

# 1 INTRODUCTION

## 1.1 *Background to the investigation*

Heavy petroleum residues originating from crude oil and coal tar are processed by delayed coking to produce lighter petrol, diesel intermediates, hydrocarbon gases and a solid carbonaceous product called “green coke”. Delayed coking involves a multitude of chemical reactions, including cracking and polycondensation of Polycyclic Aromatic Hydrocarbons (PAH) to form green coke between 450 and 500 °C. Green coke is calcined at approximately 1 350 °C to form calcined coke which is sold into a variety of industrial markets.

Needle coke in particular is differentiated (from other calcined cokes) by its highly ordered microstructure and its visual resemblance to a collection of vertically aligned needles. Needle cokes are industrially used as carbonaceous filler for the production of graphite electrodes in the steel smelting industry.

The demand for and value of synthetic delayed coke is driven by the market requirement for carbon intermediates in the energy, foundry, steel and aluminium industries. Of the 91 million tons (mt) of delayed coke produced globally per annum, 68 mt is sold as cheap fuel-grade green coke and 23 mt is calcined, producing 18 mt of calcined coke. Of the 18 mt, 14 mt is used as anode coke (for aluminium smelters), 3 mt is used as carbon raisers (in foundries) and only 1 mt meets the stringent quality specifications to be utilised as **needle coke** for the production of graphite electrodes in the steel smelting industry (Driscoll, 2007).

Compared with other commodity delayed (calcined) cokes produced for the aluminium, recarburiser or foundry industries, the comparative value of needle coke is differentiated by the following considerations:

- Needle coke has the highest comparative market value per metric ton and is in the shortest supply (Driscoll, 2007).
- There are only a limited variety of petroleum and coal-tar pitch residues which, based on their molecular and chemical composition, are suited for the production of needle coke (Driscoll, 2007).
- Needle coke precursors attract the greatest process cost prior to delayed coking (Mochida *et al.*, 1990).
- Needle coke is in certain cases (depending on the international crude oil price) more valuable than the hydrocarbon distillates (petrol and diesel) produced during delayed coking.
- The generally accepted philosophy of delayed coking is to maximise the production of petrol and diesel intermediates. However, needle coke production requires the operation of the delayed coker in the “carbon”<sup>1</sup> mode, given the quality requirements and value of the calcined coke.

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<sup>1</sup> It is the author’s experience that the operation of commercial delayed cokers is either in the “carbon” or “white product” mode. White products are defined as the hydrocarbon distillates produced during delayed coking. They include petrol intermediates, diesel intermediates and heavy recycle oil. Hydrocarbon gases are not included in this definition, although they are produced in the process.

- Electrodes produced from needle coke are required to withstand temperatures in excess of 3 000 °C (Frohs *et al.*, 2007). By contrast, anodes produced from sponge cokes<sup>2</sup> in the aluminium industry operate at only 960 °C (Hulse *et al.*, 2000).
- Needle coke has the most stringent specifications in respect of sulphur, nitrogen, ash content and especially the Coefficient of Thermal Expansion (CTE) (Frohs *et al.*, 2007).
- Needle coke has attracted the greatest amount of funding for academic research.

It thus stands to reason that the identification of a potentially new feedstock which could produce needle coke with appropriate characteristics would attract research interest. Accordingly, the current research has been conducted to study Sasol Synfuels Waxy Oil and determine its potential for the production of highly anisotropic needle-like coke.

The aliphatic composition of Waxy Oil is in stark contrast to the preferred aromatic composition of needle coke precursors (Mochida *et al.*, 1990). As discussed in this study, the industrial and academic focus on aromatic residues has historically been justified by availability and the natural predisposition thereof for intrinsic molecular self-assembly during carbonisation, producing anisotropic or highly ordered carbon. Thus the diminutive academic drive to develop needle cokes from aliphatic residues cannot necessarily be ascribed to technical incapacity, but rather to lack of industrial necessity.

However, as viable reserves of needle coke precursors diminish due to availability, environmental legislation and quality deterioration, the nature of research has evolved to maximise the viable lifespan of these residues by developing ever-more-costly and technically advanced interventions to maintain coke specifications (Mochida *et al.*, 1989). The philosophy of knowledge advancement to address ever-worsening quality symptoms is finite and may in future increasingly require reconsideration.

Waxy Oil is a heavy aliphatic by-product produced by the gas phase reaction of carbon monoxide and hydrogen over an iron-based catalyst. It is produced on a commercial scale at Sasol's Coal-to-Liquid refinery at Secunda, South Africa. Waxy Oil is currently utilised to produce calcined coke and serves as a recarburiser, although high catalyst contents frequently diminish the market value. Waxy Oil produces a calcined coke with negligible sulphur and nitrogen content; this was the overriding consideration when choosing this feed for the study.

## 1.2 Feedstock quality

Precursors for needle coke production have historically been limited to available residues whose aromatic molecular composition naturally predisposes them to form highly anisotropic carbon during carbonisation. However, further requirements of the feedstock include:

- Low ash content (Mochida *et al.*, 1987) and (Martinez-Escandell *et al.*, 1999)
- Low Quinoline Insoluble (QI) content (Crelling, 2008)
- Low asphaltene content (Seshardi *et al.*, 1982)
- Reduced content of stable nitrogen or sulphur heterocyclics (Weinberg *et al.*, 1988)
- Low oxygenate content (Marsh *et al.*, 1973) and (Sima *et al.*, 2003)

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<sup>2</sup> While there are many ways of defining types of coke, it is common practice to assign a descriptive name, e.g. needle and sponge cokes.

- Low air and carboxy reactivity of the coke during calcination (Hippo and Walker, 1975) and (Walker *et al.*, 1983)

Feedstocks historically utilised for needle coke production include Coal-Tar Pitch (CTP), Fluidised Catalytic Cracker Decant Oil (FCCDO), petroleum vacuum residues and ethylene tar. Theoretically, it should be possible to convert any heavy carbonaceous residue into needle coke given the appropriate pre-carbonisation modifications (Mochida *et al.*, 2000).

In evaluating the characteristics of Waxy Oil for the production of needle coke, it may be compared against known commercial needle coke precursors to determine the degree of modification that may be required. Waxy Oil exhibits a comparative dissimilarity to the abovementioned feedstocks and the generally accepted quality requirements listed above. This provides a natural template against which a problem statement may be defined.

### **1.3 Problem statement**

The aim of the study is to identify the characteristics of Waxy Oil that retard the formation of anisotropic coke and remediate them prior to carbonisation. These characteristics may include the molecular composition (e.g. the presence of oxygenates, multi-alkylated alkanes) but the overriding concern is the lack of aromaticity. Another source of concern is the presence of substantial iron oxide catalyst. These areas of concern form the basis of the problem statement as detailed below:

- The iron oxide catalyst content of Waxy Oil is particularly erratic. This increases the ash content which ranges from 0.05–2.0% in Waxy Oil and, due to the low yield, may increase to between 5–20% in the calcined coke. This is far in excess of the required ash content for needle coke, which is 0.20% (Frohs *et al.*, 2007). The iron oxide induces further detrimental effects on coke characteristics, including rapid oxidative polymerisation (Wang *et al.*, 2001), leading to an isotropic microstructure and an increased CTE. It is also capable of modifying the mechanism of graphitisation as it induces catalytic graphitisation (Wang *et al.*, 2001).
- The porosity of Waxy Oil “green coke” increases the surface area available for oxidative carbon consumption during calcination (which is normally carried out in oxidising conditions), further compounding carbon loss which, by default, increases the relative ash content and enhances greenhouse gas emissions.
- Compared with the carbonisation cycle of aromatic residues, the aliphatic nature of Waxy Oil requires an extra aromatisation step prior to the formation of pre-mesogens (Domine *et al.*, 2002).
- Although Waxy Oil is composed predominantly of alkanes, the potential for the formation of oxygenated hydrocarbons is enhanced as one of the co-reactants in the Fischer-Tropsch process is carbon monoxide. While the effect of oxygenated alkanes is unknown, oxygenated aromatics are known to increase the reaction rate, forming mosaic cokes, as previously described by Sima *et al.* (2004)
- Furthermore, there is a potential for the presence of iso-alkanes. Aliphatic side chains on aromatic molecules are known to form radicals and increase the rate of reaction, forming mosaic microstructures, as previously determined by Obara *et al.* (1981)
- However, of all the potential reactivity promoters, the lack of Waxy Oil aromaticity is the greatest potential concern. Although there is abundant literature promoting the importance of aromaticity in determining the anisotropy of coke, the molecular

range of certain needle coke precursors, e.g. coal-tar pitch, is vast (200–2 000 amu). By contrast, both Wang and Eser (2007) and Lewis (1987) denote the importance of three- to six-ring aromatic precursors for the production of anisotropic microstructures. So, in the author's opinion, the question of total aromaticity vs. the type of aromaticity remains unanswered.

- Waxy Oil is a synthetic product and vastly different from favoured feeds for needle coke production, including petroleum decant oils (originating from crude oil) and coal-tar residues (originating from blast furnaces). Thus, comparing the carbonisation chemistry of Waxy Oil with the bulk of available published academic literature requires caution.

## **1.4 Scope of the investigation**

The development of a commercially acceptable needle coke from an unknown residue such as Waxy Oil is a multi-disciplined process. A simplified list of basic phases<sup>3</sup> is given below.

