergoes a sharp fall from 933 to 30.6 mOhm cm as the HTT increases from 650°C to 800°C, beyond which it decreases gradually to about 7.0 and 2.4 mOhm cm at 1000 and 2700°C respectively.

7. The crystalite parameters La and Lc increase from 1.57 and 1.59 nm at about 1000°C to 24.1 and 20.5 nm at 2700°C, respec-

tively. The doo2 spacing decreases from a value of about 351 pm at 1000°C to 337 pm at 2700°C.

8. The plates heat-treated to 2700°C reveal homogeneity and fine isotropic texture.

CHAPTER - V

STUDIES CONCERNING THE SUITABILITY OF EXTRACTION AND CALCINATION CONDITIONS OF MESOCARBON MICROBEADS

5.1 INTRODUCTION

In the investigations presented in this chapter, studies have been conducted to see the effect of type of Tar Oil (in respect of its boiling range) used in the extraction of the mesocarbon microbeads on the characteristics of the resulting carbon and graphite products. The same are discussed in Section 5.2. Further, to find out suitable calcination conditions, namely, time, temperature and atmosphere during the calcination of meso-carbon microbeads, some more studies were carried out which are discussed in Section 5.3. Having optimised processing conditions for the production of isotropic graphite, an effort was made to reproduce the results, which are discussed in Section 5.4. The conclusions of all above studies are given in Section 5.5.

5.2 EFFECT OF TYPE OF TAR OIL ON THE CHARACTERISTICS OF CARBONS BASED ON MESOCARBON MICROBEADS

In this study the aim was to see the effect of type of Tar Oil (in respect of its boiling range), used in the extraction of mesocarbon microbeads out of the heat-treated pitch, on the characteristics of the resulting carbons (77). For this purpose, two coal tar pitches A and B, having characteristics given in Table 5.1, were heat-treated at 425°C for 3.0 and 3.5 h respectively, in an inert atmosphere to generate mesophase spherules in them. The size of these mesophase spherules in each of the pitch-es was determined by optical microscopy of the heat-treated (mesophase) pitches. The properties of the mesophase pitches are also given in Table 5.1 along with those of precursor coal tar

Pitches. Both the mesophase pitches were then extracted with each of the two Tar Oils, named I and II, having relatively lower (180-230°C) and higher (230-280°C) boiling ranges, to obtain four batches of mesocarbon microbeads in all, namely AI, AII and BI, BII, respectively. The microbeads of all the batches were subsequently calcined in an inert atmosphere at a temperature of 300°C and then characterised with respect to quinoline and toluene insoluble contents and volatile matter content. These values are given in Table 5.1. The mesocarbon microbeads of all the four batches were finally hot-moulded into small rectangular plates of size 60 mm x 20 mm x 4 mm using a conventional hydraulic press, and the plates obtained were heat-treated in an inert atmosphere to a temperature of 1000°C and some of them to a further higher temperature of 2700°C. Both these types of plates were then characterised with respect to various parameters, the values of which are summarised in Tables 5.2 and 5.3 respectively.

5.2.1 EFFECT OF HEAT-TREATMENT OF PRECURSOR COAL TAR PITCHES 'A' AND 'B'

The heat-treatment of the precursor coal tar pitch A and B at 425°C generates mesophase spherules, as is seen in the optical micrographs of the mesophase pitches shown in Fig 5.1. It is seen from the size distribution curves of the mesophase spherules, shown in Fig 5.2, that the spheres generated in mesophase pitch 'A' have a predominant size range of 3-10 μm with mean (average) size of 5.6 μm, and in the mesophase pitch 'B', they have a size lying predominantly in the range of 3-12 μm with a mean value of

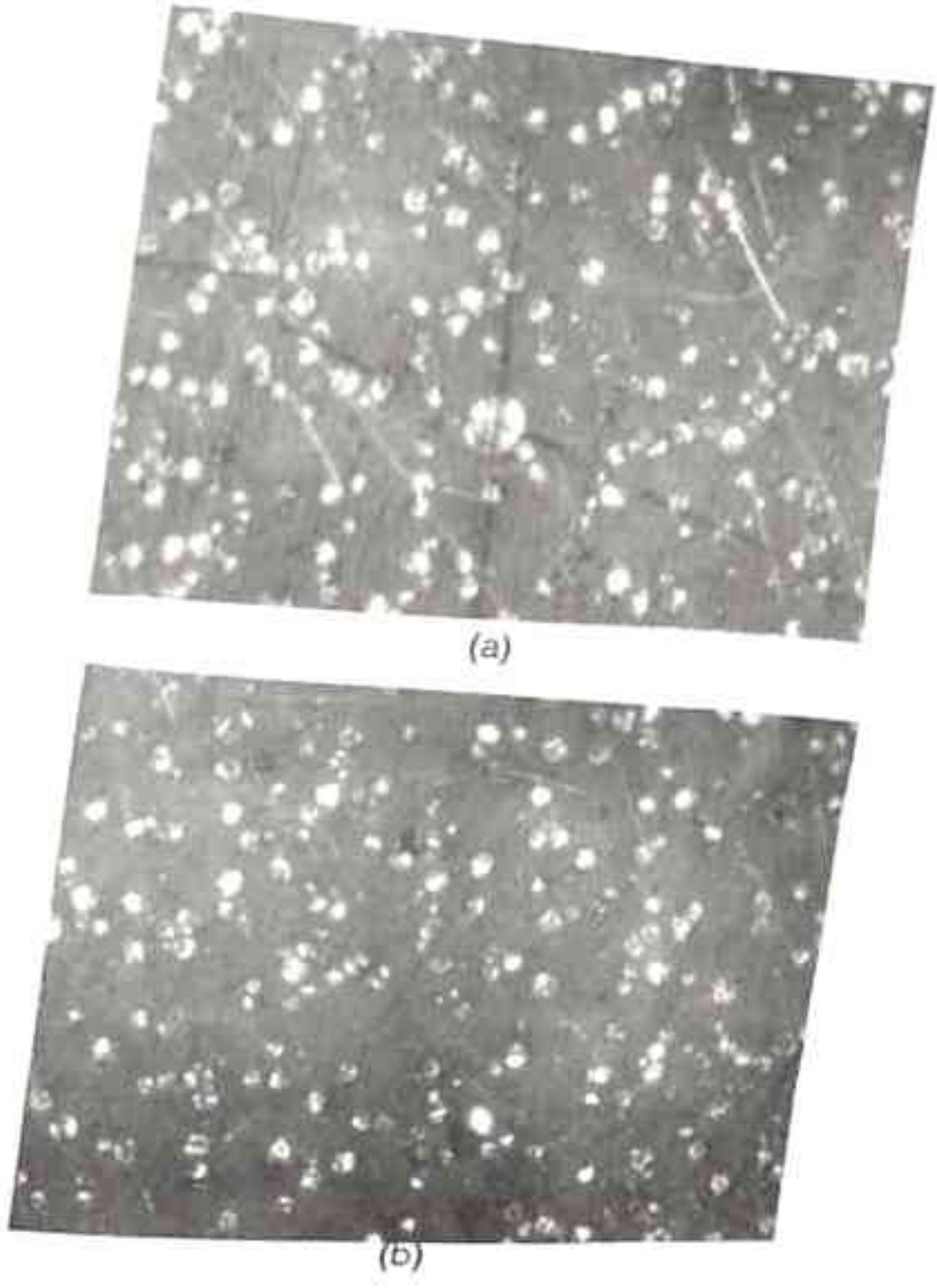


Fig 5.1 Optical micrographs of the mesophase pitches based on (a) coal tar pitch A, and (b) coal tar pitch B, at a magnification of 400.

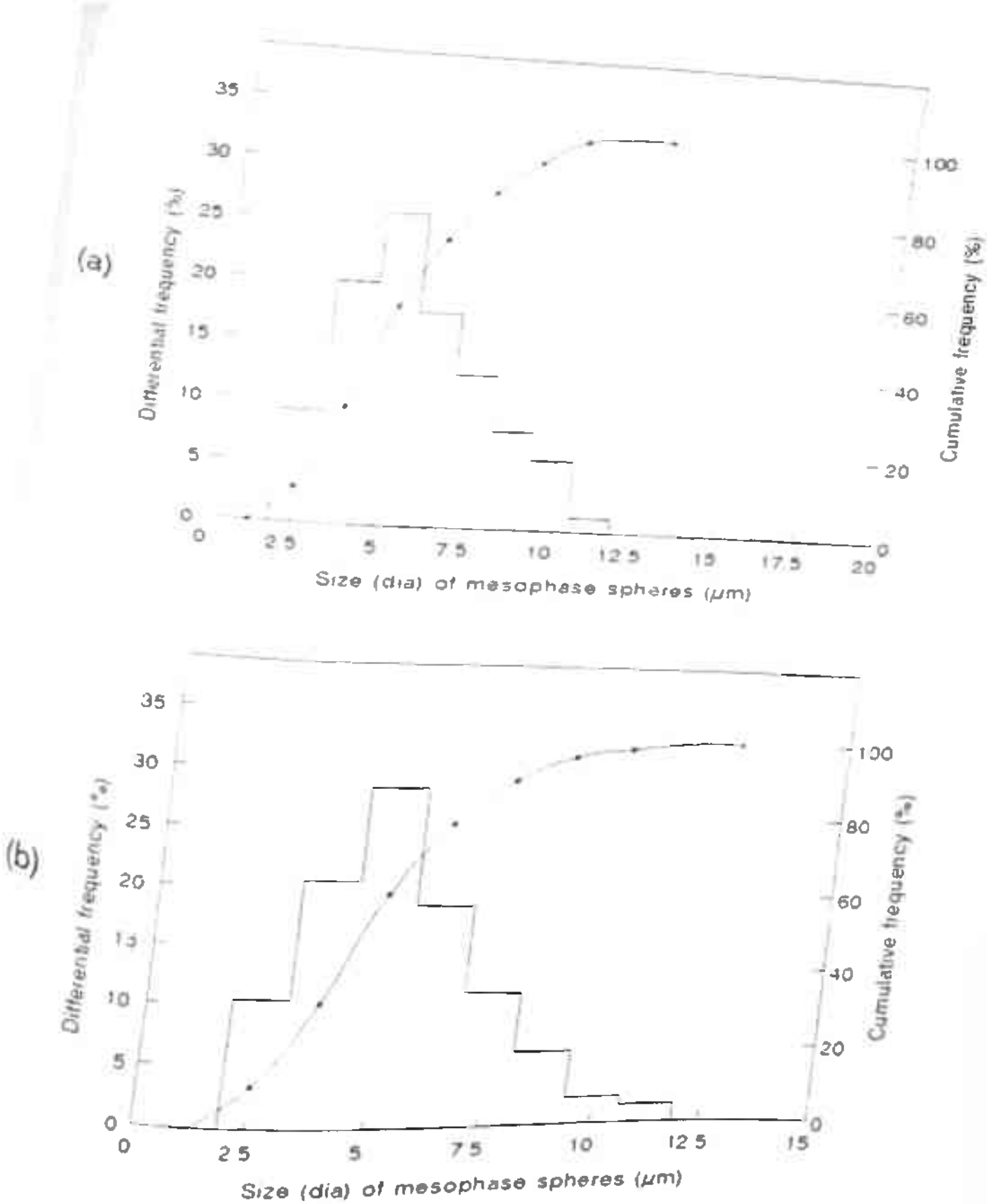


Fig 5.2 Differential and cumulative frequencies of mesophase spherules formed by heat-treatment of (a) coal tar pitch A. (b) coal tar pitch B

5.4 μm. Further, as expected, the heat-treated (mesophase) pitch-
es contain increased amounts of quinoline and toluene insolubles
and decreased amounts of the volatile matter when compared with
the precursor coal tar pitches (Table 5.1).

