

On the Importance of Mesophase State on Coke Structure

Alexandra Boytsova¹, Sergey Strokin^{*1}, Jorge Ancheyta²

¹*Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya street 29, 195251, Saint Petersburg, Russia*

²*Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, México City 07730, México*

Received May 27, 2020; Accepted August 6, 2020

Abstract

Different literature sources on the topic of carbon mesophases were reviewed and analyzed. Information about structure of coke and mesophases, properties of basic structural units, mechanism and chemistry of formation, industrial application and recent developments in carbon science was discussed. It was found that the development of mesophase state of pitch determines the coke structure.

Keywords: Carbon mesophase; Semi-coke; Coke structure; Liquid crystals.

1. Introduction

Carbon materials are widely used in modern life. They play an important role in various industrial spheres, such as metallurgy, building, atomic power engineering, nanotechnology. Delayed cokes of petroleum (petcoke) are used in production of carbon anodes, which are central to the aluminum industry. Moderation of nuclear reactions is partially provided with graphite rods. Carbon fibers are used as components for different products from sports equipment to details of passenger jets. Unique physical, chemical and structural features of carbon materials explain their popularity.

The main feedstocks for carbon materials manufacturing are pitches and cokes, which are basically products of oil and coal refinery. The application of final product of coking absolutely depends on the coke composition, which can be either isotropic or anisotropic. Structure type is somehow determined by the ability of cokes to graphitize, or to form graphene layers situated parallel to each other. If the graphitization degree is low, the structural unit of coke is a grain. Carbon grains with a size of up to 10 μm form isotropic structure (fine and medium-grained coke). High-extent graphitization provides the formation of anisotropic needle cokes with long thin grains (>60 μm length) [1].

The percentage of impurities, such as sulfur, in pitches and cokes used in production of carbon materials, is proportional to the one found in parent oil. Impurities influence the quality of resultant materials. High content of sulfur, for example, leads to corrosion of electrode pins, premature cure of rubber and, what is vitally important, restrains the graphitization process. It should be considered that petroleum industry has reached the stage where mining of heavy sulfurous oils is quite common. Processing of heavy oils is troublesome and needs high capital outlays, but due to depletion of light oil deposits new methods for heavy oil refining should be developed [2]. This fact preconditions the importance of understanding of carbon structure formation during carbonization processes.

Various research papers containing information about carbon structure have been reported in the literature. Most of them concluded that coke texture strongly depends on mesophase state of pitch development under heat treatment, and in this respect information about structure of mesophases, mechanism and chemistry of formation and some recent developments

and examples of industrial application are presented. Then the aim of the present work is to review the available information and discuss all of these aspects.

2. Theoretical aspects

2.1. Structure of mesophases

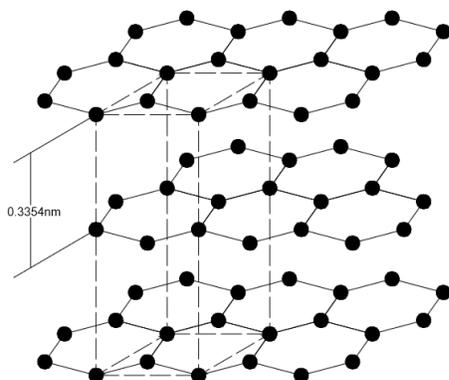


Figure 1. Scheme of hexagonal unit cell of graphite [1]

The optical anisotropy of coke was described by various scientists who independently investigated polished surfaces of cokes and coke-like materials. Still, their developments did not suggest any explanation for the process of formation of anisotropic structure which is a vital aspect of carbon industry.