- Evaluating the molecular chemistry of the residue
- Evaluating the carbonisation chemistry of the residue
- Modification of the molecular composition to enhance coke anisotropy
- Pilot plant production of delayed coke
- Production of trial coke on a commercial scale

It is for the most part unnecessary to conduct extensive academic investigations into known needle coke precursors as they are limited to coal tar or petroleum residues which have historically been the subject of numerous academic research projects and published articles.

It would be myopic to expect success based on immediate pilot plant experimentation while negating the value of a prior understanding of Waxy Oil chemistry and its carbonisation mechanism.

As the chemistry of Waxy Oil has not previously been studied, the scope of this research encompasses identifying Waxy Oil characteristics that are detrimental to the production of anisotropic carbon and then identifying modifications to promote anisotropy, as well as a reasonable description of the reaction mechanism. It is only with this knowledge that future larger-scale investigations may prove worthwhile. Thus, the scope of work in this study does not include pilot plant delayed coking.

The thesis is divided into chapters and a brief description of each is given below.

### ***Introductory chapters***

#### **Chapter 1. Introduction**

This chapter serves as a general introduction to needle coke and compares Waxy Oil with other needle coke precursors. This information is then used to define the problem statement, objectives and scope of work.

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<sup>3</sup> The list of basic phases for this development is by no means definitive. It is given for descriptive purposes only to identify phases that are evaluated by the current scope of investigation.

## **Chapter 2. The needle coke value chain**

This chapter provides a basic overview of needle coke production from feedstock selection to the use of electrodes in an arc furnace. The aim of the chapter is to lay a foundation in needle coke chemistry for readers who may not previously have been exposed to this science. It is the author's opinion that a basic chemistry approach, including aspects of commercial production, enhances the understanding of the review of previous academic research discussed in the next chapter.

## **Chapter 3. The Waxy Oil value chain**

Given the unique characteristics of Waxy Oil, this chapter provides a brief description of its origin through to the production of calcined coke. It also provides a "specification sheet" approach to Waxy Oil and calcined coke. The chemistry of Waxy Oil is not discussed in any detail as it has not been the subject of academic research prior to this study.

## **Chapter 4. Review of previous work**

This chapter examines previously published academic research within the field of needle coke chemistry and the relevance thereof to Waxy Oil as a precursor for highly anisotropic coke. As Waxy Oil is vastly different from any known needle coke precursors, direct comparisons are not possible. However, the literature study serves to identify experimental interventions that may aid the formation of coke anisotropy.

### ***Main Chapters***<sup>4</sup>

## **Chapter 5. Experimental**

This chapter describes the experimental procedures and analytical techniques used to examine the chemistry of Waxy Oil and Waxy Oil coke. The results of the laboratory research are reported in Chapters 6 to 9.

## **Chapter 6. The influence of catalyst concentration on the characteristics of commercial Waxy Oil coke**

This chapter examines the effect of increasing the concentration of iron oxide catalyst on the chemical and physical properties of Waxy Oil green coke, as well as thermally treated variants. The effect of iron oxide on the characteristics of Waxy Oil coke is one of the major factors contributing to its ineligibility as a needle coke. The technical viability of particle graphitisation as a potential process for reducing the catalyst content of Waxy Oil coke and the effects on the chemical, physical and crystal characteristics of the graphite produced are discussed.

## **Chapter 7. Waxy oil modification**

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<sup>4</sup> At the end of each of the main chapters, both conclusions and recommendations based on the knowledge gained in that chapter are presented. These are used to determine the optimal set of experimental conditions for the following chapters. Thus the thesis attempts to present a "golden line" leading up to the production of needle coke from Waxy Oil.

This chapter discusses various experimental procedures utilised to reduce the catalyst concentration and modify the organic molecular composition of Waxy Oil. These interventions include filtration, distillation and thermal treatment. The molecular composition of these modified Waxy Oils is compared with heavy residue characteristics known to promote coke anisotropy. This chapter also discusses the modified Waxy Oil samples produced for “static” carbonisation.

### **Chapter 8. “Static” carbonisation of modified Waxy Oils**

This chapter evaluates the potential of “static” carbonisation of modified Waxy Oils to provide a semi-quantitative procedure for determining the quality of green coke produced, based mainly on a microstructural analysis through the longitudinal plane of the coke.

### **Chapter 9. The carbonisation mechanism of Waxy Oil**

This chapter examines the carbonisation mechanism of filtered and thermally treated Waxy Oil. In comparison with highly aromatic feedstock, the mechanism of Waxy Oil carbonisation is complex in that it includes an aromatisation step.

### *Concluding chapters*

### **Chapter 10. Conclusions**

### **Chapter 11. Contribution to original knowledge**

### **Chapter 12. References and bibliography**

## **1.5 Objectives of the investigation**

The main objectives of the investigation are broadly divided into creating an understanding of the effects of (i) catalyst concentration and (ii) the organic molecular composition of Waxy Oil on the structural characteristics and properties of coke. The objectives may be further be subdivided as follows.

- An initial objective of this study is to determine how **increasing catalyst concentration** influences the characteristics of Waxy Oil green coke with reference to the carbon macrostructure, microstructure, crystal development, real density and air/carboxy reactivity.
- **Graphitisation as a process to remove catalyst from green coke** – It is the objective of this part of the research to establish whether graphitisation is a viable solution to reducing the catalyst content.
- **Modification of Waxy Oil prior to carbonisation** – It is the primary objective of this part of the research to reduce the catalyst concentration (as determined by the ash content) of Waxy Oil to needle coke precursor specifications. Furthermore, the characteristics of filtered and virgin Waxy Oil are compared.

- Based on the fulfilment of the primary objective, the secondary objective is to create an understanding of the **organic molecular composition** of filtered Waxy Oil and to identify reactivity promoters that, during carbonisation, may have a detrimental effect on the anisotropy of the carbonised product.
- Based on the fulfilment of the secondary objective of the research, the tertiary objective is to determine the effect of distillation and thermal treatment of filtered Waxy Oil on the **molecular chemistry** thereof. Furthermore, the objective is to provide an explanation of how these interventions lower the carbonisation rate.
- **“Static” carbonisation of modified Waxy Oils** – The objective of this part of the research is show how “static” carbonisation in test tubes can be used to determine the difference in the quality of coke based on modified Waxy Oils.
- **The carbonisation mechanism of Waxy Oil** – The objective of this part of the research is to provide a reasonable explanation for the variance between the carbonisation mechanism of filtered Waxy Oil and the modified Waxy Oil that produced the greatest degree of anisotropy in the coke.

## 2 INTRODUCTION TO NEEDLE COKE

In this chapter, two main focus areas relating to needle coke are discussed, namely:

- The value chain of graphite electrode production
- The chemistry of needle coke formation from heavy residues

### 2.1 *The industrial value chain of graphite electrode production*

#### 2.1.1 Feedstock selection

Feedstocks used for the production of needle coke include:

- Petroleum Fluidised Catalytic Cracker Decant Oils (FCCDO)
- Petroleum Low-Sulphur Vacuum Residues (LSVR) or Vacuum Residues (VR)
- Coal-Tar Pitches (CTP)
- Ethylene Tar Pitches (ETP)
- Solvent Refined Coals (SRC)<sup>5</sup>

##### 2.1.1.1 Fluidised Catalytic Cracker Decant Oil (FCCDO)

Petroleum FCCDO is a heavy residue formed by catalytic cracking of either VR, atmospheric residues or a blend of both. The primary function of the catalytic cracking reaction is the production of naphtha: the greater the severity of the reaction, the more aromatic the FCCDO. Less severe cracking conditions produce a greater abundance of long alkyl side chains bound to parent aromatic molecules of which the FCCDO is predominantly composed. The catalyst is a powdered alumino-silicate which contributes to the ash content (to varying degrees, based on the efficacy of removal within the decanter or upstream removal processes) and may have a detrimental effect on the coke quality. Cokes with high catalyst contents may also form lower density graphites due to the sublimation of metals during graphitisation, forming voids within the graphite electrode.

Chemically, FCCDO is generally characterised by high concentrations of Polycyclic Aromatic Hydrocarbons (PAH) of >70%, (Mochida *et al.*, 1987), with a negligible concentration of reactive asphaltenes. These precursor characteristics aid in the formation of anisotropic needle coke with a lower CTE (compared with VR or LSVR). FCCDO has even been known to produce cokes with negative CTEs (Mochida *et al.*, 1987) in the longitudinal direction.

##### 2.1.1.2 Low-Sulphur Vacuum Residues (LSVR) and Vacuum Residues (VR)

Petroleum Vacuum Residues (VR) are produced as the residue product of vacuum distillation of atmospheric residue. Compared with other feedstocks, they are usually composed of higher

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<sup>5</sup> There is no evidence in the literature cited that the production of needle coke from SRC is conducted on a commercial scale. The literature (Hoover, 1988) refers only to laboratory investigations.



asphaltene concentrations and sulphur contents. They are further characterised by a high concentration of aliphatic molecules and a lower concentration of aromatics compared with their more stabilised downstream counterpart, FCCDO (Mochida *et al.*, 1987).

While they are known to produce inferior needle cokes (CTE typically  $5.0\text{--}8.0 \times 10^{-7} \text{.}^\circ\text{C}^{-1}$ ), they are, in comparison with the other commercial precursors, relatively abundant. The LSVR may be used in a blend with a more aromatic decant oil to increase the quality of the resultant needle coke, with specific reference to the sulphur content. The ash content of LSVR or VR feedstocks is totally dependent on mineral matter originating from crude oil and the efficacy of upstream desalination.

