



### 3.1.2 Delayed coking of Waxy Oil

The processes for distillation of SDO, as well as the delayed coking and calcination of Waxy Oil, are similar to those used in many delayed cokers worldwide. A simplified process flow diagram is shown in Figure 3-2.

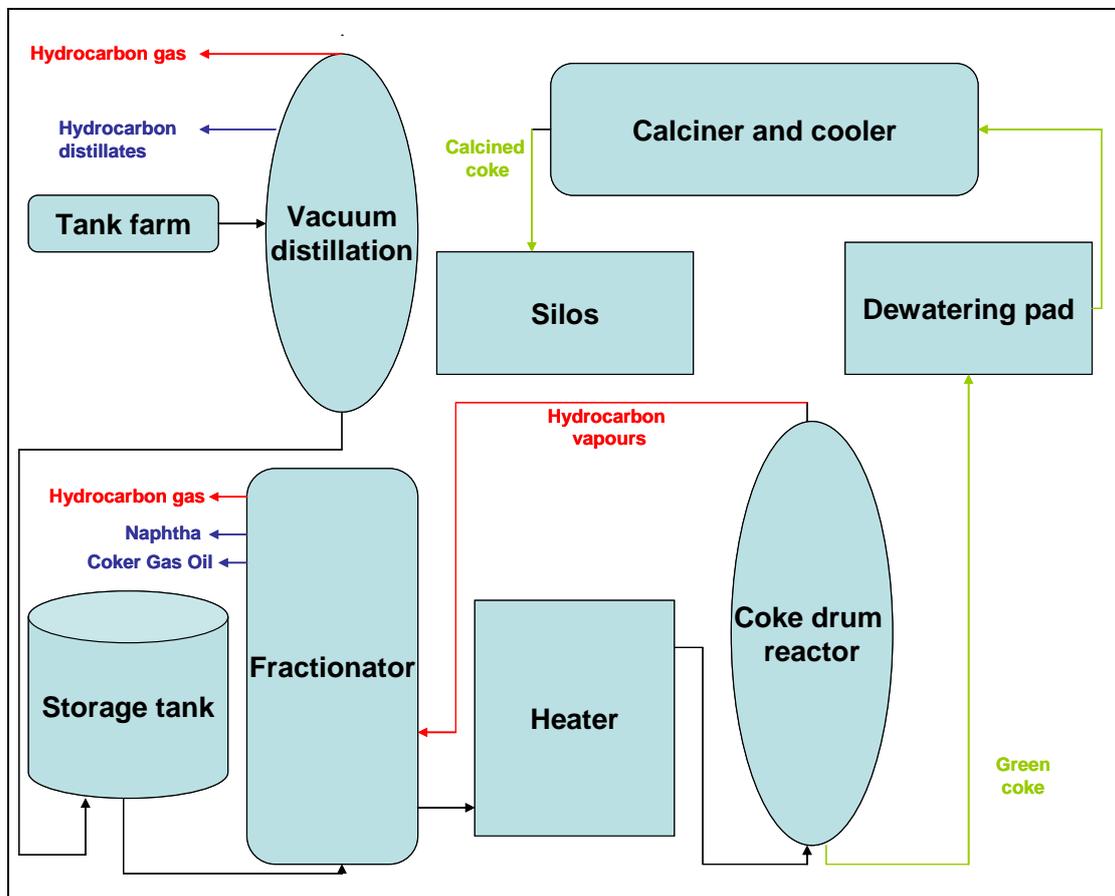
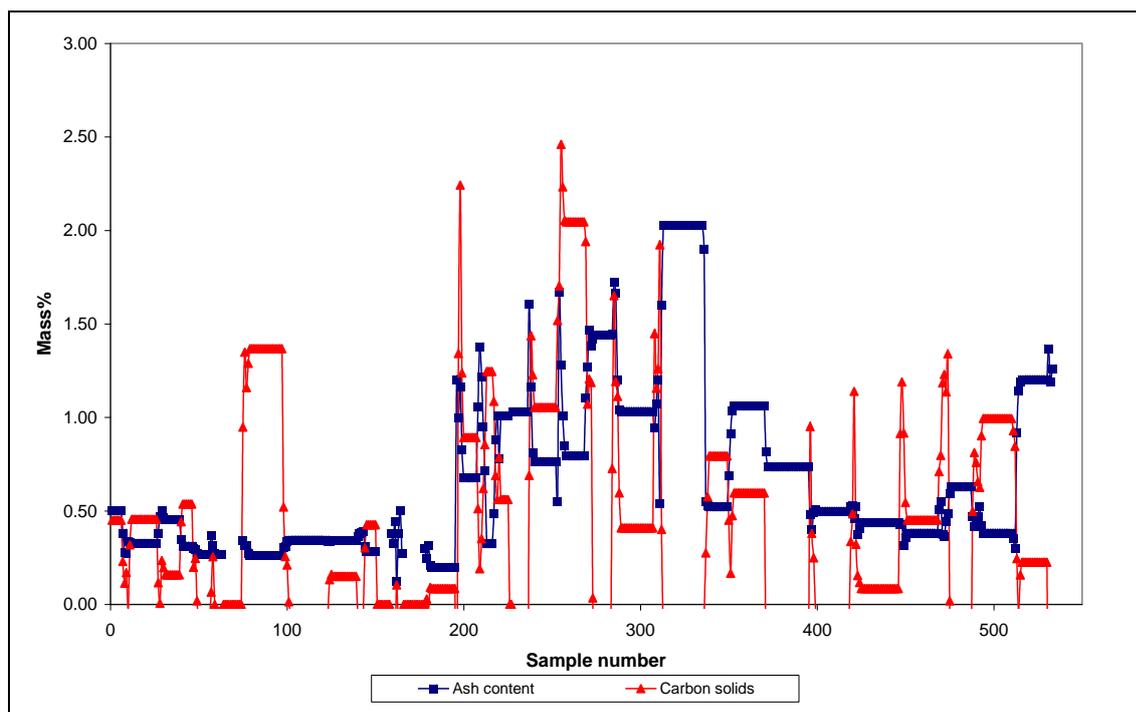


Figure 3-2 Simplified process flow diagram of SDO distillation, delayed coking of Waxy Oil and calcining of Waxy Oil green coke

The SDO is distilled in a vacuum flash column and the heavy residue (Waxy Oil) residue is pumped to the storage tanks on the delayed coker plant. Waxy Oil is processed by the delayed coker and calcined according to prescribed conditions.

### 3.1.3 Waxy Oil delayed coker feed

Feedstock consistency is integral in determining the variation in the characteristics of calcined Waxy Oil coke. By way of example, the variation in the ash and carbonaceous solids content of Waxy Oil is shown in Figure 3-3. The viscosity variation of Waxy Oil is shown in Figure 3-4. The data were compiled from 550 datum points, each representing a daily average.



**Figure 3-3 Ash content and carbon solids content of Waxy Oil feed to the delayed coker**

As shown in Figure 3-3, the ash content of Waxy Oil varies between 0 and 2.00%. As Waxy Oil has an approximate calcined coke yield of 11%, the ash content by far exceeds the requirement for the re-carburiser market (less than 0.2% in the Waxy Oil feed) or the needle coke market (less than 0.02% in the Waxy Oil feed). The carbon solids content (as determined by subtracting the ash content from the Mass Insoluble in Quinoline – MIQ – of Waxy Oil) is on average below 1.0%.