5.2.2 EFFECT OF TYPE OF TAR OIL ON THE CHARACTERISTICS OF MESOCARBON MICROBEADS

It is seen from Table 5.1 that for both the precursor pitches 'A'
and 'B', the characteristics of the mesocarbon microbeads when
extracted using Tar Oils I and II differ significantly. With tar
Oil-II, having relatively higher boiling range, for both me-
sophase pitches, the values of toluene and quinoline insoluble
contents are on the higher side and that of the volatile matter
on the lower side of the values obtained using Tar Oil-I. Fur-
ther, for both the mesophase pitches, the extraction with Tar
Oil-II results in mesocarbon microbeads having toluene insoluble
content of more than 98% and volatile matter content of around
10%. These microbeads are capable of resulting in good quality
graphite (superior to that involving the extraction by tar Oil-
II), as will be discussed in the next Section 5.2.3.

5.2.3 CHARACTERISTICS OF CARBONS BASED ON MESOCARBON MICROBEADS OBTAINED USING DIFFERENT TAR OILS - I AND II

The mesocarbon microbeads of all the batches, obtained by using
Tar Oils I and II differ in their characteristics, as has been
discussed in Section 5.2.2. Further, all of them on moulding
resulted in good green plates. However, on carbonisation and

TABLE 5.1

CHARACTERISTICS OF COAL TAR PITCHES, MESOPHASE PITCHES AND MESOCARBON MICROBEADS USED IN THE EXTRACTION STUDY

S.NO.	CHARACTERISTICS	COAL TAR PITCH		MESOPHASE PITCH		MESOCARBON MICROBEADS			
		A	B	A	B	AI	AII	BI	BII
1.	Softening point (°C)	84	82	--	--	--	--	--	--
2.	Heat-treatment / Extraction yield (%)	--	--	76	70	40	36	42	37
3.	Quinoline insolubles (%)	4.0	5.3	31.4	42.0	81.8	86.0	78.8	84.0
4.	Toluene insolubles (%)	18.2	20.4	61.1	69.0	95.5	98.4	95.6	98.0
5.	Beta-resin content (%)	13.9	15.1	30.3	27.0	13.7	12.6	16.8	14.0
6.	Coking yield (%)	48.0	49.0	75.0	78.7	89.2	91.0	88.0	90.5
7.	Specific gravity	1.270	1.276	1.290	1.293	--	--	--	--
8.	Size of mesophase spherules (μm)								
	a) Predominant range	--	--	3-10	3-8	3-10	3-10	3-8	3-8
	b) Mean (Average)	--	--	5.6	5.4	5.6	5.6	5.4	5.4

further graphitisation, they showed significant differences in the properties of the plates based on them, as is discussed below.

It is clear from Table 5.2 that though for both the pitch-es, A and B, the green density of the plates is almost the same (1.21-1.22 g cm^{-3}) with the two Tar Oils, the baked density is significantly different. For pitch A, the baked density of the plates is 1.61 g cm^{-3} using Tar Oil-II as against 1.55 g cm^{-3} using Tar Oil-I. For pitch B, it is 1.60 g cm^{-3} for Tar Oil-II and 1.51 g cm^{-3} for Tar Oil-I. In both the cases of pitches (A and B), it is found that there is a significant improvement (enhancement) in the apparent density upon carbonisation when Tar Oil-II is used, compared to Tar Oil-I. This is due to relatively lower weight loss and higher volume shrinkage taking place with Tar Oil-II compared to Tar Oil-I. Because of this very reason, the bending strength of the plates is seen to improve from 69 to 73 MPa for pitch A and from 52 to 73 MPa for pitch B, as the Tar Oil-I is replaced by Tar Oil-II. The relatively lower values of weight loss and higher values of volume shrinkage with Tar Oil-II, compared to Tar Oil-I, for both the pitches, are in complete agreement with relatively lower values of volatile matter (around 10%) and higher values of quinoline and toluene insoluble cont-ents of the mesocarbon microbeads obtained using Tar Oil-II, compared to Tar Oil-I. Further, the Young's modulus and Shore hardness are also seen to be higher for Tar Oil-II than for Tar Oil-I for both the pitches. Finally, the electrical resistivity of the plates is found to decrease, though slightly, from 7.3 to 6.8 m Ohm cm for pitch A, and from 7.0 to 6.6 m Ohm cm for pitch

S. No.	CHARACTERISTICS	HTT = 1000 °C		
		AI	AII	BI
1.	Green density (g cm^{-3})	1.22	1.21	1.22
2.	Baked density (g cm^{-3})	1.55	1.61	1.51
3.	Weight loss (%)	12.0	11.5	13.4
4.	Volume shrinkage (%)	28.6	29.9	28.8
5.	Linear shrinkage (%)	10.0	10.4	11.4
6.	Bending strength (MPa)	69	78	52
7.	Young's modulus (GPa)	12.8	15.5	11.7
8.	Shore hardness	79	88	68
9.	Elect. resistivity (m ohm cm)	7.3	6.8	7.0

	HTT = 2700°C			
BII	AI	AII	BI	BII
1.21	1.22	1,21	1.22	1.21
1.60	1.78	1.82	1.75	1.80
11.4	18.0	17.1	18.6	17.5
29.7	40.9	40.5	41.8	40.8
10.1	16.4	16.0	16.8	16.1
73	49	60	38	54
15.0	20.0	22.8	18.8	21.1
85	56	66	50	65
6.6	3.6	3.3	3.7	3.6

B, as the Tar Oil-I is replaced by Tar Oil-II. Thus, it is seen that whatever be the pitch, A or B, the characteristics of the plates based on mesocarbon microbeads are superior with Tar Oil-II, compared to Tar Oil-I

Further, the results of graphitisation of the baked plates (also given in Table 5.2) show that the product is isotropic for both the Tar Oils. The plates obtained by using Tar Oil-I possess apparent densities of 1.78 and 1.75 g cm^{-3} for Batch AI and BI, respectively, which are again lower than the values of 1.82 and 1.80 g cm^{-3} for Batch AII and BII, respectively, with Tar Oil-II. The bending strength of plates also shows higher values of 60 and 54 MPa with Tar Oil-II, compared to values of 49 and 38 MPa with Tar Oil-I for pitch A and B, respectively. The Young's modulus and Shore hardness, as in the case of baked plates, are also seen to be higher for Tar Oil-II than for Tar Oil-I for both the pitches. Finally, electrical resistivity does not show considerable difference with values of 3.6 and 3.7 using Tar Oil-I and 3.3 and 3.6 m Ohm cm with Tar Oil-II for pitch A and B, respectively.

The microstructures of the two batches of graphitised plates do not show any significant difference, as seen in the optical micrographs of the plates shown in Fig 5.3. Both the batches of mesocarbon microbeads give carbon plates with homogeneous and fine microstructure.

From the above discussion, it is clear that the type of tar oil has a significant effect on the properties of the mesocarbon microbeads as well as on the monolithic carbons based on them. The coal tar pitch, the mesophase pitch and the tar oil

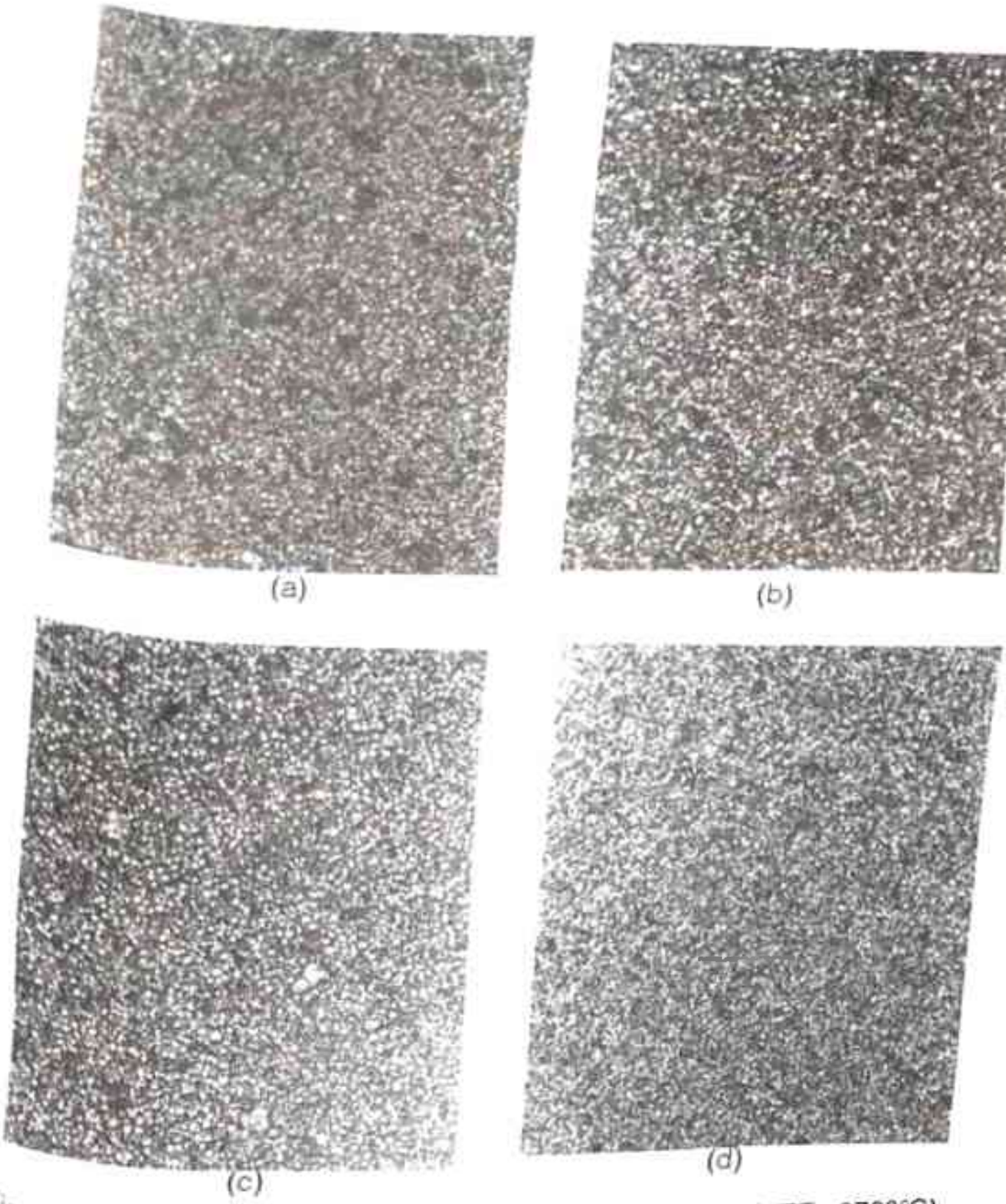


Fig 5.3 Optical micrographs of MCMB-based plates (HTT=2700°C) using tar oils I and II based on
(a) MCMB AI (b) MCMB AII
(c) MCMB BI (d) MCMB BII, at a magnification of 100.

are all complex mixtures of a large number of chemical compounds. The solvent, tar oil, plays very important role by providing a medium for the dissolution of low molecular weight components of the heat-treated pitch and leaving behind mesophase spherules along with some amount of binding components. However, the above discussed results show that not all the fractions of tar oil are equally effective for the purpose of separating mesocarbon microbeads. The carbon and graphite plates based on the two batches of MCMB show considerable difference in most of their properties which are critical for many applications. Monolithic product with relatively inferior characteristics are obtained from microbeads prepared by using lower boiling fraction of tar oil. Thus, tar oil-II with boiling range 230-280°C is a better solvent for the separation of mesocarbon microbeads out of the mesophase pitch for the production of high density - high strength - isotropic graphite.

