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Production and Sintering of Mesophase Pitch from Anthracene Oil

MR Delport

Production and Sintering of Mesophase Pitch from Anthracene Oil

A thesis submitted in partial fulfilment of the requirements for the degree MEng (Chemical Engineering)

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Production and Sintering of Mesophase Pitch from Anthracene Oil

Synopsis

When certain oils and polymers are heated under an inert atmosphere, a high viscosity liquid forms. Examples include crude oil, coal tar, and PVC. Upon further heating, this liquid becomes a progressively harder solid called pitch. Pitch that contains crystalline areas is called mesophase pitch. Mesophase pitch is required for the production of graphite. The purpose of the research was to investigate whether anthracene oil can be used for the production of mesophase pitch for sintering purposes. Sintering involves heating a powder under pressure to produce a solid. Anthracene oil is a low-value by-product of coke production from coal. Despite its low market value, it has unique properties. It consists primarily of polycyclic aromatic hydrocarbons and it is free of primary quinoline insoluble material. Polycyclic aromatic hydrocarbons are the precursors for mesophase pitch formation, while quinoline insoluble material hinders mesophase growth. These attributes make it a good potential starting material for the production of mesophase pitch, which may be used for sintering and carbon fibre production.

In the search for a mesophase pitch that can be sintered, a variety of pitches were produced from anthracene oil. This was done by varying the heat treatment time and temperature. The pitches produced were characterised to determine their glass transition temperature, melting temperature, carbon yield and optical microstructure. This was done to determine their sintering potential. A high mesophase content, high softening temperature and high carbonisation yield were considered essential for effective sintering.

Pitches with a high mesophase content were produced. Longer heat treatment led to higher carbon yields, higher glass transition temperatures, higher softening temperatures and higher mesophase content.

Pitches were prepared with and without 5 wt% $AlCl_3$ as a catalyst. The use of 5 wt% $AlCl_3$ lead to a decrease in the temperature at which mesophase forms. The use of the catalyst changed the structure of the mesophase from large bulk mesophase regions to small mesophase spheres. The catalyst retarded the coalescence of the mesophase spheres, while increasing their formation rate.

In order to produce sufficient material for sintering the reactor loading was increased from 60 g to 200 g. It was found that increasing the amount of anthracene oil used reduces the carbon yield, glass transition temperature, softening temperature and mesophase content. For a heat treatment time of 120 minutes at a temperature of 475 ^{o}C, carbon yield decreased from 92% to 73%, while the mesophase content was reduced from 100% to 12%.

The prepared pitches were pressed into rectangular test bars with dimensions 4 cm x 1 cm for various times and temperatures. Selected bars were carbonised at 1500 ^{o}C, which in some cases resulted in warping. Bars without severe warping were subsequently graphitised at 2700 ^{o}C. Meso carbon micro beads (MCMB) were pressed and carbonised under the same conditions. This was done in order to compare the pitch produced to a widely available commercial material. None of the conditions investigated were capable of repeatedly producing crack-free bars with smooth outer surfaces and reasonable strength from MCMB.

Bars of reasonable strength were produced from anthracene oil pitch using a low temperature ramp rate (2,6 ^{o}C/minute) to 450 ^{o}C. These bars were carbonised at 1500 ^{o}C and graphitised at 2700 ^{o}C. Their changes in length, mass, and density (both apparent and skeletal) were recorded. An increase in the skeletal density from 1500 kg/m^3 to 2200 kg/m^3 was recorded upon graphitisation. This is close to the density of ideal graphite at 2260 kg/m^3, which indicates a well organised structure. However, the graphitised test bars had a low apparent density of 1719 kg/m^3. The graphitised bars had large pores, which limited their strength to 4,5 MPa. The microstructure of the sintered, carbonised and graphitised specimens was compared. The ordered stacking of pitch particles on top of one another due to the application of pressure is clearly visible in the scanning electron micrographs of the sintered product. An increase in the number of cracks was observed upon carbonisation. This trend continued upon graphitisation.

In summary, it is possible to produce mesophase pitch suitable for sintering from anthracene oil. Coke and graphite with high porosity and low strength can be produced from the sintered specimens. The structure of the mesophase pitch is affected significantly by reactor loading, catalyst presence and heat treatment time. It is recommended that other temperatures should be used in order to establish the kinetics of mesophase formation from anthracene oil.

Keywords: MCMB, anthracene oil, mesophase

Contents

Nomenclature

b	Coalescence rate constant	1/(no. of spheres.s)
c_a	Concentration of reactant A	mol/L
c_{a0}	Concentration of reactant A at t = 0	mol/L
cy	Carbon yield	-
DMA	Dynamic Mechanical Analysis	-
E_a	Activation energy	J/mol
$E_{a,dead}$	Dead time activation energy	J/mol
F	Force	N
FEG-SEM	Field Emission Gun – Scanning Electon Microscope	-
g	Radius change rate constant	µm/s
H	Sample height	mm
J	Number of coalesced mesophase spheres	-
k	Reaction rate constant	1/s
k_{dead}	Dead time constant	s
k_p	Sphere number rate constant	1/s
L	Lever arm length	mm
MALDI-TOF	Matrix Assisted Laser Desorption/Ionisation Time of Flight	- -
MCMB	Meso carbon micro beads	-

MP	Mesophase pitch	-
N	Total number of spheres	-
n_1	Number of 1 µm spheres generated	-
n_a	mols of A	mol
n_p	Number of purging cycles	-
P	Pressure	kPa
R	Universal gas constant	8.314 J/(mol.K)
$r1$	1 µm Spheres	-
$-r_a$	Reaction rate	mol/(L.s)
dr/dt	Rate of radius change of all spheres	µm/s
t	Time	s
T	Temperature	K
T_g	Glass transition temperature	K
TGA	Thermogravimetric analysis	-
TMA	Thermomechanical analysis	-
t_r	Residence time	s
T_s	Softening temperature	K
t_{dead}	Dead time	s
V	Anthracene oil volume	m^3
x	Conversion	-
σ	Stress	MPa
ρ	Density	kg/m^3

1. Introduction

Synthetic graphite is currently manufactured from a mixture of petroleum coke and coal tar pitch. Coke and pitch are mixed and heated to 150 °C, which is above the pitch softening temperature. It is then extruded through a die. This mixture is then baked at 450 °C to bond the pitch and coke. In the process, the volatile components of the coal tar pitch evaporate. This results in the formation of cracks in the extruded part. The mixture is then carbonised at 1500 °C to remove chemical bonds between carbon and nitrogen, oxygen, hydrogen or sulphur. This results in the formation of more cracks. These cracks can be filled by pumping in molten coal tar pitch under pressure from the outside while pulling a vacuum on the inside. This process is called impregnation. The carbonised mixture can then be graphitised by further heat treatment to 2700 °C. Both carbonisation and graphitisation result in an increase in porosity, and it may be necessary to reimpregnate the structure multiple times to get a high density by filling all the cracks. This process can take a month or more to go to completion. This is due to the slow heating required to allow all of the volatiles to escape without causing cracking. The material must also be cooled down slowly to prevent uneven contraction, which could lead to cracks (Pierson, 1993: 87-96).

MCMB have been investigated as a possible graphite starting material (Mochida, Fujura, Kojima, Sakamoto & Yoshimura, 1995). MCMB powder is compacted in a press. When the compacted powder is heated, the spherical particles stick together. This is called sintering. Sintered articles are carbonised and subsequently graphitised. Articles with a high density can be produced. The MCMB fulfils the roles of both coke and pitch in traditional synthetic graphite manufacturing. Another potential single starting material is mesophase pitch produced from anthracene oil. It can be used in the same way as MCMB.

The purpose of the investigation was twofold. Firstly, it had to be determined whether a pitch with high mesophase content could be produced from the anthracene oil produced by Arcellor Mittal South Africa (AMSA). The method used was heating anthracene oil under an inert atmosphere. Secondly, it had to be determined whether this pitch was suitable for sintering. This would then serve as a first step towards making graphite from anthracene oil.

If graphite produced from anthracene oil using hot sintering as the forming step has suitable properties, anthracene oil may become a valuable commodity. At present, anthracene oil is a low-value by-product formed in the production of coke from coal. Its main use is as a source of naphthalene and anthracene. Anthracene oil is also used for the production of carbon black, which is used to reinforce tires (Industrial Quimica del Nalon S.A., 2010). Naphthalene is used as the starting material for MCMB production (Wang, Egashira, Ishida, Korai & Mochida, 1998).

2. Theory

2.1 Graphite precursors

2.1.1 Mesophase precursors

Large polycyclic aromatic hydrocarbon molecules form via chain growth polymerisation when smaller molecules are heated in an inert atmosphere. In order to illustrate, Figure 1 shows the first two steps in the polymerisation reaction of anthracene.

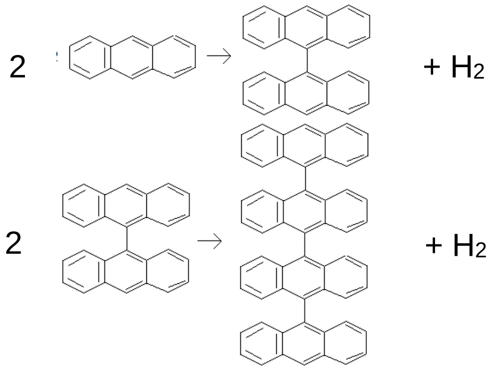

Figure 1 Polymerisation of anthracene

Due to the high degree of unsaturation of aromatic molecules, growth is not linear, but occurs in two dimensions. There is a rapid increase in viscosity as the molar mass increases. This limits the extent of growth of the molecules. Once the molar mass reaches 1100 g/mol, the molecules grow much slower (Scaroni, Jenkins & Walker, 1991). Dehydrogenation still occurs. This happens by the formation of more C-C bonds, resulting in more benzene rings. Dehydrogenation is illustrated in Figure 2.

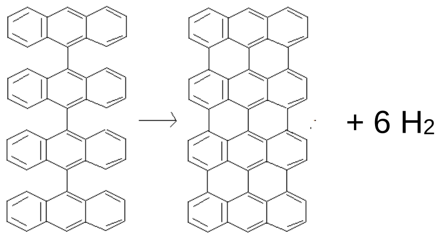

Figure 2 Dehydrogenation of anthracene Polymer

C-C double bonds consist of one sigma and one pi bond. As the number of connected benzene rings grows, the electrons involved in the pi bond start to lose their attachment to a particular set of carbon atoms. This is due to an increase in the number of possible resonance structures. Eventually, the electrons become completely delocalised. Similar to metals, the electrons now float around in a molecular cloud. This causes an increase in electrical and thermal conductivity.

The starting material may contain a mixture of different molecules. In this case, a large variety of products of different structures and molar masses will form. This will result in melting occurring over a wide temperature range (Marsh, Dachille, Marvin & Walker, 1971).

2.1.2 Mesophase (liquid crystals)

Mesophase refers to small crystals that appear inside a liquid. This happens in a variety of materials, including semi-crystalline polymers, oils and pitch. In the case of pitch, the mesophase forms due to the preferred stacking sequence of large flat molecules. It consists of large polycyclic aromatic hydrocarbon molecules. These large molecules agglomerate to form flat sheets. These sheets stack parallel to one another in the form of spheres (Marsh, 1972). The spheres join together when they collide with one another. With each collision, the shape of the combination becomes less spherical. Eventually, no more spheres are visible. This is called bulk mesophase. Both mesophase spheres (a), isotropic pitch (b) and bulk mesophase (c) can be seen in Figure 3 (Alvarez, Granda, Sutil, Menendez, Fernandez, Vina, Morgan, Millan, Herod & Kandiyoti, 2008).

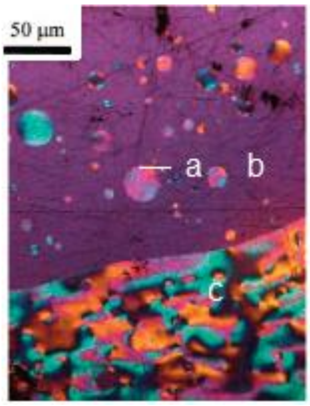

Figure 3 Differences in optical texture due to alignment during optical polarised light microscopy a: mesophase spheres b: isotropic pitch c: bulk mesophase

However, this is only in systems where there are no foreign particles. Foreign particles include dust, ash, small rust pieces, etc. They are referred to as primary quinoline insoluble material. Foreign particles agglomerate at the edges of the spheres, preventing them from coming into contact with one another and coalescing. Foreign particles also increase the rate of sphere formation by acting as nucleation points. This results in many small spheres. For the purpose of meso carbon micro beads production, the reaction conditions are chosen to produce a pitch with a low mesophase content. This reduces the probability of the mesophase spheres coalescing and growing bigger. In order to separate the mesophase spheres from the rest of the reaction products, Soxlets extraction must be carried out (see meso carbon micro beads).

2.1.3 Meso carbon micro beads (MCMB)

MCMB are produced from naphthalene heated in an inert atmosphere in the presence of HF/BF_3 (Wang et al, 1998). The reaction conditions (residence time and temperature) are chosen to produce a partial mesophase pitch. The mesophase pitch fraction must be kept low enough to prevent the formation of bulk mesophase. Mesophase spheres are the desired product. The mesophase spheres are extracted by means of a suitable aromatic solvent such as quinoline, toluene or benzene. The mesophase pitch must be insoluble in the solvent used. The isotropic pitch becomes dissolved in the solvent while the residue is the mesophase pitch. If the solvent is allowed to boil and continuously recycled by means of an overhead condenser, this is known as Soxlets extraction. This results in the agglomeration of the spherical mesophase particles into larger spheres. These spheres are called meso carbon micro beads (MCMB), as they consist of pure mesophase particles which are spherical.

2.1.4 Anthracene oil

Anthracene oil is prepared from the distillation of coal tar. It is the heaviest volatile fraction of coal tar. It is defined as the fraction of coal tar that has a boiling point at atmospheric pressure between 270 ^oC and 400 ^oC. The specific anthracene oil used here was produced by Arcelor Mittal South Africa and it has a boiling point between 220 ^oC and 250 ^oC (Mashau, 2008). This is slightly lower than the standard anthracene oil. Its main use is as a precursor of anthracene and naphthalene. It consists of a wide variety of polycyclic aromatic hydrocarbons. Polycyclic aromatic hydrocarbons are a good starting material for the production of mesophase, as they are large, planar molecules. The five main components of anthracene oil are phenanthrene, anthracene, fluoranthene, pyrene and acenaphtene (Mashau, 2008). One interesting property is that it is entirely soluble in quinoline. Material that is quinoline insoluble restricts the growth of mesophase spheres. Quinoline insoluble material also limits the extent of mesophase formation (Fernandez, Granda, Bermedjo & Menendez, 1999).

2.1.5 Anthracene oil mesophase pitch

This material is produced by heating anthracene oil under high pressure in an inert atmosphere. This process can proceed with or without a catalyst. Suitable catalysts include $AlCl_3$ (Rey Boero and Wargon, 1981), $AlCl_3$/NaCl (Cheng, Li, Hou, Jing, Zhuang & Zao, 2010), HF/BF_3 (Mochida, Oyama, Korai & Fey, 1988), S (Papole, 2009), formaldehyde (Crespo, Arenillas, Vina, Garcia, Snape & Moinelo, 2005) and O_2 (Bermejo, Menendez, Fernandez, Granda, Suelves, Herod & Kanjeo, 2001). If a sufficient heat treatment time and temperature are used, a material with a high mesophase content can be produced. If a catalyst is used, the mesophase content will be in the form of many small spheres. Without a catalyst, sphere coalescence is unimpeded, which results in regions of bulk mesophase. A high mesophase content, with or without a catalyst, results in bulk mesophase, with no spheres visible. Only a small part of the material still has the ability to melt. When heated at atmospheric pressure, the mesophase pitch remains a powder. However, when heated after sufficient compaction, the viscoelastic fraction of the mesophase acts as a glue that sticks the solid parts together. A typical pressure used for compaction is 60 MPa (Norfolk, Kaufmann, Mukasayan & Varman, 2006). When the material cools down again, a solid block of material is observed. This material has the potential to be turned into graphite via carbonisation and graphitisation.