There are three specific reasons for the high ash content of the Waxy Oil calcined coke. These are:

- Process interruption of the gunk plant resulting in catalyst breakthrough and high-ash Waxy Oil feed to the delayed coker (shown in Figure 3-3)
- The low viscosity of Waxy Oil feed to the delayed coker (shown in Figure 3-4) and the reactive aliphatic molecular composition
- The lower calcination yield due to increased macroporosity and the catalytic effect of iron and calcium on air and carboxy reactivity

The green coke yield of approximately 18% from Waxy Oil is caused primarily by the lighter composition of the molecules, which results in the lower viscosity (12–22 Cst @ 100 °C) as shown in Figure 3-4. The lower green coke yield further exacerbates the effect of an ash concentration increase.

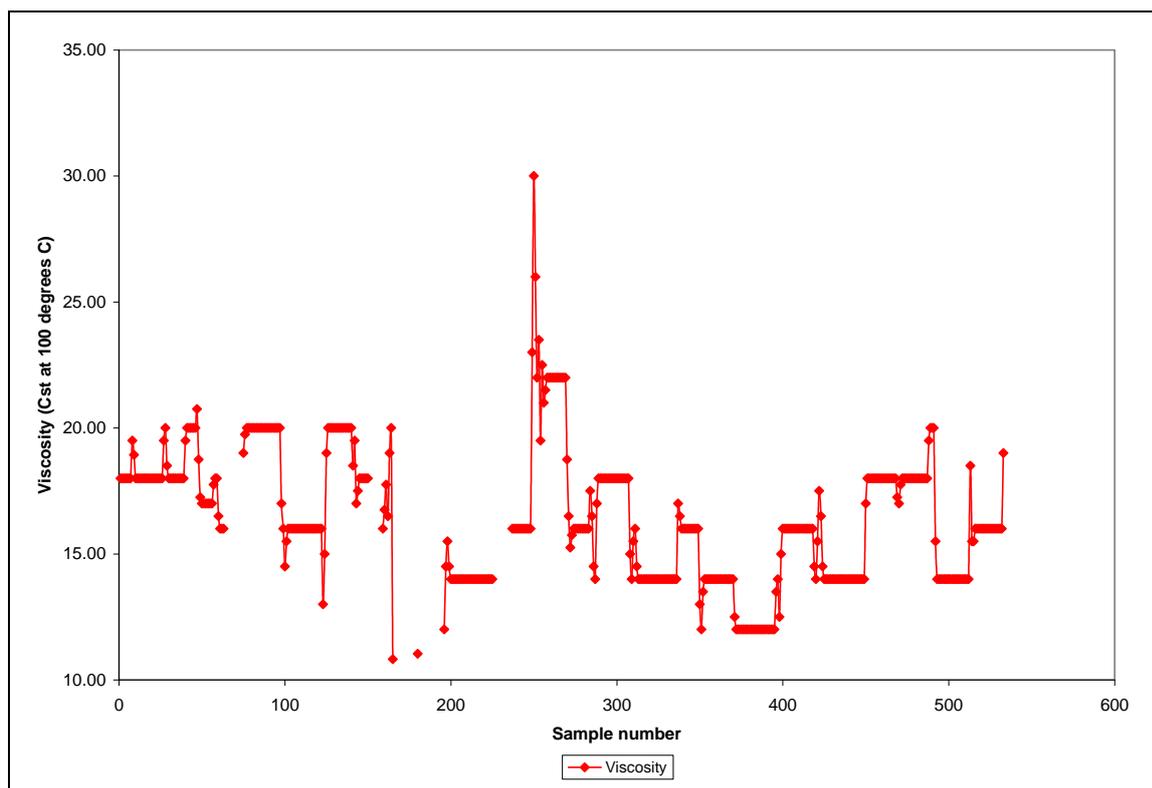


Figure 3-4 Viscosity of Waxy Oil feed to the delayed coker

The typical compositional characteristics of Waxy Oil delayed coker feedstock are shown in Table 3-1.

Table 3-1 Typical compositional characteristics and properties of Waxy Oil delayed coker feedstock

Analysis	Units	Waxy Oil
Carbon	Mass %	85.1
Hydrogen	Mass %	13.2
Sulphur	Mass %	<0.001
Nitrogen	Mass %	<0.0001
Ash content	Mass %	0.25-2.00
MIQ or QI	Mass %	3.2 <sup>2</sup>
MIT or TI*	Mass %	3.4 <sup>2</sup>
MIH or HI**	Mass %	3.7 <sup>2</sup>
Conradson Carbon Residue (CCR)	Mass %	10.7 <sup>2</sup>
Viscosity (@ 100 °C)	cSt***	22 <sup>1</sup>
Distillation: Initial Boiling Point (IBP)	°C	179
5%	°C	311
10%	°C	371
20%	°C	438
30%	°C	465

1 Viscosity is highly variable (4-25 Cst)

2 Dependant on ash content variation

\* TI = Toluene Insolubles

\*\* HI = Heptane Insolubles

\*\*\* cSt = Centistokes

Waxy Oil is composed of long-chain aliphatics (whether alkylated or not) and thus the H/C ratio is high. It is the heavy residue product of a catalysed gas-phase reaction at 300 °C and thus the carbonaceous MIT and MIQ content is low. This is especially true for the asphaltene content which is low due to the lack of heavy macromolecular aromatics. Waxy Oil, being the product of a flash distillation, has a comparatively low Initial Boiling Point (IBP) (approximately 179 °C) and requires a substantial temperature increase to yield 5% distillation product (approximately 311 °C). The viscosity of the Waxy Oil is determined primarily by the specification for the diesel intermediates from the distillation of SDO, especially the Ramsbottom carbon content. Thus, the compositional characteristics of the heavy residue are not determined by the requirements of the delayed coker.