5.3 EFFECT OF CALCINATION OF MESOCARBON MICROBEADS ON THE CHARACTERISTICS OF MONOLITHIC CARBONS OBTAINED THEREFROM

It has been seen in the previous Section 5.2 that the properties of the MCMB based monolithic carbons depend to a great extent, besides other factors, on the properties of the mesocarbon microbeads such as quinoline and toluene insoluble contents, beta-resin content, and volatile matter content, which, in turn, can be controlled to desired values to large extent by controlling the conditions of their extraction. However, in addition to

extraction, another important step in the overall process of production of MCMB-based high density isotropic graphite is calcination of the mesocarbon microbeads under suitable conditions. The main purpose of this calcination is to remove any tar oil components entrapped in the mesocarbon microbeads. Another objective is to adjust the amount of binding components adhering to the microbeads. In the present investigations, systematic studies were carried out to see the effect of calcination conditions of mesocarbon microbeads, namely, time, temperature and atmosphere (inert/vacuum) of calcination on the characteristic of the resulting MCMB-based isotropic graphite. The calcination study was carried out in two parts. In the first part, the calcination was done in an inert atmosphere under flow of nitrogen (78), and in the second part, the calcination was carried out under reduced pressure of nitrogen (79).

5.3.1 MONOLITHIC CARBONS FROM MESOCARBON MICROBEADS CALCINED AT DIFFERENT TEMPERATURES UNDER INERT ATMOSPHERE

The effect of calcination of mesocarbon microbeads in an inert atmosphere on the properties of monolithic carbons obtained therefrom has been investigated in the present study. A coal tar pitch with low QI content of 2.6% with its other characteristics given in Table 5.3 was heat-treated at a temperature of 425°C in an atmosphere of nitrogen for 2.5 h to generate the mesophase spherules. The properties of the heat-treated pitch (mesophase pitch-I) are also given in Table 5.3. The optical micrograph of the mesophase (heat-treated) pitch and the differential and

Cumulative frequencies of mesophase spherules as a function of the size of mesophase spherules are shown in Fig 5.4. The mesophase pitch was then extracted with a Tar Oil boiling in the temperature range of 230 - 270°C to obtain mesocarbon microbeads MCMB-I. A part of MCMB-I was subsequently calcined in separate lots at temperatures of 240, 280 and 320°C in inert atmospheres for a period of 0.5 h each, to obtain three different batches of the calcined MCMB, designated as IA, IB, and IC, respectively. These MCMB were characterised with respect to the contents of quinoline and toluene insolubles, beta-resins and volatile matter. The calcination conditions and the characteristics of the calcined MCMB are given in Table 5.4.

The MCMB of all the batches were then hot-moulded into small rectangular plates of size 60 mm x 20 mm x 4 mm using a conventional hydraulic press. These plates were carbonised to a temperature of 1100°C and some of them were graphitised to 2700°C. The resulting carbon and graphite plates were tested with respect to various characteristics, the values of which are compiled in Table 5.5 and 5.6.

5.3.1.1 CALCINATION OF MESOCARBON MICROBEADS AT DIFFERENT TEMPERATURES UNDER INERT ATMOSPHERE

The heat-treatment of the precursor coal tar pitch (with characteristics given in Table 5.3), at 425°C for 2.5 h generates mesophase spherules of about 4-16 μm size, as also shown in Fig 5.4. It is also seen from the Table 5.3 that the heat-treatment results in the increased values of QI, TI and CV of the resultant

TABLE 5.3

CHARACTERISTICS OF PRECURSOR COAL TAR PITCH-I AND MESOPHASE PITCH-I

S.No.	CHARACTERISTICS	COAL TAR PITCH	MESOPHASE PITCH
1.	Softening point (°C)	76	--
2.	Quinoline insoluble content (%)	2.6	25.3
3.	Toluene insoluble content(%)	21.7	59.3
4.	Beta-resin content (%)	19.1	34.0
5.	Coking yield (%)	47.6	71.1
6.	Ash content (%)	0.06	0.15
7.	Specific gravity	1.28	1.30
8.	Size of mesophase spherules a) Predominant range (μm) b) Median (μm) c) Mean (μm)		4-16 7.4 9.4

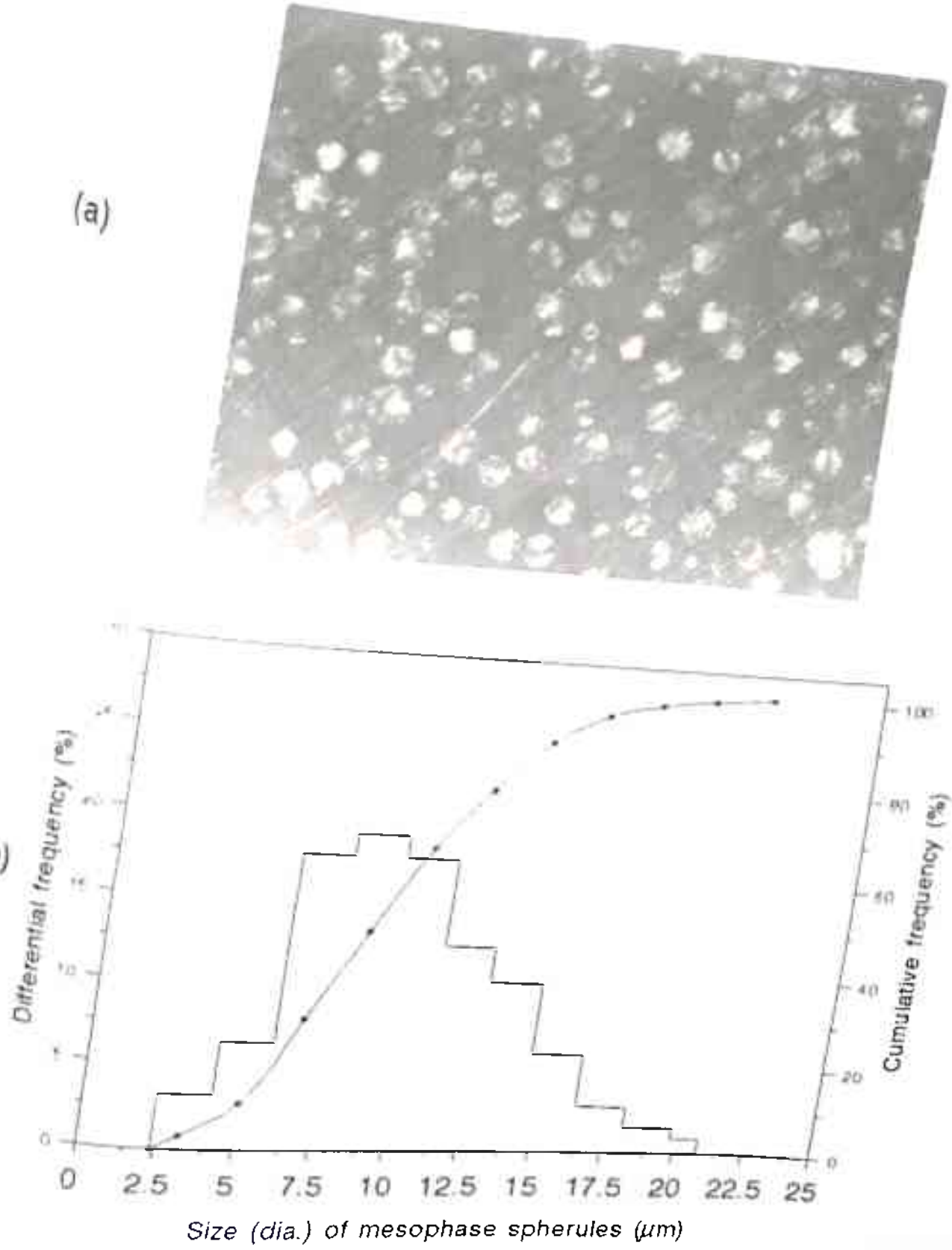


Fig 5.4 (a) Optical mirograph of mesophase pitch I (magnification = 400)
(b) Differential and cumulative frequencies of mesophase spherules as a fuction of their size.

mesophase pitch, which is obviously due to the removal of volatile constituents as well as condensation and polymerisation reactions among the molecules.

The characteristics of the uncalcined mesocarbon microbeads as well as those calcined under nitogen atmosphere are given in Table 5.4. It is seen from this table that the quinoline insoluble content of the microbeads increases from an initial value of 74.9% to values of 81.3, 85.9 and 89.0% as the calcination temperature increases from 240 to 320°C and the toluene insoluble content increases from initial values of 93.6% to values of 97.7, 97.8 and 99.7% at the above temperatures. The volatile matter content, in turn, decreases from an initial value of 15.4% to values of 11.4, 11.1 and 10.8% at the above mentioned temperatures. These variations in the characteristics of microbeads are obviously due to the removal of some volatile molecular species.

5.3.1.2 CHARACTERISTICS OF MONOLITHIC CARBONS USING MESOCARBON MICROBEADS CALCINED UNDER INERT ATMOSPHERE

The characteristics of carbon plates are given in Table 5. . It is seen from this table that the apparent density of the plates based on different MCMB, does not show any significant difference with values lying in the range of 1.28 - 1.30 g cm^{-3} and 1.69 - 1.70 g cm^{-3} at green and carbonised states respectively. However bending strength of the carbon plates shows a significant improvement from 28 MPa for uncalcined microbeads (MCMB-I) to values of 70, 84 and 85 MPa for the microbeads calcined at 240,

TABLE 5.4

CHARACTERISTICS OF MESOCARBON MICROBEADS (MCMB-I) CALCINED AT DIFFERENT TEMPERATURE UNDER NITROGEN ATMOSPHERE

S.No.	CHARACTERISTICS	BATCH			
		I	IA	IB	IC
1.	Calcination parameters:				
	(i) Temperature (°C)	-	240	280	320
	(ii) Residence time (min.)	-	30	30	30
	(iii) Yield (%)	-	92.5	91.5	91.0
2.	Quinoline insolubles (%)	74.9	81.3	85.9	89.0
3.	Toluene insolubles (%)	93.6	97.7	97.8	99.7
4.	Beta-resin content (%)	18.7	16.4	11.9	10.7
5.	Volatile matter (%)	15.4	11.4	11.1	10.8

TABLE 5.5

CHARACTERISTICS OF CARBON PLATES BASED ON MESOCARBON MICROBEADS-I *CALCINED AT DIFFERENT TEMPERATURES UNDER INERT ATMOSPHERE (HTT=1100°C)*

S.No.	CHARACTERISTICS	BATCH			
		I	IA	IB	IC
1.	App. green density (g cm^{-3})	1.30	1.28	1.29	1.28
2.	App. baked density (g cm^{-3})	1.69	1.69	1.69	1.70
3.	Specific gravity	1.76	1.74	1.72	1.76
4.	Weight loss (%)	15.6	11.4	11.0	10.1
5.	Volume shrinkage (%)	32.0	32.5	31.5	34.0
6.	Linear shrinkage (%)	13.4	12.8	12.2	11.9
7.	Bending strength (MPa)	28	70	84	85
8.	Young`s Modulus (GPa)	10	14	14.6	15.3
9.	Elect. Resistivity (mOhm cm)	--	6.8	6.7	6.9
10.	Scleroscopic hardness	50	78	82	85

280 and 320°C respectively. These variations in the bending strength of the carbon plates are probably due to the difference in the ß-resin contents of the microbeads. It is seen from Table 5.3 that the MCMB-I have a ß-resin content of 18.7%, which is probably higher than what is required to get strong, crack-free and high density carbon. However, calcination of these MCMB-I at increasing temperatures of 240, 280 and 320°C reduces the content of beta-resins to values of 16.4, 11.9 and 10.7%, respectively, which results in increase in the bending strength of the plates.