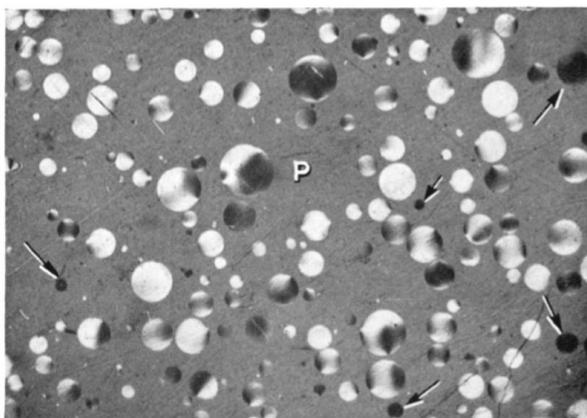


Figure 2. Spheres at an intermediate stage of development. The grey matrix is pitch-like material (P). The spheres are in random orientations. A few show almost total absorption of polarized light (arrowed). Reflected polarized light [4]

The process of formation of cokes with anisotropic features includes some important stages. When pitches, which are optically isotropic, are heated, their softening and transmission to a liquid-like state is observed [1]. As is normal for liquids, the viscosity of the feedstocks rapidly decreases until the whole system suddenly solidifies and forms a semi-coke that forms graphite layers with interlayer spacing of 3.354 Å if the heat treatment temperature is increased (Figure 1) [3].

A tremendous contribution to understand the formation of graphitizable carbons was made by Brooks and Taylor [4]. They researched the structure of coal and oil feedstocks on different stages of carbonization. It was taken into account that substances which form graphitizing carbons were reached in polynuclear aromatic compounds. The growth and appearance of spherical bodies with $d_{\min} = 0,1 \mu\text{m}$ in the plastic carbonaceous material was reported (Figure 2). The size of spheres increased until a three-dimensional mosaic formation was reached, that remained as solidified semi-coke.

Observations of spheres were done by means of electron diffraction microscopy and polarized light absorption. The described diffraction patterns observed on different sections of spheres (Figure 3) were not those

observed for crystalline materials but still indicated a considerable degree of order. After analyzing the diffraction patterns the authors came to the conclusion that the kind of order existed in spheres varied from lamellar (at the center) to radial (at the surface), as observed in Figure 4. A response to surface tension forces seems to be due to spherical shape and the surface tension effects can be seen as further evidence in the coalescence of two spheres, and subsequently returning to spherical shape. A characteristic molecular orientation at their surfaces seems to be exhibited by the spheres, thus having many of liquid crystals characteristics [5]. The boundary condition seems to achieve in different spheres (small, large, and composite), and at the pitch and mosaic mesophase interface, the surface with uniform molecular arrangement, in which aromatic planes edges are perpendicular to interface.

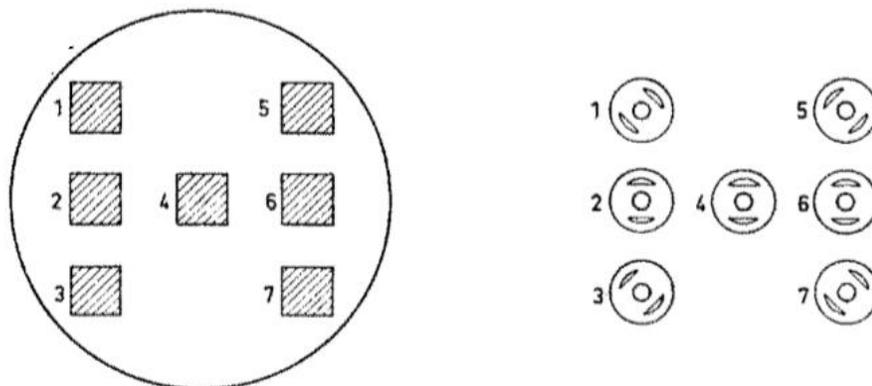


Figure 3. Variation in electron diffraction patterns over disk of sphere, oriented with lamellae parallel to beam [4]

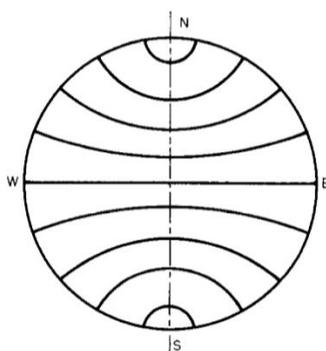


Figure 4. The model of mesophase suggested by Brooks and Taylor [4]