2.1.6 Coke

Coke is produced from the bottoms product of oil distillation (petroleum pitch). Petroleum pitch is heated to 450 ^{o}C for several days in a delayed coker. The low molar mass molecules evaporate while the high molar mass molecules react with one another to form even larger molecules. The evaporation of the low molar mass molecules results in the vertical alignment of the larger molar mass molecules. The coke thus produced is highly structured. When observed using an optical microscope with polarised light, it is seen to contain long narrow strips of material lined up in the same direction. These strips are embedded in unaligned material. Material with this optical texture is called needle coke after the shape of the aligned material. This aligned material is mesophase. Not all materials rich in carbon display this behaviour upon heating. Alkanes evaporate, while linear polymers disintegrate into smaller molecules and form chars (unordered small carbon particles). Coal is classified into two categories, coking and non-coking coal. The non-coking coal forms a char upon heating. Coke is no longer capable of softening. It must therefore be crushed and mixed with pitch, which can still soften, in order to produce an item of a desired shape. The pitch commonly used is coal tar pitch (Pierson, 1993: 74-85).

2.1.7 Coal tar pitch

Coal tar pitch is produced by the distillation of coal tar. When coal is heated, the liquid dissolved in it evaporates. This liquid consists of a non-polar and a polar fraction. The non-polar fraction is known as coal tar. The polar fraction is known as ammonia liquor. It is separated from the polar fraction using a decanter. When coal tar is distilled, the heavy bottoms product which remains is known as coal tar pitch. This pitch is formed by the heating required to evaporate the volatile components. It can be described as a polymerisation reaction. Coal tar is notable for consisting largely of aromatic hydrocarbons. This includes smaller molecules such as benzene, toluene, phenol and cresol, and larger ones such as naphthalene and anthracene. Coal tar pitch consists of the reaction products of these molecules (Pierson, 1993: 74-85).

2.2 Graphite

Graphite is one form of carbon. It consists of carbon atoms bonded to one another with sp^2 covalent bonds. Every carbon atom is bonded to three other carbon atoms, with a bond angle of 120°. This bonding results in large flat sheets of carbon atoms arranged in a series of hexagons. These sheets are stacked parallel to one another in an alternating pattern. The sheets are held together by weak covalent bonds between alternating sheets. This distinguishes it from diamond, which is carbon bonded together with sp^3 covalent bonds. sp^3 bonding results in carbon atoms bonding to one another in a three-dimensional matrix, with each atom bonded to four other atoms at an angle of 109,5°.

Graphite does not react with most chemicals, except with hot air and strong oxidising agents. It is the only material capable of withstanding the thermal shock of being removed from molten aluminium into air repeatedly. This makes it suitable for use as electrodes in steel and aluminium smelters. In this application, the electrode burns away slowly over a period of a month. Graphite has a low in-plane shear strength. This makes it easy to remove single layers of graphite. This is why it is used in pencils. Writing with a pencil involves shearing off a layer of graphite. Graphite is also an excellent lubricant. Due to its high temperature stability, it can be used at nearly all temperatures. Unlike liquid lubricants, it does not evaporate. Unlike polymers and greases, it does not degrade at high temperatures.

There are two sources of graphite, natural graphite and synthetic graphite. Natural graphite is mined. Synthetic graphite is produced by the heat treatment of a mixture of pitch and coke (see the introduction) (Manocha, 2003).

2.3 Polymers

Polymers are molecules that consist of the same chemical structure repeated over and over. Monomers are the molecules that the polymers are formed from. Polymers are formed by two main methods. These are step growth and chain growth polymerisation.

Step growth polymers are formed when bifunctional molecules react with one another. One example of this is when terephthalic acid reacts with ethylene glycol to make poly ethylene terephthalate, also known as PET. A bifunctional carboxylic acid reacts with a bifunctional alcohol to form a polyester and water. Figure 4 illustrates the first step.

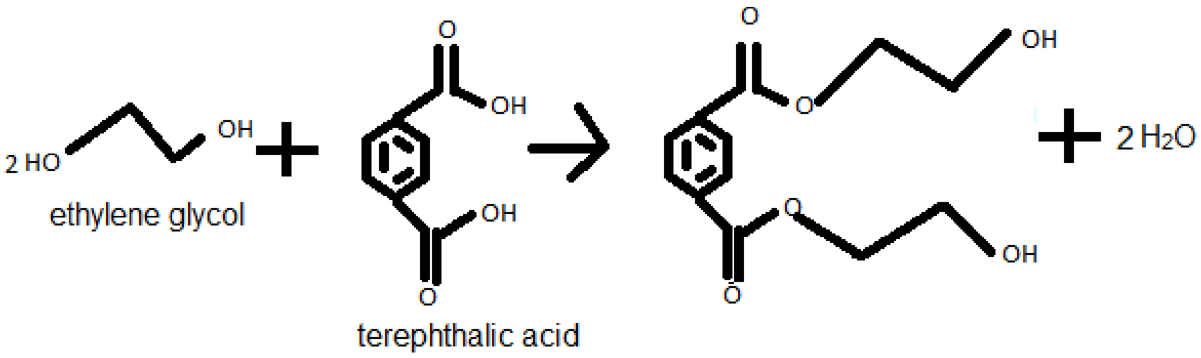

Figure 4 The first step in the production of polyester

Chain growth polymers are formed when free radicals react with organic molecules containing a double bond. These organic molecules then become free radicals themselves, reacting with other organic molecules of the same type to form a larger free radical molecule. With every reaction, the length of the chain is increased by one monomer unit. This then continues until two free radicals collide with one another. They react, forming a large, stable polymer molecule. The mechanical and thermal properties of a polymer depend on the length of the chain formed, as well as the structure of the monomers from which it is composed (Young and Lovell, 2011:19).

Pitch and coke are special forms of polymers. The main distinguishing feature of the abovementioned polymers is that they consist almost entirely of carbon. Most other polymers have repeating units that contain significant amounts of other elements, mainly oxygen and hydrogen. Another special feature of pitch and coke is that they have polycyclic aromatic hydrocarbons in their backbone. This refers to multiple benzene rings joined together. The production of pitch and tar proceeds nominally via chain growth. However, attachment is not limited to one or two sites and molecule growth happens in two dimensions (Mochida, Nakamura, Maeda & Takeashita, 1976).

Another important difference is the relatively low molar mass, which was measured as 1100 g/mol (Scaroni et al, 1991). Anthracene (178 g/mol) and naphthalene (128 g/mol) are typical precursors for pitch formation. Each mesophase unit contains roughly 6 anthracene molecules or 9 naphthalene molecules. This is in stark contrast to most chain growth polymers, which can have molar masses in excess of 10^6 g/mol. For polyethylene, the repeat unit is C_2H_4 (28 g/mol). At a typical molar mass of 10^6 g/mol, 35714 repeat units are present. The small number of repeat units in pitch is largely due to the size of the repeat units involved. Large polyaromatic molecules have multiple resonance structure. This stabilises the free radicals that cause chain growth, reducing their reaction rate. Also, pitch exhibits high viscosity in the liquid phase, which hinders movement of molecular segments. This results in a low collision rate between molecules capable of reacting, hindering the growth of the polymer chains. However, the main problem preventing large polymers molecules in pitch is that pitch becomes a permanent solid (coke) while the chains are still short. Molecules of coke can however join together to form large planar molecules that stack on top of one another. This process is called graphitisation. This occurs at a temperature of 2500 °C (Pierson, 1993: 74-84).

2.4 Heat treatments carried out on anthracene oil

A three-step method (Fernandez and Alonso, 2004) can be used for making pitch continuously. First, air is blown over hot anthracene oil for 5 seconds at 300 °C. Next, the pitch is kept for 5 hours at 400 °C. Finally, distillation is used to separate the anthracene oil from the pitch, with the anthracene oil being recycled

Another three-step method (Alvarez, Granda, Sutil, Santamaria, Blanco & Menendez, 2011) involves heating anthracene oil under an applied atmosphere of N_2 at 500 kPa at 450 °C while stirring. The second step involves continued heating under N_2 at atmospheric pressure while stirring. The final step involves an unstirred reactor at 420 °C at atmospheric pressure. This unstirred reactor causes the mesophase to separate from the isotropic phase due to the density difference between the two phases. This was confirmed by optical microscopy using polarised light. The yield of mesophase obtained was between 7% and 25%. The mesophase pitches also showed higher softening points, in the range 230 °C to more than 350 °C.

An alternative (Fernandez et al, 1999) is to heat anthracene oil in the presence of $AlCl_3$, from 5% to 10% on a weight basis at 250 °C to 350 °C for 2 to 6 hours. The amount of hydrogen lost during polymerisation is reduced by the catalyst.

2.5 Various factors affecting the polymerisation of aromatic hydrocarbons

2.5.1 Effects of catalysts

$AlCl_3$

Naphthalene was heated (Rey Boero and Wargon, 1981) with and without $AlCl_3$ under a N_2 atmosphere at atmospheric pressure. Without $AlCl_3$, complete conversion to mesophase was obtained at 550 °C after heating at 1 °C/minute. 4.75 wt% $AlCl_3$ reduces the temperature to 420 °C after heating at 1 °C/minute. This shows that the addition of $AlCl_3$ greatly reduces the temperature at which mesophase forms at a reasonable rate, though it can still be a very slow process at times.

$AlCl_3$ should theoretically be evaporated during heat treatment at high temperatures and atmospheric pressure, as its boiling point is 180 ^{o}C. However, it remains in the mixture (Mochida, Oyama, Korai & Fei, 1988).

Using $AlCl_3$ (Fernandez et al, 1999) results in pitches with a low melting temperature. The pitches only have small mesophase spheres due to the high viscosity that results from using $AlCl_3$.The treatment consisted of 5%, 8% and 10% weight $AlCl_3$ at 250, 325 and 350 ^{o}C for 2 to 6 hours. The conversion was calculated by measuring the carbon yield of the pitches obtained at 350 ^{o}C. The strength of the resulting pitch was measured by crushing the pitch using steel ball bearings and analysing the size distribution of the pitches with a sieve. The strength was found to be lower than the strength of commercial pitches used for impregnating coke. The air reactivity was evaluated by heating samples in air while recording the mass loss using a TGA. The air reactivity was similar to commercial binder and impregnation pitches.

Needle and mosaic cokes are produced with $AlCl_3$. Isotropic cokes are produced with Potassium (Mochida et al, 1976).

A strong magnetic field (Kovak & Lewis, 1978) was applied to anthracene and naphthalene polymerised with $AlCl_3$. The polymerised anthracene and naphthalene was heated to 300 ^{o}C in a 1 Tesla magnetic field. The temperature was maintained for 30 minutes. After cooling, the sample was mounted. The effect of using $AlCl_3$ was believed to change the shape of the mesophase spheres. Instead of the stacks making up the spheres being perpendicular to the surface at the sphere circumference, they are parallel to it. However, no control experiment was done to prove that the structure results from $AlCl_3$ as a catalyst rather than the magnetic field applied.

Polycyclic aromatic hydrocarbons containing oxygen, nitrogen and sulphur atoms were carbonised (Mochida, Inoue, Maeda & Takeshita, 1977) at 600 ^{o}C for two hours after 4 hours of heating. In the first instance, no catalyst was added. In the second instance, $AlCl_3$ was added in equimolar amounts as a catalyst. Using $AlCl_3$, it was possible to carbonise the pitches formed. In the absence of $AlCl_3$, the yield upon carbonisation was limited or non-existent. The degree of carbonisation was measured from the solubility in benzene.

$AlCl_3$/NaCl

An equimolar mixture of NaCl and $AlCl_3$ was used (Cheng et al, 2010) to catalyse the formation of mesocarbon micro beads from coal tar pitch. The ratio of mixed salts to coal tar pitch used was varied from no mixed salts to 5 kg mixed salts: 1 kg pitch. The reaction was carried out for 1 hour at 300 ^oC, with the heating taking 4,5 hours. At a higher salt concentration, the size of the organised structures (mesophase) formed decreased. With a low salt concentration, only a few large spheres were formed. These large spheres were also less symmetrical than the small ones.

HF/BF_3

It is not possible to recover all of the $AlCl_3$ via washing with HCl. Also, the catalyst cannot be reused, as it is recovered as $Al(OH)_3$. More than 0.1% $Al(OH)_3$ remains behind. HF-BF_3 as a catalyst has the advantage that it can easily be recovered by distillation, with boiling points of 20 ^oC for HF and -100 ^oC for BF_3 at 101,325 kPa respectively (Mochida et. al., 1988). This is also the catalyst that is used commercially to produce MCMB from pure naphthalene. The process involves heat treatment followed by Soxlets extraction.

Methanal (formaldehyde)

Methanal is not a catalyst in that it is consumed in a polymerisation reaction. However, its use in coal tar pitch increases the extent of mesophase formation in a subsequent heat treatment. The average size of mesophase spheres is also reduced, and the extent of coalescence is increased (Crespo et al, 2005).

Sulphur

Sulphur catalyses the polymerisation of anthracene oil. However, some sulphur becomes incorporated in the pitch. This is undesirable as sulphur causes puffing during graphitisation, which reduces the strength of graphite formed (Papole, 2009).

Hexachlorocyclohexane (C6H6Cl6)

Hexachlorocyclohexane reacts with components like anthracene and naphthalene, causing them to polymerise. However, it also releases hydrochloric acid in the reaction, and chlorinates the anthracene. This can cause corrosion. Therefore this reaction must be carried out in equipment constructed from an inert material, such as glass or stainless steel (Mashau, 2008).

Oxygen

Oxygen reacts with aromatic molecules, linking them together through ether linkages. It can also cause the formation of alcohol and carboxylic acid groups, which can link together aromatic molecules via ester formation. When these molecules become large enough, they can form mesophase. However, if too much oxygen reacts, the molecules become too large and therefore infusible. This is called a cross-linked solid. The material will then no longer be an appropriate graphite precursor. Too much oxygen during heat treatment will also result in a fire. A typical treatment consists of only 0.7 kg air/kg Anthracene oil added over a period of 5 hours at 300 ^{o}C (Bermejo et al, 2001), which amounts to only 21% of the oxygen required for complete combustion. This is for the simplifying assumption that anthracene is the only component.

2.5.2 Effects of pressure

The effect of suddenly dropping the pressure or temperature during the heating of vacuum residue was investigated (Bagheri, Gray & Mcaffery, 2011). This was done for both H_2 (4.1 MPa) and N_2 (4.8 MPa) atmospheres. The mesophase fraction was estimated from the area of spheres observed relative to the total area using an on-line microscope. Dropping the pressure suddenly results in a large increase in the rate of mesophase formation. Decreasing the temperature suddenly just stops the reaction, as would be expected.

Heat treatment on a petroleum pitch was performed at 1 MPa and atmospheric pressure under a N_2 atmosphere (Santamaria-Ramirez, Romero-Palazon, Gomez-De-Salazar, Rodriguez-Reinoso, Martinez-Escandell & Marsh, 1999). Low pressure heat treatment resulted in more individual spheres than coalesced spheres. It also resulted in more individual spheres of larger size than was the case for the same heat treatment time and temperature at a single high pressure. There were fewer spheres in total. Depressurisation therefore seems to prevent coalescence of mesophase spheres to form bulk mesophase. The fraction of mesophase was measured by calculating the area of spheres and coalesced spheres from microscopic observation. The number of spheres per millimetre and their size distribution was also determined.

The effect of pressure on the carbonisation of anthracene without a catalyst was investigated (Scaroni et al, 1991). It was found that a pressure above the vapour pressure of anthracene does not change the conversion to coke achieved at 510 ^{o}C. When only the vapour pressure of anthracene (1.1 MPa) was used, the results were no different from that for 6.9 MPa of applied N_2.

2.5.3 Effects of gas flow rate

A study of gas flow rates on coal tar pitch polymerisation was done (Moriyama, Hayasi, Goda & Chiba, 2005). Coal tar pitch was heated to 430 ^{o}C under flowing N_2. Exposed surface area relative to sample mass (original pitch depth) and gas flow rates were changed to determine the effect on mesophase sphere size, number and coalescence. Higher gas flow rates evaporated more of the coal tar pitch. This increased the average molar mass of the remaining coal tar pitch. The viscosity of the pitch increased. Mesophase sphere movement was impeded. This resulted in reduced coalescence amongst spheres. Larger individual spheres were formed. If the intention is the formation of large individual mesophase spheres, then it is beneficial to increase the rate of evaporation by using more N_2. Alternatively, flatter reaction containers with more exposed surface area relative to the mass of coal tar pitch can be used. Conversely, the absence of flow may favour the formation of bulk mesophase.