### 2.1.1.3 Coal-Tar Pitch (CTP)

Coal tar is a heavy by-product of coke oven furnaces used to produce metallurgical coke for the blast furnace and other applications. The properties of coal-tar pitch are very much determined by conditions in the furnace. Low-rank coals processed at lower temperatures may yield pitches with a large number of alkyl functions bound to the aromatic ring, higher oxygen contents and higher reactivity rates during carbonisation, leading to less appropriate coke for electrodes. By contrast, pitches produced at excessive temperatures may produce highly stable aromatic molecules which produce less gas during carbonisation, thus affecting pore morphology.

Coal-tar pitches are characterised by comparatively high densities (approximately  $1.18 \text{ g.cm}^{-3}$ ), higher nitrogen (1.5–1.70%) and lower sulphur (0.50%) contents in comparison with petroleum residues. The oxygen content may vary according to furnace conditions but is typically in the 1.0–2.0% range. Carbon aromaticity is high (93–96%) and the average molecular weight is in the 200–2 000 amu (atomic mass unit) range.

There are two main challenges faced in the production of needle coke from coal-tar pitch. The pitches usually require removal of primary quinoline insolubles (QI), which is solid carbonaceous matter carried over from the coke oven. QI is known to impede mesophase development which is essential in controlling the coke morphology, by presenting a three-dimensional inert obstruction to parallel alignment of mesogenic molecules, thus producing a coke with a higher CTE. Various methods for QI removal are utilised, including filtration, centrifugation and aliphatic/aromatic solvent precipitation.

The other challenge is the stability of nitrogen heterocyclics and their subsequent inclusion in the coke matrix. During graphitisation (of the electrode), nitrogen is released (1 600–1 800 °C) which leads to puffing of the electrode. Inhibitors utilised to suppress puffing include iron (III) sulphate, boron compounds and sodium salts.

From a market perspective coal tar is used as both binder and impregnation pitch as it is the only residue historically deemed to have the correct specifications.<sup>6</sup> It is also less favoured for cracking owing to its aromatic stability compared with that of petroleum residues. Furthermore, the exclusive use of coal tar and the size of the binder market presents competition to its use as a needle coke feedstock.

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<sup>6</sup> Heavy petroleum residues, for example, have been used as extenders in the binder pitch market. However, their comparative volume is low.

#### 2.1.1.4 Ethylene Tar Pitch (ETP)

Ethylene tar is the residue product from the production of ethylene (via steam cracking) and is characterised by high reactivity rates during the onset of carbonisation, limiting the extent of mesophase formation by prematurely increasing the viscosity of the developing mesophase and leading to less anisotropic carbon. Ethylene tar precursors may be upgraded when used in blends with more aromatic feedstock, e.g. FCCDO.

#### 2.1.1.5 Solvent Refined Coal (SRC)

It is not certain whether needle coke is commercially produced from SRC; however, it has been the subject of substantial research. It is usually considered an inappropriate feedstock due to the high process cost associated with solvent recovery. While SRC typically has high oxygen (3.0%) and nitrogen (2.2%) contents, it requires hydrogenation to promote formation of a needle coke as it is relatively hydrogen-deficient. Needle cokes produced from SRC are typically in the premium and regular grades (CTE of  $5.0\text{--}8.0 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$ ) as previously described by Hoover *et al.* (1988).

### 2.1.2 Delayed coking

The quality characteristics of needle coke are determined by its microstructure, which in turn is controlled by mesophase development of the precursor during carbonisation. While this research relates to specific facets of needle coke mesophase chemistry, for readers not familiar with this science a general description may be found in the literature cited (Marsh *et al.*, 1997; Clark, 2008; Mochida *et al.*, 1994).

Delayed coking is the onset of molecular transition from a complex mixture of aromatic molecules to the production of a solid carbon. All the processes, including delayed coking, calcining and graphitisation, only provide a source of thermal energy. Thus, the chemical composition of the molecules in needle coke precursors determines the characteristics of the eventual graphite electrode. All needle coke feedstocks (or for that matter any delayed coker feedstock) may be described as having a specific “predisposition” towards the formation of a certain green coke microstructure.

An empirical diagram of a delayed coker is shown in Figure 2-1, but note that the design of commercial delayed cokers may vary according to volumes of feedstock processed.

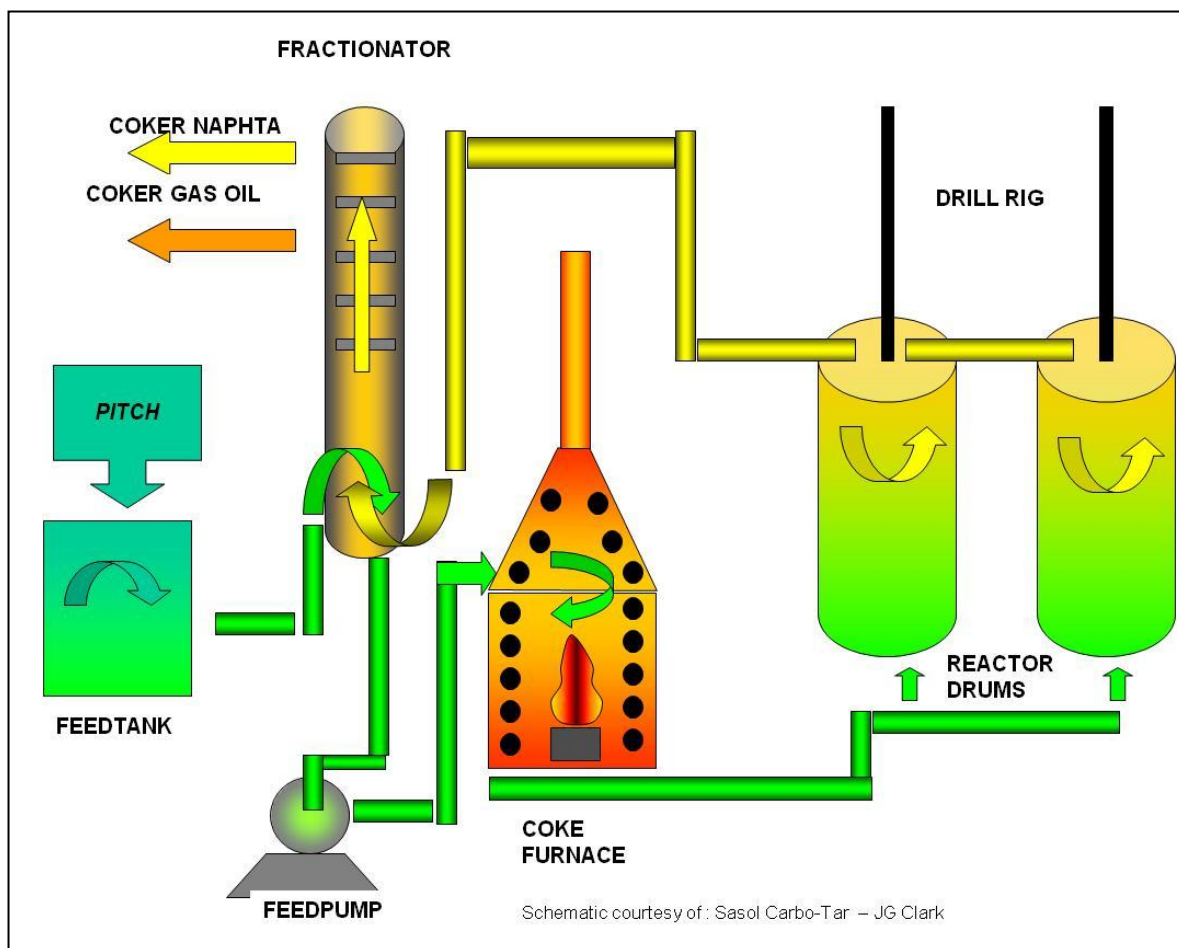


Figure 2-1 Diagram of a delayed coker (Clark, 2008)

Feedstock is stored in heated tanks and pumped via a series of pipes through two or more pre-heaters into the fractionator. The feed is pumped through gas-fired heater tubes and into the reactor drum. In the drum both exothermic cracking and dealkylation reactions provide vapours which are removed at the top of the drum and condensed in the fractionator. These vapours form hydrocarbon gases, naphtha (petrol intermediate) and coker gas oil (diesel intermediate). Naphtha and coker gas oil require hydrogenation prior to utilisation as petrol and diesel blend components, as delayed coking is a dehydrogenative process. The heavier molecules, which are not removed at the top of the drum, undergo polycondensation reactions. The coke forms from the bottom of the drum towards the top in a vertical direction.

Within the reactor several progressive phases of the carbonisation cycle are present: at the bottom is green coke, on top of this is the developing mesophase (a liquid crystalline state) and above this is virgin feedstock. The level of the coke in the reactor increases to approximately 70% of the drum's volume. On the completion of a cycle, feed is switched to another drum to prevent carryover of solid carbonaceous solids to the fractionator and risk of damage to the fractionator plates. The drum is then steamed and water is injected to cool the coke and remove some of the volatile organic matter. Although the diameter of various drums may vary, the coke is usually cut with a water jet using a two-stage process. The first stage cuts a "pilot hole" down the centre of the drum, followed by removal of the rest of the coke usually using a process called "undercutting", which cracks the coke rather than pulverising it, in order to minimise the production of fine carbon.