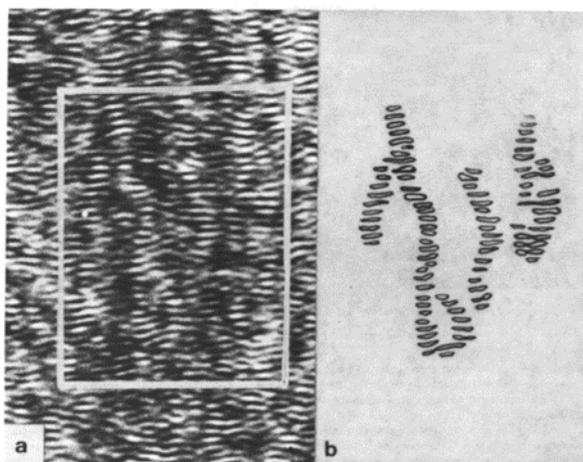


Figure 5. a) Transmission electron micrograph of a thin section of a single mesophase sphere; b) drawing of the thin area, showing columns [6]

Single mesophase spheres prepared by thin sectioning were studied by Augie et al. by means of transmission electron microscopy [6]. The observed lattice fringes showed a peculiar order of disk-like molecules, they were stacked in long distorted columns, and their optical diffraction pattern obtained with a laser beam displayed a good parallelism of the carbon layers (Figure 5). Such an organization of molecules is reminiscent of smectic properties. When the spheres coalesce, some disclinations are produced at the spheres' boundaries. Also, the nematic order destroys and replace the short-range peculiar order [3]. So that, it can be stated that mesophases have discotic, aromatic, nematic properties with transient smectic behavior.

The formation of mesophase is neither a process of crystallization, nor a precipitation reaction, but it is a process of molecular self-assembly, which is an important property of macromolecules [7].

The polarity possessed in spherical mesophases results from π - π interactions between polynuclear aromatic type of molecules which are recurring units of carbonaceous liquid crystals [8].

2.2. Mechanism of mesophase formation

The initial stage of mesophase spheres formation is their nucleation owed to pitch volatiles physical distillation with maximum molecular weight (MW) of 400 and the molecules thermal polymerization in the range of 400-1100 MW. The average molecular weight (AMW) of the isotropic phase is increased by both distillation and polymerization, which results in the initial

development of long-range molecular order in the pitch. In the coalesced mesophase and mesophase spheres, polymerization of the 400-1100 MW molecules causes a temporary increase in the mesophase AMW. The transfer due to stirring and generated gas percolation of similar size molecules from the isotropic phase reestablishes molecular equilibrium in mesophase. The transfer of these smaller pitch molecules, which are unreacted original pitch components, provokes the growth of mesophase spheres and coalesced mesophase. The lack of reactivity of the largest molecules in the mesophase also contributes to the constant MW distribution [8].

2.3. Coalescence

Coalescence of spheres leads to the formation of larger regions of extended order bulk mesophases (Figures 6 and 7). Due to multiple acts of coalescence, the formation of bulk mesophases is possible through the whole volume of a pitch sample. These margins possess regions with almost constant parallel orientation of carbon layers. The larger the bulk mesophases, the more graphitizable the semi-coke produced as a result of carbonization. However, real pitch samples often contain insoluble impurities, which aggregate on the surface of mesophases and might either modify the final coke structure or prevent individual mesophases from coalescence. As a result, spheres adhere to each other and produce multicrystalline mesophase with different orientation of layers in individual regions. Obviously, a single mesophase system is much more ordered than a multicrystalline one and its ability to graphitize is higher.