### 3.1.4 Waxy Oil calcined coke

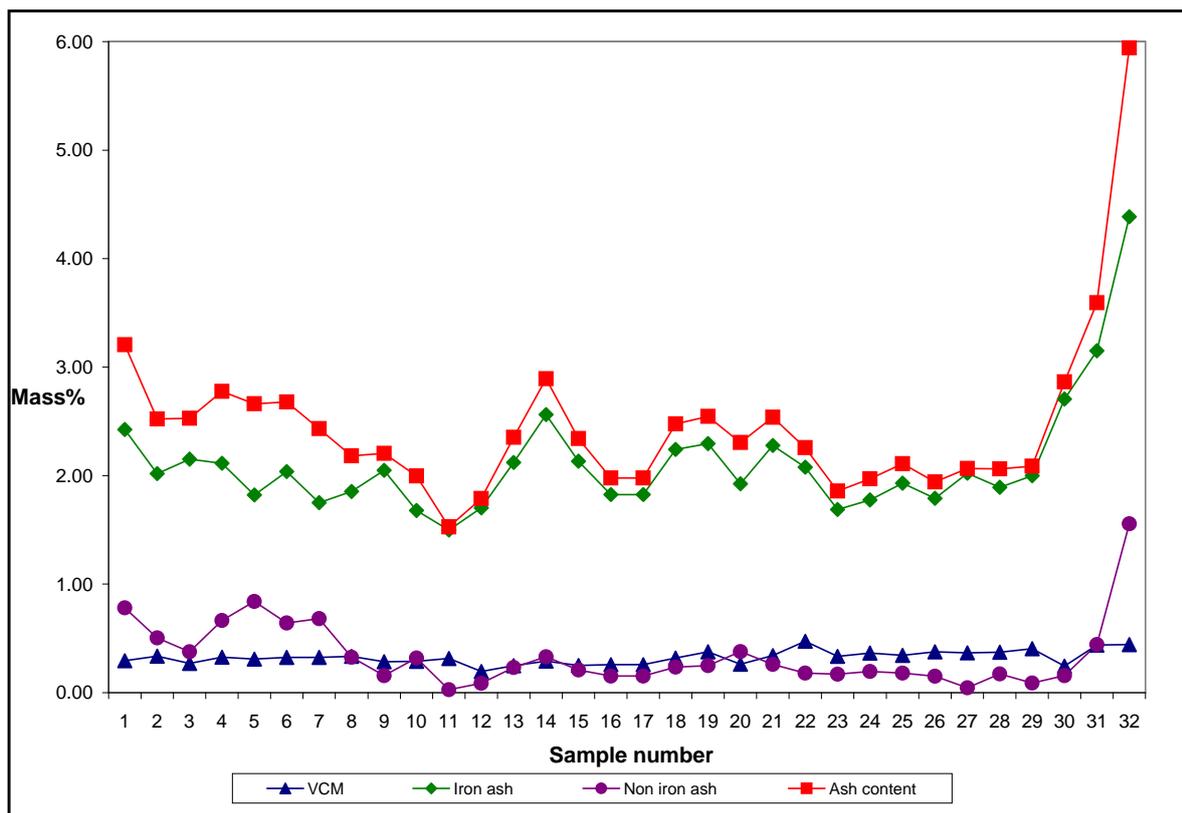
The compositional variation of Waxy Oil calcined coke is shown in Table 3-2.

**Table 3-2 Typical compositional variation of Waxy Oil calcined coke**

Analysis	Units	Waxy Oil calcined coke
Fixed carbon	Mass%	87–99
Hydrogen <sup>1</sup>	Mass%	0.200
Sulphur	Mass%	0.064
Nitrogen	Mass%	0.003
CO <sub>2</sub> reactivity <sup>1</sup>	Mass %. 100 min <sup>-1</sup>	67–91
Air reactivity <sup>1</sup>	Mass%	> 1.2
Real density (He)	g.cm <sup>-3</sup>	2.08–2.17
Ash content	Mass%	1-13
Vibrated Bulk Density (VBD) <sup>1</sup>	g.cm <sup>-3</sup>	≈ 0.56

<sup>1</sup> Analyses not conducted on a routine basis

The major influence on the compositional variation of the Waxy Oil calcined coke is the ash content, which typically ranges between 1 and 13% with a reciprocal influence on the fixed carbon content. Both the nitrogen and sulphur contents are comparatively low. The carboxy and air reactivities are comparatively high given the macro-porosity of the coke and the presence of both iron and calcium catalysts. The influence of the catalyst concentration on the ash content of Waxy Oil calcined coke is shown in Figure 3-5.



**Figure 3-5 Total ash content (comprising non-iron ash and iron ash) and Volatile Carbon Matter (VCM) of Waxy Oil calcined coke**

The iron ash component of the total ash content is approximately 90–95%. The non-iron ash content is substantially lower and is composed of contributions from both silicon and calcium.

### 3.2 Concluding remarks – The Waxy Oil value chain

Analysis of the Waxy Oil production process and compositional characteristics of the feedstock and calcined coke form a template on which the carbonisation chemistry is determined in later chapters. The two predominant detrimental factors in considering Waxy Oil as a needle coke precursor are the catalyst content and the lack of aromaticity.

While catalyst removal would appear a natural process step, it is the author’s opinion that a determination of the effect thereof on the characteristics of Waxy Oil coke is necessary as an initial investigation. This is especially true given that the catalyst is iron oxide, which is known to both retard the extent of mesophase formation and promote multi-phase graphitisation, as demonstrated by Wang *et al.* (2001). These effects are further discussed in Chapter 6. The efficacy of graphitisation to sublimate iron from Waxy Oil coke is also discussed in Chapter 6.

However, catalyst removal from heavy residues is not unique to Waxy Oil and thus is more of a general requirement. The “art” will reside in the ability to modify the organic molecular composition of Waxy Oil in such a way as to effect a change in the kinetics of the carbonisation cycle.

If the effects of other reactivity promoters (e.g. hydroxyl substituents) are for the moment discounted, the given the fact that the literature provides convincing arguments to indicate that increasing the aliphatic nature of heavy residues is correlated with the production of isotropic carbon (Martinez-Escandell *et al.*, 1999), it may well be argued that the probability of producing highly anisotropic carbon from Waxy Oil is indeed remote. However, the author asserts that the aliphatic nature of previously studied residues may well differ substantially from that of Waxy Oil, with specific reference to its unique origin. Thus it would be myopic to merely discount Waxy Oil without evaluating its molecular composition and carbonisation chemistry. Waxy Oil modification, subsequent carbonisation and determination of the reaction mechanism are discussed in Chapters 7 to 9.

A comparison of Waxy Oil characteristics with research results provided in the cited academic literature is discussed in Chapter 4.

## 4 REVIEW OF PREVIOUS WORK

### 4.1 *Introduction*

The science of needle coke has been the subject of academic research for many years. Most of the literature cited emphasises the dependence of needle coke characteristics on pre-carbonisation feedstock variables, which in turn are governed largely by their origin and upstream processing, whether the coke is based on crude oil or coal.

This chapter compares what is known about Waxy Oil chemistry at the onset of this study against relevant knowledge described in the published literature. The structure of the chapter includes a short paragraph at the beginning of each section relevant to Waxy Oil (*provided in italics*), followed by a comparison with the literature.

### 4.2 *The chemistry of needle coke precursors*

#### 4.2.1 **The influence of feedstock aromaticity on needle coke quality**

*The molecular composition of Waxy Oil is not well understood. However, it is thought to be composed predominantly of normal and multi-alkylated alkanes of varying chain length. This is in stark contrast to the dependence of needle coke on the aromaticity of the carbonisation precursor as described below.*

Wang and Eser (2007) used High-Pressure Liquid Chromatography (HPLC) with Photodiode Array (PDA) coupled with Laser Desorption Mass Spectroscopy (LDMS) to determine some of the molecules present in FCCDO, a known precursor for needle coke production. The major compounds present were three- to six-ring PAHs, inclusive of phenanthrene, pyrene, chrysene, perylene, benzopyrene and benzoperylene or multi-alkylated homologues thereof.

Mochida *et al.* (1987) showed the influence of aromaticity on the concentration of microstructural flow domains and the CTE of coke using carbonisation in a tube bomb; FCCDO with 71% aromatic content produced the highest concentration of microstructural flow domains and the lowest CTE in the coke. Comparatively, the same research evaluated two LSVRs, comprising lower aromatic contents (44 and 52% respectively), which produced cokes with more randomly orientated domains (than flow domains) and a higher CTE. The most isotropic of the cokes (displaying fine isotropic microstructural mosaics) was produced from Gilsonite composed almost entirely of reactive asphaltenes. The CTE of the Gilsonite coke was approximately an order of magnitude higher than that of the FCCDO calcined coke.