2.5.4 Effects of temperature

The effect of temperature upon carbonisation for various pure aromatic compounds was investigated (Mochida, Kudo, Fukuda & Takeshita, 1975). The extent of carbonisation was taken as the solubility in benzene. A higher temperature led to a greater extent of carbonisation. The optical microstructure of the pitches produced was monitored. Some pitches formed mosaics without making spheres first. This was the case for pyrene. However, most pitches made spheres which subsequently flowed together to make mosaics. All the starting materials formed benzene insoluble material, except for benzene.

2.5.5 Temperature-pressure interdependence

A study was done (Mochida et al, 1988) where fluidised catalytic cracking decant oil, low sulphur vacuum residue and coal tar pitch were carbonised in a tube bomb. The effect of pressure and temperature on the degree of order in the resultant cokes was analysed. The coefficient of thermal expansion decreases with increased ordering. It was found that for every temperature, there was an optimum pressure that gave the lowest coefficient of thermal expansion. Both higher and lower temperatures had higher values of the coefficient of thermal expansion. The same can be said for the variation of temperature at constant pressure.

2.5.6 Effect of volatile release after heat treatment completion

A study was done (Liedtke et al, 1996) where Ashland A-240 pitch was heated under Ar at a pressure of 1 MPa to 490 ^{o}C at 10 ^{o}C/minutes with no residence time at this temperature. The volatiles in the reactor vessel were them flashed off at various temperatures by opening up the reactor. The following trends in the properties of the pitch produced were observed:

1. A higher reactor opening temperature increases the glass transition temperature observed with a TMA.
2. A higher opening temperature increases carbon yield.
3. The product yield decreases at a higher opening temperature.
4. The product of the carbon yield and the product yield remains constant.

From this information, it can be concluded that small volatile molecules which remain in the pitch after heat treatment tend to reduce its glass transition temperature. They also do not survive the process of coking. Flashing off these molecules can increase the glass transition temperature and hence the strength of the pitch.

2.6 Kinetics

2.6.1 Kinetics of the model compound anthracene

The various factors that can influence the kinetics of anthracene carbonisation without a catalyst were investigated (Scaroni et al, 1991). The effect of sample mass was investigated. A higher sample mass led to higher yields. This is due to the fact that at a low sample mass, a large fraction of the anthracene is evaporated. The reactor was equipped with a motorised cradle that allowed it to be rocked back and forth at a predetermined frequency. Conversion became independent of rocking frequency above 1 Hz. The fraction of pyridine insoluble material was taken as an analogue for conversion to coke. Equation 1 shows that the reaction rate is a standard temperature-dependent first-order reaction in anthracene concentration after an initial dead time. Equation 2 shows the temperature dependence of the dead time.

$$-r_a\,(t-t_{dead}) = k\,c_a\,e^{-\frac{E_a}{RT}} \qquad (1)$$

$$t_{dead} = k_{dead}\,e^{\frac{-E_{a,dead}}{RT}} \qquad (2)$$

The value of the constants were: $k = 4 \times 10^9$/s E_a = 192 kJ/mol $E_{a,dead}$ = 167 kJ/mol k_{dead} =5.12 x 10^{15}s .

Gel permeation chromatography was used to determine the molar mass distribution of the pyridine insoluble fraction that had reacted with lithium in diethyl amine to make it soluble in quinoline. The gel permeation chromatograph was calibrated by using fractionated pitch, with molar mass determined by vapour pressure osmometry. The average molar mass of anthracene polymerised for 5 hours at 485 ^oC was 1100 g/mol, corresponding to roughly six anthracene molecules joined together.

2.6.2 Kinetics of coal tar pitch

A mathematical model of the kinetics of mesophase formation from coal tar pitch was set up (Moriyama et al, 2004). This model was for coal tar pitch at 430 ^oC treated under constant N_2 flow. The coal tar pitch was separated into two fractions by washing in quinoline before the heat treatment. The one fraction contained quinoline insoluble material while the other did not. The model consists of three steps. First, small spheres 1 µm across are generated. Then, these spheres grow. Finally, they join together. The model predicts the total number of spheres, their volume and their number-based size distribution. Equation 3 gives the rate at which spheres 1 µm across are generated. Equation 4 gives the concentration of coal tar pitch. Equation 5 predicts that spheres increase in diameter at a constant rate.

Equation 6 predicts the rate of coalescence, which is proportional to the square of the number of spheres.

$$\frac{dn1}{dt} = \frac{-dc_a}{dt}\left[\frac{4\pi(r1)^3}{3}\right]^{-1} \tag{3}$$

$$c_a = c_{a0}e^{-k_p(t-t_{dead})} \tag{4}$$

$$\frac{dr}{dt} = g \tag{5}$$

$$\frac{dj}{dt} = bn^2 \tag{6}$$

This model was successful in predicting the number of spheres generated for pitch containing quinoline insoluble material, but not for quinoline soluble pitch. Quinoline insoluble material increased the rate of sphere generation but it decreased the rate of sphere growth and coalescence. Therefore, quinoline insoluble material results in many small spheres

2.7 Methods for investigating pitch

To determine whether a pitch contains mesophase, two methods can be used. The first method involves mounting the pitch in epoxy. The epoxy is then polished to expose the surface. This can then be viewed under polarised light with a microscope. Areas that are aligned parallel to the light source will have one colour, whereas areas aligned at right angles to the abovementioned areas will have a different colour. If the entire pitch consists of areas of alternating colour, then the pitch is said to be anisotropic. This is also called bulk mesophase. If the whole pitch is a single colour, then this is classified as an isotropic pitch. Mesophase spheres are small regions larger than 1 µm across that have a different colour from the rest of the pitch. The fraction of mesophase in a pitch can be determined by calculating the total area of mesophase spheres observed and dividing this by the total area observed under the microscope. This method is not possible when the mesophase is highly non-spherical. In this case, the image must be divided by a grid of vertical and horizontal lines. The image is evaluated at every intersection to determine whether mesophase appears at that intersection. The fraction of intersections that contain mesophase is then determined and taken as the fraction of the pitch that contains mesophase. This method is easier to use, as there is no need to approximate the area of non-spherical regions. The second method involves determining the fraction of the pitch that is insoluble in quinoline. This fraction is classified as mesophase or anisotropic material. There is some disagreement between the two methods. A material can be 100% anisotropic according to its optical texture, but it may still remain soluble in quinoline (Cheng et al, 2010).

The glass transition temperature is the word used to describe the temperature at which a pitch shows a drastic decrease in its elastic modulus. This is similar to the glass transition temperature in polymers. Polymers are processed at 50 ^{o}C above this temperature in order to allow them to flow into the required shape. It can be determined by dynamic mechanical analysis (DMA). This involves imposing a time-varying sinusoidal strain on the pitch while increasing the temperature. The resulting stress is measured. The phase angle ϴ between the stress and the strain is recorded. When the value of tan ϴ goes through a maximum, the material has reached its glass transition temperature. Tan ϴ is the ratio of the loss modulus to the storage modulus. The loss modulus determines the amount of energy that is not returned when an object experiences an impact. (Young and Lovell, 2011: 494).

The softening temperature of a pitch is the minimum temperature at which it can flow. The main method for measuring this is described by ASTM D 3104. This method involves heating pitch placed on a hollow ring with a weight placed on top of it. A video camera is used to determine the temperature at which the pitch starts to fall through the ring. An alternative method (Bragga et al, 2009) involves using a rotational rheometer to measure viscosity. The temperature at which a pitch reaches a viscosity of 1000 Pas was taken as the softening point. The softening point determined in this way was close to the value determined using ASTM D 3104. The method could also be used at higher temperatures than ASTM D 3104, which only works up to 180 ^{o}C. Softening points up to 340 ^{o}C were measurable with this method.

The softening temperature of a pitch can be determined using thermal mechanical analysis (TMA). This works by measuring the length of a pitch sample while continuously changing the temperature. When there is a sudden decrease in the length of the sample, this is an indication that it has melted. Due to the wide molar mass distribution and large variety of molecules, no single melting point can be assigned to a pitch. The onset of melting is taken as the temperature where the sample starts to shrink. This temperature is within 5 °C of the glass transition temperature recorded on a DSC. The absolute softening temperature recorded using TMA or DSC is 80% of the absolute softening temperature recorded using ASTM D 3104. This is somewhat similar to the trend observed for polymers, where the glass transition temperature is 65% of the melting temperature (Barr and Lewis, 1981). Care must also be taken to avoid oxygen when using a TMA, as oxygen causes the pitch to crosslink. It can no longer melt. The information gathered at other temperatures gives the thermal expansion coefficient. If the sample continues to expand, this implies that it is a coke. It will not melt or soften at any temperature.

The fraction of volatile material in a pitch is determined by thermogravimetric analysis (TGA). The sample is weighed continually while being heated in an inert atmosphere. The volatile components evaporate, leaving behind the solid residue. The thermogravimetric analysis can also give an indication of the melting point, as once the pitch has melted it starts to evaporate and loses mass rapidly. The peak mass loss rate temperature corresponds to the temperature at which a significant fraction of the pitch has melted.

The energy required to melt the pitch can be determined by differential scanning calorimetry (DSC).In heat flux DSC, the pitch and a reference sample are heated up simultaneously with the same heat flux(power input), and the temperature difference is determined. In power compensation DSC, the power difference required to keep the reference sample and the pitch at the same temperature is recorded (Young & Lovell, 2011: 435 – 439).

Elemental analysis can be performed to determine the relative amount of hydrogen, carbon, and sulphur in a pitch. This consists of burning the pitch and measuring the amount of CO_2, SO_2 and H_2O produced (Ciucci, Corsi, Palleschi, Rastelli, Salvetti & Tognari, 1999).

Gel permeation chromatography (GPC) can be used to determine the average molar mass of a pitch. For pitches prepared from pure starting materials, this allows the degree of polymerisation to be determined. A column is packed with beads with miniature holes in them. The pitch is dissolved in a solvent at low concentration and pumped through the column at a constant flow rate. Larger molecules are less likely to get stuck in these holes. Therefore, they have a shorter residence time in the column than smaller molecules. At the exit, a detector determines the concentration of pitch in the solvent. The instrument is calibrated with pitch fractions of known molar mass. One potential problem is the small average molar mass of pitch in comparison to regular polymers. Another potential problem is that pitch has a very high viscosity (Scaroni et al, 1991).

Gas Chromatography (GC) can be used to determine what compounds make up a pitch. The compounds that are produced by heat treatment can also be identified. Comparison of the results of the pitch before and after heat treatment allows an estimate to be made of the degree of conversion of the compounds in the original pitch. The pitch is heated until it vaporises and runs through a long, thin packed tube in the presence of a carrier gas, such as methane or helium. The molecules of the components get adsorbed onto the packing. Larger molecules spend a longer time adsorbed on the packing. Therefore their residence time in the column is greater. At the end of the column is a detector, which determines the presence of a molecule by one of a large number of different methods. The fractional area of the peak measured by the detector for a specific molecule is an indication of its concentration (Fernandez et al, 1999).

A related method is MALDI-TOF (Matrix Assisted Laser Desorption/ionisation Time of Fight). This method involves mixing less than 1 wt% of the material under investigation into a solvent that contains a dissolved crystal with a low melting and boiling temperature (the matrix). A salt of sodium, silver or potassium is also added. The solvent is first evaporated, resulting in the matrix and the material under investigation crystallising together. When the mixture is heated using a laser, the salt causes the material under investigation to ionise. The laser causes the material under investigation, the solvent and the salt to evaporate. The ions produced are accelerated using an electric field. The final velocity the ions reach is determined by their size. All ions gain the same amount of kinetic energy in the electric field, as they all have the same charge. However, smaller ions have a lower mass and therefore they reach a higher velocity. Their time of flight to the detector is therefore reduced. The mass of an ion can be determined by the time it takes to reach the detector. The number of ions of each mass reaching the detector allows the molar mass distribution of the sample to be determined (Young & Lovell, 2011: 335-337). A potential problem when applying this approach to pitch is that there are few suitable solvents in which pitch can dissolve. Most pitches also have no polar groups which makes them harder to ionise. An exception might be PVC pitch.

Helium pycnometry works by placing an object of known mass in a chamber of known volume. All gas is first evacuated from the chamber. Then, gas is added until the chamber is at some desired starting pressure. A valve to a second chamber that is under vacuum is then opened. The gas is allowed to flow into the second chamber until the pressure in the second chamber is equal to the pressure in the first chamber. By measuring this new pressure and comparing it to the original pressure, it is possible to calculate the volume in the first chamber that was originally occupied by helium. The sample volume is the difference between the chamber volume and the volume originally occupied by helium. As the sample mass is known, the skeletal density can be calculated. It is the ratio of the sample mass to the sample volume with open pores excluded from the sample volume. This calculation is based on the assumption that the ideal gas law holds. The ideal gas law only holds for moderate pressures and temperatures, where forces of attraction and repulsion between molecules are insignificant. It is important to take note of the temperature and pressure when using a pycnometer to make sure that the ideal gas law holds. Another limitation is that helium cannot enter closed pores (Tamari, 2004).

Scanning Electron Microscopy (SEM) is an alternative to light microscopy that uses electrons instead of visible light. This allows for greater magnification than visible light. The resolution of visible light is limited by its wavelength. Objects with a similar size to the wavelength of light interfere with it, causing visual distortions. Also, samples for SEM do not need to be perfectly flat.

SEM works by bombarding the sample with electrons. The electrons are made to go to a specific point on the sample using two electromagnets. One magnet deflects the electron in the x direction and the other deflects the electron in the y direction. By varying the voltage to the two electromagnets, electrons are sent to each point on the sample surface in a grid pattern. The electrons bounce off the sample, losing some of their energy in the process. They are then detected using a photomultiplier tube. Each point on the sample is assigned a number, which reflects the energy left in the electron. Every number corresponds to a shade of grey. This allows an image of the sample to be generated. Samples need to be electrically conductive for this to work (Holler, Skoog & Crouch: 608-612, 2007).

3. Experimental

3.1 Apparatus

A reactor vessel (80 mm outer diameter x 135 mm height x 5 mm wall thickness) with an inlet for gas was used to produce the pitch by keeping anthracene oil under a high pressure atmosphere (N_2 admitted at 0,6 MPa). Heating was supplied by means of an electric heating mantle. Figure 5 illustrates the apparatus used for mesophase pitch production.

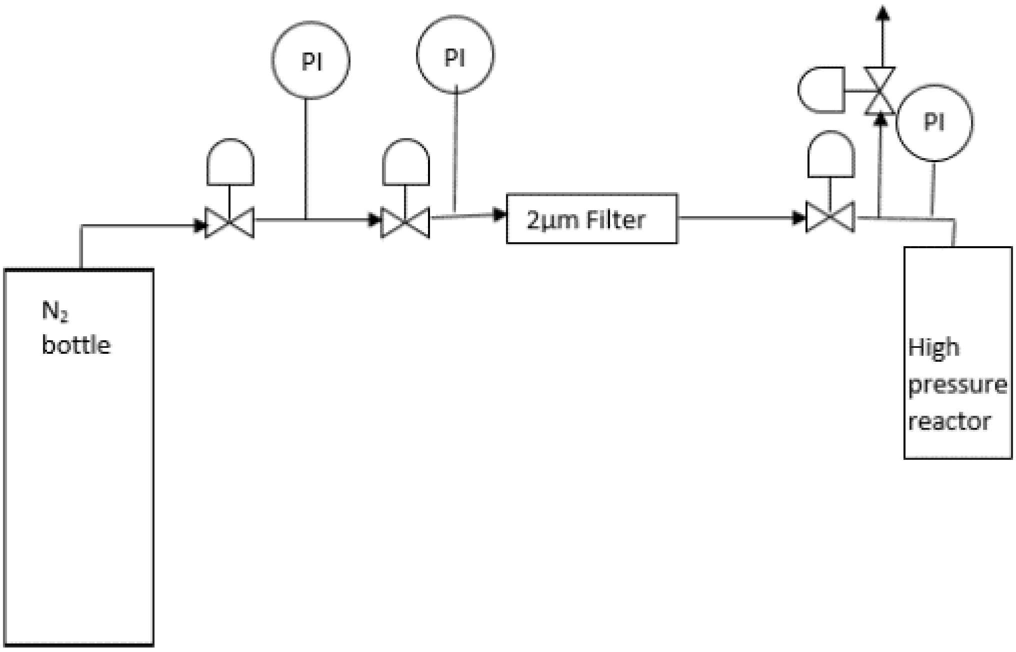

Figure 5 High Pressure reactor schematic

A ball mill (MRC Scientific Large Ball Mill) was used to reduce the particle size of the pitch formed. Alumina spheres were used as the milling media. A cylindrical container was used. It was rotated at 350 rpm.