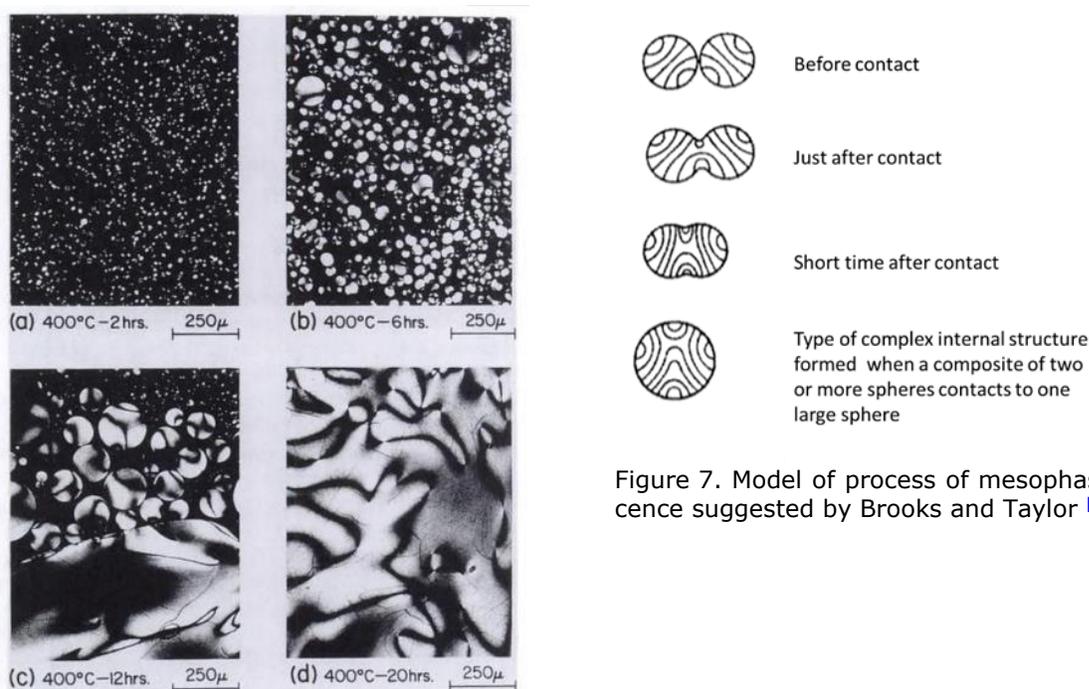


Figure 6. Growth and coalescence of mesophases into bulk mesophase system [8]

2.4. Properties of structural units

From the moment of mesophase nucleation the polymerization reactions occur in and between planes of mesogens, resulting in increasing of molecular weight of structural units [8]. The average molecular weight of mesophase components was calculated by Greinke during the process of carbonization of residuum obtained from catalytic cracking of petroleum distillates and residues. It was observed that molecules with molecular weight less than 400 distilled quickly. The content of components with MW of 1200 greatly increased, resulting in AMW reaching the value of more than 800 (Figure 8).

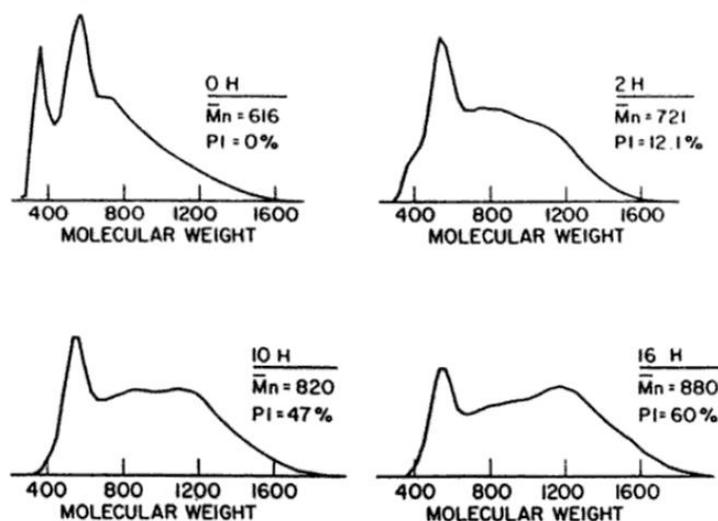


Figure 8. Molecular weight distributions obtained from Gel Permeation Chromatography curves of a petroleum pitch as a function of heat treatment at 400°C [8]

Numerous researches were done to determine the type of chemical bonds formed by polymerization of pitch molecules. Delhaes *et al.* [9] using diamagnetic susceptibility measurements, have shown that the polymerized molecules in mesophase pitch do not possess too highly condensed pitch monomers by single chemical bond. Later, application of depolymerization reaction of *p*-toluene-sulfonic acid to mesophases exhibited that chemical bonds in polymerized and dimerized molecules were proposed by aryl-aryl bridges with smaller amount of methylene bridges. Thermal cracking and gas formation studies of alkyl groups on aromatic molecules with molecular weight higher than 400 have indicated that the side chains break at the alpha position to the aromatic ring, which leads to aryl-aryl bridges formation in the pitch dimers and not methylene bridges [8].

