

8 “STATIC” CARBONISATION OF MODIFIED WAXY OILS

8.1 *Introduction*³³

The aim of this chapter is to provide a correlation between the chemical composition of modified Waxy Oils (produced in Chapter 7) and the microstructure of coke produced by “static” carbonisation.

The chapter is divided into two main themes:

- Firstly, the effect of **catalyst concentration** on various characteristics of Waxy Oil coke is determined, including the coke yield, macrostructure, microstructure, crystal development, carboxy reactivity and air reactivity. The carbonised products of Sample A (unfiltered Waxy Oil) and Sample B (filtered Waxy Oil) are therefore compared.
- Secondly, the effect of **organic modification** of filtered Waxy Oil on the green coke yield, macrostructure and microstructure is determined. The carbonised products of Samples C1, C2, D1, D3, D4, E2 and E1b are compared. The substantial effect of organic modification on the microstructural characteristics of the cokes produced is determined.

The unmodified and modified Waxy Oils produced in accordance with the procedures previously described (Chapter 7) were subjected to “**static**” carbonisation at 480 °C and 5 bar in a test tube, with a heat soaking time of 2 h. A detailed description of the procedure is given in Chapter 5.

Small quantities of the unmodified and modified Waxy Oil samples (approximately 100 g) were placed in separate Pyrex glass test tubes. The modified Waxy Oil samples were carbonised in the same reactor used for the thermal treatments (discussed in Chapter 7). Green cokes A and B were removed from the Pyrex glass tubes and calcined in a muffle furnace at 1 350 °C in argon.

8.2 *The role of “static” carbonisation*

The mode of carbonisation has a distinct influence on the characteristics of coke produced. In this chapter the fundamental effect of Waxy Oil composition on the coke microstructure is determined and thus “static” carbonisation was preferred to “dynamic” or delayed coking. “Static” carbonisation of heavy residues is by no means novel, neither is the expression of overall anisotropy based on the height percentage of a piece of coke against the longitudinal plane produced in a tube bomb, as determined by Mochida *et al.* (1989). During “static” carbonisation, molecules with a higher reactivity polycondense, initially forming a semi-solid second phase of slightly higher density. The molecules gravitate towards the bottom of the test tube, in much the same way as asphaltenes have been noted to precipitate out of ethylene

³³ The research for Chapter 8 was conducted by the author at the Instituto Nacional del Carbón (INCAR) in Oviedo, Spain under the tutorship of Dr. Ricardo Santa-Maria Ramirez.

tars, as determined by Obara *et al.* (1981), or out of low-sulphur petroleum residues, as determined by Mochida *et al.* (1989).

Although the molecular composition of Waxy Oil is certainly different from that of better known needle coke precursors, certain molecular families (included in Waxy Oil) have previously been shown to increase the reactivity during the onset of carbonisation and tend to form mosaic microstructures at the bottom of the longitudinal plane of the green coke sample. These families include oxygenates, as determined by Dumont *et al.* (2005) and Sima *et al.* (2003), and multi-alkylated hydrocarbons, as determined by Guo *et al.* (2010). In contrast, thermally stable molecules react at higher temperatures within the carbonisation cycle, producing anisotropic coke towards the top of the coke section, as described by Mochida *et al.* (1989).

“Static” carbonisation thus shows the effect of these reactivity promoters (discussed in Chapter 7) in forming a layered microstructure with isotropic coke at the bottom of the test tube and anisotropic coke towards the top of the test tube.

8.3 Effect of catalyst removal on coke characteristics

8.3.1 Green and calcined coke yields of filtered and unfiltered Waxy Oil

The yields of green and calcined cokes from “static” test tube carbonisation and calcination of Samples A and B are shown in Table 8-1.

Table 8-1 Yield of green and calcined cokes from Samples A and B modified Waxy Oil

Experiment number	Sample	Residue yield (%) ¹	Green coke yield	Green coke yield	Calcined coke yield	Calcined coke yield
			(%) ¹	(%) ²	from green coke (%)	from Waxy Oil (%)
A	Unfiltered Waxy Oil	100	22.5	22.5	92.0	20.7
B	Filtered Waxy Oil	98.3	19.8	19.8	91.2	18.1

¹ Based on carbonisation residue feed

² Base on fresh Waxy Oil feed

The green coke yield of unfiltered Waxy Oil (Sample A) is slightly higher than that of filtered Waxy Oil (Sample B) which may be ascribed to both the influence of the catalyst and its propensity to increase the coke yield during carbonisation, as previously determined by Wang *et al.* (2001). The calcined coke yield (from green coke) is similar for both A and B. Due to the reactive nature, molecular composition and lower viscosity of Waxy Oil, the green coke yield is low compared with that of better known needle coke feedstocks. With the exception of Low Sulphur Vacuum Residue (23%), the yields of Waxy Oil green cokes are notably lower, e.g. FCCDO (40%) (Mochida *et al.*, 1989).