The velocity of gases through the delayed coker drum is dependent on both the volume of cracked gases from the feedstock and other non-oxidising gases injected, e.g. steam. Steam has two main functions: to increase the velocity of the feed through the heater tubes to prevent coke laydown; and to strip lighter organic volatiles from green coke in the reactor drum. As a consequence, the increased flow of gases through the drum has a substantial effect on the coke microstructure and pore morphology by affecting the alignment of mesophase domains.

During delayed coking, the top layers exercise pressure on the coke towards the bottom of the reactor. Because of thermal distribution within the drum, the coke in the bottom of the drum is usually denser due to constant pitch intrusion. Higher CTE coke at the bottom of the drum may also be affected by the precipitation of asphaltenes during carbonisation, producing fine isotropic, high CTE shot coke. Shot coke at the bottom of a drum may present a further safety concern as the coke forms in the shape of balls which may vary in size from a couple of millimetres to over 0,5 m in diameter.

Typical drum cycle times may last between 18 and 24 h, depending on the viscosity and green coke yield from the fresh feed. Each feedstock will have an optimum temperature for carbonisation, the more stable feeds requiring greater activation energy. However, delayed coking temperatures usually range between 460 and 500 °C. While it is optimum to operate the delayed coker at the minimum temperature for a specific feed, cognisance needs to be taken of the Volatile Carbon Matter (VCM) of the green coke. If the reaction temperature is too low, the VCM will increase to levels at which the green coke may become uncalcifiable (due to instability in the calciner). Another reason for controlling the VCM of the green coke to between 7 and 10% is that during calcination the VCM is combusted, causing porosity which decreases the bulk density of the calcined coke and may increase the binder pitch demand during electrode forming.

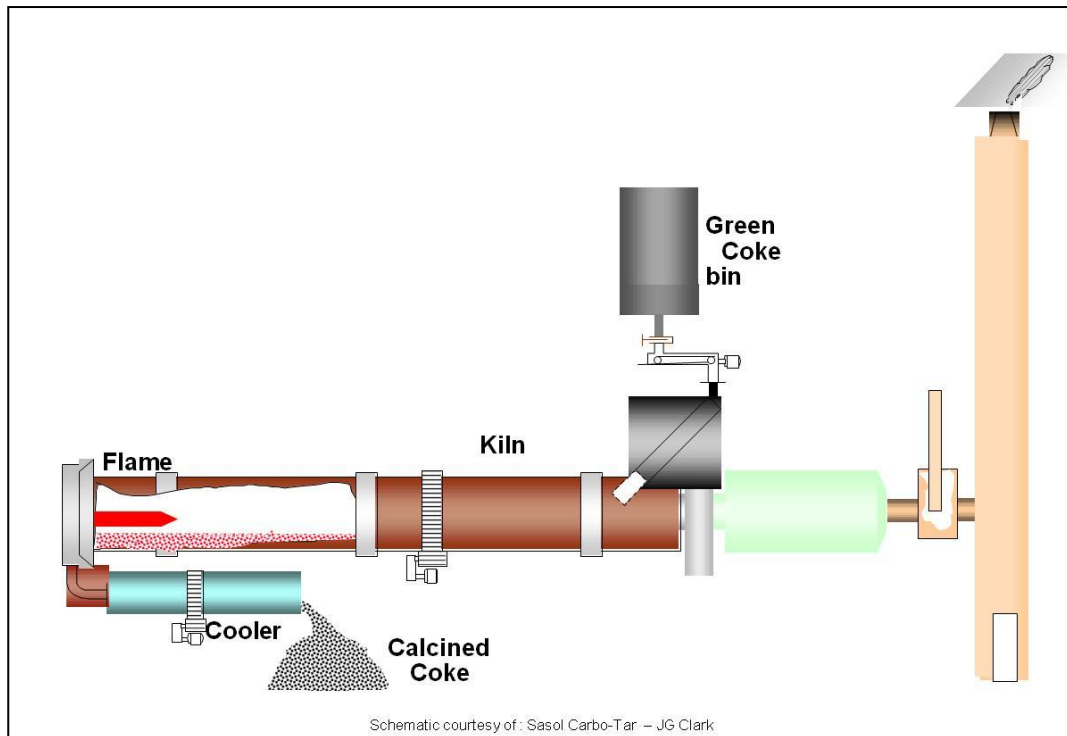
Pressure over the delayed coking system serves to increase the yield by retaining vapours in the drum. All delayed cokers producing needle coke are operated to maximise coke yield and thus the pressure remains constantly high (approximately 500 kPa). Decreasing the system pressure can lead to green coke yield losses, while increasing the pressure too much may retard the release of vapours and affect the pore morphology of the coke.

The drum vapour of heavier molecular weight is called the “recycle oil”. As the name implies, it is recycled to the fresh feed stream, given its propensity to increase the green coke yield of the virgin feedstock.

The control of carbonisation **temperature** and **pressure** is critical for producing coke with a low CTE. As each of the feedstocks has a different molecular composition, their specific optimum kinetics for carbonisation differs.

### 2.1.3 Calcination

Calcination is the process of VCM reduction and graphene layer densification between temperatures of 600 °C and approximately 1 350 °C. A diagram of a typical kiln calciner is shown in Figure 2-2.



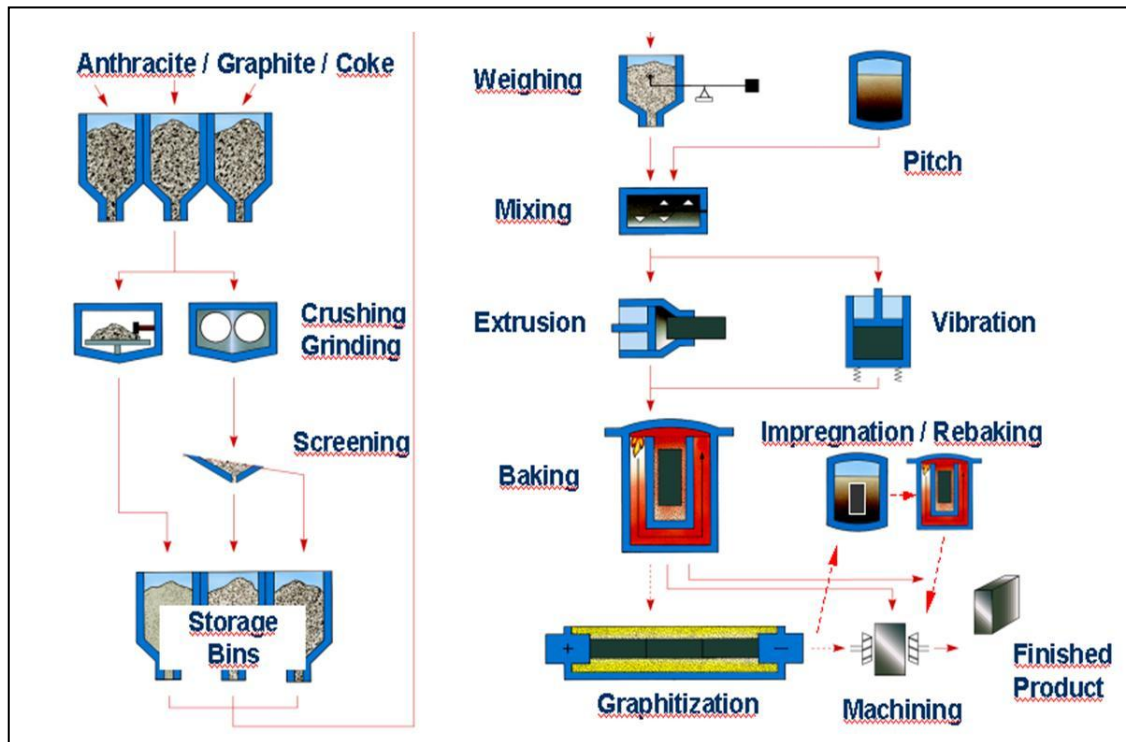
**Figure 2-2 Diagram of a counter-current calciner (Clark, 2008)**

Coke enters the kiln at 600 °C and is immediately dehydrated. At 700–800 °C dehydrogenation occurs. The temperature and atmosphere within the rotary kiln have a distinct effect on the properties of the calcined coke. Densification of the graphene planes occurs in the 1 100–1 400 °C range and is especially significant for the production of needle coke due to crystallite development.

Upon exiting the kiln at 1 400 °C, the coke enters a cooler where rapid shrinkage occurs, yielding cracks and determining the friability of the coke. While the coke is at 1 400 °C, the temperature is not high enough to affect the release of stable heteroatoms. Rapid cooling may induce microcracks either parallel or perpendicular to the flow domain of the coke, which provide a pathway for the escape of the gases released in the early stages of electrode graphitisation, thereby decreasing the puffing phenomenon.

### 2.1.4 Electrode production

The production of electrodes is a closely controlled process. While exact formulations and process conditions are closely guarded intellectual capital, it is possible to present the general flow scheme of electrode production, shown in Figure 2-3.



**Figure 2-3** Diagram showing the manufacturing process for graphite electrodes (Frohs *et al.*, 2007)

After crushing, needle coke is classified according to particle size and separated into bins. The “dry recipe” is then formulated according to a predetermined programme. The larger the diameter of an electrode, the higher the thermal stress it will need to withstand (without significant expansion or cracking), both during graphitisation and within an Electric Arc Furnace (EAF). The “ceramic toughening” principle to hinder crack propagation on bigger particles has led to the formulation of larger electrodes with larger coke particles (up to 20 mm). This has had a knock-on effect on the producers of calcined coke to reduce the friability thereof.