The pitch produced during heat treatment was pressed at 5 MPa in one of two moulds. One mould consisted of a cylindrical die (internal diameter = 10 cm) and the other was a rectangle 4 cm x 1 cm. Figures 6 and 7 illustrate the moulds.

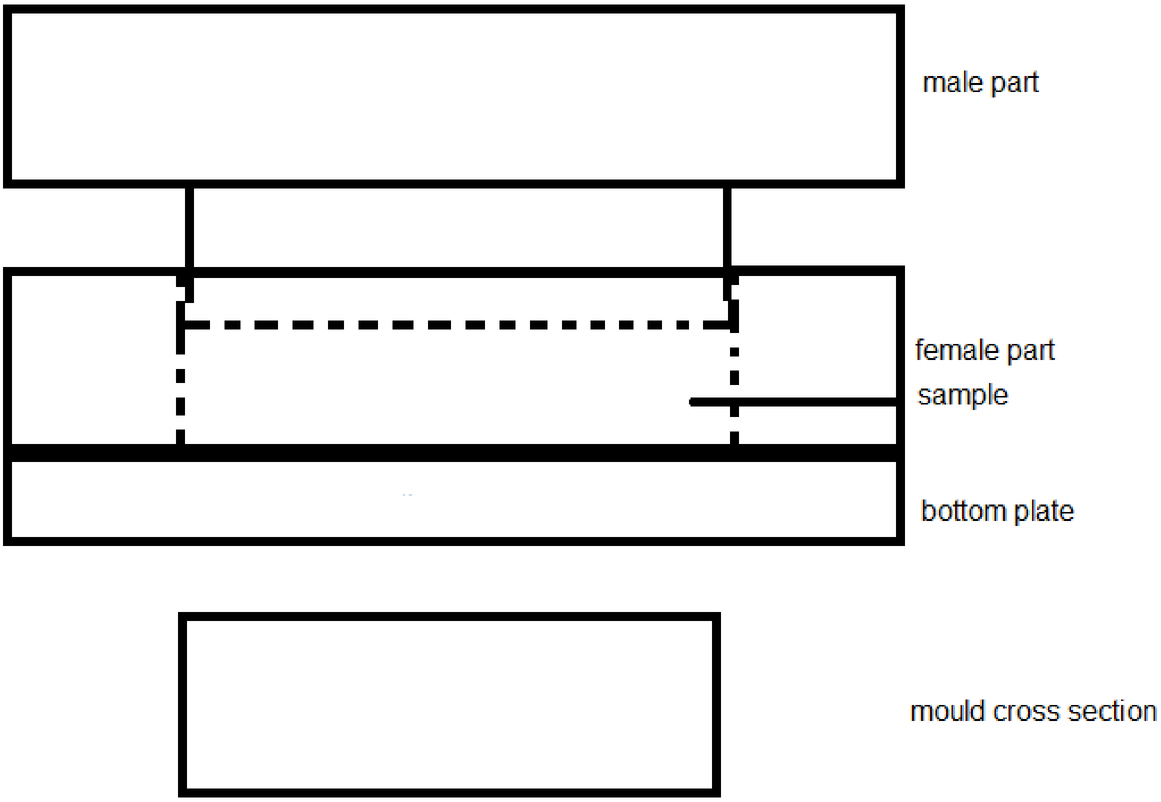

Figure 6 Rectangular mould

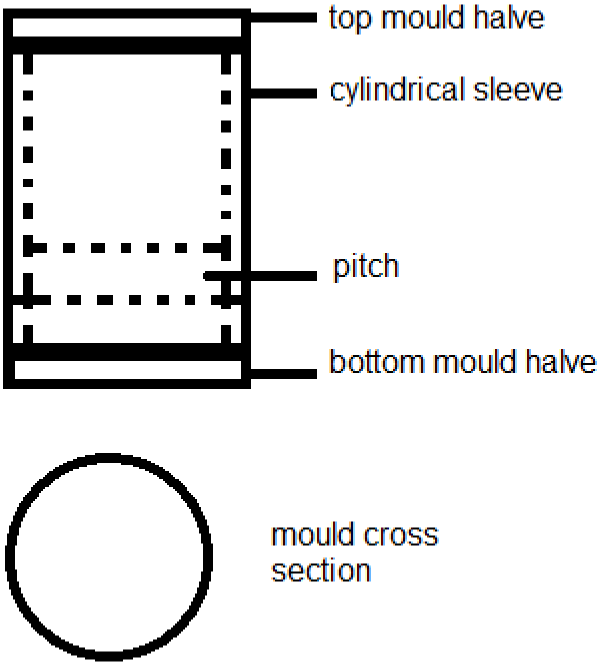

Figure 7 Cylindrical mould

The mould was placed in a press (Vertex). The pressure was increased to 5 MPa. The press was then heated to the desired temperature and maintained at this temperature for times ranging from 30 minutes to 180 minutes. The mould was then allowed to cool down while still at 5 MPa. Glass wool was used to line the interior of the press in order to increase cooling time and prevent cracking from rapid contraction. Rectangular bars of 40 mm x 10 mm were then cut from the cylinders using a Beuhler linear precision saw with a 0.6 mm wide toothless ceramic blade. Sintered samples were carbonised (Thermal Technology inc.) by heating them to 1500 ^{o}C in flowing helium at a rate of 10 ^{o}C/minute. This temperature was maintained for 30 minutes. Samples were graphitised (Thermal Technology inc.) by heating them to 2700 ^{o}C in flowing helium at 10 ^{o}C/minute. This temperature was maintained for 2 hours. Samples of pitch, sintered pitch, carbonised pitch and graphitised pitch were mounted in epoxy and polished using a polishing machine (Beuhler Alpha 2-speed grinder-polisher) and various grits of sandpaper in order to prepare them for microscope examination. Table 2 (in section 3.3.6) gives the polishing procedure.

Polarised light microscopy (Leica DM 2500) was performed on the samples to determine their mesophase content. FEG-SEM microscopy (Zeiss Ultra Plus 55 High Resolution FEG-SEM) was used to determine specific physical features of the sintered, carbonised and graphitised pitch. For this purpose, samples were mounted on aluminium plates using carbon tape. The sintered samples had to be sputter coated with a thin layer of graphite to improve their conductivity. A TGA (TA Instruments SDT Q600) was used to determine the carbon yield of the pitch prepared. A TMA (TA Instruments TMA Q400) was used to determine the melting behaviour of the pitch formed. A DMA (TA Instruments DMA 800) was used to determine the glass transition temperature of the pitch formed.

3.2 Planning

The following objectives were attempted:

1. Obtain the minimum time and temperature that causes the formation of mesophase pitch from anthracene oil using 5 wt% $AlCl_3$ as a catalyst.
2. Determine the effect of heat treatment temperature on pitch structure using 5 wt% $AlCl_3$.

3. Obtain the minimum time and temperature that causes in the formation of mesophase pitch from anthracene oil without a catalyst.
4. Determine the effect of heat treatment time on pitch structure and thermal properties without a catalyst.
5. Identify conditions of time, temperature and pressure that can be used to sinter mesophase pitch in a press.
6. Determine whether the mesophase pitch formed can be carbonised and graphitised without warping.
7. Determine the effect of oil load on pitch structure and thermal properties.

To achieve objective 1, a total reaction time of 3 hours was used, with the temperature increasing from 200 °C in increments of 50 °C. The total experiment time remained constant while the temperature was varied to achieve objective 2. The value found from achieving objective 1 was used as a starting point for objective 3, with the time and temperature increased until mesophase pitch formed. The temperature from objective 3 was maintained, while the time was varied to prepare material for objective 4. A variety of conditions were tested to achieve objective 5. Carbonisation and subsequent graphitisation were used to achieve objective 6. Objective 7 was pursued by keeping the temperature and heat treatment time constant while using either 60g or 200g of oil.

3.3 Processing Methods

3.3.1 Producing mesophase pitch

Mesophase pitch was produced from anthracene oil by heating anthracene oil in a reactor vessel to a specified temperature and maintained at this temperature for a specified heat treatment time. The reactor vessel was pre-pressurised with N_2 gas to 0,6 MPa. Pressure increased to 2 MPa during the experiment. Gas was vented to keep the pressure at an average value of 2 MPa. This was done by decreasing the pressure to 1.6 MPa every time it increased to 2.4 MPa. Total experiment time reported is the sum of the time to reach the indicated temperature and the time spent at this temperature. As many batches of pitch were produced, the work was broken down into numbered sets of connected experiments in order to aid the reader in understanding their purpose. In set 1, an attempt was made to find the minimum conditions that produce mesophase pitch from anthracene oil using 5 wt% $AlCl_3$ as a catalyst. The temperature was increased in increments of 50 °C from 200 °C to 400 °C. A total experiment time of 3 hours was used, which resulted in variable heat treatment times due to a variable heating rate. Table 1 illustrates the conditions. In set 2, the effect of increased temperature on mesophase structure was determined. A total experiment time of 3 hours was used. In set 3, the catalyst was removed while the same temperatures as set 2 were used. Due to the failure of set 3 to produce a room temperature solid, the temperature was increased to 475 °C while the heat treatment time was increased to 289 minutes. This resulted in a material that was 100% bulk mesophase. An effort was made to determine what other microstructures can be obtained. This resulted in sets 4 and 5. The difference between sets 4 and 5 is that set 4 experiments were run for a specific total time, whereas in set 5 the time at 475 °C was controlled. In set 6 experiments, the amount of oil used was increased in order to produce more pitch for use in hot pressing. Set 7 consists of a single experiment that was run in order to explain the change in properties seen when using different amounts of oil at the same heat treatment time and temperature.

Table 1 Pitch production method descriptions

Set	Objective	Experi-ment name	Temper-ature (°C)	Total experiment time (minutes)	Heat treatment time (minutes)	Oil load (g)	Wt% $AlCl_3$
1	1	200-57c	200	180	57	40	5
1	1	250-63c	250	180	63	40	5
1	1	300-112c	300	180	112	19	5
1	1	350-117c	350	180	117	19	5
1	1	400-125c	400	180	125	19	5
2	2	420-93c	420	180	93	19	5
2	2	440-120c	440	180	120	19	5
3	3	420-131	420	180	131	19	5
3	3	440-136	440	180	136	19	0

Set	Objective	Experi-ment name	Temper-ature (°C)	Total experiment time (minutes)	Heat treatment time (minutes)	Oil load (g)	Wt% $AlCl_3$
4	3	475-289	475	350	289	19	0
4	3	475-190	475	240	190	60	0
4	3	475-134	475	180	134	60	0
4	3	475-51	475	120	51	19	0
5	4	475-70	475	89	70	60	0
5	4	475-80	475	112	80	60	0
5	4	475-90	475	133	90	60	0
5	4	475-110	475	147	110	60	0
5	4	457-120	475	155	120	60	0
6	5	475-120B	475	171	120	200	0
6	5	475-180B 2 MPa	475	210	180	354	0
6	5	475-180B 0,6 MPa	475	210	180	354	0
7	7	475-120B2	475	161	120	200	0

Mixtures of some of the pitches were made up in order to determine their sintering potential. Table 2 lists the mixtures.

Table 2 Pitch mixtures

Name	Objective	Mixture
MIX1	5	90% 475-180B 2 MPa + 10% 475-180B 600kPa
MIX2	5	83,3% 475-180B 2MPa + 16,7% 475-180B 600 kPa
MIX3	5	50% 475-180B 2 MPa + 50% 475-180B 600 kPa
MIX4	5	50% 475-180B 2 MPa + 50% 475-120B

3.3.2 Pressing mesophase pitch

Mesophase pitch produced from anthracene oil and MCMB were pressed after heating. This was done at various times and temperatures. The materials were pressed into rectangular bars with dimensions 4 cm x 1 cm and variable thickness at a pressure of 5 MPa. This was for the purpose of preparing specimens for flexural strength testing on a single cantilever bending rig (see Figure 9). This was done to achieve objective 5.

Table 3 lists the pressing conditions for the pitch:

Table 3 Pitch pressing conditions

Temperature (°C)	Time (minutes)	Heating rate (°C/minute)	Repeats	Pitch	Experiment name	Drying	Pressing Pressure (MPa)
30	1	0	1	475-110	475-110-s1	-	5
270	30	5	1	475-90	475-90-s1	-	5
300	30	5	1	475-134	457-134-s1	-	5
350	180	5	1	475-120	475-120-s1	-	5
450	1	5	1	475-134	475-134-s2	-	5
450	120	5	1	475-120	475-120-s2	-	5
450	180	5	1	475-110	475-110-s2	-	5
450	180	5	1	475-120	475-120-s3	-	5
300	30	5	1	475-180 2 MPa	475-180B 2 MPa-s1	-	5
350	180	5	1	475-180 2 MPa	475-180B 2 MPa-s2	-	5
400	180	5	1	475-180 2 MPa	475-180B 2 MPa-s3	-	5
450	180	5	1	475-180 2 MPa	475-180B 2 MPa-s4	-	5
300	180	5	1	475-180 2 MPa	475-180B 2 MPa-s5	-	5

Temperature (^{o}C)	Time (minutes)	Heating rate (^{o}C/minute)	Repeats	Pitch	Experiment name	Drying	Pressing Pressure (MPa)
250	180	5	1	475-180 2 MPa	475-180B 2 MPa-s6	-	5
300	180	5	1	475-180 2 MPa	475-180B 2 MPa-s7	-	5
350	180	5	1	475-180 2 MPa	475-180B 2 MPa-s8	-	5
400	180	5	1	475-180 2 MPa	475-180B 2 MPa-s9	-	5
450	180	2,3	10	475-180 2 MPa	475-180B 2 MPa-s10	-	5
250	180	5	1	475-180 0,6 MPa	475-180B 0,6 MPa-s1	-	5
200	180	5	1	475-180 0,6 MPa	475-180B 0,6 MPa-s2	-	5
200	180	5	1	475-180 0,6 MPa	475-180B 0,6 MPa-s3	30 minutes at 200 ^{o}C	5
450	120	5	1	475-120B	475-120B-s1	-	5
300	60	5	1	475-120B	475-120B-s2	-	0,1
350	60	5	1	475-120B	475-120B-s3	30 minutes at 250 ^{o}C	5
150	180	5	1	MIX1	m1-s1	-	5
250	180	5	1	MIX1	m1-s2	-	5
350	180	5	1	MIX2	m2-s1	-	5
150	180	5	1	MIX3	m3-s1	-	5
200	180	5	1	MIX3	m3-s2	-	5
250	180	5	1	MIX4	m4-s1	-	5

Table 4 lists the pressing conditions of MCMBs

Table 4 MCMB pressing conditions

Temperature (^oC)	Time (minutes)	Heating rate (^oC/minute)	Repeats	Experiment	Pressing Pressure (MPa)
30	1	0	1	MCMB-s1	5
300	30	5	1	MCMB-s2	5
350	60	5	3	MCMB-s3	5
400	6	5	3	MCMB-s5	5
400	180	5	1	MCMB-s6	5
450	30	5	1	MCMB-s7	5
450	60	5	5	MCMB-s8	5
450	90	5	1	MCMB-s9	5
450	120	5	2	MCMB-s10	5
450	180	5	2	MCMB-s11	5
480	30	5	1	MCMB-s12	5

3.3.3 Carbonisation

Samples were carbonised by heating them to 1000 ^oC in flowing helium at a rate of 10 ^oC/minute. This temperature was then maintained for 30 minutes. Samples were then cooled at a rate of 15 ^oC/ minute. Samples were carbonised further by heating them to 1500 ^oC at 10 ^oC/ minute. This temperature was then maintained for 30 minutes. Samples were then cooled at a rate of 15 ^oC/ minute. The samples carbonised were MCMB-s11 and 475-180B-2 MPa-s10. This was done to achieve objective 6.

3.3.4 Graphitisation

Samples were graphitised by heating them to 2700 ^oC at a rate of 5 ^oC/ minute. This temperature was then maintained for 30 minutes. Samples were then cooled at a rate of 15 ^oC/ minute. This was done to achieve objective 6.