8.3.2 Macrostructure of Waxy Oil green cokes A and B

There is substantial evidence in the literature to show the effect of precursor molecular composition (specifically utilising co-carbonisation of feeds) on the micro- and macrostructure of green coke (Mochida *et al.*, 1989; Clark *et al.*, 2002). The effect of process conditions, including the introduction of a steam or nitrogen “chaser” on the macropore morphology, has previously been reported (Fu & Newman, 1989; Karacan & Badger, 2003) during dynamic or delayed coking.

To determine whether catalyst removal from Waxy Oil prior to carbonisation has an effect on the comparative macrostructure, photos at different height sections of the coke (formed in the test tube) were taken. A diagrammatic representation of the position of the photos taken in relation to the coke height is shown in Figure 8-1. The experimental procedure is described in Chapter 5, Section 5.3.3.1.

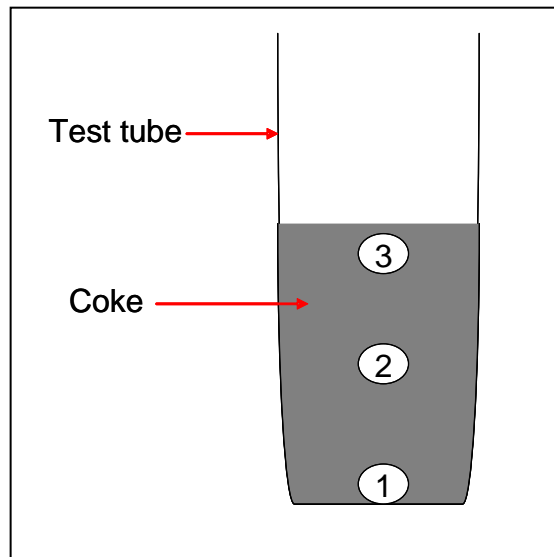


Figure 8-1 Diagram showing the height zones within the coke bed at which photos of the macrostructure were taken

Photos of the coke macrostructure were taken at the bottom (Position 1), middle (Position 2) and top (Position 3) of the coke tube.

The macromorphology of green coke A at the top, middle and bottom of the coke section are shown in Figure 8-2 (a–c) respectively and that of green coke B in Figure 8-2 (e–f) respectively.