The above discussed results shows that the extraction of the mesophase pitch with the tar oil yields mesocarbon microbeads containing an excess of relatively lower molecular weight components (tar oil components or beta-resins). However, calcination of these microbeads reduces the excess of low molecular weight components and improves the suitability of MCMB for the purpose of monolithic carbons.

Further, the microscopic examinations showed that microbeads calcined at 280 and 320°C lead to crack-free carbon plates having homogeneous and fine microstructure, whereas the microstructure of the plates based on uncalcined microbeads and those calcined at 240°C shows that these plates contain some cracks, as is revealed from in the optical micrographs of these plates shown in Fig 5.5. These cracks reflect the presence of tar oil components or other low molecular weight components in the mesocarbon microbeads. However, calcination temperatures of 280 and 320°C are effective to result in crack free carbons.

Regarding the results of graphitised plates summarised in Table 5.6 it is found that in all the cases, product is iso-

Fig 5 5 Optical micrographs of carbon plates (HTT=1100°C) using (a) uncalcined MCMB (b) MCMB calcined at 240°C (c) MCMB calcined at 280°C (d) MCMB calcined at 320°C at a magnification of 100

TABLE 5.6

CHARACTERISTICS OF GRAPHITISED PLATES BASED ON MESOCARBON MICROBEADS-I CALCINED AT DIFFERENT TEMPERATURES UNDER INERT ATMOSPHERE (HTT=2700°C)

S. No.	CHARACTERISTICS	BATCH			
		I	IA	IB	IC
1.	App. green density (g cm^{-3})	1.30	1.28	1.29	1.28
2.	App. graphitised density (g cm^{-3})	1.86	1.93	1.96	1.97
3.	Specific gravity	1.88	1.93	1.97	1.99
4.	Weight loss (%)	20.6	16.6	16.3	16.0
5.	Volume shrinkage (%)	43.2	44.2	43.6	45.9
6.	Linear shrinkage (%)	19.0	18.6	18.2	18.0
7.	Bending strength (MPa)	--	56	69	70
8.	Young's modulus (GPa)	--	27.1	28.9	29.0
9.	Coeff. of thermal Expansion ($\times 10^{-6} °K^{-1}$); ‖	--	6.9	6.9	6.6
	⊥	--	7.0	6.8	6.5
10.	Anisotropy ratio	--	1.01	1.01	1.02
11.	Elect. resistivity (mOhm cm)	--	2.6	2.5	2.6
12.	Scleroscopic hardness	--	63	68	69

tropic (anisotropic ratio = 1.01-1.02). It is seen that the plates based on microbeads calcined at temperatures above 240°C exhibit very good density of 1.93, 1.90 and 1.97 g cm^{-3}, and bending strength of 56, 69 and 70 MPa for the batches IA, IB, and IC, respectively. These plates show reasonably good hardness with values in the range of 63-69.

From the above results, it appears that the calcination of mesocarbon microbeads (obtained as tar oil insolubles) in the temperature range of 240-320°C in an inert atmosphere leaves a beta-resin content of 10-12% in the mesocarbon microbeads with a volatile matter content of less than 11-12%, and makes them suitable to be used for the production of monolithic carbons.

5.3.2 MONOLITHIC CARBONS FROM MESOCARBON MICROBEADS CALCINED AT DIFFERENT TEMPERATURES UNDER REDUCED PRESSURE OF NITROGEN

The study of the effect of calcination of mesocarbon microbeads on the properties of monolithic carbons was extended to find out suitable calcination conditions when the calcination is carried out under reduced pressure of an inert atmosphere of nitrogen. For this purpose, a low-QI coal tar pitch was heat-treated at a temperature of 425°C for 2.5 h in an atmosphere of nitrogen to generate the mesophase spherules. The properties of the coal tar pitch and the heat-treated pitch are given in Table 5.7. The optical micrograph of the heat-treated pitch (mesophase pitch-II) and the differential and cumulative frequencies as a function of the size of mesophase spherules are shown in Fig 5.6. The me-

TABLE 5.7

CHARACTERISTICS OF PRECURSOR COAL TAR PITCH-II AND MESOPHASE PITCH-II

S.No.	CHARACTERISTICS	COAL TAR PITCH	MESOPHASE PITCH
1.	Softening point (C)	76	--
2.	Quinoline insoluble content (%)	2.6	26.6
3.	Toluene insoluble content(%)	21.7	60.2
4.	Beta-resin content (%)	19.1	33.6
5.	Coking yield (%)	47.6	71.6
6.	Ash content (%)	0.06	0.16
7.	Specific gravity	1.28	1.29
8.	Size of mesophase spherules a) Predominant range (µm) b) Median (µm) c) Mean (µm)		4-16 8.5 9.8

sophase pitch was extracted with a Tar Oil to obtain the mesocarbon microbeads (MCMB-II), which were subsequently calcined in separate lots at temperatures of 215, 230, 245, 260, 285 and 310°C, under reduced pressure of nitrogen, to obtain six different batches of the calcined MCMB, designated as IIA, IIB, IIC, IID, IIE and IIF, respectively. The MCMB of these batches were characterised with respect to the contents of quinoline and toluene insolubles, beta-resins and volatile matter. The calcination conditions and the characteristics of the calcined MCMB are given in Table 5.8.

The MCMB of all the six batches (IIA to IIF) were then hot-moulded into small rectangular plates of size 60 mm x 20 mm x 4 mm using a conventional hydraulic press. These plates were carbonised to a temperature of 1100°C and some of them were graphitised to 2700°C. The resulting carbon and graphite plates were tested with respect to various characteristics, the values of which are compiled in Tables 5.9 - 5.11.

5.3.2.1 CALCINATION OF MESOCARBON MICROBEADS AT DIFFERENT TEMPERATURES UNDER REDUCED PRESSURE OF NITROGEN

It is clearly seen from the optical micrograph of the mesophase pitch (Fig 5.6) that the heat-treatment of the precursor pitch results in the formation of mesophase spherules with a smallest size of less than 2.5 μm to a size as high as about 21 μm. The average (mean) size of these spherules has been found to be 9.3 μm with the predominant size lying in the range of 4-16 μm and the median size of 8.5 μm, as seen from the graphs of differen-

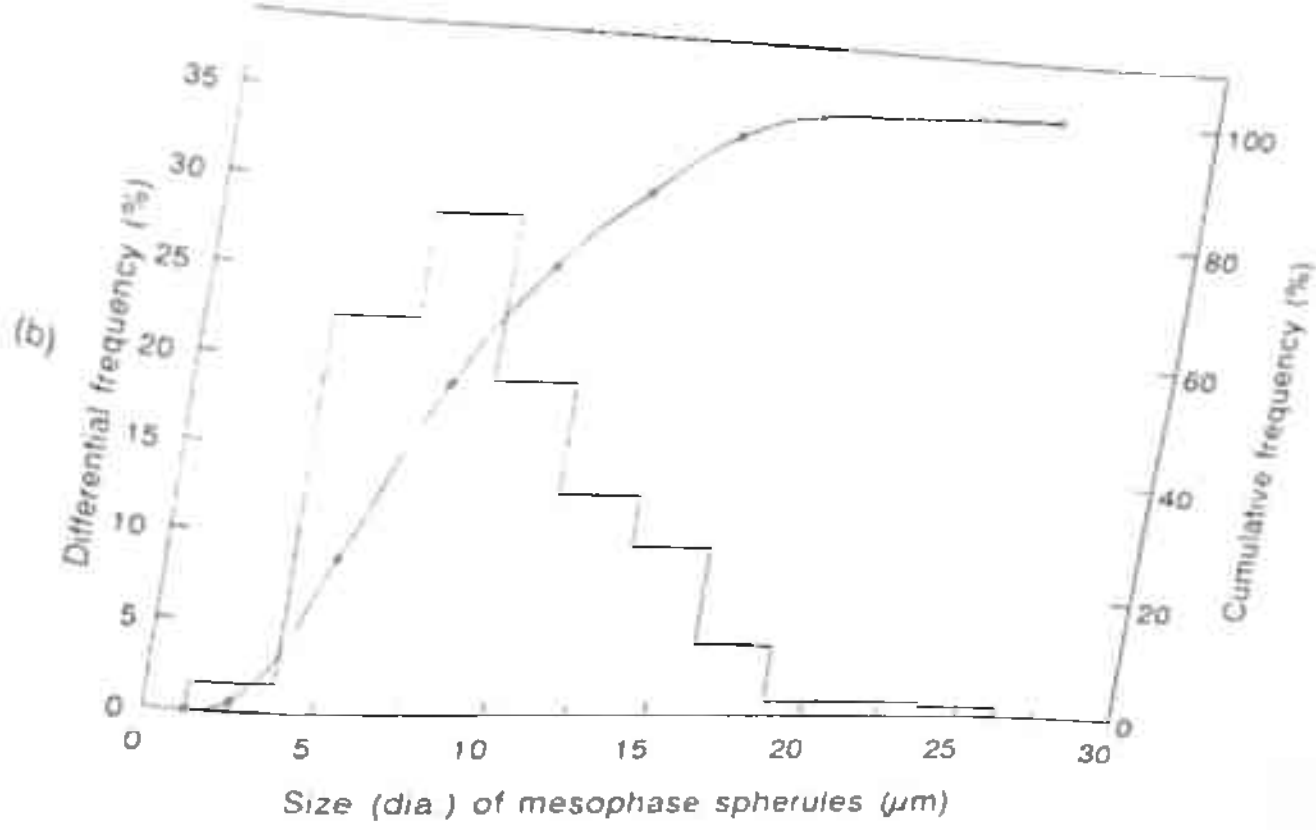


Fig.5.6 (a) Optical micrograph of mesophase pitch II (magnification = 400)
(b) Differential and cumulative frequencies of mesophase spherules formed in mesophase pitch I as a function of their size.

tial (histogram) and cumulative frequencies of these mesophase spherules as a function of their size.