3.4 Analytical methods

3.4.1 Determining softening temperature

TMA testing was done using a macroexpansion probe on the TMA Q400 from TA instruments. The material was heated to 650 ^oC at a rate of 10 ^oC/minute. A nitrogen flow was maintained to prevent oxidation. The softening onset temperature of the material was defined as the temperature where the material started to shrink. Due to the large molar mass distribution of the material, melting occurs over an interval of up to 150 ^oC. Mettler softening point equipment was not available, therefore TMA measurements were used.

3.4.2 Determining glass transition temperature

DMA testing was done by flexing a powder inside a stainless steel sleeve at 0,1 Hz using the DMA 8000 from TA Instruments. The temperature was increased to 400 ^oC at 5 ^oC/minute. N_2 flowing at 5 L/minute was used to prevent oxidation. The shift in phase angle between the applied strain and the achieved stress was measured. When this phase angle reaches a maximum, the sample changes from being hard and brittle to soft and rubbery. The tangent of the phase angle is equal to the loss modulus divided by the storage modulus (young’s modulus). This value reaches a maximum when the loss modulus is large and the storage modulus is small. The loss modulus represents the viscous (liquid) component of the response and the storage modulus represents the elastic (solid) component of the response. Therefore, above the glass transition temperature, the material behaves more like a liquid and less like a solid. It becomes soft and malleable, instead of hard and brittle. While it still has the ability to store energy, it can also flow. A material with this combination of properties is called viscoelastic.

The reason that DSC was not used to determine this property is that the glass transition of mesophase pitches is quite difficult to pick up using DSC. There is only a very small deviation visible where the transition occurs.

3.4.3 Determining carbon yield

Carbon yield is defined here as the fraction of pitch that does not evaporate below 1000 ^oC. This term is used as at this temperature the remaining material is nearly pure carbon. This was determined in a TGA by heating the specimen to 1000 ^oC at a rate of 10 ^oC/minute using N_2 flowing at 50 mL/minute. The SDT Q600 from TA Instruments was used.

3.4.4 Determining carbon microstructure

Polarised light microscopy allows the microstructure of carbon materials to be determined. For a detailed explanation of how this works see section 2.7.

Samples of the mesophase pitch were mounted in epoxy and polished using an Alpha 2 speed grinder-polisher from Beuhler. Table 5 explains the polishing procedure.

Table 5 Polishing procedure

Grit	Time (minutes)	Liquid	Force (N)
400	2	water	5
600	2	water	5
1200	2	water	5
rubber	5	3 µm SiC suspension	5
satin	5	0.05 µm polycrystalline diamond suspension	5

Microscope photos were then taken (Leica DM 2500) at 20x magnification using polarised light.

Optical microscopy is unable to show the surface texture of specimens due to the requirement for a flat surface. Electron microscopy overcomes this limitation. It is also possible to achieve higher magnification. Electron microscopy was performed using a FEG-SEM (Zeiss Ultra Plus 55 High Resolution FEG-SEM). Samples were mounted on Aluminium plates with carbon tape. Where needed, samples were carbon-coated using an electrical discharge to improve electrical conductivity.

3.4.5 Determining mesophase content

In order to determine the mesophase content, the images were superimposed on a grid of 11 x 11 rectangles. This gave 100 intersection points on the inside of the image. The intersection points on the perimeter were ignored. The number of these intersections containing mesophase were counted and taken as the percentage mesophase pitch.

3.4.6 Strength testing

Single cantilever bending was conducted using a purpose-built rig.

The rig consisted of two clamps. One clamp was connected to each end of a rectangular test specimen. One clamp was bolted to a table. The other clamp was connected to a platform for holding weights. Applying weights to the second clamp resulted in a torque in the rectangular bar. The mass used was increased in increments of 102 g until the sample broke. Mechanics of Materials principles (Hibbeler, 2004: 1) were then applied (equation 7) to determine the breaking stress σ of the sample using the force F, the distance between the clamps L, the sample width W and the sample height H.

$$\sigma = \frac{6FL}{WH^2} \tag{7}$$

Figure 8 shows an illustration of single cantilever bending.

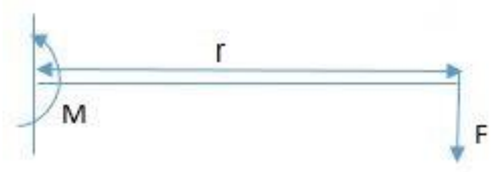

Figure 8 Single cantilever bending illustration

Figure 9 shows the device employed.

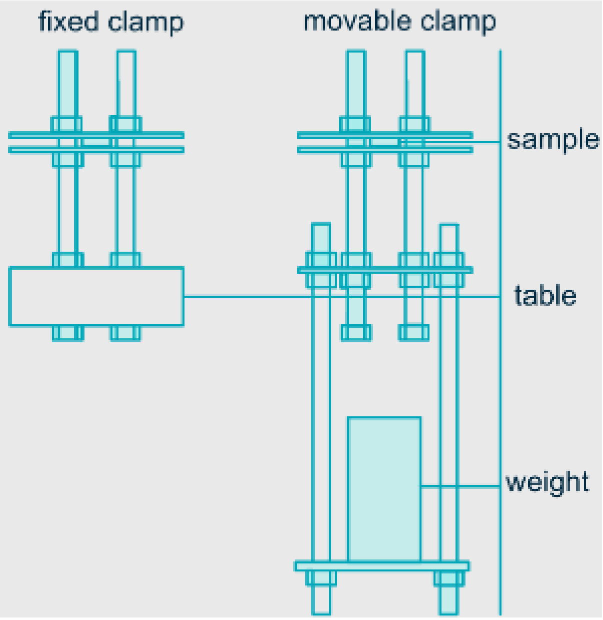

Figure 9 Single cantilever bending rig (scale=1:2.6)

3.4.7 Determining C:H ratio

The C:H ratio is determined by means of elemental analysis. Elemental analysis involves combustion of pitch in pure O_2. The amount of CO_2 and H_2O produced is measured using infrared absorption spectroscopy. The ratio of carbon to hydrogen atoms in the pitch is then determined from the relative amounts of CO_2 and H_2O produced. This procedure was performed by the University of Johannesburg.

3.4.8 Determining density

The bulk density of a sample was determined by measuring its volume using a pair of Vernier calipers (Duratool DC150) with an accuracy of 0,01 mm and measuring its mass using a scale with an accuracy of 0,1 mg (Mettler Toledo XS105 Dual Range). The pycnometric density of the samples was determined by using a helium pycnometer (micrometrics AccuPyc 1340). This device uses helium to fill all of the open pores in the sample. The volume of a sample is the difference between the volume of helium in a chamber with the sample in it and the actual volume of that chamber. This volume can be calculated by passing the helium in one chamber into another evacuated chamber and measuring the pressure drop. The helium fills all the open pores in the sample. The pycnometric density is the ratio of the sample mass to the sample volume. The scale mentioned earlier was used to determine the mass before testing.

4. Results and Discussion

4.1 Thermal properties of pitches

Table 6 gives the thermal properties of the pitches prepared with small and large amounts of anthracene. The following code identifies the pitches: xxx-yy-a

xxx: heat treatment temperature (°C) yy: heat treatment time (minutes) a: pressure (MPa) (2, unless indicated)

Table 6 Thermal properties of pitches

Powder	Oil load (g)	T_s (°C)	T_g (°C)	% CY	% MP	C:H ratio
475-50	19	48	101	56	8±1	1,92
475-70	60	67	123	57,5	27±6	-
475-80	60	100	150	72,3	37±2	-
475-90	60	105	201	84,6	100	3,86
475-110	60	117	350	89,1	100	-
475-120	60	114	>400	91,7	100	-
MCMB	N/A	>450	239	92	100	-
475-180	354	114	194	89	34	2,46
475-180-0,6	357	60	97	80	45	-
475-120	200	64	170	72,8	12	-

Figure 10 gives the results of TGA analysis for small pitch batches. A clear pattern can be seen. An increase in heat treatment time leads to higher carbonisation yields. This is due to molecules growing to the size where they can no longer evaporate. Small molecules with a low boiling point either react to form larger molecules or evaporate.

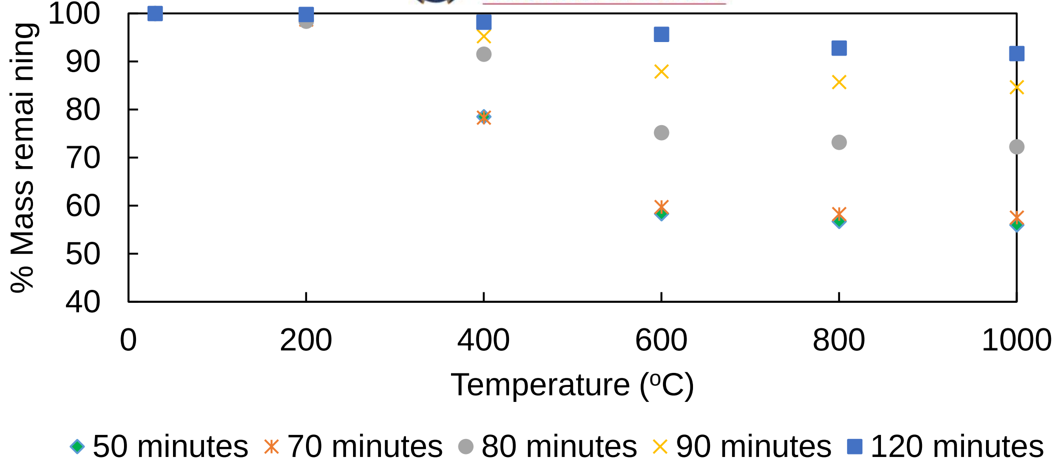

Figure 10 Thermogravimetric analysis of small batches

A similar pattern is detectable from DMA analysis in Figure 11. A longer heat treatment time results in molecules with a greater degree of polymerisation and therefore a higher average molar mass. Molecules with the same shape and chemical bonds show an increase in melting temperature as molar mass increases. A hard, glassy polymer such as polystyrene and polycarbonate does not really melt. Rather, it reaches a temperature where it becomes soft and easily deformed. This is called the glass transition temperature. Just like the melting temperature of other molecules, the glass transition temperature of a polymer increases as the molar mass goes up. Pitch behaves in a similar manner. Pitch can be considered to be a thermoplastic, and the glass transition temperature serves as a measure of the average molecular mass of the material.

However, pitch contains a very wide variety of different molecules. It behaves as a mixture of different materials, with multiple glass transitions visible on a DMA test result. Interpreting the results can be difficult.

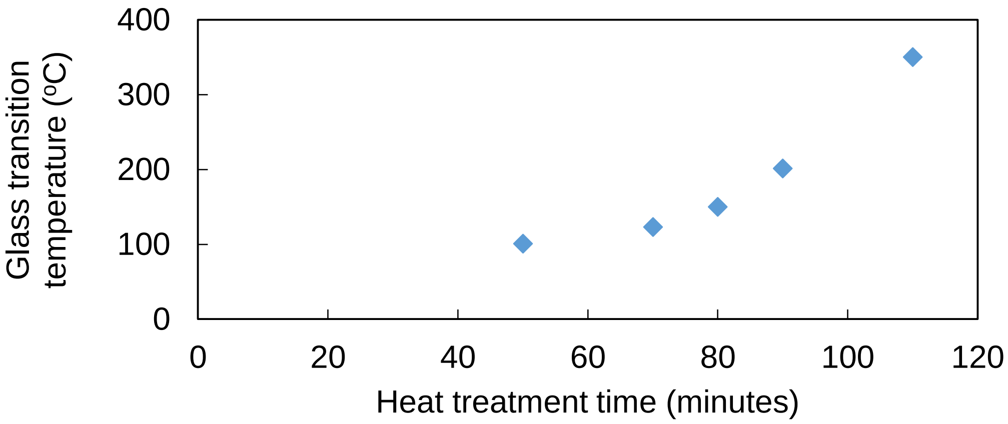

Figure 11 Dynamic mechanical analysis of small pitch batches

TMA analysis in Figure 12 corroborates the pattern seen from the DMA analysis. There was expected to be a strong correlation between TMA and DMA results due to the similarities between the two properties. The TMA presses down on the pitch and measures its length while ramping up the temperature. The point taken as the softening point was the temperature at which the pitch starts to shrink. Most materials expand as they get hotter. However, above a certain temperature pitch starts to deform under its own weight and the applied force. This is called the softening onset temperature. The increase in softening onset temperature is due to an increase in the average molecular mass of the pitch.

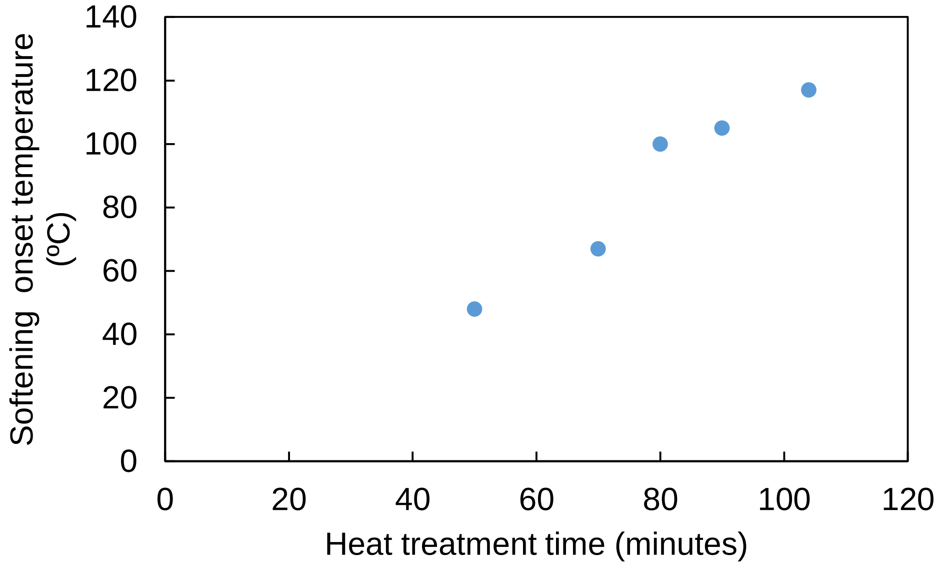

Figure 12 Thermal Mechanical Analysis of small pitch batches

Figure 13 compares the softening onset temperature from the TMA with the glass transition temperature from the DMA. A higher softening temperature is correlated with a higher glass transition temperature.

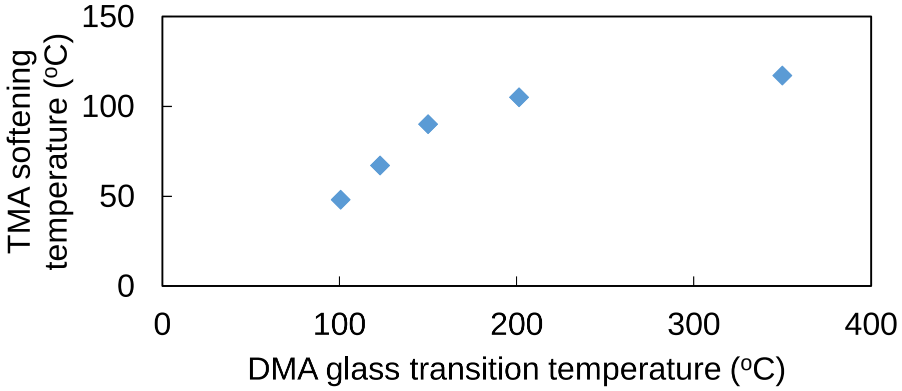

Figure 13 Comparison of TMA and DMA results

The C:H ratios of the small batches increase with heat treatment time. This is due to an increase in the degree of polymerisation of the anthracene oil. For every step in the reaction, more hydrogen is lost. For comparison, anthracene has a C:H ratio of 1,4C:1C, and the main molecules in anthracene oil have ratios from 1,2 – 1,6 C:1H.

4.2 Thermal analysis of the effect of reactor loading

Figure 14 displays the result on carbon yield of altering the amount of anthracene oil charged to the reactor.