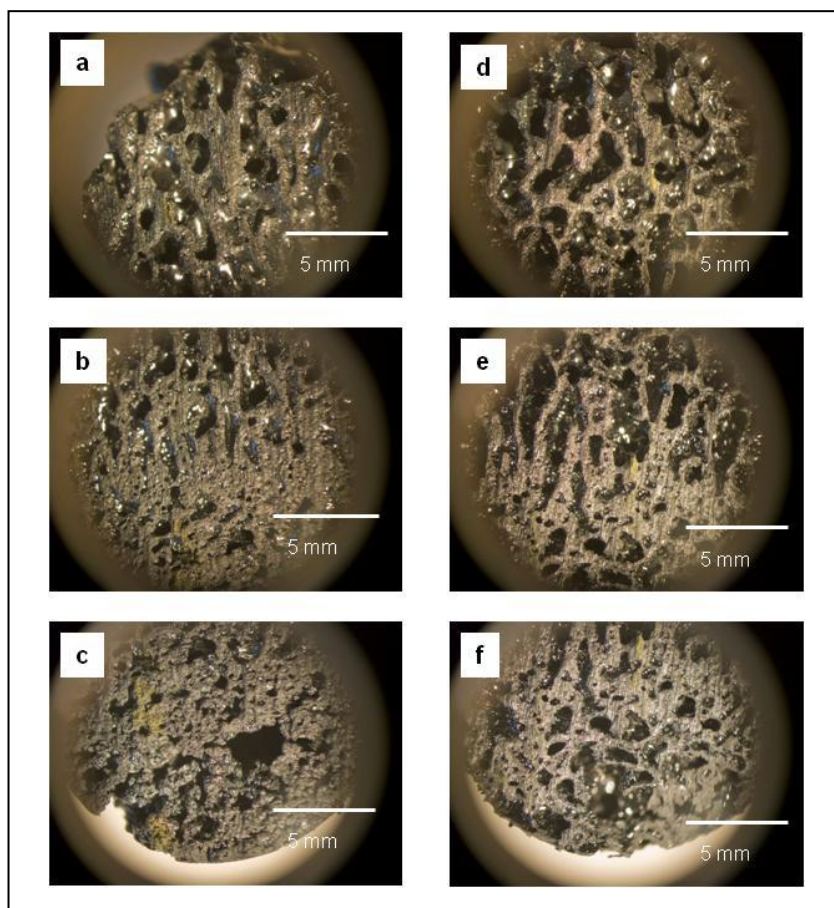


Figure 8-2 Macromorphology of green coke A at the top, middle and bottom of the coke section (a–c) respectively and of green coke B at the top, middle and bottom of the coke section (d–f) respectively

Comparing the macropore morphology of cokes A and B at the top of the coke section (Figures 8-2a and d); green coke B shows a minimal difference in visible macroporosity compared with its green coke A counterpart. The same is true for the middle sections of both green cokes (Figures 8-2b and e). At the bottom of the coke section, however, there is a discernable difference in the macrostructure of the cokes. Green coke A (Figure 8-2c) exhibits a macrostructure that resembles clusters of coke agglomerates, with a grainy texture loosely bonded together, reminiscent of shot coke formation. By contrast, the bottom section of green coke B (Figure 8-2e) shows macrodomain flow.

8.3.3 Optical microscopy of Waxy Oil green cokes A and B

Optical microscopy was used as the method of determining the relative degree of anisotropy through the height of the coke formed in the test tube. The optical micrographs presented **do not**, however, represent the quality of the coke that would be produced by delayed coking. As reactive molecules react to form semi-carbons at a lower temperature than thermally stable molecules, examination of a longitudinal section of the **whole piece of green coke (from bottom to top)** provides an indication of the overall reactivity of the feed from the green coke microstructure which deposits in horizontal layers. As the optical microscopic procedure is central to the determination of the coke microstructure, it is described (in full detail) below and a photo depicting an example of a longitudinal coke section is provided for reference in Figure 8-3.