It is seen from Table 5.8 that an increase in the calcination temperature of the MCMB from 215°C to 310°C results in a corresponding increase in the quinoline insoluble content from 78.0% at 215°C to values of 82.2, 83.6, 84.3, 86.2 and 91.8% at the temperatures of 230, 245, 260, 285 and 310°C, respectively. and the toluene insoluble content from 89.9% at 215°C to values of 93.7, 94.4, 94.9, 96.4, and 96.6%, respectively, at the above temperatures. The volatile matter content, in turn, decreases from a value of 14.0% at 215°C to values of 13.7, 13.5, 13.0, 12.0 and 10.2%, respectively, at the above mentioned temperatures. These variations in the characteristics of the MCMB are obviously due to the removal of molecular species which are volatile at these calcination temperatures. Gradually increasing values of the quinoline or toluene insoluble contents with the calcination temperature show that these volatile molecular species are soluble in quinoline or toluene. It is further seen from this table that the beta-resin content of the MCMB undergoes only a marginal decrease from 11.9% to 10.2% as the calcination temperature is increased from 215 to 285°C. This could be because of the simultaneous conversion of some of the toluene soluble components of the MCMB to beta-resins and the beta-resins components to quinoline insolubles, resulting thereby in only a marginal change (decrease) in the beta-resin content. However, as the calcination temperature is increased further to 310°C, the beta-resin content gets reduced to a significantly low value of 4.8%. This may be due to more of the beta-resin components getting

S. No.	CHARACTERISTICS	BATCH					
		IIA	IIB	IIC	IID	IIE	IIF
1.	Calcination Temperature (°C)	215	230	245	260	285	310
2.	Quinoline insoluble content (%)	78.0	82.2	83.6	84.3	86.2	91.8
3.	Toluene insoluble content (%)	89.9	93.7	94.4	94.9	96.4	96.6
4.	Beta-resin content (%)	11.9	11.5	10.8	10.6	10.2	4.8
5.	Volatile matter content (%)	14.0	13.7	13.5	13.0	12.0	10.2

converted to quinoline insolubles than the toluene solubles changing to beta-resins, because of the polymerisation and condensation reactions.

5.3.2.2 CHARACTERISTICS OF MONOLITHIC CARBONS USING MESOCARBON MICROBEADS CALCINED UNDER REDUCED PRESSURE OF NITROGEN

It is seen from Table 5.9 that the apparent baked densities of the carbons of Batches IIB to IIF lie in a narrow range of 1.71-1.74 g cm^{-3}, except for Batch-IIA, which has the highest baked density of 1.80 g cm^{-3}. This behavior is in parallel with that of the green densities of these carbons, which means that the higher the green density, the higher is the baked density. In fact, it is quite reasonable also as one would see from the data shown in Table 5.10. The ratio of the fractional residual weight to the fractional residual volume for various batches (corresponding to different calcination temperatures) given in Table 5.10 works out to be almost constant (lying in the range 1.32-1.35), showing thereby that the baked density is directly proportional to the green density. Further, the values of the expected baked density are found to be quite close to the actual (observed) values.

Furthermore, it is seen from Tables 5.8 and 5.9 that the MCMB of Batch-IIA with a volatile matter content of 14.0% results in carbon plates bearing visible cracks, with an apparent baked density of 1.90 g cm^{-3} and a bending strength of 20 MPa. Looking at the characteristics of the MCMB of Batch-A from Table 5.8 and the cracks in the resulting carbons, this high value of the apparent density coupled with a low value of the bending strength

CHARACTERISTICS

CALCINED AT DIFFERENT TEMPERATURES UNDER REDUCED PRESSURE OF NITROGEN (HTT=1100°C)

S. No.	CHARACTERISTICS	BATCH					
		IIA	IIB	IIC	IID	IIE	IIF
1.	App. green density (g cm^{-3})	1.36	1.30	1.32	1.31	1.33	1.28
2.	App. baked density (g cm^{-3})	1.80	1.74	1.72	1.72	1.72	1.71
3.	Specific gravity	1.80	1.75	1.74	1.72	1.72	1.72
4.	Weight loss (%)	15.9	15.4	13.3	13.5	14.4	13.8
5.	Volume shrinkage (%)	36.8	36.1	34.2	33.6	33.7	35.6
6.	Linear shrinkage (%)	13.8	13.5	13.0	12.6	12.7	13.7
7.	Bending strength (MPa)	20	45	78	81	84	79
8.	Young's modulus (GPa)	4.3	8.6	9.4	10.7	11.9	10.7
9.	Scleroscopic hardness	---	58	56	64	68	75
10.	Elect. resistivity (mOhm cm)	5.4	5.1	4.4	5.1	4.1	4.0

TABLE-5.10

DATA SHOWING CORRELATION OF APPARENT BAKED AND GREEN DENSITIES IN TERMS OF WEIGHT LOSS AND VOLUME SHRINKAGE

BATCH	CALCINATION TEMPERATURE (°C)	APPARENT GREEN DENSITY (GD) ($g\ cm^{-3}$)	FRACTIONAL RESIDUAL WEIGHT (a)	FRACTIONAL RESIDUAL VOLUME (b)	DENSITY AMPL. FACTOR (c=a/b)	EXPECTED BAKED DENSITY (GDXc) ($g\ cm^{-3}$)	ACTUAL BAKED DENSITY ($g\ cm^{-3}$)
A	215	1.36	0.841	0.632	1.335	1.81	1.80
B	230	1.30	0.865	0.639	1.354	1.76	1.74
C	245	1.32	0.870	0.658	1.322	1.75	1.72
D	260	1.31	0.874	0.664	1.316	1.72	1.72
E	285	1.33	0.873	0.663	1.316	1.75	1.72
F	310	1.28	0.863	0.664	1.340	1.72	1.71

NOTE: Fractional residual weight (a) = 1 - wt. loss (%)/100
Fractional residual volume (b) = 1 - vol. shrinkage (%)/100
Density amplification factor (c) = a/b

suggests that these MCMB (calcined at 215°C) contain an excess amount of low molecular weight components like tar oil or toluene solubles, which while improving the binding and fusion of the MCMB during compaction (as seen from the highest value of the green density) also result in the formation of visible cracks in these carbons during carbonisation. These cracks, in turn, lead to a poor bending strength of only 20 MPa of these carbons.

The increase in the calcination temperature from 215 to 230 and 245°C, results in improvement in apparent density and bending strength of plates, but microstructure of these plates reveals the presence of some cracks even at calcination temperature of 245°C (Fig 5.7). Further, calcination of the microbeads at temperatures above 245°C results in a decrease in the tar oil or toluene solubles content, which helps in eliminating the formation of any visible crack in the carbonised product, resulting thereby in an increase in the bending strength of the carbons upto a value of 84 MPa for Batch IIE (285°C). However for the MCMB of Batch-IIF calcined at 310°C, the bending strength decreases slightly to 79 MPa from the highest value of 84 MPa (for Batch-IIE), which could be attributed to a substantially reduced value (4.8%) of the beta-resin content.

Regarding, the results of the graphitised plates, Table-5.11 shows that the plates based on MCMB-IID to IIF (calcined at temperatures of 260-310°C) possess high density of 1.93-2.02 g cm^{-3} and high bending strength of 65-68 MPa respectively. These high values of density and strength are critical requirements expected of a high density . high strength - isotropic graphite needed for critical applications.

Optical micrographs of carbon plates (HTT=1100°C) using mesocabon microbeads
a) calcined at 230°C
b) calcined at 245°C, at a magnification of 100.

S. No.	CHARACTERISTICS	BATCH					
		1A	IB	IC	ID	IE	IF
1.	App. green density (g cm^{-3})	1.36	1.30	1.32	1.31	1.33	1.28
2.	App. graphitised density (g cm^{-3})	--	1.90	1.89	1.93	2.02	1.99
3.	Specific gravity	--	1.91	1.90	1.94	2.03	2.00
4.	Weight loss (%)	--	21.0	18.0	18.2	18.6	18.0
5.	Volume shrinkage (%)	--	46.0	46.3	45.0	45.6	47.0
6.	Linear shrinkage (%)	--	18.7	18.4	18.0	18.2	19.0
7.	Bending strength (MPa)	--	32	62	65	69	68
8.	Young's modulus (GPa)	--	20.2	24.0	24.4	26.3	26.0
9.	Scleroscopic hardness	--	50	48	57	55	58
10.	Elect. resistivity (mOhm cm)	--	2.5	2.2	2.3	2.2	2.1

In view of the above discussion, it can be concluded that for the given mesocarbon microbeads, the properties of the final product depend quite significantly on the calcination conditions, which in turn, fix the contents of volatile matter and quinoline and toluene insoluble contents. A temperature in the range of 260-310°C with a preferable value of 285°C under reduced pressure of nitrogen appears to be suitable for the calcination of microbeads (obtained by using a tar oil of 230-280°C boiling range) for the production of high density graphite.

5.4 HIGH DENSITY GRAPHITE PREPARED BY USING OPTIMISED PROCESSING CONDITIONS

Having optimised the conditions of extraction of a mesophase pitch (Section 5.2) and then the conditions of calcination of the mesocarbon microbeads (Section 5.3), an attempt was made to study the characteristics of carbons made from mesocarbon microbeads having a mean size of about 5 μm, extracted and calcined under optimum conditions found under studies discussed in the above sections. For this purpose a coal tar pitch containing 3.1% of primary QI (Table 5.12) was heat-treated at 420°C for 3 h to form mesophase spherules with a mean size of about 5 μm. The heat-treatetd pitch was extracted with a tar oil having a boiling range of 230-280°C to obtain the mesocarbon microbeads, which were then calcined at a temperature of 285°C under reduced pressure of nitrogen. The characteristics of the coal tar pitch, mesophase pitch and the mesocarbon microbeads are summarised in Table 5.12.

TABLE 5.12

CHARACTERISTICS OF COAL TAR PITCH, MESOPHASE PITCH AND MESOCARBON MICROBEADS

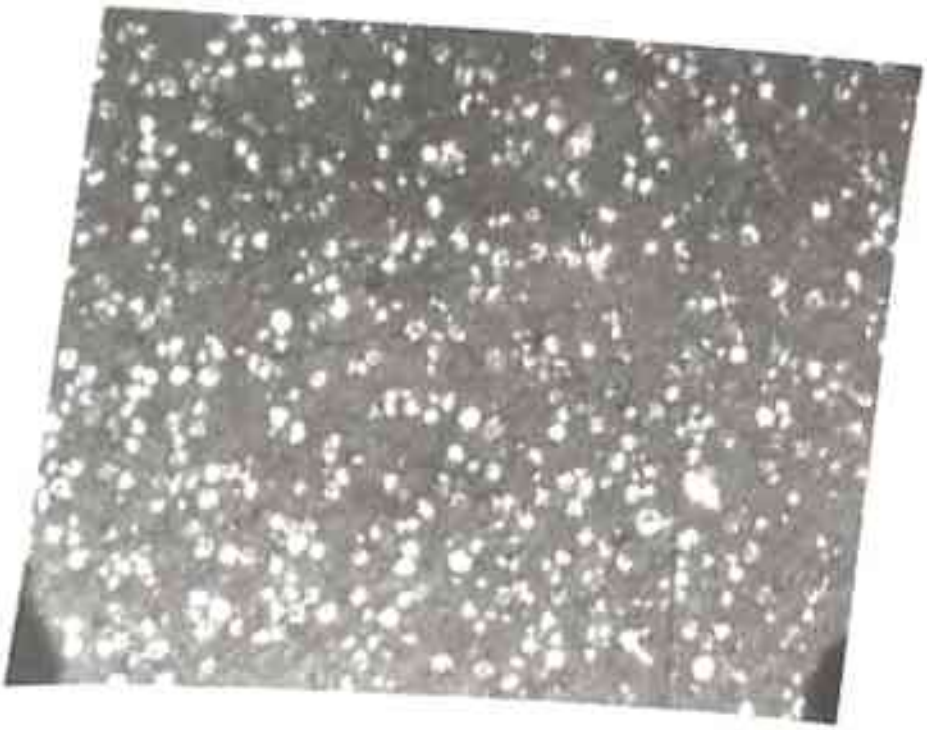
S. No.	CHARACTERISTICS	COAL TAR PITCH	MESOPHASE PITCH	MESOCARBON MICROBEADS
1.	Softening point (°C)	76	--	--
2.	Heat-treatment/ Extraction yield (%)	--	78.0	39.0
3.	Quinoline insoluble content (%)	3.1	19.5	90.4
4.	Toluene insoluble content (%)	20.7	50.3	97.9
5.	Beta-resin content (%)	17.6	30.8	7.5
6.	Coking yield (%)	48.0	68.1	90.0
7.	Size of mesophase spherules	--	3-8	3-8
	Predominant range (μm)	--	4.2	4.2
	Median (μm)	--	5.3	5.3
	Mean (μm)	--	2.27	2.67
8.	Atomic C/H ratio			

The calcined MCMB were then hot-moulded into small rectangular plates of size 60 mm x 20 mm x 4 mm using a conventional hydraulic press. These plates were carbonised to a temperature of 950°C, and some of them graphitised to 2700°C. The resulting carbon and graphite plates were finally tested with respect to various characteristics, the values of which are compiled in Table 5.13.