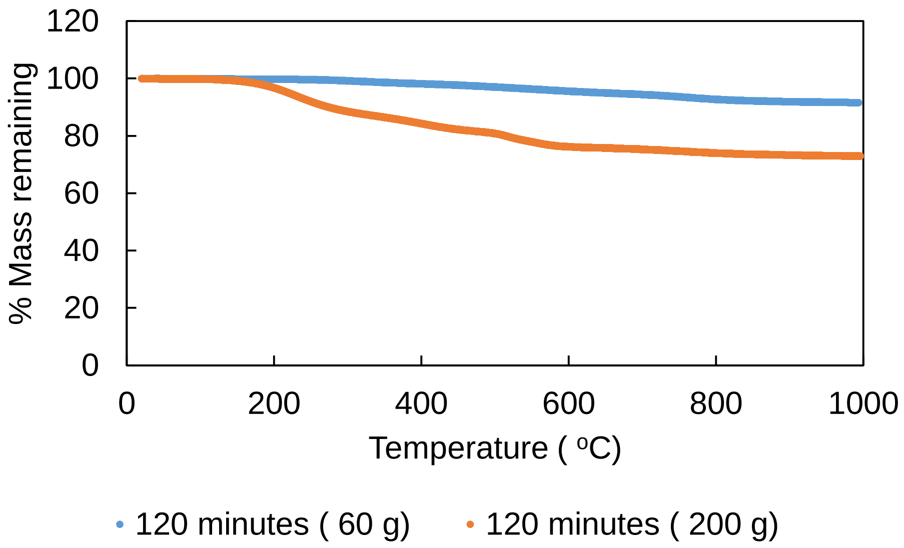

Figure 14 Effect of changing the reactor loading

The carbonisation yield drops from 91% to 73 % if the oil used is increased from 60 g to 200 g. If a batch reactor is loaded with reactants that react in the liquid phase to form a solid, for a reaction that is first-order in terms of one reactant, the conversion is not influenced by the level to which the reactor is loaded. This is due to conversion depending only on the temperature. Equations 8 through 14 give the derivation.

$$\frac{dn_a}{dt} = -r_a V \tag{8}$$

$$-r_a = k\, c_a \tag{9}$$

$$k = k_0 e^{\frac{-E_a}{RT}} \tag{10}$$

$$\frac{dn_a}{dt} = k_0 e^{\frac{-E_a}{RT}} c_a V \tag{11}$$

$$dn_a = c_a V dx \tag{12}$$

$$c_a = c_{a0}(1 - x) \tag{13}$$

$$\frac{dx}{dt} = k_0 e^{-\frac{E_a}{RT}}(1 - x) \tag{14}$$

This derivation shows that batch reactor loading does not influence the conversion of a first-order reaction. By assuming ideal gas behaviour, the same conclusion will be arrived at for a batch reactor containing only a gas reagent. However, the situation is different for a gas-phase reaction where the gas must first evaporate and the pressure remains constant. In this situation, the fixed pressure means that the concentration of reagent gas remains constant. If it is assumed that the headspace volume remains constant, the total reaction rate will be constant. This means that the amount of product formed increases linearly with time. A higher loading would then require more time to reach the same level of conversion. Equations 15 through 20 give the derivation.

$$\frac{dn_a}{dt} = -r_a V \tag{15}$$

$$-r_a = kc_a \tag{16}$$

$$c_a = \frac{P_{AO}}{RT} \tag{17}$$

$$P_{AO} = constant \tag{18}$$

$$\therefore c_a = constant \tag{19}$$

$$\therefore \frac{dn_a}{dt} = constant \tag{20}$$

An inert gas is used to pressurise the anthracene oil and prevent air from entering the reactor. This gas is gradually replaced by anthracene oil with each purge cycle. In the case of a gas phase reaction, this will result in a gradual increase of anthracene oil vapour concentration, and subsequently the reaction rate. Equations 21 and 22 show how to calculate the anthracene oil pressure after n purge cycles.

$$P_{AO}(n) = P_{total} - P_{N_2}(n) \tag{21}$$

$$P_{N_2}(n) = P_{N_2}(0) \times \left(\frac{P_{total}(lower\ limit)}{P_{total}(upper\ limit)}\right)^n \tag{22}$$

The frequent purging required to keep the pressure at a constant value also limits the residence time that reagent gas spends in the reactor. For the specific case where the pressure is decreased to 1,6 MPa every time it rises to 2,4 MPa, it can be shown that the gas remains behind for 2,5 purging cycles. If the purge interval is known, the total gas phase residence time can be calculated using equation 23.

$$t_r = purge\ interval \frac{P_{avg}}{\Delta P} \qquad (23)$$

Table 7 shows the required purging schedule.

Table 7 Purging requirements with varying oil loads in order to maintain the pressure between 1,6 MPa and 2,4 MPa

Oil load (g)	Time between first and last purge (minutes)	Number of purges	Purge interval (minutes)
60	152	4	38
200	111	13	8,5

From table 7, it can be seen that more oil results in more frequent purging of gas from the reactor in order to maintain a constant average pressure. This would reduce the final conversion of reagent for a gas phase reaction due to the reduced residence time. It should be noted that this is a simplified model of the real situation. Once the molecules reach a certain size, their boiling point at 2 MPa would exceed 475 ^{o}C, and they will condense. The reaction will then proceed in the liquid phase, and the kinetics will change.

The reaction under consideration is a polymerisation reaction. An increased conversion in the model used would translate to a larger degree of polymerisation. Subsequently, larger molecules would form. Larger molecules have a higher boiling point and consequently produce a pitch with a higher carbonisation yield. They also have an increased melting point, and this would increase the glass transition temperature and softening temperature of the pitch. This is confirmed by table 8.

Table 8 changes in material properties due to reactor loading

Material	T_g (^{o}C)	T_s (^{o}C)
120 minutes 60 g	>400	114
120 minutes 200 g	170	64

4.3 Micrographs

Figure 15 shows how a completely amorphous material looks under optical polarised light.

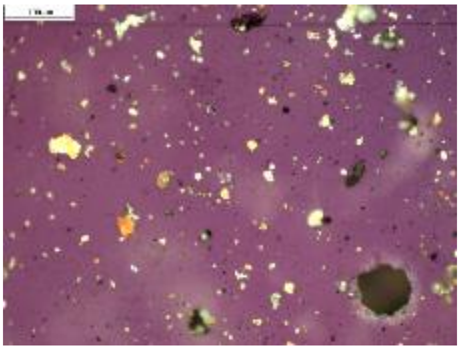

Figure 15 Epoxy containing some dirt (green) as an example of a completely amorphous (isotropic) material

A gradual increase in mesophase content with heat treatment time can be observed (Figure 16). After 50 minutes, only a few small spheres are visible. After 80 minutes, a clear distinction between the mesophase regions and the isotropic region can be seen. Coalesced mesophase spheres are also visible. After 90 minutes, all the isotropic material has been converted to mesophase.

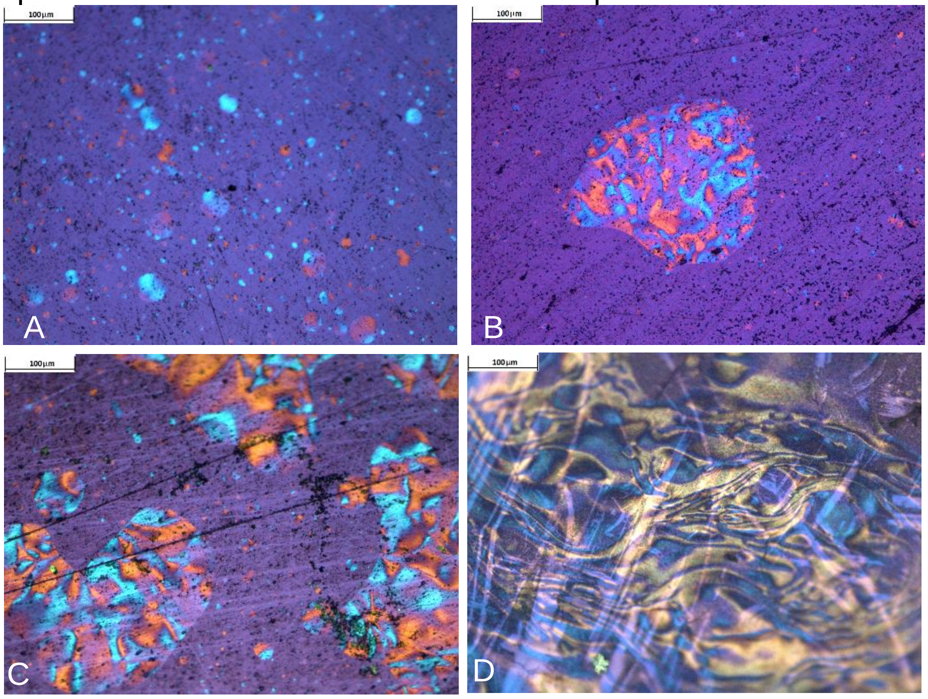

Figure 16 Polarised light optical micrographs showing the development of mesophase pitch at 475 °C for various heat treatment times (20x magnification). A: 50 minutes B: 70 minutes C: 80 minutes D: 90 minutes

Changes in mesophase structure were expected with increased heat treatment time. It was expected that an extended heat treatment would lead to narrow, elongated regions, forming a structure similar to needle coke (Martin & Shea, 1958). This was observed to a limited extent after 180 and 293 minutes of heat treatment (Figure 17).

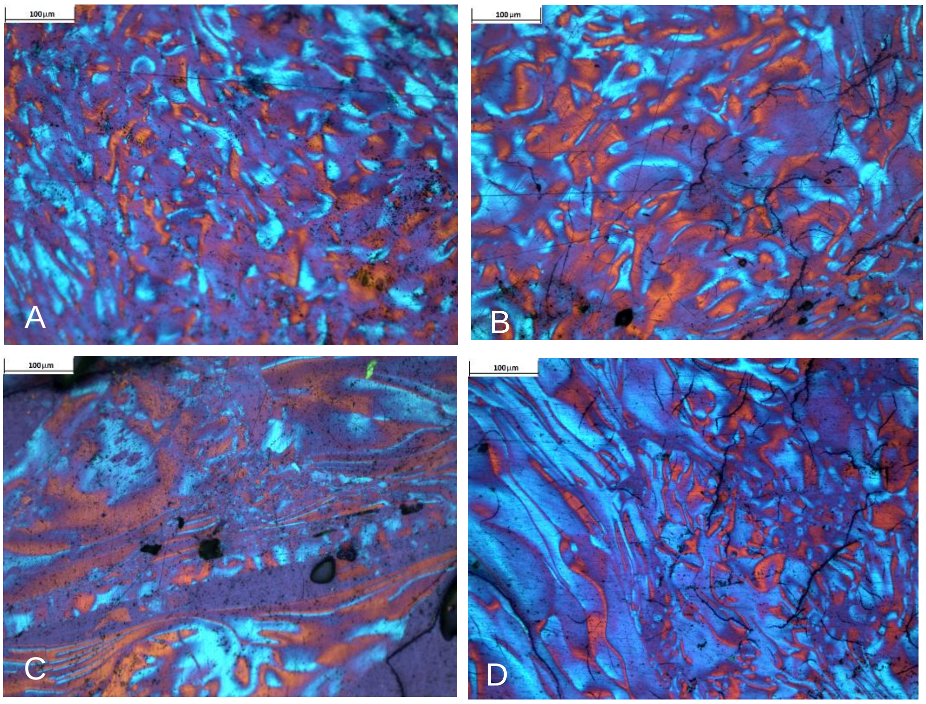

Figure 17 Polarised light optical micrographs showing the change in mesophase pitch structure at 475 ^{o}C for various heat treatment times (20x magnification). A: 120 minutes B: 134 minutes C: 180 minutes D: 293 minutes

Using 5 wt% $AlCl_3$ as a catalyst results in a different microstructure (Figure 18). Many small mesophase spheres are visible, which develops into large bulk mesophase with longer heat treatment times and higher temperatures. At 420 ^{o}C after 93 minutes (pitch 420-93c), many small mesophase spheres are visible. At 440 ^{o}C after 120 minutes of heat treatment time (pitch 440-120c), bulk mesophase forms, which is separated from the isotropic pitch.

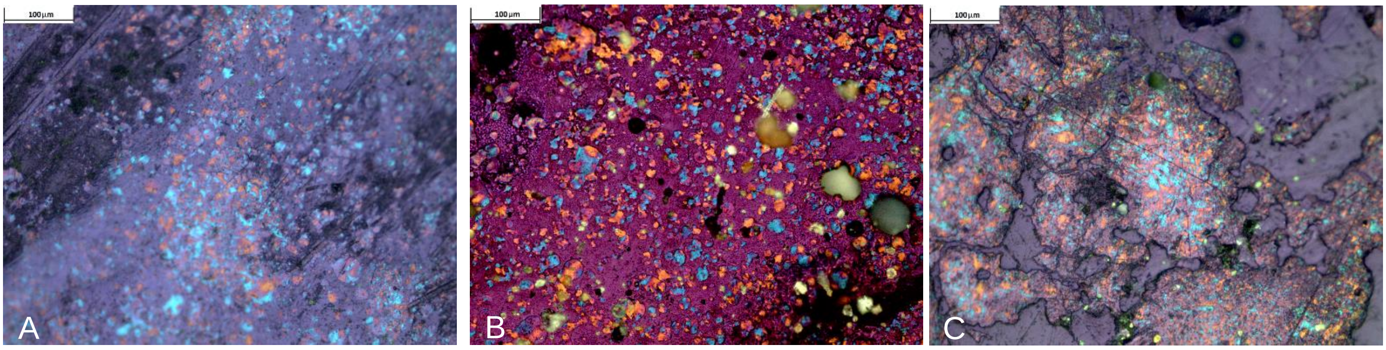

Figure 18 Polarised light optical micrographs of pitches prepared from anthracene oil with 5 wt% AlCl3 for the temperatures and heat treatment times indicated. A: 400 °C 125 minutes B: 420 °C 93 minutes C: 440 °C 120 minutes

Figure 19 shows a comparison between MCMB and anthracene oil mesophase pitch sintered at 450 °C. The separated mesophase spheres are clearly visible in the sintered MCMB. The sintered anthracene oil mesophase pitch has no distinguishing features.

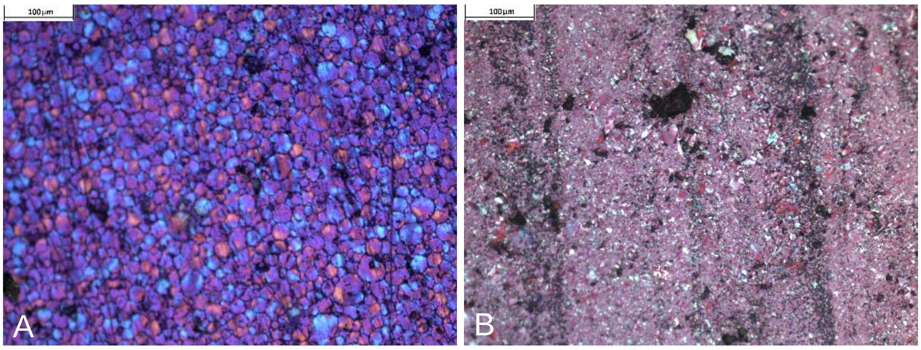

Figure 19 Polarised light optical micrographs of sintered pitches A: MCMB sintered at 450 °C and 5 MPa for 180 minutes (MCMB s-11) B: Mesophase pitch prepared at 475 °C by 120 minutes of heat treatment time sintered stepwise to 450 °C (475-180B 2 MPa-s10).

Figure 20 Shows that the number of cracks and the degree of order increases as the pitch is first carbonised and then graphitised.