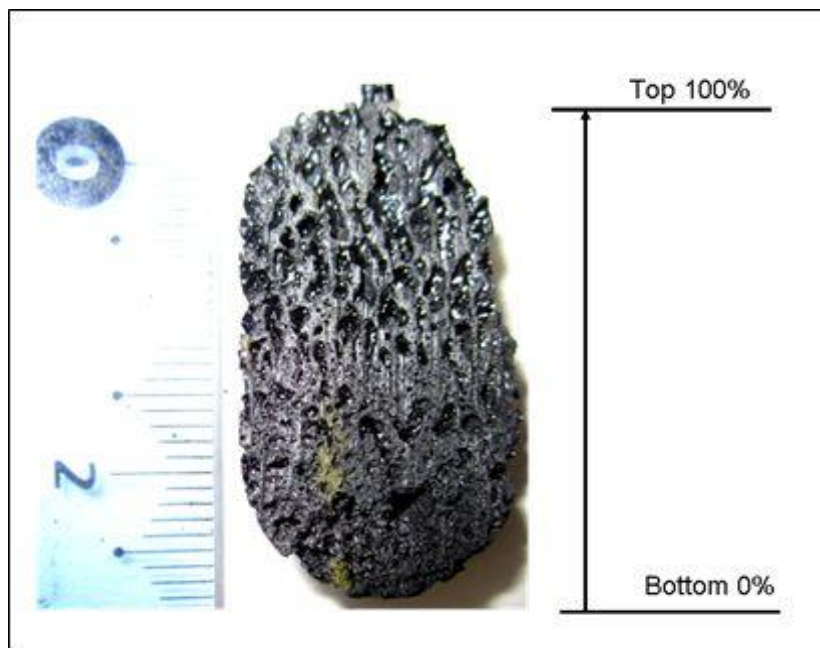


Figure 8-3 Photo of a longitudinal section of green coke

Optical microscopy was done using the longitudinal plane of the whole green coke particle which was mounted in epoxy resin using a Buehler mounting press (150 °C; 29 MPa; 15 min). It was conducted on polished samples using a Zeiss Axioplan microscope with a Liera DC100 monitor. Micrographs were taken of the coke particle from the bottom (0%) to the top (100%), as represented in Figure 8-3, using an automatic step counter every 14 μm along the length. Where the micrograph either contained totally mosaic microstructures or was a mixture of mosaic and flow domains, it was determined to be mosaic. Where the microstructure of the coke (towards the top of the coke section) contained only flow domains, it was determined to have a domain microstructure.

The relative height percentages of mosaic vs. domain flow microstructures for green cokes A and B are shown in Table 8-2.

Table 8-2 Percentages of mosaic vs. domain flow microstructures within a longitudinal section of green cokes A and B

Sample	Waxy Oil modification	Green coke	
		Microstructure	
		Mosaic (%)	Domain (%)
A	No modification	78	22
B	Filtered through 0.5 μm sieve	46	54

A comparison of the quantitative microstructural development of green cokes A and B (Table 8-2) shows that the removal of catalyst from Waxy Oil substantially reduces the height percentage of mosaic microstructures. The dominance of mosaic microstructures in green coke A (78%) is ascribed to the compound effect of the iron oxide catalyst and the thermal reactivity of Waxy Oil molecules. The iron-based catalyst promotes an increase in the height percentage of mosaic microstructures by two means: firstly as an inert barrier to mesophase

formation (specifically visible in Figure 8-5c), limiting the amount of hydrogen transfer, as described by Obara *et al.* (1985) and Menendez *et al.* (1997); and secondly by promoting catalytic dehydrogenation, as described by Wang *et al.* (2001).

Catalyst filtration (green coke B) removes one of the reactivity promoters, as evidenced by the reduction in the height percentage of mosaic microstructures to 46% (ascribed solely to the thermal instability of organic molecules in Waxy Oil) during carbonisation.

8.3.3.1 Optical microscopy of green coke A

Optical micrographs of the top and bottom sections of green coke A are shown in Figure 8-4. Figure 8-4a–c shows micrographs of green coke A at the **bottom** of the longitudinal section of coke with increasing magnification. Figure 8-4d–f shows micrographs of green coke A at the **top** of the longitudinal section of coke with increasing magnification.