Although Martinez-Escandell *et al.* (1999) provide a convincing argument as to the effect of aromaticity in reducing the reactivity of petroleum residues during carbonisation, the relationship is not absolute and requires qualification. By way of example, Gilsonite composed almost entirely of aromatic asphaltenes is very reactive, forming highly isotropic coke as described above. The influence of asphaltenes is discussed in more detail in Section 4.5.

Eser and Jenkins (1989) used Fourier Transform Infra Red (FTIR) spectroscopy to determine the degree of aromaticity of various heavy residues and further correlate them with the CTE of the resultant cokes. They also determined that the presence of reactive asphaltenes (producing fine mosaics) had a dominating effect on the optical texture of the coke microstructure. Seshardi *et al.* (1982) used  $^{13}\text{C}$  Nuclear Magnetic Resonance (NMR) to determine the carbon aromaticity of various needle coke precursors and showed that an increase in the percentage of  $^{13}\text{C}$  aromatic carbons promoted the formation of more anisotropic coke with a reduced CTE. Other studies have also established a similar relationship between increased hydrogen aromaticity and a decrease in the CTE of resultant cokes (Eser & Jenkins, 1989; Mochida *et al.*, 1977; Eser & Hou, 1996). Studies using high-resolution  $^1\text{H}$  NMR demonstrate the ability to predict the CTE of cokes based on the hydrogen aromaticity (denoted as “bay” protons) of the precursor (Stecker, 1984). The importance of bay protons or hydrogen donors is to cap radical intermediates produced during the onset of carbonisation, preventing extensive premature cross-linking and increasing the duration of the mesophase in a liquid crystalline state. This allows the growth of mesophase spheres and eventual coalescence of the mesophase as determined by Eser and Jenkins (1989).

Mochida *et al.* (2000) state that optimal precursors for the production of anisotropic mesophase include naphthalene and methylnaphthalene. These molecules are particularly suitable as they comprise two-ring aromatics and utilise the alkyl function to create bridges with other aromatics during polycondensation. An added advantage of these molecules is the relative abundance of hydrogen donors (hydrogen bound directly to the aromatic ring structure) (Mochida *et al.*, 2000; Lutz & Wilson, 1986; Eser and Jenkins, 1989).

Given the complexity of both coal tars and decant oils, Lewis (1987) studied the mesophase reaction of some of the most basic of aromatic building blocks, namely naphthalene or dimethyl naphthalene, in order to elucidate a reaction mechanism. This research showed that aromatic polycondensation was integral in the carbonisation process, forming dimers of single aromatic molecules during the onset of carbonisation. Dimethyl naphthalene was found to carbonise at a faster rate than naphthalene due to the activating effect of methyl groups, as explained below.

The initiation step in the carbonisation of alkyl aromatics is thought to be governed by free radical chemistry, involving the abstraction of aromatic hydrogen or the cleavage of the C-H bond on the methyl side chain (Wang & Eser, 2007). These initial reactions include the formation of aryl-aryl bonds, as in the case of naphthalene polymerisation, or methyl-aryl bonds, as in the case of methyl naphthalene carbonisation (Lewis, 1987; Mochida *et al.*, 2000). Further polycondensation and hydrogen loss create the first precursors of the graphene sheet, which is the basic two-dimensional unit of the graphitic crystal structure. Further development of the mesophase has been described by Mochida *et al.* (1977) as the growth and coalescence of spheres composed of these planar aromatic molecules (6-15 Å) with molecular weights in the range of 400 to 3 000 atomic mass units (amu).

The higher thermal stability of aromatic residues compared with aliphatic residues and the propensity thereof to produce anisotropic coke has been previously established by several authors, including Rodriguez-Reinoso *et al.* (2001), Torregrosa-Rodriguez *et al.* (2000) and Martinez-Escandell *et al.* (1999) who studied the carbonisation chemistry of various petroleum residues. These residues varied from a totally aliphatic soft wax to a mostly aromatic FCCDO.

## 4.2.2 The influence of aromatic hydrogen on mesophase development

*Based on the aliphatic nature of Waxy Oil, the absence of aromatic protons is by default a “fait accompli”. However, by their very nature aliphatic heavy residues have relatively high hydrogen-to-carbon ratios. The production of coke from aliphatic Waxy Oil will naturally include an aromatisation step prior to mesophase formation. The duration of mesophase fluidity will thus depend on the “reservoir” of stable hydro-aromatic bay protons produced.*

Although the role of carbon aromaticity in the development of the mesophase has already been established, the substantial contribution of aromatic hydrogen as a rate-determining factor is integral to the development of the mesophase. Obara *et al.* (1981) described the role of hydrogen-transfer reactions in “extending the temperature zone of maximum fluidity” while stabilising radicals produced during carbonisation. Indeed, Diez *et al.* (1999) further argue that the increased mobility of the pitch system during mesophase development allows aromatic sheets to stack parallel to each other, increasing the anisotropy of the resultant coke

The study of these hydrogen-transfer reactions has been based on the role of aromatic molecules in acting both as hydrogen donors and hydrogen acceptors. Various authors have described these transfer reactions using model compounds, including 9, 10-dihydroanthracene/1, 2, 3, 4-tetrahydroanthracene as the hydrogen donor and anthracene as the acceptor molecule in various precursors – coal-tar pitch (Machnikowski *et al.*, 2001; (Yokono & Marsh, 1979), hydrogenated ethylene tar pitch (Obara *et al.*, 1981) and petroleum pitch (Diez *et al.*, 1999; Yokono *et al.*, 1980).

Mochida *et al.* (2000) used a pure compound, namely tetrahydroquinoline, to show how it reduced the rate at which the carbonisation reaction proceeds and allowed a greater extent of mesophase development. Pure low-order polycyclic aromatics, inclusive of naphthalene, tetralin or anthracene, may be used as a source of aromatic hydrogen (Lutz & Wilson, 1986; Legin-Kohler *et al.*, 1999); however, they are prohibitively expensive on a commercial scale. McConaghy *et al.* (1979) showed how aromatic distillate fractions of either coal tar or petroleum decant oils added to petroleum vacuum residuum (which would usually produce a sponge coke: CTE  $20.0 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$ ) using a process called Hydrogen Donor Diluent Cracking (HDDC) produced a premium needle coke with a reduced CTE of  $5.0 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$ .

Hishiyama *et al.* (1983) demonstrated that the temperature at which hydrogenation is conducted can similarly affect the microstructure and graphitisability of the coke. Thermal treatment of ethylene pitch at 400 °C, as opposed to lower temperatures (200–300 °C), was shown to promote the development of flow textures, which formed cokes with mosaic microstructures. The significance is the ability of a precursor to allow these hydrogen-transfer reactions during the formation of pre-mesogens and prior to mesophase development.

## 4.3 The influence of heteroatoms on needle coke quality

Heteroatoms present in needle coke feedstock originating from either crude oil or coal tar play a vital role in the carbonisation process and may influence the texture of the resultant coke.