Binder pitch is mixed with the dry recipe at a temperature of 160–180 °C, which is 50–65 °C above the softening point of the pitch. The amount of pitch used is specific to the recipe and the macroporosity of the coke.

Forming of a green electrode is conducted by extruding the paste through a die with a specific diameter, producing a green electrode. The electrode is cut to size (in length) and usually rolled into a water bath to cool the pitch matrix down, allowing the green electrode to maintain the integrity of its shape.

Green electrodes are placed in metal cylinders and baked (in a vertical position) for a number of days at a slow temperature gradient, eventually reaching 900–1 000 °C. During the baking process the binder pitch is carbonised, providing a solid infusible carbon cylinder with the filler coke. The slow temperature gradient is particularly important in controlling the dimensions and possible shrinkage of the electrode as a result of pitch pyrolysis. Binder pitch dosage is equally important: if the mix is too wet, deformation during baking may occur and if the mix is too dry, the baked electrode will have a lower mechanical strength and bulk density.

Impregnation of baked electrodes is conducted to increase the bulk density and ultimately the mechanical strength. Baked electrodes are placed in an autoclave in the vertical position. The hood is closed and a vacuum drawn on the system. Impregnation pitch is introduced to the system covering the electrodes under a pressure of up to 10 atmospheres. The softening point of impregnation pitch (approximately 95 °C) is lower than that of binder pitches (approximately 115 °C) and contains a substantially lower percentage of primary QI. The combination of the lower softening point, negligible primary QI and pressure allows penetration of the inner macropores of the electrode. After impregnation, excess pitch is drained and the electrode is re-baked. This process may be repeated until the required bulk density is reached.

The purpose of graphitisation is to transform the filler needle coke and carbonised pitch into graphite. The process heats electrodes to approximately 2 900–3 000 °C, at a predetermined heating gradient, and keeps it at that temperature, allowing it to cool afterwards.

## **2.2 The chemistry of needle coke formation**

In this section the chemistry of needle coke formation is discussed with sequential reference to feedstock composition, mesophase formation, microstructure and characteristics of needle coke.

### **2.2.1 Composition of needle coke feedstock**

The molecular composition of needle coke feedstock has by far the greatest influence on the coke's performance as a filler material in an electrode. Furthermore, feedstock aromaticity is a leading indicator in predicting the anisotropy of needle coke produced.

However, the mere determination of total aromaticity either using  $^1\text{H}$  (Stecker, 1984) or  $^{13}\text{C}$  (Seshardi *et al.*, 1982) Nuclear Magnetic Resonance (NMR) or Fourier Transform Infra-Red (FTIR) spectroscopy to determine the Aromatic Index (Sima *et al.*, 2003) does not solely produce an adequate explanation as the type of aromaticity is equally important.

Needle coke feedstocks are heterogeneous systems composed of (in some cases) many thousands of different aromatic molecules (Domine *et al.*, 2002) and may, as in the case of coal-tar pitch, be composed of a wide molecular weight distribution – between 200 and 2000 amu as determined by Gullien *et al.* (1998), which means that compounds from 2-25-ring aromatics may be present. Secondly, the presence of asphaltenes (large molecular weight aromatics, highly contaminated by heteroatoms and minerals) as determined by Dickakian (1984) increases the thermal reactivity of the heavy residue, thus prematurely increasing the viscosity and having a dominating effect on the microstructure of the coke.

As determined by Gullien *et al.* (1998), coal-tar pitch is also composed largely of three- to six-ring aromatic compounds. Comparatively, petroleum decant oil is composed largely of alkylated three- to six-ring aromatic compounds (Wang & Eser, 2007). Both the abovementioned authors determined this range of aromatics to be the preferred molecular weight precursors for the production of highly anisotropic needle coke. These aromatic compounds are referred to as “pre-mesogens” meaning, those Polycyclic Aromatic Hydrocarbons (PAH) from which the mesophase is generated. A compilation of typical gas chromatography-amenable PAH compounds present in needle coke feedstocks is shown in Figure 2-4.

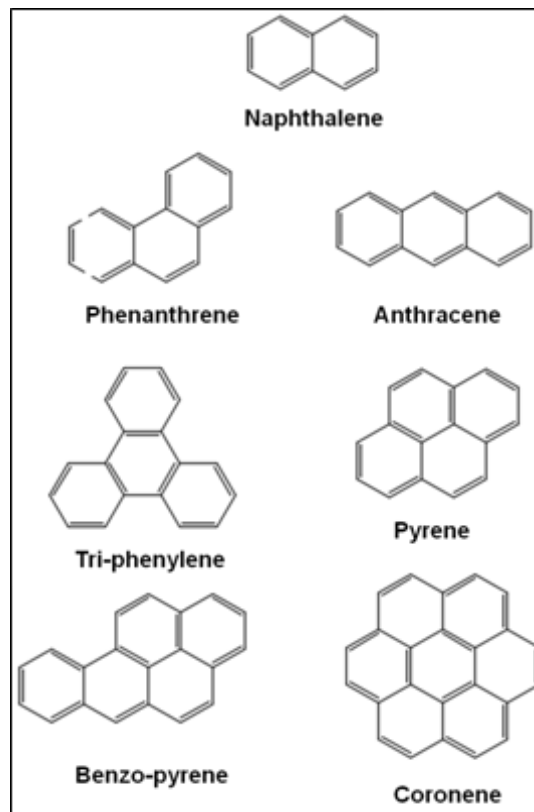
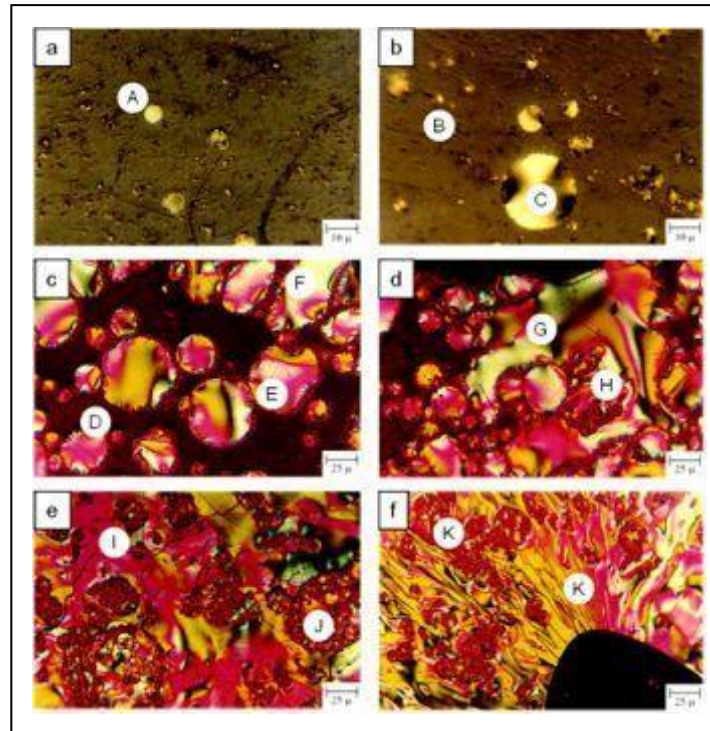


Figure 2-4 Typical aromatic pre-mesogens in needle coke feedstock

## 2.2.2 Mesophase formation

Mesophase is the intermediate liquid crystal phase formed by polycondensation of PAHs before solidification to form coke as defined by Mochida *et al.* (1994). Mesophase grows from an isotropic phase in the form of small spheres as seen in Figure 2-5.





**Figure 2-5 Mesophase development and the influence of primary Quinoline Insolubles (QI)**  
(Crelling, 2008)

Incipient mesospheres grow by incorporating mesogens from the isotropic matrix, as seen in Figure 2-5 (Positions A, B and C). The spheres coalesce to form larger spheres (shown in Positions D and E), eventually forming semi-coke (as seen by Position F). The degree to which the spheres grow and coalesce while maintaining maximum fluidity is defined as the “extent” of mesophase formation. This defines the morphology of the microstructure as seen in Positions G, H, I, J and K.

The extent of mesophase formation is not dependent solely on the type of aromaticity, but may also be affected by other feedstock compositional factors, including:

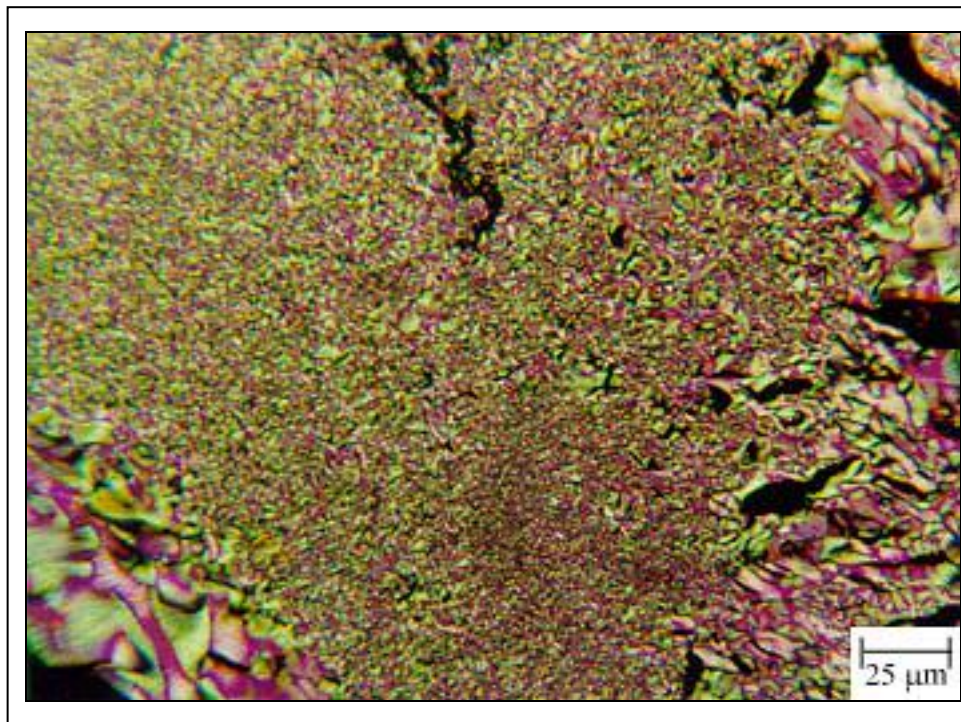
- The oxygen, nitrogen and sulphur content of the feedstock (Sima *et al.*, 2003)
- The asphaltene content of the feedstock (Dickakian, 1984)
- Alkyl side chains bound to the parent aromatic compounds, e.g. in VR (Mochida *et al.*, 1989) or ethylene tars (Mochida *et al.* 1989)
- The mineral concentration in the feedstock either chemically modifying mesophase development (e.g. iron oxide as described by Wang *et al.*, 2001) or providing an inert barrier to mesophase development (e.g. silica gel as described by Obara *et al.*, 1985)
- QI, which are small solid particles of carbon especially predominant in coal-tar feedstock due to the temperature of formation (approximately 1 100 °C). QI is pushed towards the edge of the developing spheres (as shown in Positions E and H) and may prevent further coalescence, thus producing mosaic coke

### 2.2.3 Coke microstructure

Any one or a combination of the factors listed above will affect the kinetics (or the rate) at which heavy residues are transformed into coke. If the mesophase “cures” too quickly, its viscosity will prevent further coalescence of mesogenic spheres. By so doing coalescence is retarded and this gives rise to the family of microstructures known as “mosaics”, which include:

- Fine mosaic
- Medium mosaic
- Coarse mosaic

These appear as a “collection of balls” of varying sizes. This type of material is **isotropic** (on a micro/milli-dimensional scale) as seen in Figure 2-6, but within the “balls” on a smaller dimensional scale there are anisotropic regions.

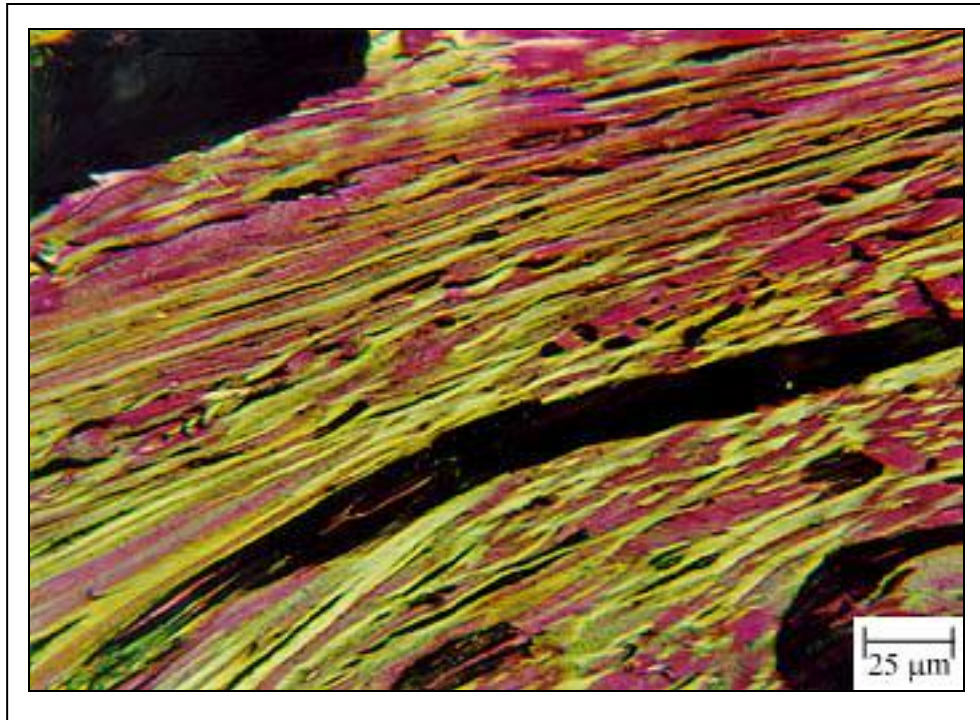


**Figure 2-6** Micrograph of an isotropic coke showing fine mosaic structures (Crelling, 2008)

If the mesophase kinetics allows unhindered coalescence of spheres, microstructures resembling flow domains are produced. **Flow** patterns include:

- Coarse
- Granular
- Laminar

These thus appear as a collection of elongated domains and are common in higher order sponge and needle cokes. These cokes are typically referred to as **anisotropic** (with order) as shown in Figure 2-7. Needle coke microstructure is typically composed of these flow domains.



**Figure 2-7 Micrograph of anisotropic coke showing flow domain microstructures (Crelling, 2008)**

Historically, one of the most reliable methods for evaluating the microstructure of cokes is the Optical Texture Index (OTI). The procedure entails setting the carbon in an epoxy resin mould and then polishing the flat surface of a piece of carbon with fine alumina powder. The polished surface of the carbon is then examined under a light microscope at low magnification within a drop of oil. Under magnification the carbon reveals “shapes or structures” which are point-counted to determine an “index value” and reveal the relative anisotropy/isotropy of the material on a milliscale. The OTI reference table is given in Table 2-1. The higher the OTI factor, the more ordered or anisotropic the coke, as discussed by Marsh *et al.* (1997).

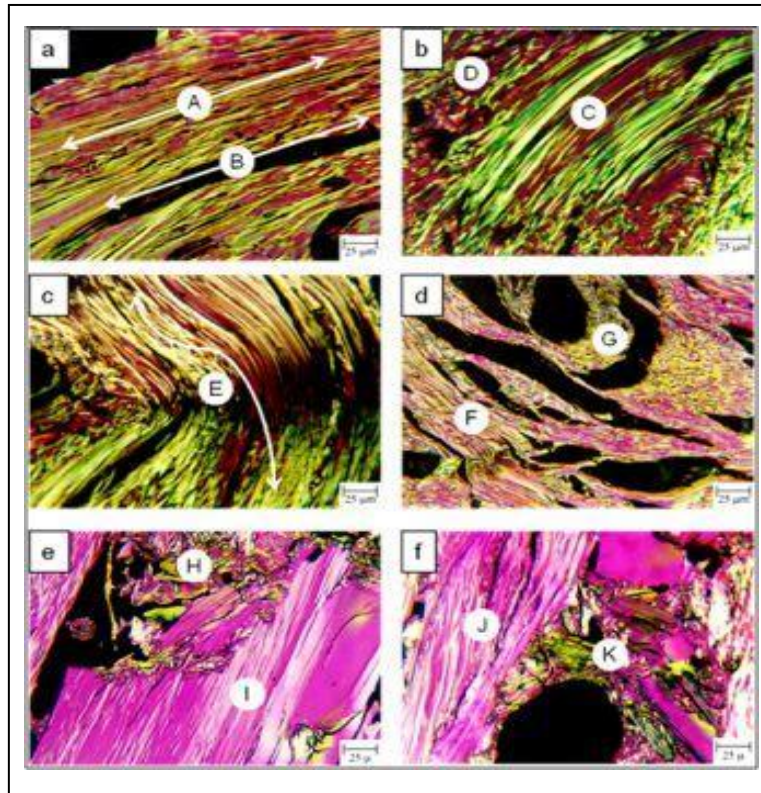
**Table 2-1 Optical Texture Index (OTI) (Marsh *et al.*, 1997)**

Category	Description	OTI Factor
<b>Fine mosaics</b>	Small circular < 0.8 μm in diameter	0
<b>Medium mosaics</b>	Circular > 0.8 μm < 2.0 μm in diameter	1
<b>Course mosaics</b>	Large circular > 2.0 μm < 10 μm in diameter	3
<b>Granular flow</b>	> 2.0 μm in length and > 1 μm in width	7
<b>Course flow</b>	> 10.0 μm in length and > 2 μm in width	20
<b>Lamellar flow</b>	> 20.0 μm in length and > 10 μm in width	30

The relative degree of anisotropy within a carbon matrix has significant effects on the in situ performance of the carbon filler within the graphite electrode, including the Coefficient of Thermal Expansion (CTE) discussed later in this chapter.

## 2.2.4 Microstructure of needle coke

A montage of needle coke micrographs is shown in Figure 2-8.