Fig 5.8 shows that the heat-treated pitch contains mesophase spherules with a predominant size range of about 3-8 μm with mean size of 5.3 μm. Extraction of the mesophase pitch with tar oil followed by calcination of microbeads at 285°C under reduced pressure results in mesocarbon microbeads having quinoline and toluene insoluble contents of 90.4 and 97.9% respectively, with a volatile matter of 9.0% and atomic C/H ratio of 2.69. The heat-treated pitch contains mesophase spherules to an extent of 39% by weight of it, as also given in Table 5.12 showing the characteristics of coal tar pitch, mesophase pitch and mesocarbon microbeads.

It is seen from this Table 5.13 that the green plates made from these microbeads, possess an apparent density of 1.27 g cm^{-3}. On carbonisation to 950°C, the green plates undergo a weight loss of 10.2% with a large volume shrinkage of 31.9% on carbonisation to 950°C, which increases the apparent density of the plates to 1.68 g cm^{-3}. The carbon plates are found to have a good bending strength of 112 MPa and a Shore hardness of 105. On further heat-treatment from 950 to 2700°C, the plates show a cumulative weight loss of 15.1% accompanied by cumulative volume and linear shrinkages, of 44.1 and 16.6%, respectively. The

(a)



(b)

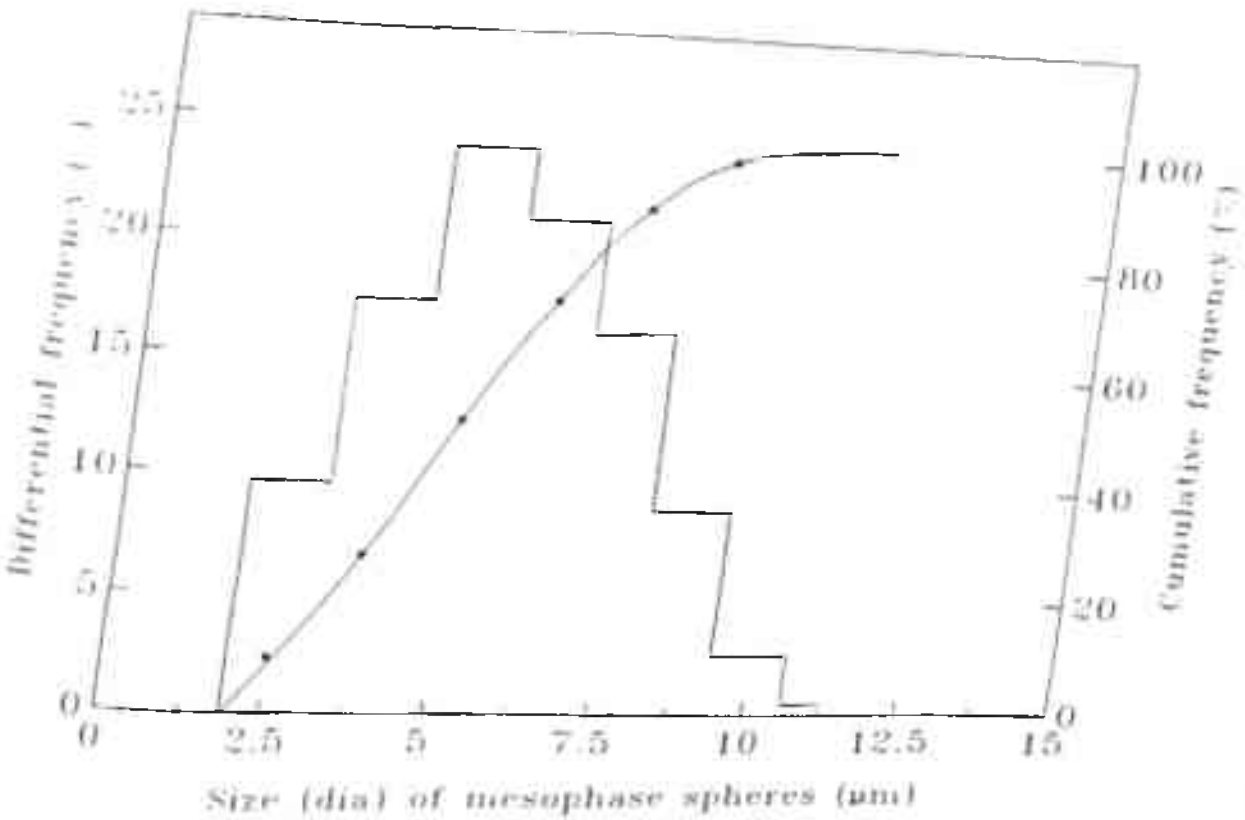


Fig.5.8 *(a) Optical mirograph of heat-treated pitch (magnification = 400)*
(b) Differential and cumulative frequencies of mesophase spherules as a fuction of their size.

TABLE 5.13

CHARACTERISTICS OF CARBON PLATES USING MCMB PREPARED UNDER OPTIMUM PROCESSING CONDITIONS (HTT = 950°C AND 2700°C)

S.No.	CHARACTERISTICS	VALUE AT HTT (°C) OF	
		950	2700
1.	App. green density ($g\ cm^{-3}$)	1.27	1.27
2.	Apparent density ($g\ cm^{-3}$)	1.68	1.93
3.	Specific gravity	1.69	1.94
4.	Weight loss (%)	10.2	15.1
5.	Volume shrinkage (%)	31.9	44.1
6.	Linear shrinkage (%)	10.5	16.6
7.	Bending strength (MPa)	112	88
8.	Young's modulus (GPa)	20	28
9.	Coeff. of thermal Expansion ($\times 10^{-6} °K^{-1}$) ∥	--	6.9
	⊥	--	6.8
10.	Anisotropy ratio	--	1.01
11.	Scleroscopic hardness	105	80
12.	Elect. resistivity (mOhm cm)	6.8	2.4

apparent density, in turn, increases from 1.68 g cm^{-3} at the HTT of 950°C to a value of 1.93 g cm^{-3} at 2700°C, whereas, the bending strength of the plates decreases from 112 to 88 MPa by further heat-treatment from 950 to 2700°C.

The microstructure of these MCMB based monolithic carbons in both carbonised (HTT=950°C) as well as graphitised (HTT = 2700°C) states is found to be quite homogeneous with a fine isotropic texture as also seen in Fig 5.9 showing optical micrograph of the graphite plate. It must be mentioned here that in the present investigations conventional hydraulic press has been used. It can expected that the overall characteristics like apparent density, bending strength and fine-isotropic structure of the product would be further improved if isostatic press is used for moulding of mesocarbon microbeads.

5.5 CONCLUSIONS

1. The mesocarbon microbeads obtained by extraction of two different mesophase pitches with a tar oil of boiling range 230 - 280°C result in good carbon plates having better values of the critical characteristics as compared to carbons obtained by using another tar oil with relatively lower boiling range of 180-230°C. The solvent tar oil for extraction of mesophase pitch should predominantly boil in the temperature range of 230-280°C.

2. The calcination of the mesocarbon microbeads in the temperature range of 280-320°C in inert atmosphere removes the entrapped tar oil as well as adjust the binding components to an

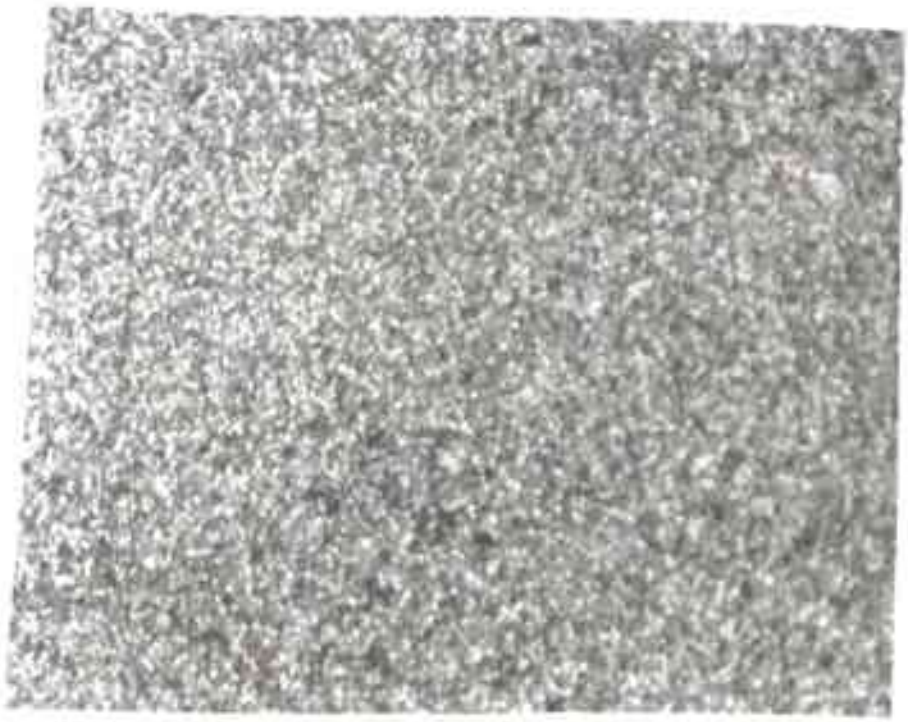


Fig 5.9 Optical micrograph of MCMB-based plate (HTT=2700°C) using mesocabon microbeads prepared under optimum condition (at a magnification of 100).

optimum level, thereby making the MCMB suitable for the production of high density isotropic graphite.

3. A temperature in the range of 260-310°C with a preferable value of 285°C under reduced pressure (about 5 cmHg) of nitrogen appears to be suitable for the calcination of microbeads for the production of high density graphite.

4. The heat-treatment of a coal tar pitch containing about 3% of primary QI at 420°C for 3 h forms mesophase spherules with a mean size of about 5 μm.