2.5. Chemistry of mesophase formation

Various analysis methods may be used to obtain enough information about the pitch composition, e.g. chromatographic analysis, mass spectrometry and nuclear magnetic resonance. The abundance of chemical compounds of pitch might produce multiple chemical reactions, so the complexity of composition of feedstocks is a stumbling block to understanding the chemistry of conversion of pitches to cokes. This is why observation of general properties of pitch is more beneficial than specific molecular analysis [10].

The influence of asphaltenes on mesophase development was investigated by Eser and Jenkins [11-12]. It was concluded that feedstocks asphaltene does not appear to be critically important for the determination of mesophase development degree. However, the feedstocks asphaltene fractions have a controlling influence in determining the mesophase development degree during the feedstocks carbonization. The mesophase development degree during the feedstock asphaltenes carbonization is dependent on the asphaltenes chemical constitution. particularly, the asphaltenes hydrogen aromaticity seems to be a multifaceted parameter in reflecting the structural differences among the asphaltenes, which are critically substantial for the mesophase development. The mesophase development degree increased steadily with the enhanced hydrogen aromaticity of the asphaltenes of various sources (residue from vacuum distillation, bottoms from catalytic cracking, etc.)

By means of electron spin resonance, the presence of unpaired electrons in carbonizing pitches was appointed, which probably indicates the formation of free radicals [13-14]. Free radicals production is enhanced by alkyl, naphthenic, phenolic, carboxylic and other groups and heteroatoms (sulfur, oxygen, nitrogen). Existence of free radicals increases the reactivity of the mesophase systems, resulting in chemical reactions that lead to molecular growth in

pitches in particular. The velocity of those reactions depends on reactivity of radicals. The faster the polymerization reactions occur, the greater molecules appear at low temperatures, which also increases the viscosity of the system. The resultant coke optical structure depends directly on the rheological properties of the preceding mesophase [15]. Highly viscous mesophases are unable to coalesce, and optical texture of resultant coke is smaller. Marsh and Walker [10] made an important conclusion that it is difficult to determine the quantity of compounds required to keep the balance between the carbonization rate, controlled by the reactivity of components of carbonizing systems, and the viscosity of the resultant pitch. Highly reactive and viscous pitches produce non-graphitizable semi-cokes and cause solidification even before formation of mesophases. The polymerization reactions can be moderated by hydrogen-donor molecules. Transferring hydrogen atoms to active free radicals stabilizes them and allows to reach lower viscosity at higher temperatures, promoting graphitizability [16-19].

It was reported by Marsh *et al.* [20] that the rate of carbonization is connected with the optical size of produced coke. Some volatile compounds remain in the system or transform due to thermolysis, decreasing its viscosity and promoting the formation of cokes with large optical texture.

The parameter of pressure affects the carbonization process. A closed system preventing loss of volatile materials is created by the effect of a pressurized carbonization. The normally lost material as volatiles in open systems is now preserved and its effect by reducing turbulence and bubble formation, is to improve the resultant optical textures size. Such an effect was reported when the applied gas pressure reached 150 bar. But higher pressures (300 bar) provide the enhancement of viscosity and this prevents the coalescence of mesophase [21].

It was analyzed by Marsh and Latham [21] that pitch material can be basically separated into three groups of components:

- Low molecular weight fraction, which decreases viscosity (solvent) and either becomes incorporated into mesophase or volatilizes
- Higher molecular weight fraction – the main material for pitch formation
- An insoluble in benzene and tetrahydrofuran fraction, which gives isotropic carbons when carbonized separately
- The formation of quinoline-insoluble fraction during thermal processes was also considered.