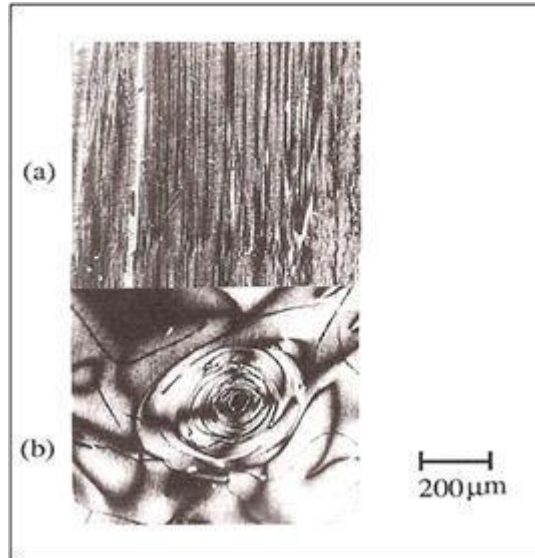
**Table 2-8** Montage of needle coke microstructures (a–d) and needle coke in an electrode (e–f) (Crelling, 2008)

Needle coke has a microstructural morphology dominated by long thin flow domains of indeterminate length as shown in Position A. This morphology is largely the result of the hydrocarbon gases produced during cracking escaping in a vertical direction, as seen from the parallel long thin pores formed (Position B), as previously determined by Mochida *et al.* (1998 and 1999).

Depending on the composition of the feedstock, the morphology of needle coke may contain a mixture of flow domains (Position C) and domains of a shorter length yet wider breadth (Position D). The morphology of the flow domains is determined by the path of the escaping gases and may appear straight (as previously shown by Position A) or curved (Position E). Feedstocks producing inferior needle cokes, e.g. ethylene tar (Mochida *et al.*, 1990a), often have lower coke yields and a mixture of coke microstructures as seen from the flow domains (Position F) and medium to coarse mosaics (Position G). Lower green coke yields are often characterised by the production of highly porous morphologies, as described by Mochida *et al.* (1987) and shown in Figure 2-8d.

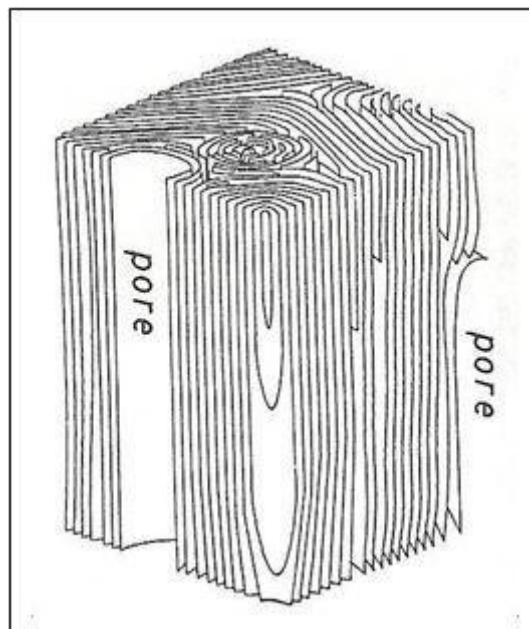
Figure 2-5 (e–f) shows needle cokes (Positions I and J) as filler material in an electrode. The filler particles are bound by carbonised binder pitch (Positions H and K). The carbonised binder forms a coke with a microstructure that is less anisotropic than the filler material.

The morphology of needle coke is entirely dependent on the angle from which it is viewed as shown in Figure 2-9.



**Figure 2-9** Scanning electron micrograph of perpendicular sections of needle coke, (a) in the longitudinal section and (b) in the transverse section (Mochida *et al.*, 1994)

When viewed along the longitudinal a-axis (Figure 2-9a), the microstructure appears entirely composed of long thin flow domains. However, when viewed in the transverse c-axis (Figure 2-6b), the microstructure appears as concentric rings surrounding a central pore. This difference in the microstructure is further explained by examining a three-dimensional diagram of needle coke structure as shown in Figure 2-10.



**Figure 2-10** Diagram of the structure model of needle coke (Mochida *et al.*, 1994)

Examination of the longitudinal axis of needle coke shows that both pores and cracks run parallel to this axis, providing evidence that gas evolution in the final stages of mesophase solidification determines the uni-axial arrangement of the coke microstructure.

Crystal development is dependent on the graphitisability of the green coke microstructure, which is determined by the mesophase formation, as previously described by Murthy *et al.* (2001).

### 2.2.5 Needle coke crystallography

Graphitisation depends on the efficacy of thermal energy to produce slight incremental adjustments to the alignment of the graphene planes (Mochida *et al.*, 1994). The mobility of aromatic molecular planes is fixed when the coalesced mesophase solidifies to form the green coke and thus it is impossible to produce a more highly aligned structure from an isotropic coke by increasing the temperature alone.

As optical microscopy is able to show the basic alignment of planes at various heat treatment temperatures on a micron-scale, X-Ray Diffraction (XRD) is able to follow the growth of crystals on a nanoscale (Murthy *et al.*, 2001). The effect of graphitisation on CTE is more easily understood using XRD, which is able to provide finite values ( $L_a$ ,  $L_c$ ,  $d_{002}$ ) rather than relying on point counting of aligned planes using Scanning Electron Microscopy (SEM) or optical microscopy, which provides qualitative aspects of the nano/milli-structure. The effect of increasing the temperature on the XRD indices of a petroleum coke is shown in Table 2-2.

**Table 2-2 Crystalline development as a function of heat treatment temperature for an anisotropic petroleum coke (modified from Inagaki, 2000)**

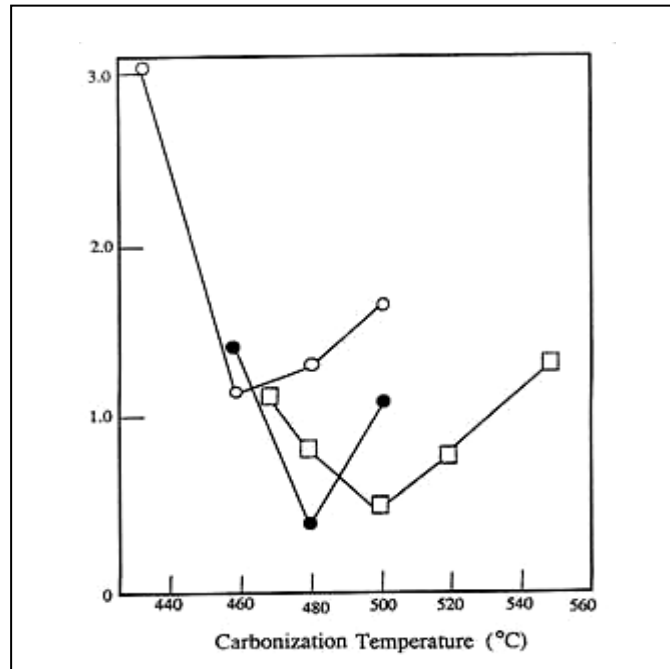
Heat treatment temperature (°C)	$d_{002}$ (Å)	$L_c$ (Å)	$L_a$ (Å)
2 300	3.369	440	310
2 400	3.363	490	310
2 500	3.359	550	330
2 600	3.358	560	350
2 700	3.357	610	360
2 800	3.352	670	420

As the heat treatment temperature increases, the interlayer spacing ( $d_{002}$ ) between the graphene sheets decreases while the height ( $L_c$ ) and the width of the crystal increase. The anisotropy of the microstructure is fundamental in allowing these modifications of the crystal structure with increasing temperature.

### 2.2.6 The Coefficient of Thermal Expansion (CTE) of needle coke

The CTE of needle coke is one of the most important, yet most commonly misunderstood, characteristics of needle coke. The CTE is dependent on the orientation of the pores and cracks within a specific particle of coke. It cannot be measured directly but is inferred from

the CTE value of a synthetic electrode manufactured with the coke in question as a filler. The effect of carbonisation temperature on the CTE of test rods produced from coke carbonised at various temperatures is shown in Figure 2-12.



**Figure 2-11** CTE values of test electrode rods produced from cokes formed at various temperatures, at a pressure of  $16 \text{ kg.cm}^{-2}$  from feedstocks. ○ LSVR; ● FCCDO; □ Coal-tar pitch (QI free) (Mochida *et al.*, 1994). The Y-scale is the Coefficient of Thermal Expansion and is measured in units of  $\text{mm/mm} \times 10^{-6} \cdot ^\circ\text{C}^{-1}$

The CTE of particulate needle coke or a graphite electrode has the effect of increasing thermal stress on the expansion thereof in both the *a*- and *c*-axes (Mochida *et al.*, 1994). The CTE of a graphite electrode along the direction transverse to the extrusion axis is of importance owing to the extremely high temperatures (approximately  $3\ 000\ ^\circ\text{C}$ ) it has to withstand without cracking.

Figure 2-11 shows that the optimum carbonisation temperatures for producing the lowest CTE coke for various needle coke precursors is different. LSVR and ethylene tar are reactive and thus necessitate carbonisation at lower temperatures (Mochida *et al.*, 1989 and 1990b). However, heavy residues that have undergone some sort of catalyst cracking, e.g. FCCDO (Mochida *et al.*, 1989) or heat treatment during their formation, e.g. coal-tar pitch (Mochida *et al.*, 2000), are less reactive and thus are carbonised at higher temperatures. The optimum temperature for carbonisation is modified when mixtures of residues with higher reactivity residues (e.g. vacuum residues) and residues with lower reactivity (e.g. FCCDO) are mixed to reduce the CTE of the coke, as described by Mochida *et al.* (1989).

At temperatures either below or above the optimum, the CTE of the coke increases. At higher carbonisation temperatures, mesophase development is comparatively rapid. This has the following consequences:

- Gases are evolved before they may have an effect on the pore aspect ratio of the coke (during solidification of the mesophase).
- Due to limited growth of isochromatic areas, their distribution may appear random.
- Microstructures form elongated mosaics rather than domains or flow domains.
- The rapid viscosity increase of the mesophase does not allow optimum growth of mesophase spheres within the liquid crystalline state.
- The lower anisotropy of the coke increases the CTE.