*Waxy Oil differs from either coal-tar or petroleum residues in that it is synthetically produced from a gas-phase reaction, and thus the typical nitrogen content (0.009%) and sulphur content (0.08%) of Waxy Oil calcined coke is comparatively minimal. It is this fact that makes Waxy Oil a potentially attractive residue as a needle coke precursor. Inasmuch as Waxy Oil is devoid of stable nitrogen and sulphur heterocyclics, it is important to define the action of these heteroatoms in better known needle coke precursors to establish the comparative value. While the predominance of oxygen-containing organics in Waxy Oil is not known (at least at the onset of the project), the fact that carbon monoxide is one of the co reactants in the process would indicate the possibility of their presence.*

Whereas Lewis (1987) is of the opinion that the optimum aromatic precursor molecule for the production of a highly anisotropic needle coke is naphthalene or methyl naphthalene, based on carbon and hydrogen alone, in reality this feed would be prohibitively expensive and there would not be enough to sustain the demand for needle coke. The two major sources of needle coke precursors are petroleum products originating from crude oil (which by virtue of their origin contain a substantial concentration of stable sulphur heterocyclics) and coal-tar products (which by virtue of their origin contain a substantial concentration of stable nitrogen heterocyclics), as described by Weinberg *et al.* (1988). The inevitable presence of these heteroatoms in these available precursors has attracted substantial research interest with respect to their effect on both the mesophase formation and puffing.

The oxygen content of most delayed coker feedstocks, and certainly those deemed suitable for the production of needle coke, is comparatively low (below 1%) due to loss of the hydroxyl function during production. Both Clark *et al.* (2002) and Wolters & Van der Walt (2007) studied the effect of heavy residues formed by the low-temperature gasification of coal on mesophase formation, in which the oxygen content was substantially higher (5%), dominated by hydroxyl functions.

Studies to determine the effect of heteroatoms on mesophase formation are broadly characterised into two groups:

- Heteroatoms bound as heterocyclics (e.g. furans, thiophenes and pyridines)
- Heteroatoms bound as functionalities to a parent aromatic (e.g. hydroxyls, thiols and amides)

### **4.3.1 The influence of sulphur on needle coke quality**

Mizuntani *et al.* (2007) conducted research into the cracking reaction on petroleum Fluid Catalytic Cracker (FCC) feed and gasoline products using both Field Desorption Mass Spectroscopy (FDMS) and Gas Chromatography-Atomic Energy Detection (GC-AED). The predominant sulphur species found were polycyclic thiophenes, benzothiophenes with alkyl functions up to C<sub>4</sub> and dibenzothiophenes with alkyl side functions up to C<sub>8</sub> in the heavier FCC feed. Using sulphur-selective ligand exchange chromatography, Ma *et al.* (1997) concluded that the major non-polar species present in petroleum vacuum residue were alkyl benzothiophenes, benzonaphtha thiophenes and phenanthrothiophenes.

Sulphur may also present as less-stable side functions bound to the parent aromatic. These sulphydral groups, due to their valency differing from that of carbon, react during the onset of carbonisation with aromatic carbon of the same or neighbouring molecules, disturbing the

planar geometry and resulting in three-dimensional faults in the graphitic structure, as determined by Weinberg *et al.* (1988).

Hossain and Podder (1989) carbonised elemental sulphur with model anthracene and phenanthrene to show the cross-linking effect of sulphur functionalities using Differential Thermal Analysis (DTA). The mesophase microstructures of the sulphur anthracene/phenanthrene compounds were found to be disrupted and disordered, showing mosaic domains as compared with those of the model compounds alone whose mesophase structures appeared to have coarse flow domains.

Furthermore, Marsh *et al.* (1973) reported that carbonisation of model sulphur-containing organic compounds (dibenzothiophene and thianthrene) produced only isotropic carbon. However, the literature is not in complete agreement with respect to the role of sulphur in disrupting mesophase formation. Studies conducted on Khafti asphalt by Oi and Oinishi (1978) determined that sulphur-containing organics have no effect on mesophase development due to these molecules having a similar nature to those in the Khafti asphalt. However, this research has further shown the catalytic effect of vanadium in the presence of sulphur to promote the formation of  $\beta$ -resins, known as the “building blocks” of the developmental mesophase, as suggested by Lewis (1987). The same author also suggests that non-polar heterocycles containing sulphur may readily be incorporated into the macromolecular matrix during mesophase development and thus become stabilised with no substantial reduction in the sulphur content below 1 100 °C.

Didchenko and Lewis (1992) indicated the maximum sulphur concentration for needle coke feedstock to be 1%, producing a calcined premium-grade needle coke with a maximum sulphur content of 0.8%. The same authors emphasise the need to direct hydro-desulphurisation reactions towards the heavier sulphur-containing molecules as the lighter sulphur-containing molecules are vaporised during the delayed coking process.

Given the comparatively low levels of sulphur in Waxy Oil, desulphurisation processes are only of passing interest. Worldwide crude oil resources are known to be getting heavier and more sour (higher concentrations of sulphur), according to the work of Nylen *et al.* (2004). Hydro-desulphurisation reactions using catalysts based on oxides of cobalt and molybdenum supported on an alumina substrate have been utilised to decrease the sulphur content of decant oil (2.35%) to between 0.79 and 1.27%, as described by Didchenko and Lewis (1992).

### **4.3.2 The influence of nitrogen on needle coke quality**

Studies evaluating the role of nitrogen-containing heterocycles on the extent of mesophase formation have for the most part been conducted on either model compounds or coal-tar needle coke feedstock.

While the list is by no means definitive, Murti *et al.* (2005) report pyridines, anilines, quinolines, indoles and carbozoles to be the dominant species.

Marsh *et al.* (1973) showed how the carbonisation of model nitrogen-containing polyaromatic hydrocarbons (carbazole) produced isotropic mosaics, while phenazine produced anisotropic mosaics. The addition of carbozole to model anthracene was found to impede the development of the mesophase. However, as with studies of the carbonisation reactions of

aromatic compounds containing sulphur and oxygen bound as a side chain, Weinberg *et al.* (1988) showed nitrogen in the form of amide groups to be disruptive to mesophase formation.

### 4.3.3 The influence of oxygen on needle coke quality

Studies pertaining to the effect of oxygen-containing aromatics with hydroxyl/aldehyde side chains have historically been of lesser significance given that the temperatures under which coal-tar and FCCDO residues are produced largely eliminate these functionalities.

However, studies conducted to identify the nature of oxygen-containing aromatics (Murti *et al.*, 2005; Weinberg *et al.*, 1988; Marsh *et al.*, 1973) have identified the presence of furans and coumarin. Oxygen bound as side chain functionality to aromatic molecules has been identified as phenolics, hydroxyl naphthalenes, phthalic anhydrides, various derivatives of anthraquinone and carboxylic acids associated with two- to four-ring aromatics, e.g. naphthoic acid.

Both Weinberg *et al.* (1988) and Marsh *et al.* (1973) reported carbonisation of aromatics with bound hydroxyl functions to produce isotropic microstructures. This characteristic has been explained by the ability of a hydroxyl function (for instance) to form ether linkages during the initial phase of carbonisation, resulting in intermediates that are not planar and cannot be incorporated into the ordered graphene structure. The effect is to increase the viscosity of the developing mesophase prematurely, thereby decreasing molecular mobility.