(i) The extraction of heat-treated pitch with tar oil of optimum boiling range (230-280°C) leads to mesocarbon microbeads with a yield of 39%.

(ii) Calcination of these microbeads at a temperature of 285°C under reduced pressure of 5 cm Hg of nitrogen makes them suitable for the production of high density - high strength - isotropic graphite.

(iii) The plates made from these microbeads, possess an apparent density of 1.27 g cm^{-3}, 1.68 g cm^{-3} and 1.93g cm^{-3} at green stage and heat-treated to 950 and 2700°C repectively. The bending strength of 112 MPa and 88 MPa is obtained at HTT of 950 to 2700°C. The anisotropy ratio w.r.t. coefficient of thermal expansion is 1.02 indicating that the product is isotropic.

CONCLUSIONS

1. EFFECT OF HEAT - TREATMENT CONDITIONS ON MESOPHASE FORMATION IN DIFFERENT COAL TAR PITCHES

(i) The heat-treatment of a coal tar pitch results in increased values of the quinoline and toluene insoluble contents, as well as the coking value of the resultant heat-treated or mesophase pitch, compared to those of the original (starting) pitch.

(ii) The size and concentration of mesophase in any heat-treated pitch increases as the soaking time at a particular heat-treatment temperature (420°C) increases. However, the increase in the mesophase size with heat-treatment temperature is dependent upon the QI content in the precursor pitch.

(iii) In a coal tar pitch having a QI content of 0.5%, the mean size of the mesophase spherules increases to a value as high as 24.2 μm for a heat-treatment period of 3h, whereas, it reaches a value of only 12.8 μm for a pitch having a QI content of 6.5%, even after 7h of the heat-treatment. For a QI content of 3.3%, however, the mean size of the spherules is found to be 9.1 μm for a heat-treatment period of 5h. Thus, the presence of quinoline insolubles is useful to control the size of mesophase spherules to a desired value.

2. DEVELOPMENT OF MESOPHASE POWDERS OBTAINED USING DIFFERENT SOLVENTS

(i) Quinoline insolubles of a mesophase pitch do not contain adequate wetting and binding components and fail to give a dense and strong monolithic carbon. Toluene insolubles, on the other hand, even after calcination upto 350°C, contain an excess of wetting and binding components, which lead to severe bloating (swelling) of the product during carbonisation. Thus, toluene and quinoline are not suitable for the extraction of a mesophase pitch.

(ii) The extraction of a mesophase pitch with a tar oil yields a mesophase powder (also called "mesocarbon microbeads, MCMB") suitable for producing a dense and strong monolithic carbon. Thus, tar oil is a suitable solvent for the extraction a mesophase pitch to obtain mesocarbon microbeads.

3. MONOLITHIC CARBONS FROM PRECURSOR COAL TAR PITCHES HAVING DIFFERENT CONTENTS OF QUINOLINE INSOLUBLES

(i) A very low QI content of 0.5 % in the precursor coal tar pitch leads to mesophase spherules (mesocarbon microbeads) of higher size lying predominantly in the range of 6-21 μm with a mean size of 13.5μm, due to ease of coalescence of the mesophase spherules in the presence of only few QI particles, besides resulting in a low yield of 23% of the mesocarbon microbeads. The coal tar pitches containing 3.3 %, 6.5 % and 9.2% of QI lead to 40 %, 47 % and 52 wt.% of mesocarbon microbeads with an average size of about 5 μm,

respectively. The weight percent of inert QI matter in the MCMB as well as the yield of the microbeads increases with the increase in the QI content of the precursor pitch.

(ii) The mesocarbon microbeads based on the coal tar pitch having 0.5 % of QI particles, contain 86.2% of quinoline insolubles and 99.4% of toluene insolubles with a volatile matter of 10.6 %. The monolithic carbon plates (at HTT of 950°C) made using these MCMB possess an apparent density of 1.58 g cm^{-3}, bending strength of 62 MPa and anisotropy ratio of 1.01 along with a homogeneous and fine microstructure.

(iii) The mesocarbon microbeads based based on a precursor coal tar pitch having 3.3% of QI contain a volatile matter of 11.0% and have quinoline and toluene insoluble contents of 93 and 96%, respectively. The monolithic carbons made using these microbeads exhibit apparent densities of 1.66 and 1.85 g cm^{-3}, bending strengths of 88 and 68 MPa, Shore hardness of 95 and 70, electrical resistivities of 6.7 and 2.7 mOhm cm, and open porosities of 7.9 and 14.5% at the heat-treatment temperatures of 950 and 2700°C respectively.

(iv) A coal tar pitch containing 6.5% of QI results in MCMB having quinoline and toluene insoluble contents of 88.9 and 95.0%, respectively, with a volatile matter of 9.7%. Using these microbeads, the product is isotropic possessing an apparent density of 1.63 and 1.80 g cm^{-3}, bending strength of 73 and 55 MPa and Shore hardness of 85 and 66 at heat-treatment temperatures of 950 and 2700°C respectively.

(v) A coal tar pitch containing 9.2 % of quinoline insolubles yields microbeads having quinoline and toluene insoluble contents of 84 and 98% respectively, with a volatile matter content of 9.5%. These MCMB lead to an isotropic product with apparent density of 1.60 and 1.78 g cm^{-3}, bending strength of 70 and 49 MPa and a Shore hardness of 84 and 60 at heat-treatment temperatures of 950 and 2700°C, respectively.

(vi) The microstructure of all the MCMB based carbons reveals homogeneity and fine isotropic texture in the carbonised as well as graphitised states.

(vii) The presence of very low QI (0.5 %) in the precursor coal tar pitch, gives a low yield of 23 % of the MCMB, that too with relatively higher mean size of 13.5 μm. This low yield makes the process economically unviable. A small increase in the content of QI particles to about 3 % leads to a significant increase in the yield of MCMB (40 %) of the desired size (about 5 μm). The presence of QI in excess of 3 % in the precursor pitch, while slightly improving the yield of MCMB of similar size causes an appreciable fall in the density and strength of the product at both 950°C and 2700°C. Therefore, from techno-economical consideration, it may be concluded that a coal tar pitch containing around 3 % of quinoline insolubles can act as a good precursor for the production of high density - high strength - isotropic graphite.

4. EFFECT OF SINTERING TEMPERATURE ON THE CHARACTERISTICS OF CARBONS BASED ON MESOCARBON MICROBEADS

(i) The plates heat-treated to 1000 and 2700°C exhibit apparent density of 1.64 and 1.78 g cm^{-3}, with weight loss of only 11.5 % and 15.3 % and enormous volume shrinkage of 32.4 % and 45.0 %, respectively.

(ii) The open porosity has a value of 7.6 % at the HTT of 1000°C which is close to its minimum value of 7.2 % in the green stage, and a maximum value of 14.0% at an HTT of 2700°C.

(iii) The atomic C/H ratio of the plates increases from an initial value of 2.4 in the green stage to 30 and 417 at the HTT of 1000 and 2700°C, respectively.

(iv) The bending strength is found to have a maximum value of 72 MPa at an HTT of about 1000°C, above which it decreases gradually to attain a value of 50 MPa at 2700°C.

(v) The Shore hardness gradually increases from an initial high value of 93 at 500°C to attain a maximum value of 102 at 1000°C, beyond which it decreases almost linearly to a value of 70 at 2700°C.

(vi) The electrical resistivity undergoes a sharp fall from 933 to 30.6 mOhm cm as the HTT increases from 650°C to 800°C, beyond which it decreases gradually to about 7.0 and 2.4 mOhm cm at 1000 and 2700°C respectively.

(vii) The crystalite parameters La and Lc increase from 1.57 and 1.59 nm at about 1000°C to 24.1 and 20.5 nm at 2700°C, respectively. The d_{002} spacing decreases from a value of about 351 pm at 1000°C to 337 pm at 2700°C.

(viii) The plates heat-treated to 2700°C reveal homogeneity and fine isotropic texture.

5. EFFECT OF THE TYPE OF TAR OIL ON THE CHARACTERISTICS OF CARBONS BASED ON MESOCARBON MICROBEADS

(i) The mesocarbon microbeads obtained by extraction of two different mesophase pitches with a tar oil of boiling range 230 - 280°C result in good carbon plates having better values of the critical characteristics as compared to carbons obtained by using another tar oil with relatively lower boiling range of 180-230°C.

6. EFFECT OF CALCINATION OF MESOCARBON MICROBEADS ON THE CHARACTERISTICS OF RESULTING MONOLITHIC CARBONS

(i) The calcination of the mesocarbon microbeads in the temperature range of 280-320°C in inert atmosphere removes the entrapped tar oil as well as adjust the binding components to an optimum level, thereby making the MCMB suitable for the production of high density isotropic graphite.

(ii) A temperature in the range of 260-310°C with a preferable value of 285°C under reduced pressure (about 5 cmHg) of nitrogen appears to be suitable for the calcination of microbeads for the production of high density graphite.

7. HIGH DENSITY GRAPHITE PREPARED BY USING OPTIMISED PROCESSING CONDITIONS

(i) The heat-treatment of a coal tar pitch containing about 3 % of primary QI at 420°C for 3 h forms mesophase spherules with a mean size of about 5 μm.

(ii) The extraction of heat-treated pitch with tar oil of optimum boiling range (230-280°C) leads to mesocarbon microbeads with a yield of 39 %.

(iii) Calcination of these microbeads at a temperature of 285°C under reduced pressure of 5 cmHg of nitrogen makes them suitable for the production of high density - high strength - isotropic graphite.

(iv) The plates made from these microbeads, possess an apparent density of 1.27 g cm^{-3}, 1.68 g cm^{-3} and 1.93 g cm^{-3} at green stage, and heat-treated to 950 and 2700°C repectively. The bending strength of 112 MPa and 88 MPa is obtained at HTT of 950 to 2700°C repectively. The anisotropy ratio w.r.t. coefficient of thermal expansion in graphitised samples is 1.02 i.e. the product is isotropic.

REFERENCES

1. W.H. Bragg and W.L. Bragg, Proc. Royal Soc. London, A89, (1913), 277.
2. M.Seal, Nature, 185 , (1960), 522.
3. H.T Hall, Proc. Third Carbon Conf (Pergamon Press, New York, 1959), P.75.
4. A.W. Hull, Phys. Rev., 10, (1917), 661.
5. J.D. Bernal, Proc. Royal Soc. London, A106, (1924), 749.
6. H. Lipson and A.R. Stockes, Proc. Royal Soc. London, A181, (1942), 101.
7. H.P. Boehm and U. Hofmann, Z. Anorg. Allgemein. Chem., 278, (1955), 58.
8. H.P. Boehm and R.W. Coughlin, Carbon, 2, (1964), 1.
9. M.J. Basset, J.Phys. Radium 10, (1939), 217.
10. M.T. Jones and W. Weltner, Proc. 4th Carbon Conf. (Pergamon Press, New York, 1960), Unpublished.
11. H.P. Biorenkerk, F.P. Bundy, H.T. Hall, H.M. Stong and R.H. Wentorf (Jr.), Nature, 184, (1959), 1094.
12. F.P. Bundy, J.Chem.Phys., 38 (1963), 618.
13. T. Noda and H. Matsuoka, Proc. Int. Symposium on High Temp. Technol. (McGraw Hill Book Co., New York, (1959), P.286.
14. F.P. Bundy, W.A. Bassett, M.S. Weathers, R.J. Hemley, H.K. Mao and A.F. Goncharov, Carbon, 34 (1996), 141.
15. H.W. Kroto, J.R. Heath, S.C. O'Brein, R.F.Curl and R.E. Smalley, Nature, 318, (1985), 162.