By individual carbonizing of fractions a conclusion was made: low molecular weight fraction not only provides physical fluidity of system, but also chemical stability. Its carbonization result was coke with the largest optical texture which was even bigger than that one of carbon produced from parent pitch. It also was noticed by Kakuta *et al.* [22] that the low aromaticity saturate fraction produces a coke with a needle structure.

There exist a great variety of pitches with high content of impurities which can be converted into carbons of low economical and industrial value, and production of such pitches is expanding due to depletion of light oil deposits. However, most industrial spheres need to imply cokes of high purity and long-flow anisotropy. Three main ways of improving the quality of the resultant coke are:

1. To extract separate fractions and produce isotropic and anisotropic cokes from components of one parent pitch
2. To add materials that up-grade the quality of the resultant coke
3. To modify the chemical composition by alkylation, hydrogenation etc.

The separation of parent feedstocks into benzene-soluble (BS) and benzene-insoluble fractions (BI) an attempts for co-carbonization of blends of these fractions was reported in the literature [23-26]. Certain fractions were also hydrogenated or alkylated and the resulting alkylated fractions were hydrogenated. They investigated the ability of blends of fractions to co-carbonize in order to obtain needle-coke structure. The following conclusions were pointed out:

1. Co-carbonization compatibility of solvent refined coal with benzene insoluble fractions were significantly improved by hydrogenation, which give isotropic coke

2. Co-carbonization compatibility of BS fractions is destroyed by alkylation, which suggests that pitches poor compatibility could be associated with alkylation in constituent pitch molecules

3. The compatibility is restored by hydrogenation of the alkylated material

Impact of catalysts on carbonization process was observed by Mochida *et al.* [27] Their experiment with carbonization of sulfur containing pitch in the presence of aluminum chloride showed an improvement of optical structure.

Kumar and Srivastava [28] investigated the influence of transition metals, Co and Ni in particular, on the mesophase formation. The time of thermal treatment to form mesophase pitch was reported to be reduced due to acceleration of polymerization reactions. The addition of Co and Ni salt catalysts improved the crystal assembly of mesophase.

A spinnable mesophase pitch could be produced from aromatic hydrocarbons by using HF/BF₃ as a condensation catalyst (Figure 9) [29].

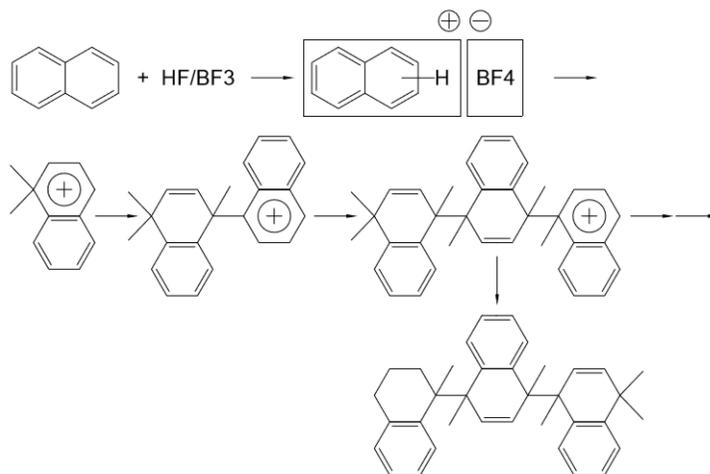


Figure 9. Catalytic condensation of aromatic hydrocarbon with HF/BF₃ [29]

3. Industrial application

3.1. From theory to reality

Understanding the theoretical aspects of formation of carbon structure made a significant impact on the industry of carbon and graphite. Scientifically reasonable methods of moderation of different processes are now applied and new processes were also created.