Wolters and Van der Walt (2005) showed that carbonisation of low-temperature coal gasification pitch, which has a comparatively high concentration of phenolics, produced coke with a mixture of fine and medium isotropic mosaics. Using the same feedstock containing up to 5% oxygen, Clark *et al.* (2001) showed on a commercial scale that adding a lesser percentage of FCCDO to this feed increased the anisotropy of the coke. Further work by the same authors demonstrated the ability to determine microstructural variations along the height of a commercial delayed coker drum (Clark *et al.*, 2002).

## 4.4 Interventions to control puffing of needle coke

Research to control the puffing reaction during the graphitisation of needle cokes may broadly, irrespective of the precursor, be classified into three main categories:

- Choosing a feed with a low heteroatom content, specifically those bound as heterocyclics
- Removing heterocycles from the feedstock, referring to various hydro-desulphurisation/hydro-denitrification reactions (depending on the origin of the needle coke precursor)
- Treating the symptom, referring to the control of the puffing reaction aided by the addition of inhibitors that control the release of heteroatom gases

The least costly option would involve the identification of needle coke precursors with reduced concentrations of stabilised heterocycles; however, this is not always an option due to limited availability. Furthermore, the quality of a needle coke precursor is not determined solely by either nitrogen or sulphur content, but depends on a range of feedstock characteristics as discussed earlier.

Academic research into controlling the puffing reaction during graphitisation with the aid of additives mainly concentrates on either sulphur puffing (as is the case with petroleum needle cokes) or nitrogen puffing (as is the case with coal-tar pitches). A detailed description of the puffing reaction has been given in Chapter 2, but this section concentrates on inhibitors that are used to control puffing during graphitisation.

With respect to the graphitisation of petroleum cokes, the addition of iron oxide (2% by weight) to calcined coke is the preferred remedy for suppressing puffing in calcined cokes containing more than 0.3% sulphur, based on work conducted by Orac *et al.* (1992). This research also proposes the use of sodium carbonate (either in the form of a fine powder or as an aqueous slurry) as a puffing inhibitor. Sodium carbonate is sprayed onto the calcined coke within the cooler section after the calciner. Sodium is able to penetrate the matrix of the coke particle (via porosity) and inhibit the puffing reaction from “within”, reacting with sulphur and stabilising it during graphitisation (especially in the 1 600–1 800 °C range). Orac *et al.* (1992) showed how the addition of 1% sodium carbonate to calcined coke under prescribed conditions was effective in reducing the puffing rate from 62 (with no additive) to 0 (with additive).

Kawano *et al.* (1999b) used boric acid (0.9%) to suppress puffing of petroleum-derived needle cokes from 1.5 to 0.8%. The same authors (Kawano *et al.*, 1999a) showed that the addition of boric acid, followed by heat treatment to 400, 600 and 950 °C, was effective in reducing puffing by 22, 40 and 41% respectively, using the untreated petroleum needle coke as a reference.

Hsu (1982) showed that the addition of iron oxide to decant oil (prior to carbonisation) was effective in reducing coke puffing. However, Wang *et al.* (2001) also showed that the addition of iron oxide to petroleum residues (prior to delayed coking) inhibited mesophase development by increasing the rate of oxidative polymerisation.

#### **4.5 The influence of asphaltenes on needle coke quality**

*As shown in Chapter 3, Waxy Oil is composed of a negligible percentage of asphaltenes. There are two probable reasons for this. Firstly, during the Fischer-Tropsch reaction, the maximum temperature is 320-350 °C which, secondly, produces long-chain aliphatics not possessing the activity for aromatisation. While asphaltenes are thus important in relation to Waxy Oil (by their absence), this study also identifies molecular groupings that act as reactivity promoters, of which asphaltenes are one. Another reason for describing the contribution of asphaltenes during carbonisation is their tendency to precipitate prematurely out of solution, forming mosaic microstructures and shot coke at the bottom of the coke section. The current study uses much the same methodology to determine the effect of Waxy Oil modification on the microstructure, using “static” carbonisation (discussed in Chapter 8).*

Dickakian (1984) described asphaltenes as a group of reactive heavy molecular weight aromatic molecules containing between 3 and 4% heteroatoms, which are soluble in quinoline and therefore cannot be described as solids. Asphaltenes are further characterised by their solubility in paraffinic solvents but insolubility in toluene. Although asphaltenes are highly aromatic (which has previously been described as beneficial in terms of the

anisotropicity), they are large non-planar molecules with high reactivity. Seshardi *et al.* (1982) therefore argue that they are detrimental to the anisotropy of the coke.

Although most polynuclear aromatics absorb ultraviolet light in the region between 280-400 nanometres (nm), asphaltenes have been detected at specific wavelengths of 292, 324 and 340 nm in accordance with ASTM method D2008 (Sien & McGinley, 1983).

Seshardi *et al.* (1982) conducted quantitative  $^{13}\text{C}$  NMR to show that the asphaltene fraction of decant oil and pyrolysis tar had a higher average molecular weight than the parent residue. The asphaltene fraction had an average molecular weight of 515 amu vs. 331 amu for the parent decant oil. The average molecular weight of the pyrolysis tar asphaltene fraction (984 amu) was also shown to be substantially higher than that of the parent pyrolysis oil (300 amu).

The effect of asphaltenes on mesophase development has been evaluated previously by several authors and the findings are summarised below.

- They show higher reactivity and the ability to increase the rate of carbonisation (Eser and Jenkins, 1989; Mochida *et al.*, 1989).
- They tend to form isotropic mosaics within the coke structure leading to higher CTE cokes (Eser and Jenkins, 1989; Mochida *et al.*, 1989; Mochida *et al.*, 1987; (Eser *et al.*, 1989).
- They have a “dominating” influence on the microstructure morphology of a coke (Mochida *et al.*, 1987; Mochida *et al.*, 1989).
- They tend to precipitate out of the developing mesophase and settle at the bottom of a coke drum, producing a highly isotropic dense region of coke, commonly referred to as “shot” coke (Mochida *et al.*, 1989)

Eser *et al.* (1989) thermally treated petroleum vacuum residues containing asphaltenes at sub-carbonisation temperatures (350–400 °C) to increase the concentration of aromatic hydrogen, lower the reactivity and promote self-condensation of reactive asphaltic molecules. Compared with the reference coke (produced from the untreated vacuum residues), the cokes produced showed a greater degree of anisotropy (as determined by an increase in flow domains) and a greater graphitisability (as determined by lower  $d_{002}$  values and higher  $L_c$  values).

Several other processes have been described to reduce the reactivity of asphaltenes, including:

- Hydrogenation followed by catalytic cracking (Murukami *et al.*, 1989)
- Solvent separation using heptane (Dickakian, 1984)
- Hydro-treating followed by asphaltene extraction with pentane (Goyal *et al.*, 1994)
- Solvent extraction of asphaltenes with light naphtha or  $\text{C}_4$  to  $\text{C}_6$  paraffinic solvents (Bonilla & Elliot, 1987).