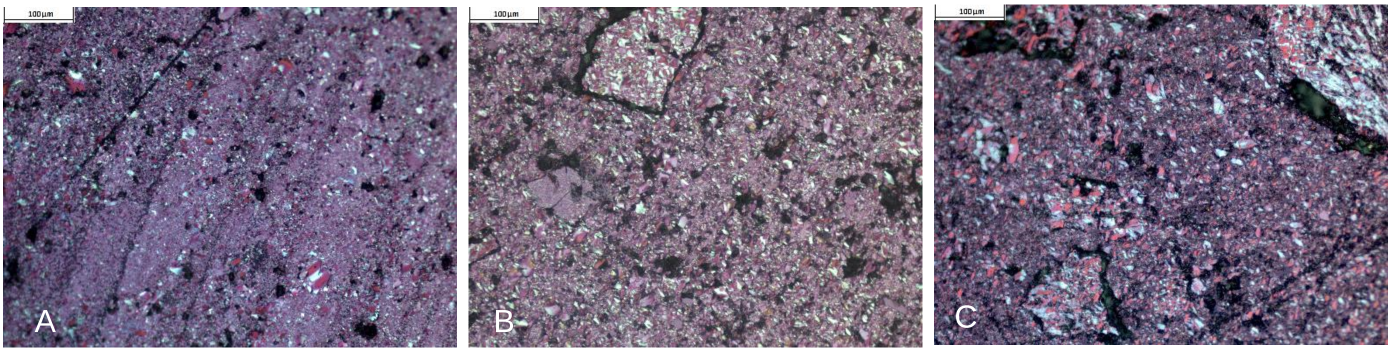

Figure 20 Polarised light micrograph of mesophase pitch 475-180B-2 MPa A: sintered stepwise to 450 ºC B: carbonised to 1500 ºC C: graphitised to 2700 ºC.

Figures 21 through 29 shows field emission gun scanning electron microscopy (FEG-SEM) images. Figure 21 shows images of sintered (A), carbonised (B) and graphitised (C) mesophase pitch. The sintering method employed was a stepwise temperature ramp from 200 ºC to 450 ºC in 50 ºC increments with a 15 minute residence time at each temperature. After carbonisation at 1500 ºC, there is an increase in the number of cracks seen. This continues upon graphitisation.

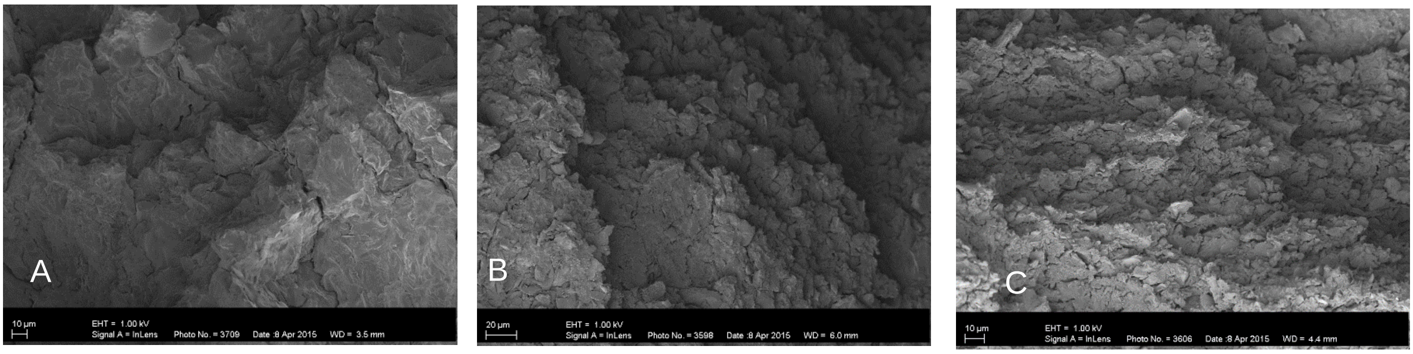

Figure 21 FEG-SEM images of fractured mesophase pitch (1000x magnification) A: sintered stepwise B: sintered stepwise and carbonised at 1500 ºC C: sintered stepwise, carbonised at 1500 ºC and graphitised at 2700 ºC.

In figure 22, it can be seen that the sintered mesophase pitch has some surface texture. It is not as featureless as figure 21A suggests.

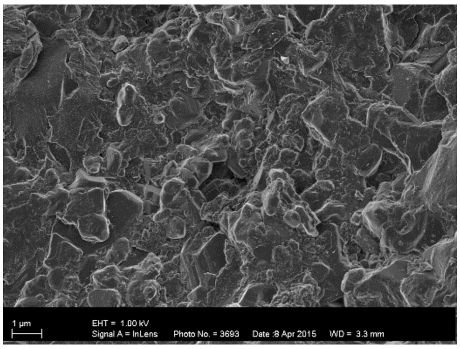

Figure 22 FEG-SEM close-up image of sintered mesophase pitch surface texture (20 000x magnification).

Figure 23 shows that the pressure applied during the sintering process contributes to the stacking of particles parallel to one another. This is a more detailed view of the stacked parallel plates seen in Figure 21A.

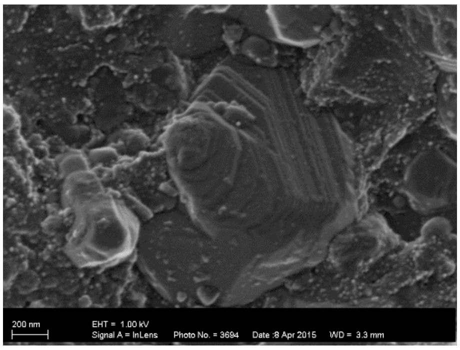

Figure 23 FEG-SEM image of columns formed via sintering in fractured mesophase pitch (120 000x magnification)

Figure 24 shows that the milled pitch particles used for sintering are still visible after carbonisation and graphitisation. This feature shows that the milled particles used in sintering maintain their external structure, even though their internal structure changes dramatically.

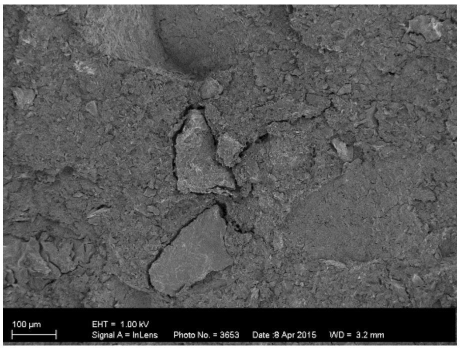

Figure 24 FEG-SEM image of fractured graphitised mesophase pitch (300x magnification)

A common feature found on the fracture surfaces of carbonised and graphitised samples was an abundance of mesophase spheres. It is believed that these mesophase spheres act to bind the particles of pitch together during sintering. When the material fails, these bonds are broken, revealing the mesophase spheres. This would be similar to the failure at a glue line for laminated wood. In order to enable the reader to identify mesophase spheres, Figure 25 was included. Figures 26 and 27 show mesophase spheres on a carbonised and a graphitised sample.

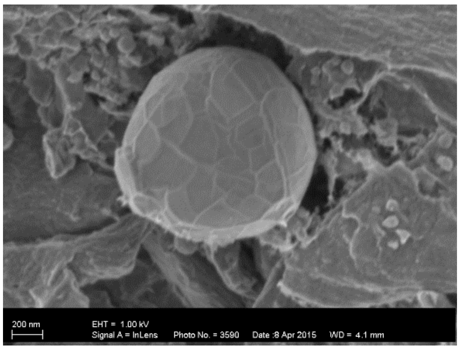

Figure 25 FEG-SEM image of a mesophase sphere (100 000x magnification)

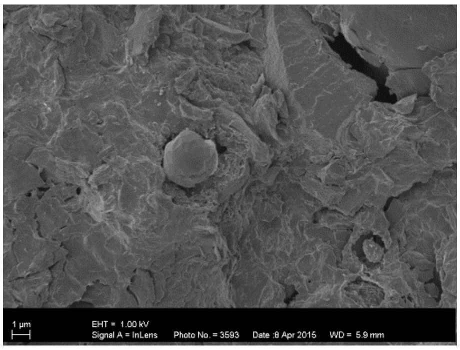

Figure 26 FEG-SEM image of a mesophase sphere on fractured carbonised mesophase pitch (12 000x magnification)

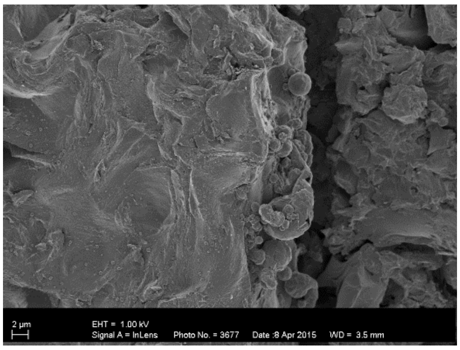

Figure 27 FEG-SEM image of mesophase spheres on graphite fracture surfaces (5000x magnification)

In graphitised samples, many small cavities (visible as small black dots) were found. These cavities formed when small impurities in the graphite with boiling points below 2700 ^{o}C evaporated. It should be noted that this temperature can remove some but not all metals. Figure 28 shows these cavities inside the white circle. The large cracks may have formed due to the difference in thermal expansion of graphite in and perpendicular to the basal plane (ab and c directions).

Figure 28 Cavities and cracks formed upon graphitisation (80 000x magnification)

Some of the sintered pitch particles pull away from one another due to the shrinkage that occurs during carbonisation. The direction in which the particles pull is perpendicular to the direction in which their grains are orientated. This can be seen clearly in figure 29.

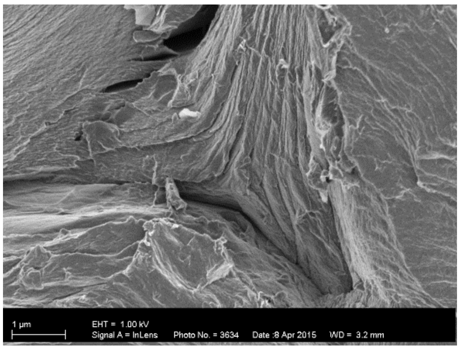

Figure 29 FEG-SEM image of sintered particles pulling apart during carbonisation (35 000x magnification)

4.4 Sintering

Table 9 shows all attempts to sinter MCMB's at 5 MPa. An x indicates success and a 0 indicates failure. Success was identified as the formation of an intact bar. Failure is seen by a cracked or crumbling bar. The procedure involved placing the MCMB under a pressure of 5 MPa. The MCMB were then heated to the indicated temperature and maintained at this temperature for the indicated time. They were allowed to cool down using natural convection. Glass wool was used as insulation to reduce the cooling rate. A pressure of 5 MPa was used. It is clear from the table that there is no reliable way to sinter MCMB at this pressure. Even those methods which gave some success failed at other times under identical conditions.

Table 9 Results of pressing MCMB

Experiment	Attempts	Failures	Successes
MCMB-s1	1	1	0
MCMB-s2	1	1	0
MCMB-s3	3	1	2
MCMB-s4	1	1	0
MCMB-s5	3	3	0
MCMB-s6	1	1	0
MCMB-s7	1	1	0
MCMB-s8	5	4	1
MCMB-s9	1	0	1
MCMB-s10	3	2	1
MCMB-s11	2	1	1
MCMB-s12	1	1	0

Table 10 shows the same results for the mesophase pitches.

Table 10 Results of sintering mesophase pitches

Experiment	Result
475-110-s1	failed to sinter
475-90-s1	failed to sinter
457-134-s1	failed to sinter
475-120-s1	failed to sinter
475-134-s2	failed to sinter
475-120-s2	failed to sinter
475-110-s2	failed to sinter
475-120-s3	sintered
475-180B-2 MPa -s1	crumbled during removal
475-180B-2 MPa -s2	crumbled during removal
475-180B-2 MPa -s3	cracked
475-180B-2 MPa -s4	cracked
475-180B-2 MPa -s5	cracked die
475-180B-2 MPa -s6	crumbled during removal
475-180B-2 MPa -s7	cracked but intact bar
475-180B-2 MPa -s8	cracked but intact bar
475-180B-2 MPa -s9	cracked but intact bar
475-180B-0,6 MPa-s1	melted
475-180B-0,6 MPa-s2	melted
475-180B-0,6 MPa-s3	melted
475-120B-s1	melted
475-120B-s2	melted
475-120B-s3	melted
m1-s1	crumbled during removal
m1-s2	crumbled during removal

Experiment	Result
m2-s1	crumbled during removal
m3-s1	cracked and crumbled during removal
m3-s2	cracked and crumbled during removal
m4-s1	melted

It was hypothesised that melting occurred due to the presence of a low-boiling component. Therefore, the pitch 475-120B was dried at 250 ºC for one hour under a N_2 atmosphere. The pitch melted and solidified into the shape of a perfect cylinder upon cooling. This was then crushed and pressed at 250 ºC. It melted and flowed out the mould, proving that the low viscosity of the pitch at this temperature was due to a component that boils at a temperature greater than 250 ºC at atmospheric pressure. It was realised that simply melting the pitch was a potential sintering method. Table 11 shows the results of this and various other potential sintering methods.

Table 11 Various potential sintering methods

Temperature (°C)	Compaction	Atmosphere	Container	Result
250	no	nitrogen	Aluminium cylinder	perfect smaller cylinder shorter + narrower
250	no	nitrogen	mould	intact bar
300	yes	air	mould	cracked bar
250	yes	air	mould	intact bar
250	no	air	mould	crumbled bar
250	no	nitrogen	cobalt foil	chunks
250	no	nitrogen	aluminium foil	chunks

Without compaction, the pitch does not adhere to the walls of the container when it melts. For all shapes except the cylinder, the pitch did not retain the shape of the container and it did not remain in one piece. In the presence of air, the pitch must be compacted. Without compaction, there are too many gaps for oxygen to get in to the mould. The product formed simply crumbles. When the pitch is compacted and heated to 250 ºC, it forms an intact bar. Some oxidation does take place. When the temperature is raised to 300 ºC, the product formed is seen to contain surface cracks. It also cracked in half when removed from the mould. This happens when the mould is not being pressed during heating. When it is pressed during heating, the pitch simply flows out. From these results we know that 475-120B is a fluid at 250 °C. The viscosity is so high that it will not flow under its own weight or a pressure below 10 kPa (the pressure supplied by the weight of the male mould part) at this temperature. It will also not melt at a higher temperature unless pressure is applied. This was determined by reheating one of the intact bars to 450 °C without applying pressure. No melting occurred. However, when pressed, it will escape through small cavities between the two mould parts, or the bottom mould part and the plate placed beneath it. However, due to the high volatile content of this sample, it is not suitable for carbonisation.

One final attempt was made to sinter mesophase pitch. This was for the pitch 475-180B 2 MPa. The pitch was heated slowly from 200 °C up to 450 °C in increments of 50 °C. The temperature was maintained for 15 minutes at each temperature. This resulted in the production of intact bars after cooling. This was likely due to the slow release of volatile materials. The heating program used resulted in an average heating rate of 2,6 °C/minute. The rapid release of volatile materials would result in cracking. Also, the final temperature was maintained for 15 minutes instead of 180 minutes. This may have prevented excessive crosslinking due to oxygen, which can also result in a cracked bar. In order to visualise the heating program used, figure 30 illustrates the heating profile.

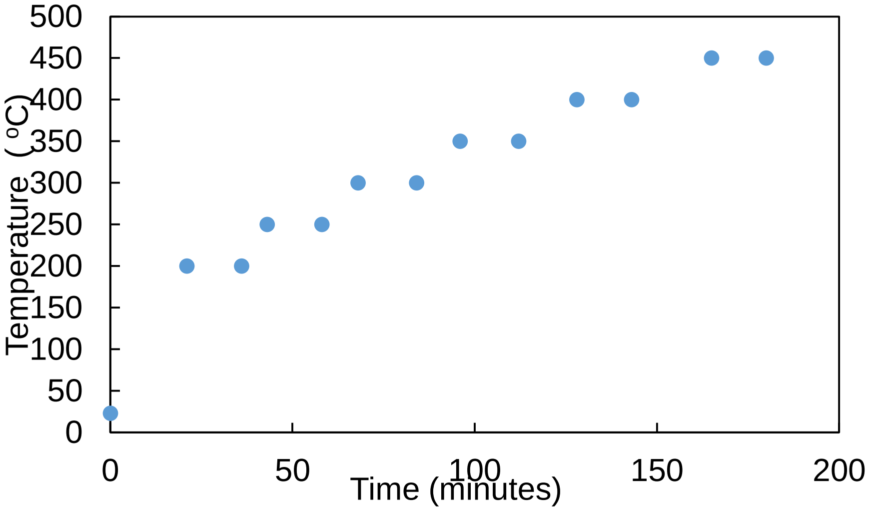

Figure 30 Heating profile for the final pressing method

The sintered test bars formed by this method were carbonised and graphitised. Three bars were produced for each state. Their flexural strength was then measured using single cantilever bending on the device described in 3.3.10. Table 12 gives the average strength obtained from these tests. A sample of traditional synthetic graphite was tested for comparison. Flexural strength of commercially available extruded graphite (Grade 6250 extruded graphite) is also given (Pierson, 1993: 100). The strength of the sintered samples was lower than the traditional synthetic graphite and the commercially available extruded graphite. This was likely due to large pores in the tested samples.