Development of production of spinnable mesophase pitch from pure aromatic hydrocarbons with the aid of HF/BF₃ is one of the most tremendous achievement in studies of carbon mesophase. Those pitches are spinned into carbon fibers with very high Young's modulus and thermal conductivity. Carbon fibers are used in construction technology, improving structural stability due to [30]:

- High strength
- Stiffness
- Tensile and compressive strengths balance, and their very light weight

Consideration of mesophase formation is vital for modeling of processes of delayed coking [30]. The commercial value of green coke (graphitizable carbon produced as result of delayed coking) depends on the size of optical texture. There are two qualities of commercial green coke [1]:

- Regular coke, with coarse-grained mosaics of 10 μm diameter or medium-flow anisotropy with less than 30 μm length
- Needle coke, with acicular flow domain anisotropy of >60 μm length).

The calcined regular cokes are the filler cokes in anode production for aluminum industry, while needle cokes are filler cokes in manufacturing of high-performance graphite electrodes for steel production.

Mesophase pitch is suitable as solid lubricant, which is employed for bearings and friction parts working at severe conditions. MoS₂ and graphite are used dispersed in mineral oil and grease as solid lubricants; but, graphite possesses unsatisfactory adhesion and malleability. Mesophase pitch keeps its liquid state up to 450°C, that provides a graphitizable carbon film on the metal surface at high yield. Blending of the mesophase pitch with graphite powder improves lubrication. Mesophase pitch is also useful as a high temperature liquid lubricant (300-400°C) [31].

Solvent fractioning of pitch matrix allows to separate the mesophase spherules or meso-carbon microbeads (MCMB) [32]. These spherules are excellent raw material for high density carbon materials, column-packing materials [33] and super-active carbon [34], while MCMB are applied as Li-ion battery anode material [35].

3.2. Recent developments in studies of carbon mesophase materials

The rheological properties of mesophase pitch and coal mixtures were reported at temperatures up to 873 K. To observe the effect of coal particles on foaming and on the development of pores in activated carbon discs (ACD) during carbonization, quench tests were conducted. High coal-to-pitch ratios caused increases of the viscosity of the mixture under low-pressure foaming process, provoking two effects: limited growth of large bubbles and stronger carbon monoliths. The highest strength ACD (56 ± 3 MPa compressive strength) was achieved with a pitch-to-coal mass ratio of 1:2 (0.91g/cm³ bulk density and 579 ± 37 m²/g surface area), whereby it was shown that the coal particles can stabilize bubble growth in an effective way during the mesophase pitch foaming and carbonization. In addition, both the bubble growth and ACD strength can be altered by adjusting the blend viscosity of pitch and coal with the addition of coal to the blend. From these results, it is anticipated that the activated carbon discs exhibit great potential for their application as gas storage and separation materials, since they possess high strength and high volumetric adsorption capability.

A petroleum pitch of naphthenic nature was separated in three fraction by sequential extraction with heptane and toluene [37]:

- Heptane-soluble (HS)
- Heptane insoluble/toluene-soluble (HITS)
- Toluene-insoluble (TI)

HITS resulted adequate and superior to HS and TI for the preparation of mesophase pitch with the following characteristics:

- Large domain structure
- Low softening point
- High H/C molar ratio
- Carbon residue and ordered microcrystal structure

The results indicated the following behavior for the three components:

- HS, possessing rich alkyl chains, could enhance the carbonization by means of breaking of chains at the beginning of the reaction
- HITS, having abundant naphthenic structures, was more prone to mitigate the carbonization via hydrogen transfer reaction during the aromatic molecules aggregation
- TI, as initial nucleus with small size, could initiate the mesophase spheres generation

The effect of asphaltenes in petroleum feeds (internally present and externally added) on mesophase formation and structure of semi-coke was also reported in the literature [38]. The results indicate that the increased asphaltenes content impacts on the semi-coke texture. For instance, a feedstock with asphaltenes content of 10.44 wt% yielded flow-type coalescence, while a feedstock with asphaltenes content of 24.57 wt%, resulted in a mosaic-type texture in the pitch. When part of these asphaltenes was removed from the feedstock, the resulting oil produced semi-cokes with large size mesophase domains.

Boytsova *et al.* [39] investigated the gasification of asphaltenes from Yarega heavy oil under different pressures in steam atmosphere. Two types of cokes were obtained as result of pyrolysis. The first one had big pore size and crumble structure. The second one presented dense spherical carbon particles with properties probably reminiscent of mesophases and significantly lower content of impurities than that of parent crude oil.