#### **4.6 The influence of mineral matter on needle coke quality**

*The potential impact of mineral matter on the carbonisation of Waxy Oil is of importance as the concentration of the catalyst (iron oxide) therein is variable and may increase to*

approximately 2%. Given the low yields during delayed coking and calcination this percentage may then convert to 10% in the calcined coke. The presence of iron contaminates in petroleum residues is limited for two reasons. Firstly, they are not naturally abundant in petroleum residues (compared with vanadium or nickel) and cracking catalysts have historically been based on alumino-silicate powders. However, based on the literature discussed below, iron oxide affects many reactive mechanisms: it may inhibit mesophase development, promote oxidative polymerisation, increase the carboxy or air reactivity of calcined cokes and substantially modify the graphitisation mechanism. Thus this study describes in detail the potential detrimental effect of the iron oxide catalyst on the carbonisation, calcination and graphitisation of Waxy Oil.

#### 4.6.1 The effect of mineral matter on mesophase development

Mineral matter in needle coke feedstock may originate either from the source itself (e.g. coal or crude oil) or from catalysts used in upstream pre-carbonisation processes.

Obara *et al.* (1985) investigated the effect of silica gel (< 45 µm) addition to FDDCO in reducing the size of the microstructural domains of the coke and reducing the amount of transferable hydrogen during carbonisation. This work is supported by that of Wang *et al.* (2001) who determined the effect of iron oxide as catalysing oxidative polymerisation, so producing fine mosaic microstructures. This research used the addition of iron oxide powder (0.1–1.0 µm) to improve the yield of the QI insoluble fraction during carbonisation. However, microstructural evidence showed the formation of anisotropic flow domains (without the iron oxide additive), the development of coarse mosaic texture with the addition of 6% iron oxide and the development of fine mosaics with the addition of 17 and 25% iron oxide respectively. Iron oxide not only presents an inert barrier to parallel stacking, but also promotes chemical oxidative polymerisation, leading to cross-linking, premature viscosity increase during mesophase development and the formation of mosaic microstructures. The severity of oxidative polymerisation is highly dependent on the concentration and particle size distribution of the catalyst, according to the research of Obara *et al.* (1985) and Wang *et al.* (2001).

Sakanishi *et al.* (2002) showed that many metals extracted from coals may bind in the form of silicates, oxides, carbonates, sulphides, sulphates and phosphates. However, the addition of various organo-metallic compounds to PVC pitch was shown to have a varied effect on mesophase formation, attributed more to the type of metal rather than the concentration thereof. Both vanadium acetylacetonate and nickelocene were further found to have a catalytic effect by increasing the thermal decomposition of sulphur heterocyclics (Oi & Onishi, 1978).

Boudou *et al.* (1998) noticed similar effects on the microstructure when iron chloride was added to a coal-tar pitch. The iron chloride converts to iron oxide, which increases the rate of carbonisation, promoting the formation of mosaic microstructures. However, Song *et al.* (2003) argue that the inclusion of iron as an organo-metallic in the form of ferrocene decreases the interlayer spacing of the crystal. In a study aimed at increasing the rate at which carbons react during gasification, Marsh *et al.* (1984) showed how both metal (Li, Na, K, Rb and Cs) hydroxides and carbonates promoted the formation of isotropic carbon when co carbonised with Ashland A240 pitch.

However, some metal oxides have much the opposite effect during carbonisation. Ramos-Fernandez *et al.* (2007) showed that both oxides and carbides of titanium enhanced mesophase development by a process thought to be concerned with facilitating hydrogen transfer and increasing the liquidity range of the pitch system during carbonisation.

#### **4.6.2 The effect of iron oxide on the carboxy and air reactivity of calcined coke**

*One of the factors contributing to the low yield of Waxy Oil calcined coke is thought to be the ability of iron to catalyse both air and carboxy reactivity during calcination. Quite apart from the loss of solid carbon, there is a substantial and unnecessary increase of the ash content and the carbon footprint of the calcination process.*

Mineral catalysts for air reactivity have historically been linked to vanadium, nickel and sodium (Hume *et al.*, 1993), specifically in petroleum cokes where the heavy metals (vanadium and nickel) originate as metal porphyrinic complexes associated with the asphaltenes of crude oil, according to Ali and Abbas (2006). The catalytic activity of sodium is often more enhanced due to its ability to intercalate between carbon lamellae and thus become better dispersed, but this activity is reduced in high-sulphur petroleum cokes (Hume *et al.*, 1993). Patrick and Shaw (1972) showed that sodium increases air reactivity, increases meso/microporosity and reduces the ignition temperature of coke. However, the vanadium, nickel and sodium content of Waxy Oil calcined coke is low.

The carboxy reactivity of the Waxy Oil calcined cokes is far in excess of the normal specification for petroleum calcined cokes (10–15%) in the aluminium industry, as reported by Hume *et al.* (1993). In an extract from Hume's PhD thesis, Hume *et al.* (1993) showed that the catalytic effect of increased sodium and calcium contents of calcined petroleum cokes was to increase substantially the carboxy reactivity. Indeed, the catalytic effect of calcium on the carboxy reactivity of petroleum cokes, coals and chars has been established previously by several authors, namely Walker *et al.* (1993), Hippo and Walker (1975) and Lang and Neavel (1982).

Jenkins *et al.* (1973) showed iron oxide ( $\alpha\text{-Fe}_2\text{O}_3$ ) to be a poor catalyst for air and carboxy reactivity. However, within calcined coke, iron oxide is reduced predominantly to iron, which was shown by both Hippo and Walker (1975) and Walker *et al.* (1983) to promote both reactivities. At this point it is necessary to mention that both air and carboxy reactivities are of more importance to the aluminium industry and given the relatively low concentration of iron compared with other metals in delayed cokes, its effect has not been widely studied. Another factor is that no petroleum cokes for either the aluminium or electrode industries have catalyst contents as high as Waxy Oil calcined coke.

#### **4.6.3 Iron oxide as a driving force for multi-phase graphitisation**

*Iron oxide is listed as one of the 31 minerals that promote multi-phase graphitisation during thermal treatment of green coke. The unusually high concentration of iron oxide in Waxy Oil increases the potential for it to affect the graphitisation mechanism of coke during thermal treatment. The predominant graphitisation mechanism during thermal treatment of needle cokes depends on the anisotropy of the carbon microstructure. Any departure from this mechanism may well provide disingenuous results when trying to compare the*

*crystallographic indices of Waxy Oil coke with those of other needle cokes. This characteristic is investigated in Chapter 6.*

While the addition of chromium, manganese, molybdenum, vanadium and iron oxides has been shown to reduce the temperature at which graphitisation is initiated (increasing the  $L_c$  and reducing the  $d_{002}$ ), this form of catalytic graphitisation is on a localised scale of approximately 1  $\mu\text{m}$ , as reported by Mochida *et al.* (1980). Thus the influence of iron in promoting catalytic graphitisation will depend both on its particle size distribution and on the concentration, as reported by Wang *et al.* (2001).