16. W.Kratschmer, K.Fostiropoulos, and D.R. Huffman, Chem Phys, Lett., 170, (1990), 167.

17. W.Kratschmer, L.D. Lamb, K.Fostiropoulos, and D.R. Huffman, Nature 347 (1990), 354.

18. A.K. Dutta, Phys. Rev., 90, (1953), 187.

19. W. Primak and L.H. Fuchs, Phys, Rev., 95 (1954), 22.

20. De Combarieu, A. J. Phys. (France), 28, 931 (1968).

21. T. Nihara and T. Itawa, Japanese J. Applied Phys., 14, 1099, (1975).

22. C. L. Mantell, "Carbon and Graphite Handbook" (Interscience, New York, 1968).

23. L.M. Liggett, in "Kirk-Othmer Encyclopedia of Chemical Techonology", Vol. 4 (Interscience, New York, 1964).

24 J.M. Hutcheon, in "Modern Aspects of Graphite Technology" edited by L.C.F. Blackman (Academic Press, London, 1970), pp. 49-78.

25 E.I. Shobert II, in "Modern Materials", Vol.4, edited by B.W. Gonser and H.H. Hausner (Acadamic Press, New York, 1964), pp. 1-99.

26 Carbon, 13, (1975), 251.

27. R.E. Franklin, Proc. Royal Soc. London, 209, (1951),196.

28. S. Mrozowski, Proc. 2nd Carbon conf. (University of Buffalo, New York, 1956), 195.

29. F.A. Smith, Manufacture of coal-tar and pitches, "Bituminous materials", Ed. J. Hoiber, Vol. 3, R.E. Krieger, Huntington, New York, pp.57-116.

30. S.S. Chari, G. Bhatia and R.K. Aggarwal, Journal of scientific and Industrial research, 37 , 10, (1978), 502.

31. J. Newman, "Petroleum derived carbons", edited by M.L. Deviney and T.M. O'Grady, SCS symp. Ser. 21 (Amer. chem. 500), pp. 52-62.

32. J.D. Brooks and G.H. Taylor, in "Chemistry and Physics of Carbon", Vol.4, edited by P.L.Walker Jr., (Marcel Dekker, New York, 1968), pp.243-286

33. J.D. Brooks and G.H. Taylor, Carbon, 3, (1965), 185.

34. J.L.White, "The formation of microstructure in graphitisable carbon", Aerospace Corporation, Air Force Contract No.FO470, 73 C 0074, SAMSO-TR-74-93, April 15, 1975.

35. H. Marsh and J.Smith, in Analytical methods for coal and coal products, Vol.2, edited by C.Karr (Jr.Academic Press, New York, 1978), 371.

36. H. Marsh And P.L. Walker Jr., in "Chemistry and Physics of Carbon", Vol. 15, edited by P.L.Walker (Jr.) and P.A.Thrower (Marcel Dekker, New York,1979), pp.229-286.

37. I.C. Lewis, Journal de chimie Physique, 81C (1984), 751.

38. H. Honda, Carbon, 26 (1988), 139.

39. J.B.Barr, S. Chwastiak, R. Didchenko, I.C.Lewis R.T.Lewis and L.S.Singer, Proc., Applied Polymer Symposium No. 29, 1976, p.161.

40. P.L.Walker, Carbon, 10, 1972, 161.

41. G. Bhatia, E. Fitzer and D. Kompalik, Carbon 24 (1986), 489.

42. E.L.Shea (Jr.), US PAT. 2, 775, 549 (1956).

43. J.B.Donnet and A. Voet, Carbon Black, Marcel Dekker, New York.

44. H. Honda and Y. Yamada, Jol. Japan Petrol.Inst., 16

(1973), p.392.

45. H. Honda and Y. Yamada, Ceramic Data Book (Kogyoseihio Gijutsh Kyokai, Tokyo, 1973), p 377.

46. T. Hoshikawa, "Isotropic Graphite", Extended Abstracts, Int. Symposium on Carbon Toyohashi Japan (Carbon Society of Japan 1982) p.531.

47 T. Hoshikawa and T. Nagaoki, Recent Carbon Technology, English Editor: I.C.Lewis), JEC Press, 1983.

48 Y. Nakagawa, K.Fujita and M.Mori., "An industrial process of mesocarbon microbeads", Proc. 17th Biennial Conf. Carbon, June 16-21, 1985, Kentucky, USA (American Carbon Society, 1985), 409.

49 N. Fukuda, M. Honma and K. Nakayama, "Carbon spherules made from coal tar pitch for high density isotropic carbon blocks" Proc. Int. Conf. Carbon, Newcastle Upon Tyne, U.K., September 18-23, 1988, p.620.

50. A. Oya, "High density isotropic graphite- An overview" "Pitch and Pitch Based Products", Proc. of the Indo Japanese Workshop on pitch and pitch based products, Nov.24-25,1989, New Delhi, India (Indian Carbon Society, NPL, New Delhi, India,1989), p.58.

51. G. Bhatia, R.K. Aggarwal and O.P. Bahl "Special pitches for newer carbon products", "Pitch and Pitch Based Products", Proc. of the Indo Japanese Workshop on pitch and pitch based products, Nov.24-25,1989, New Delhi, India (Indian Carbon Society, NPL, New Delhi, India,1989), p.22.

52. K. Fujimoto "The Optical texture and physical properties of graphites" Proc. 19th Biennial Conf. Carbon Pennsylvania, U.S.A. (American Carbon Society, 1989), p.124.

53. B. Rand, "Microstructural studies of high strength monolithic carbons from mesophase powders" Extended Abstracts - Int. symp. Carbon, Tsukuba, Japan, Nov.4-8, 1990 (Carbon Society of Japan, 1990), p.260.

54. T. Takekawa, T. Shiode, H. Morotomi and T. Kato., "ROMS for super grade carbon artifacts", Int. symp. Carbon, Tsukuba, Japan, Nov.4-8, 1990 (Carbon Society of Japan, 1990), p.252.

55. T. Kato, N.Morishita, T. Takekawa, T.Shiode, Y.Owifama and Y.Sekiguchi, N.K.K. technical review No. 57 (1989) p.50.

56. K. Nagayama, T. Torii, H. Hatano and N.Fukuda, "A Study of the Sintering Mechanism of KMFC Green Compacts made from Mesocarbon Microbeads", IBID., Extended Abstracts and Program, 20th Biennial Conf. Carbon, June 23-28, 1991, California, USA, (American Carbon Society, 1991), p.206.

57. B. Rand and C. Stirling "Sintered Carbon from Mesophase Powders", ibid., p.204.

58. W.R. Hoffman and K.J. Huttinger, Carbon, 34, 1994, 1087.

59. A. Gschwindt and K.J. Huttinger, Carbon, 32, 1994, 1103.

60. I. Mochida, R. Fujiura, T. Kojima, H. Sakamoto, and K. Kanno, Carbon, 32, 1994, p.961.

61. M. Braun and K.J. Huttinger, "Sintered carbons from catalytically produced mesophase", 22nd Biennial Conf. Carbon, July 16-21, 1995, San Diego, USA, (American Carbon Society, 1995), p.234.

62. B. Rand and D.N. Ting, "Fabrication of fine grained carbon/graphite from mesophase microbeads" ibid., p.280.

63. R. Fujiura, T. Kojima, M. Komatsu and I. Mochida Carbon 33, 1995, p.1061.

64. G. Bhatia, R.K. Aggarwal, N. Punjabi and O.P. Bahl, "Development of High Density - High Strength - Isotropic Graphite", Presented at 2nd Annual General Meeting of Material Research Society of India, February 9-10, 1991, New Delhi, India.

65. G. Bhatia, R.K. Aggarwal N. Punjabi and O.P. Bahl, J. Mat Sci. 29, (1994), 4757.

66. G. Bhatia, R.K. Aggarwal, O.P. Bahl and N. Punjabi, Patent applied for.

67. J.W. Stadelhofer, Fuel, 59 (1980), 360.

68. M. Forest and H. Marsh, Fuel, 62 (1983), 612.

69. H.Marsh, C.S.Latham and E.M. Gray, Carbon, 23 (1985), 555.

70. R. Menendez, E.M. Gray, H. Marsh, R.W. Pysz and E.A. Heintz, Carbon, 29 (1991), 107.

71. G.H.Taylor, G.M.Pennock, J.D.Fitz Gerald and L.F.Brunckhorst, Carbon, 31, (1993), 341-354.

72. N.El Horr, C.Bourgerette and A. Oberlin, Carbon, 32, 1994, 1035.

73. G. Bhatia, R.K. Aggarwal and O.P. Bahl, J. Mat Sci. 22, (1987) 3847.

74. C.Morris, J.F.Byrne, K.Goto and H. Marsh, "Ageing of mesocarbon microbeads as studied by flow microcalorimetry" Proc. 19th Biennial Carbon Conf. Pennsylvania U.S.A. (American Carbon Society 1989) p. 202 (1989).

75. G. Bhatia R.K. Aggarwal, N. Punjabi and O.P. Bahl, Proc. 5th Int. Carbon Conf. (CARBON92), Essen, Germany, June 22-26 1992, p.91.

76. G. Bhatia R.K. Aggarwal, N. Punjabi and O.P. Bahl, J. Mater. Sci. (In press).

77. G. Bhatia, R.K. Aggarwal, N. Punjabi and O.P. Bahl, Proc. 22nd Biennial Carbon Conf., San Diego, USA, June 13-18, 1995, p.731.

78. G. Bhatia, R.K. Aggarwal, N. Punjabi and O.P. Bahl, Proc. 21st Biennial Carbon Conf., Buffalo USA, June 13-18 1993, p.719.

79. G. Bhatia R.K. Aggarwal, N. Punjabi and O.P. Bahl, Proc. National conf. on Carbon'94, Bhopal, India, Feb. 17-18, 1994 p.186.

LIST OF PUBLICATIONS

1. G. Bhatia R.K. Aggarwal, N. Punjabi and O.P. Bahl, Proc. 5th Int. Carbon Conf. (CARBON92), Essen, Germany, June 22-26 1992, p.91.
2. Bhatia G., Aggarwal R.K., Punjabi N. and Bahl O.P., Proc. National Workshop on Newer Carbon Products and their Applications, Oct.9-10, 1992, Banglore (Indian Carbon Society, New Delhi, 1992) p.398.
3. G. Bhatia, R.K. Aggarwal, N. Punjabi and O.P. Bahl, Proc. 21st Biennial Carbon Conf., Buffalo USA, June 13-18 1993, p.719.
4. G. Bhatia, R.K. Aggarwal N. Punjabi and O.P. Bahl, J. Mat Sci. 29, (1994), 4757.
5. G. Bhatia R.K. Aggarwal, N. Punjabi and O.P. Bahl, Proc. National Conf. on Carbon'94, Bhopal, India, Feb. 17-18, 1994 p.186.
6. G. Bhatia, R.K. Aggarwal, N. Punjabi and O.P. Bahl, Proc. 22nd Biennial Carbon Conf., San Diego, USA, June 13-18, 1995, p.731.
7. G. Bhatia R.K. Aggarwal, N. Punjabi and O.P. Bahl, J. Mater. Sci. (In press).