Mesophase pitches from different petroleum were chemically activated to produce appropriate activated carbons to be used as electrodes in supercapacitors [40]. The effects of activating agent (NaOH, LiOH, and KOH), ratio of alkaline hydroxide-to-pitch, and temperature of activation on the properties of the obtained activated carbons were the following:

- LiOH exhibited poor efficiency as activating agent.
- NaOH and KOH produced activated carbons with more suitable properties, that is high apparent surface area and pore volume.
- The higher the KOH-to-pitch ratio the higher the chemical attack on the carbon.
- Increased KOH-to-pitch ratio produced higher burn offs and porosity development.
- Activation of petroleum pitch with 5:1 KOH-to-carbon ratio produced very high apparent surface areas.
- The higher the activation temperature the higher the burn off, with minor differences as compared with using different amounts of activating agent.

During the synthesis of carbon foams using an asphaltene pitch from Avgamasya in Turkey as a carbon precursor, it was found that initial nitrogen pressure, foaming temperature, pressure release time and inorganic content of the natural pitch affect in a considerable manner the physical properties and microstructure of carbon foams. The asphaltite inorganic components may act as filler, and thus be responsible of the enhancement of density and compressive strength. The substantial increase in the compressive strength of asphaltite foams can be then attributed to carbonization [41-42].

4. Perspectives on the study of mesophase formation

From the literature reports, it has been recognized that the carbonaceous mesophase plays an important role as a precursor for manufacturing carbon fibers and other valuable materials. The main definition of mesophase is that it is a high molecular weight planar aromatic compound with considerable molecular order. Mesophase is a general term used to describe to various intermediate phases which can be formed by the liquid crystalline materials.

Particularly, asphaltene fraction has been found to represent a high percentage of conversion into mesophase, being the best precursor to produce mesophase the fraction of asphaltenes carbonized at 400°C.

It is also reported that carbonaceous mesophase appears during the thermal treatment of crude oil in the range of 350 to 500°C as optically anisotropic spheres surrounded by an isotropic liquid matrix. The onset of mesophase is of high interest in hydrogen addition processes, because this phase can coalesce to form larger mesophase domains, which eventually deposit as coke, thus producing reactor internals fouling.

Being asphaltenes closely related to mesophase, characterization of asphaltenes is very useful to understand its mechanisms formation. But not only asphaltenes characterization is important, but also the properties of asphaltenes fractions than can be divided by using different solvent proportions (e.g. heptane and toluene). For instance, it has been reported that the least soluble asphaltene fraction has more complex structures than other fractions, the average number of carbons per alkyl side chain of the fractions is higher than that found in unfractionated asphaltenes.

By thermal analysis of the two main polar components of a heavy crude oil, it was found that asphaltenes formed 47wt% of coke during cracking reaction, while resins only 9 wt% of coke, being wider the temperature range for resins to react as compared with that of asphaltenes. From this experimental results, it can be stated that asphaltenes contribute to the generation of free radicals and that condensation reactions take place at high temperature.

In summary, to get more insights on carbon mesophase mechanism formation, separation of asphaltenes from crude oils, fractionation of the separated fractions, and their detailed characterization is recommended.

5. Conclusion

From the analysis of the literature, the following conclusions can be pointed out:

- The development of mesophase state of carbon materials is a complex process that depends on a variety of physical and chemical factors
- Understanding the stages of mesophase formation and the influence of temperature, pressure and chemical composition is fundamental for choosing the feedstocks and methods of processing in order to obtain carbons with certain structure
- Asphaltenes fraction is responsible for about 50 % of coke formation during cracking reaction
- Not only asphaltenes content but also asphaltenes properties are important to understand the mechanisms of mesophase formation
- It has been recognized that fractionation of asphaltenes is also important to study to carry out, since depending on the solubility the separated fractions they exhibit different structures that influence in different manner on mesophase formation

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To whom correspondence should be addressed: Sergey Strokin, Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya street 29, 195251, Saint Petersburg, Russia