Table 12 Flexural strength of tested samples

Sample	Apparent density (kg/m^3)	Flexural strength (MPa)
sintered sample	1288	5,1
carbonised sample	1601	2,8
graphitised sample	1719	4,5
traditional synthetic graphite	1680	12,5
Grade 6250 extruded graphite (Carbone of America)	1670	12

The changes in mass, volume and density upon carbonisation and graphitisation were tracked using a single block which was sanded to be a close approximation of a rectangle. Table 13 records the mass, apparent density, skeletal density and volume of the sintered, carbonised and graphitised block. Apparent density is the density recorded when the mass of a sample is divided by its volume. Skeletal density uses a different volume, which is the volume that excludes the open pores. This volume is determined by measuring the volume of helium that can enter the sample.

From table 13, it can be seen that the skeletal density is close to the theoretical skeletal density of perfect graphite, which is 2260 kg/m^3. However, the material has an open porosity of 21,4 %, which accounts for its low strength.

Table 13 Properties of test bar

Sample	Mass (mg)	Volume (mm^3)	Apparent density (kg/m^3)	Skeletal density (kg/m^3)
Sintered	295	229	1288	1479

Sample	Mass (mg)	Volume (mm^3)	Apparent density (kg/m^3)	Skeletal density (kg/m^3)
Carbonised	269	168	1601	1975
Graphitised	262	152	1719	2187

Table 14 records the changes in mass, volume, skeletal density and apparent density upon carbonisation and graphitisation. It can be observed that the biggest density gains were seen upon carbonisation.

Table 14 Changes upon carbonisation and graphitisation

Treatment	$\%\Delta m$	$\%\Delta V$	$\%\Delta\rho_{apparent}$	$\%\Delta\rho_{skeletal}$
Carbonisation (1500 ºC)	-8,7	-26,7	+24,5	+33,5
Graphitisation (2700 ºC)	-2,7	-9,4	+7,4	+10,7

5. Conclusion

A variety of pitches with different properties were prepared from anthracene oil. It was shown that increasing the heat treatment time resulted in a higher carbon yield. The glass transition temperature and the softening temperature also increased. The optical texture changed from isotropic to partially anisotropic and eventually to bulk mesophase.

At a temperature of 475 °C, the transition from partial to complete mesophase occurred in a small time window. Ten minutes separates 38% mesophase pitch from 100% mesophase pitch. This was for 60 g of oil. For larger oil loads, the window period was extended considerably. This was believed to be due to the reduced gas phase residence time.

A significant effect was seen of reactor loading on the product produced. With identical reaction conditions, increased reactor loading produced a pitch with a lower softening point and glass transition temperature. The carbon yield was also reduced. A possible explanation for this was that the reaction occurs in the gas phase. This fixes the total reaction rate for a given anthracene oil partial pressure and vapour headspace volume. The higher oil loading also results in more gas production, which leads to an increased venting frequency. This limits the residence time of anthracene oil vapour in the reactor, reducing the conversion and consequently the degree of polymerisation.

The differences in the optical texture of pitch produced with and without 5 wt% $AlCl_3$ as a catalyst was examined. The use of a catalyst was found to produce pitches containing many small spheres. This is due to the catalyst particles acting as nucleation points for the generation of mesophase spheres. The catalyst particles also surround the outside of the spheres, preventing them from coalescing. In this way, the catalyst behaved in the same fashion as primary quinoline insoluble material, which is not present in anthracene oil.

It was not possible to produce perfect sintered articles without cracks that do not crumble using high heating rates. Some success was achieved, but it was not repeatable. When the average heating rate was reduced to 2,3 °C/minute, the production of crack-free bars that did not crumble upon removal was possible. This was due to the reduced rate of volatile production. The flexural strength of graphitised bars produced at a low heating rate was found to be 4,5 MPa. This is significantly less than the strength of ordinary synthetic graphite in the same test (12,5 MPa). It is also lower than a value from literature of 12 MPa (Pierson, 1993: 100). This is likely due to the size of the pores, which were visible to the naked eye. No method of reliably sintering MCMB was found.

The reasons for unsuccessful sintering was investigated for one of the pitches. It was established that a high volatiles content results in pitch melting when it is heated under pressure. When samples were pressed cold and then heated without applied pressure, melting was not observed. However, embrittlement occurred due to oxygen crosslinking at 300 ^{o}C.

One of the bars that was pressed successfully using a high heating rate was carbonised at 10 ^{o}C/minute to 1500 ^{o}C. However, it showed extensive warping. The bars pressed at a low heating rate could be carbonised and graphitised without warping. A low heating rate is therefore recommended for successful sintering.

In order to scale up the production of pitches with properties similar to those produced in the small batch experiments, it is recommended that a reactor loading of 120 kg anthracene oil/m^3 reactor is used. It is known that larger loadings produce pitches with lower carbon yields, glass transition temperatures and softening temperatures.

In the event that it is uneconomical to operate with such low loadings, experiments have to be conducted with the required loading in order to determine the required heat treatment time that produces a pitch with the required properties. The present investigation shows that (for the same heat treatment time and pressure) loading has a large effect on carbon yield, microstructure, glass transition temperature and softening temperature.

An alternative way to operate a reactor for the production of mesophase pitch from anthracene oil would be with no venting. It is strongly advised that experiments are conducted to determine the maximum pressure that would be developed if this course of action is followed, bearing in mind that the pressure generated depends on the loading. The reactor would then have to be designed to resist this pressure. One possible consequence of this option could be an increase in the heat treatment time required for a given conversion to mesophase. With no mass lost through evaporation, all material will have to be converted. Smaller molecules would require a higher degree of polymerisation to become mesophase pitch.

If this proves unfeasible, pressure control must use the on-off operation mode, with the gas venting valve opening at a pressure greater than 2.4 MPa and closing at a pressure less than 1.6 MPa. It is uncertain what the effect of continuous venting would be as this was not tested.

6. Reference list

Alvarez, P, Granda, M, Sutil, J, Menendez, R, Fernandez, JJ, Vina, JA, Morgan, TJ, Millan, M, Herod, AA and Kandiyoti, R (2008) “Characterization and pyrolysis behaviour of novel anthracene oil derivatives”, *Energy & Fuels,* 22, 4077 - 4086

Alvarez, P, Granda, M, Sutil, J, Santamaria, R, Blanco, C, and Menendez, R (2011) “A unified process for preparing mesophase and isotropic material from anthracene oil based pitch” *Fuel Processing Technology*, 92, 421 - 427

Bagheri, SR, Gray, MR and McCaffery, WF (2011) “Influence of depressurisation and cooling on the formation and development of mesophase” *Energy and Fuels* Nov 2011, 25, 5541 – 5548

Barr, JB and Lewis, IC (1982). "Characterization of Pitches by Differential Scanning Calorimetry and Thermomechanical Analysis." *Thermochimica Acta,* 52, 297-304

Bhatia, G, Fitzer, E and Kompalik, K (1986) “Mesophase formation in defined mixtures of coal tar pitch fractions” *Carbon,* 28, 4, 489 – 494

Bermejo, J, Menendez, R, Fernandez, AL, Granda, M, Suelves, J, Herod, AA and Kanjeo, R (2001) “A comparative study of the composition of anthracene oil polymerised by different treatments” *Fuel*, 80, 2155 - 2162

Bragga, CP, de Castro, LD, de Castro Dutra, CHM and de Andrade, CT (2009) “Influence of heat and pressure treatment on the rheological properties of petroleum pitches”, *Fuel*, 88, 853 - 860

Cheng, Y, Li, T, Hou, X, Jing, D, Zhuang, Q and Zhao, T (2010) “Effects of $AlCl_3$-NaCl Content on the Formation of Mesocarbon Microbeads”, *International Journal of Chemical Reactor Engineering,* 8, note S7

Ciucci, A, Corsi, M, Palleschi, V, Rastelli, S, Salvetti, A, Tognari, E (1999) “New Procedure for quantitative elemental analysis by laser-induced plasma spectroscopy”, Applied Spectroscopy, 53, 960-964

Crespo, JL, Arenillas, A, Vina, JA, Garcia, R, Snape, CE, and Moinelo, SR (2005) “Effect of the polymerisation of formaldehyde on the thermal reactivity of a low-temperature Coal Tar Pitch”, *Energy and Fuels,* 19, 374 – 381

Derfus, B, Gruhl, M, Rotmair, CA, Folek, A and Singer, RF (2008) “Net-shape production of graphite parts via powder injection moulding of carbon mesophase”, *Journal of Materials Processing Technology*, 208, 444 - 449

Fanjul, F, Granda, M, Santamaria, R and Mendez, M (2003) “Pyrolysis behaviour of stabilised self-sintering mesophase” *Carbon*, 41, 413 - 422

Fernandez, AL, Granda, M, Bermedjo, J and Menendez, R (1999) “Catalytic polymerization of anthracene oil with aluminium trichloride”, *Carbon,* 37, 1247 - 1255

Fernandez, JJ, Alonso, F (2004) “Anthracene Oil Synthetic Pitch: a Novel Approach to Hybrid Pitches”, *Light Metals 2004,* 499 – 502

Fujiura, R, Kujima, T, Kanno, K, Moshida, I, Korai, Y (1993) “Evaluation of naphthalene-derived mesophase pitches as a binder for carbon-carbon composites”, *Carbon*, 31, 1, 97 -102

Gschwindt, A and Huttinger, KJ (1994) “Sintering of powders of polyaromatic mesophase to high-strength isotropic carbons”, *Carbon*, 32, 6, 1105 – 1118

Hibbeler, RC (2004) *Mechanics of Materials sixth edition,* Prentice Hall, America

Hoffmann, WR and Huttinger, KJ (1993) “Demonstration of spontaneous liquid-phase sintering of mesophase powders” *Carbon, 31, 2, 259 – 262*

Holler, FJ, Skoog, DA and Crouch, SR (2007) *Principles of Instrumental Analysis Sixth Edition*, Thomson Brooks/Cole, Canada

Industrial Quimica Del Nalon S.A. (2010) *Anthracene oil MSDS*, Spain

Kanno, K, Koike, N, Korai, Y, Moshida, I and Komatsu, M (1999) “Mesophase pitch and phenolic resin blends as binders for magnesia-graphite bricks”, *Carbon*, 37, 195 -201

Korai, Y Ishida, S, Yoon, SH, Wang, YG, Mochida, I, Nakagawa, Y, Matsumura, Y, Sakai, Y and Komatu, M (1996) “Efficient preparation of meso-carbon micro-beads from synthetic isotropic pitch derived from naphthalene”, *Carbon*, 34, 12, 1569 -1576

Korai, Y, Ishida, S, Yoon, SH, Wang, YG, Mochida, I, Nakagawa, Y Yamaguchi, C , Mamtsumara, Y Sakai, Y and Komatu, M (1997) “Preparation of mesocarbon micro beads by dispersing mesophase pitches in isotropic pitches", *Carbon,* 35, 10 -11, 1503 – 1515

Kovak, KA and Lewis, IC (1978) "Magnetic orientation studies of synthetic mesophase pitches", *Carbon, 16, 434 – 437*

Liedtke, V and Huttinger, KJ (1996) "Mesophase Pitch as Matrix Precursor of Carbon Fibre Reinforced Carbon: 1. Mesophase Pitch Preparation and Charachterisation", *Carbon*, 34, 9, 1057- 1066

Manocha, LM (2003) "High performance carbon materials", *Sadhana*, 28, 349 - 358

Marsh, H (1972) "Carbonisation and liquid crystal (mesophase) development part 1. The significance of the mesophase during carbonization of coking coal ", *Fuel*, 52, 205 - 212

Marsh, H, Dachille, F, Melvin, J and Walker, PJ (1971) "The carbonisation of Anthracene and Biphenyl under pressures of 300 MN/m^2 (3 kbar)", *Carbon,* 9, 159 – 177

Martin, SW, Shea, FL (1958) "Microstructure of Carbon Products", *Coking Methods and Products,* 50, 41 - 46

Mashau, SN (2008) "The preparation of pitches from Anthracene oil", Masters Thesis, University of Pretoria

Mochida, I Inoue, I, Maeda, K and Takeshita, K (1977) "Carbonisation of heterocyclic compounds catalysed by Aluminium Chloride", *Carbon*, 15, 9 -16

Mochida, I, Korai, Y, Ku, C, Watanabe, F and Sakai, Y (1999) "Chemistry of synthesis, structure, preparation and application of aromatic-derived mesophase pitch", *Carbon,* 38, 305 - 328

Mochida, I, Kudo, K, Fukuda, N and Takeshita, K (1975) "Carbonisation of polycyclic aromatic hydrocarbons under the presence of aluminium chloride catalyst", *Carbon,* 13, 135 - 139

Mochida, I, Nakamura, E, Maeda, K and Takeshita, K (1976) "Microscopic features of carbons obtained by the aid of catalysts", *Carbon,* 14, 341 – 344

Mochida, I, Nakamura, E, Maeda, K and Takeshita, K (1976) “Reaction path of carbonisation catalysed by alkali metals”, *Carbon,* 14, 123 - 129

Mochida, I, Oyama, T, Korai, Y and Fei, YQ (1988) “Study of carbonisation using a tube bomb: evaluation of lump needle coke, carbonization mechanism and optimisation“, *Fuel*, 67, 1171 – 1181

Mochida, I, Shimizu, K, Korai, Y, Otsuka, H and Fujiyama, S (1988) “Structure and carbonisation properties of pitches produced catalytically from aromatic hydrocarbons with HF/BF_3”, *Carbon*, 26, 6, 843 - 852

Mochida, I, Fujiura, R, Kojima, T, Sakamoto, H and Yoshimura, T (1995) “Carbon disc of high density and strength prepared from heat-treated mesophase pitch grains”, *Carbon,* 33, 3, 265 - 274

Moriyama, R, Hajasi, JI and Chiba, T (2004) “Effects of quinoline insoluble particles on the elemental process of mesophase formation”, *Carbon, 42, 2443-2449*

Moriyama, R, Hayasi, JI, Goda, R and Chiba, T (2005) “Changes in the yield and size distribution of mesophase spheres upon supressing convective motion in a fused coal tar pitch”, *Materials Chemistry and Physics,* 92, 205 -213

Muller, A, Kauranen, P, Von Ganski, A and Hell, B (2006) “Injection moulding of Graphite Composite Plates”, *Journal of Power sources*, 154, 467 – 471

Norfolk, C, Kaufmann, A, Mukasyan, A, Varman, A (2006) “Processing of Meso carbon micro beads to high performance materials: Part 3. High temperature sintering and graphitisation”, *Carbon*, 44, 301 - 306

Papole, G (2009) “Classification of medium temperature gassifier pitch”, Masters Thesis, University of Pretoria

Pierson, A (1993) *Handbook of Carbon, Graphite, Diamond and Fullerenes,* Noyes Publications, New Jersey

Rey Boero, JF and Wargon, JA (1981) “Study of the $AlCl_3$ catalytic activity on aromatic hydrocarbons-ii mesophase formation”, *Carbon,* 19, 5, 341 -346

Santamaria-Ramirez, R, Romero-Palazon, E, Gomez-de-Salazar, C, Rodriguez-Reinoso, F, Martinez-Saez, S, Martinez-Escandell, M and Marsh, H (1999)

"Influence of pressure variations on the formation and development of mesophase in a petroleum residue", *Carbon, 37, 445 – 455*

Scaroni, AW, Jenkins, RG and Walker, PL (1991) "Carbonisation of Anthracene in a batch reactor", *Carbon,* 29, 7, 969-980

Sommer, M, Kellermann, K and Singer, RF (2013) "Production of mesophase carbon by PIM – tailoring gel strength of agar binder", *Powder Technology,* 237, 228 – 232

Tamari, S (2004) "Optimum Design of the Constant Volume Gas Pycnometer for Determining the Volume of Solid Particles", *Measurement Science and Technology*, 15.3, 549

Wang, Y, Egashira, M, Ishida, S, Korai, Y, Mochida, I (1998), "Production of mesocarbon microbeads prepared from isotropic naphthalene pitch in the presence of carbon black", *Carbon*, 37, 304 - 314

Young, RJ, and Lovell, PA (2011) *Introduction to Polymers,* Taylor & Francis group, Boca Rotan