However, the converse is also true: carbonisation at temperatures below the optimum has the following consequences:

- The carbonisation reaction is slow and takes longer.
- Gas evolution is slow and may not provide sufficient gas evolved during the solidification stage of the bulk mesophase, thus affecting the aspect ratio of pore morphology.
- The green cokes produced may contain a substantial VCM content. On calcination these pockets of VCM will carbonise immediately and form areas of high-CTE mosaics.
- Unless the pressure is high enough, co-carbonisation of feedstock with differing optimum carbonisation temperatures may limit the interaction of their kinetics or produce two different types of coke in the same drum.

As indicated by Figure 2-13, CTE measurement along the longitudinal axis (or **a-axis**) yields lower CTE values than along the transverse axis (**c-axis**). Measurement of the CTE on a piece of coke is inaccurate due to porosity variation between pieces (even from the same carbonisation). The coke is thus mixed with binder pitch to produce a graphitised rod, which removes much of the inaccuracies.

However, different graphite producers and researchers are known to vary the temperature range over which the CTE is measured and thus these values are not always comparable. Examples thereof given in the literature include:

- Ambient to 400 °C (Keshun *et al.*, 1985)
- Ambient to 500 °C (Mochida *et al.*, 1989)
- Ambient to 100 °C (Mochida *et al.*, 1987)

The same characteristic may apply to the fracture mechanics of a graphite electrode in an EAF. If the electrical conductivity of a graphite electrode is not high enough, thermal stress in the electrode will translate into mechanical stress. In most instances crack propagation will progress along the longitudinal direction in which the resistance is the lowest.

### 2.2.7 Puffing

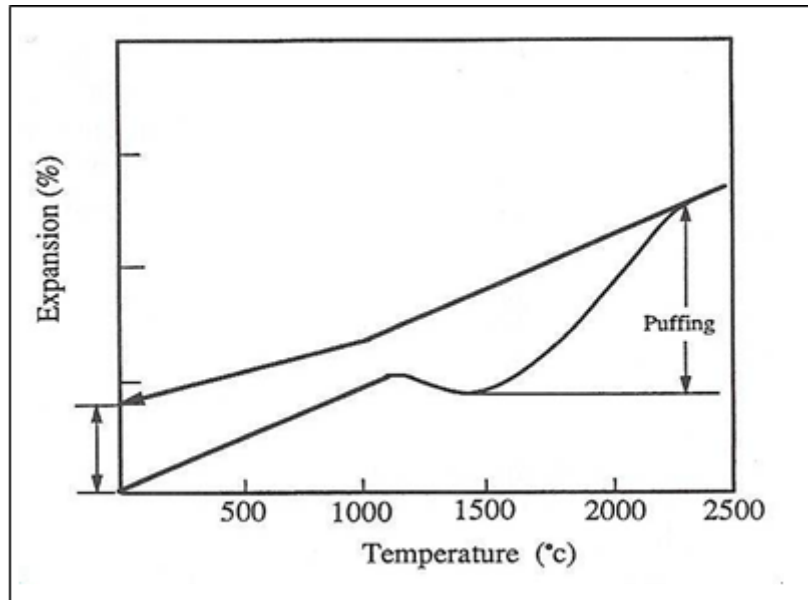
Puffing may be defined as the irreversible expansion of an electrode during graphitisation. It is caused by the release of bound heteroatoms from the carbon matrix between 1 600 and 2 300 °C, as described by Kawano *et al.* (1999a). The nature of the heteroatoms released is dependent on the origin of the needle coke precursor. Petroleum-based needle cokes tend to release higher concentrations of sulphur, as described by Orac *et al.* (1992), while coal-based



needle cokes tend to release higher concentrations of nitrogen, as described by Kawano *et al.* (1999b and 2000).

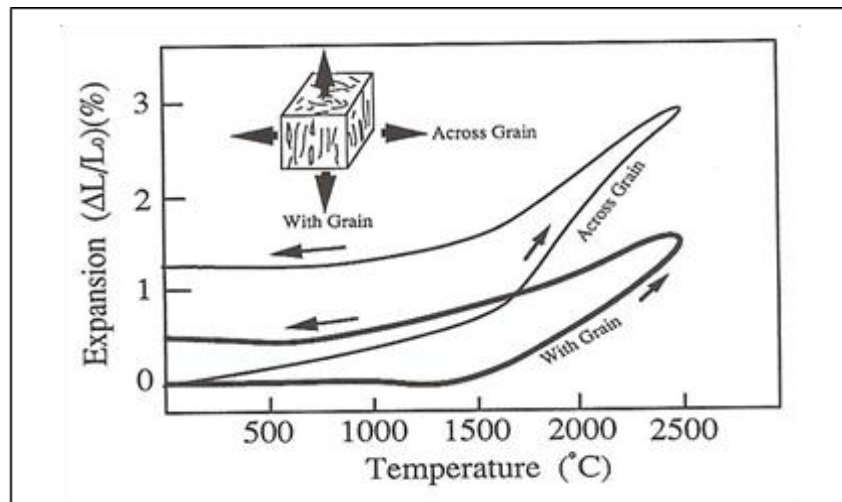
Graphitisation increases the crystal height (**c-axis**) and width (**a-axis**). This densification decreases the space between the graphene layers (**d-spacing**). Needle coke expands during graphitisation up to 1 500 °C and then from 1 500 to 1 600 °C the coke shrinks. This is followed by rapid expansion from 1 600 to 2 300 °C (dynamic puffing) and then at 2 500 °C secondary puffing occurs (Mochida *et al.*, 1994). The gases released during dynamic puffing include N<sub>2</sub>, CS<sub>2</sub>, H<sub>2</sub>S and COS, depending on the type of needle coke, as described by Mochida *et al.* (1994).

The initial puffing phase occurs between 1 500 and 1 800 °C as released gases cause a volumetric expansion of the coke on a linear curve as a result of pressure on the coke microstructure due to blocking of pathways. According to Mochida *et al.* (1994), from 1 700 to 1 800 °C, the d-spacing increases slightly due to the release of these heteroatoms. The extent of puffing in an electrode is also dependent on the ability of the released gases to escape through the carbonised binder matrix. Figure 2-13 shows the expansion and shrinkage curves of needle coke heat-treated to 2 500 °C. The coke shrinks on a linear curve on cooling.



**Figure 2-12 Profile of expansion and shrinkage curves of an electrode showing the effect of puffing (Mochida *et al.*, 1994)**

The volumetric expansion of a coke particle is not equal in all directions due to the preferred orientation of microstructural flow domains and pore morphology as shown in Figure 2-14.



**Figure 2-13** Diagram showing the influence of measuring direction on the extent of puffing (Mochida *et al.*, 1994)

The alignment of the pores in the longitudinal (with grain) direction provides a pathway for the release of gases during puffing and thus the pressure increase is less, decreasing the expansion. The opposite is true for expansion in the transverse (across grain) direction as the pathway for released gases is impeded to a greater extent by the carbon structure, causing a pressure build-up and greater expansion. The same theory holds if the expansion (in both directions) were to be measured on an electrode during graphitisation, principally due to the alignment of the coke particles in the longitudinal direction (Mochida *et al.*, 1994).

Traditional methods employed to control puffing include the use of a puffing inhibitor, as previously described by Orac *et al.* (1992) and Kawano *et al.* (1999b). Inhibitors form a chemical bond with heteroatoms and serve to control the rate at which heteroatoms are released from the coke matrix, thus reducing pressure on the inner walls of the electrode. The mineral content within needle coke may be bound in a number of ways, but under the inert conditions of graphitisation normally reduces to the metallic state and sublimates, leaving voids in the crystal structure, thus decreasing the bulk density and the mechanical strength of the electrode, while increasing the electrical resistivity.

### 2.2.8 Needle coke specifications

A summary of typical super-premium needle coke specifications is shown in Table 2-3. Needle cokes may be broadly classified into three grades which vary in the stringent quality specifications and have a considerable influence on the price. Table 2-3, however, considers only the specifications attributed to the highest grade, namely super-premium grade needle coke.

**Table 2-3 Typical super-premium grade needle coke analyses<sup>7</sup> (Frohs *et al.*, 2007)**

Analysis	Units	Typical range
CTE	X10 <sup>-7</sup> . °C <sup>-1</sup>	3–4
Real density	g.cm <sup>-3</sup>	2.140–2.145
Sulphur	%	0.4–0.5
Nitrogen	%	0.2–0.3
Hydrogen,	%	0.035–0.045
Vibrated Bulk Density (VBD)	g.cm <sup>-3</sup>	080–0.82
Ash	%	0.1-0.2

Needle cokes possess a low CTE, high electrical conductivity, high real and bulk density, low heteroatom content and low ash content (Mochida *et al.*, 1994). It is the compound effect of these needle coke characteristics that determines the in situ performance of a graphite electrode in an EAF.

## **2.2 Concluding remarks – Introduction to needle coke**

A basic understanding of needle coke science is important when discussing the results of this research project. In this chapter a sequential description has been provided, but it is by no means definitive.

The Waxy Oil value chain is discussed in Chapter 3 from production of Waxy Oil to calcined coke

<sup>7</sup> All analyses of needle coke are conducted on the particles, except the CTE which is conducted on a test rod produced by mixing needle coke with binder pitch, extruding, baking and graphitising. Particle CTE is variable due to differences in porosity between the particles.