#### **4.6.4 Methods for removing mineral matter from heavy residues**

*Apart from the effects of iron oxide on numerous characteristics of Waxy Oil green and calcined coke, the most apparent effect is simply an increase in the ash content. If Waxy Oil coke is used as a recarburiser, the high ash content is less of a problem as the iron reports to the iron melt. However, in producing a highly anisotropic carbon from Waxy Oil for use in the manufacture of carbon artefacts (e.g. needle coke for electrodes), the catalyst would have to be removed either prior to or after delayed coking. This study concentrates on the removal of iron oxide from Waxy Oil using filtration.*

Eguchi *et al.* (1997) reduced the mineral content of petroleum decant oils (prior to delayed coking) using filtration, centrifugation, electrostatic aggregation and a combination of these methods. Although the effect of minerals on the formation of isotropic mosaics and the trend towards a higher CTE has been established, this research determined the effect of reducing the alumino-silicate concentration in petroleum decant oil directly on the CTE of the coke produced. The research showed that reducing the mineral content of the petroleum decant oil from 0.0240 to 0.002% reduced the CTE from 6.7 to  $4.9 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$ . In all three of the abovementioned mineral reduction interventions, lowering the viscosity of the feed either by increasing the temperature or by the addition of naphtha was beneficial.

#### **4.7 Molecular modification of needle coke precursors**

*Molecular modification of Waxy Oil will be beneficial only once the catalyst has been removed. As little is known about Waxy Oil molecular chemistry, its characterisation will be necessary to identify potential reactivity promoters before embarking on modification processes. This study uses distillation and thermal treatment to effect molecular modification. However, it concentrates on molecular modification to increase the anisotropy of the coke.*

As the molecular make-up of feedstock determines the quality of the needle coke, modification the make-up will change the reaction kinetics of carbonisation and the microstructure of the coke.

Interventions to optimise the chemical nature of needle coke precursors and thus of coke qualities include:

- Co-carbonisation of feedstock
- Thermal treatment
- Hydrogenation/cracking
- Distillation

#### 4.7.1 Co-carbonisation of feedstock

*The co-carbonisation of heavy residues has historically proved a cheap alternative to pre-carbonisation modification processes and thus needs to be discussed in this chapter. It is unlikely that co-carbonisation of Waxy Oil with another heavy residue would be viable for two reasons. The reason for choosing Waxy Oil as a feed for this study was its comparatively negligible sulphur and nitrogen content. Co-carbonisation with another heavy residue (e.g. a petroleum FCCDO), even in small percentages, would substantially increase the sulphur or nitrogen content (given the low coking yield of Waxy Oil) and thus destroy market attractiveness. The other possible reason is that the aliphatic nature of Waxy Oil may present challenges when it is co-carbonised with an aromatic residue due to separation and independent carbonisation of the residues.*

As delayed coking of many petroleum vacuum residues produces sponge coke, FCCDO may be added to modify its composition and thus upgrade the feed for the production of needle coke. Using a step increase in the concentration of FCCDO in a blend with a petroleum vacuum residue, Mochida *et al.* (1989) established that the aromaticity of the blend increased in direct proportion to the concentration of FCCDO, the asphaltene content decreased and carbonisation produced coke with an increased percentage of flow domains. The coke produced from the vacuum residue alone yielded a CTE of  $13.0 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$ , while when 30, 50 and 70% FCCDO were added, the CTE of the coke reduced proportionately to 3.9, 2.3 and  $1.0 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$  respectively.

Similar studies investigating the effect of step increases in the addition of FCCDO to ethylene tar were reported by Dickinson and Moore (1988) who showed that it was possible to reduce the CTE of the coke formed from 100% ethylene tar (CTE  $9.4 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$ ) using an addition of 75% FCCDO, to  $4.7 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$ .

The purpose of co-carbonisation is to maximise the beneficial attributes of the feedstocks during carbonisation while providing a buffer for detrimental characteristics. A case in point is the co-carbonisation of FCCDO with gasification coal-tar pitch as determined by Clark *et al.* (2001) and in later research by the same authors (Clark *et al.*, 2002). This research describes the interaction of the beneficial attributes of FCCDO (lower nitrogen content, higher aromaticity) with those of gasification coal-tar pitch (lower sulphur content, lower metals content, higher density) to form a hybrid coke used in the production of small-diameter electrodes.

#### 4.7.2 Molecular modification of heavy residues

*It is incumbent on any process evaluated that its three main objectives are met, namely increasing the coke anisotropy, reducing the pre-carbonisation residue volume and increasing the coke yield. However, in this study the anisotropy of the coke is of the greatest importance. It may well be argued that comparing the low-temperature pyrolysis of Waxy Oil against the cited literature on the basis of aromatic residues would be superfluous. However, the aim of any thermal treatment is to induce thermal stability and thus it is the author's opinion that many parallels may be drawn with the reduction of reactivity promoters.*

The use of **catalytic cracking** reactions to produce a highly aromatic needle coke precursor and lighter distillates from petroleum gas oil has been studied by many researchers, including

Lionetti and Schrader (1983) and Beuther *et al.* (1979). Hydrogenation followed by cracking reactions has also been shown to reduce the amount of pre-asphaltenes (the TI soluble component of asphaltenes) and by so doing reduce their reactivity by introducing aromatic hydrogen (Murukami *et al.*, 1989).

**Thermal treatment** of needle coke precursors prior to carbonisation is a method of stabilising reactive species at sub-carbonisation temperatures. Thermal treatment typically increases the Beta resin (QI - TI) fraction of isotropic pitch prior to mesophase formation. This “stabilisation” of the reaction rate allows the growth of smaller polyaromatics. Eser *et al.* (1989) conducted research to show how thermal treatment of vacuum residue stabilised reactive asphaltenes, increasing the anisotropy of the coke, decreasing the interlayer spacing and increasing the  $L_c$  of the graphite produced.

Dickakian (1985) showed that apart from stabilising the reactivity of the asphaltenes, thermal treatment of petroleum pitch increased the TI content from 1 to over 30%, while at the same time increasing the carbon aromaticity from 55 to over 80%. An increase in the concentration of two six-ring aromatic compounds or dimers thereof was also noticed. Blanco *et al.* (2000a) thermally treated coal-tar pitches at 430 °C for 2 to 4 h to increase the softening point and carbon yield. This was accompanied by a similar increase in the TI content and degree of graphitisation as determined by the interlayer spacing ( $d_{002}$ ) and crystallite height ( $L_c$ ). Similar results were obtained by the same researchers (Blanco *et al.*, 2000b), comparing thermally treated (430 °C for 2 to 4 h) coal-tar pitches with air-blown (275 °C for 10–30 h) coal-tar pitches. The air-blown pitches developed isotropic microstructures (caused by oxidative cross-linking), while the thermally treated pitches developed a higher degree of structural ordering with respect to mesophase development.

Perez *et al.* (2002) evaluated the difference between thermally treated and distilled petroleum pitches and determined that thermally treated pitches transformed a substantial amount of the aryl- and alkyl-substituted aromatics into planar aromatic cata-condensed aromatic compounds. The thermally treated pitches enhanced mesophase development compared with the mesophase from distilled petroleum pitches.

#### **4.8 Concluding remarks – Review of previous work**

It is clear that the characteristics of Waxy Oil differ substantially from the general characteristics of known needle coke precursors, especially in terms of aromaticity, alkyl side functionalities, the potential of oxygenate functionalities and the presence of iron oxide. All of these differences culminate in an increase in the carbonisation rate and thus a decrease in the extent of mesophase formation. Thus it is evident that substantial pre-carbonisation modification will be required to decrease the thermal reactivity of Waxy Oil

Although the carbonisation chemistry is not known at this stage of the project, it will be determined by its origin and pre-carbonisation processes. A description of the experimental procedures used in the current research is given in Chapter 5.