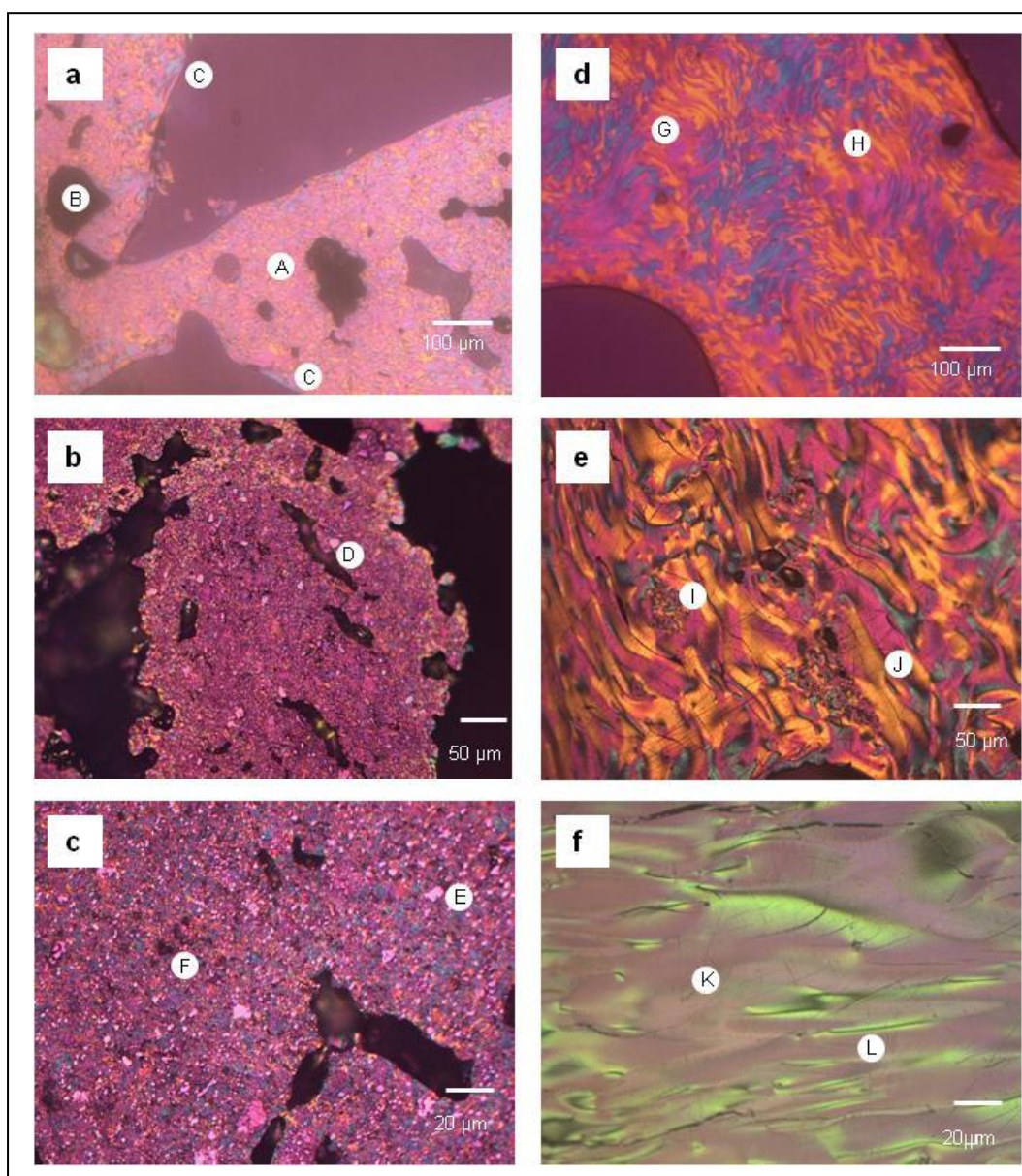


Figure 8-4 Optical micrographs of green coke A at the bottom (a–c) and top (d–f) of the coke section

At the bottom of the coke section, Figure 8-4a shows green coke A to have a fine to medium mosaic microstructure (Position A), with small areas of coarse flow domains (Position B) at the extinction contours of the pores, probably caused by shear forces (attributable to escaping gas) during solidification of the mesophase. There is also evidence of substantial porosity, as shown by Position B. At higher magnification (Figure 8-4b), green coke A displays a “grainy” texture composed of catalyst embedded in the mosaic carbon microstructure (Position D). At the highest magnification (Figure 8-4c), the variance in the size of the catalyst can be differentiated from fine (Position F) to over 6 μm (Position E) as shown by white areas.

The nomenclature used to differentiate between the mosaic and flow domain microstructures of Waxy Oil green coke in Chapter 8 is in accordance with that of Obara *et al.* (1981).

At the top of the coke section (Figure 8-4d), the microstructure is dominated by flow domains. These are composed of a collection of independent micro-domains (approximately 200 x 200 μm) surrounding Positions G and H. They are not axially orientated with one another. The lack of axial orientation (between micro-domains) at lower magnification is probably linked to the low shear rate which allows deformation due to the absence of a dominating flow vector, as previously described by Mochida *et al.* (1994). This is the result of “static” carbonisation. Obviously, as the magnification is increased (Figure 8-4e), the micrograph covers a smaller area and thus the degree of axial orientation appears greater. Also visible in the micrograph are smaller regions of mosaic microstructures (Position I) which are thought to be associated with agglomerations of very fine catalyst. However, the micrograph is dominated by flow domains of indeterminable length (Position J). At the highest magnification (Figure 8-4f), the microstructure of green coke A presents as flow domains (Position K) with uni-axial orientation. The pores (Position L) have a high aspect ratio and run parallel to the domain flow.

The formation of flow domains within the top section of green coke A shows the segregation of carbon microstructures even with the maximum reactivity promoters present during carbonisation.

8.3.4 Optical microscopy of green coke B

Optical micrographs of the top and bottom sections of green coke B are shown in Figure 8-5. Figure 8-5 (a–c) shows micrographs of green coke B at the **bottom** of the longitudinal section of coke with increasing magnification. Figure 8-5 (d–f) shows micrographs of green coke B at the **top** of the longitudinal section of coke with increasing magnification.

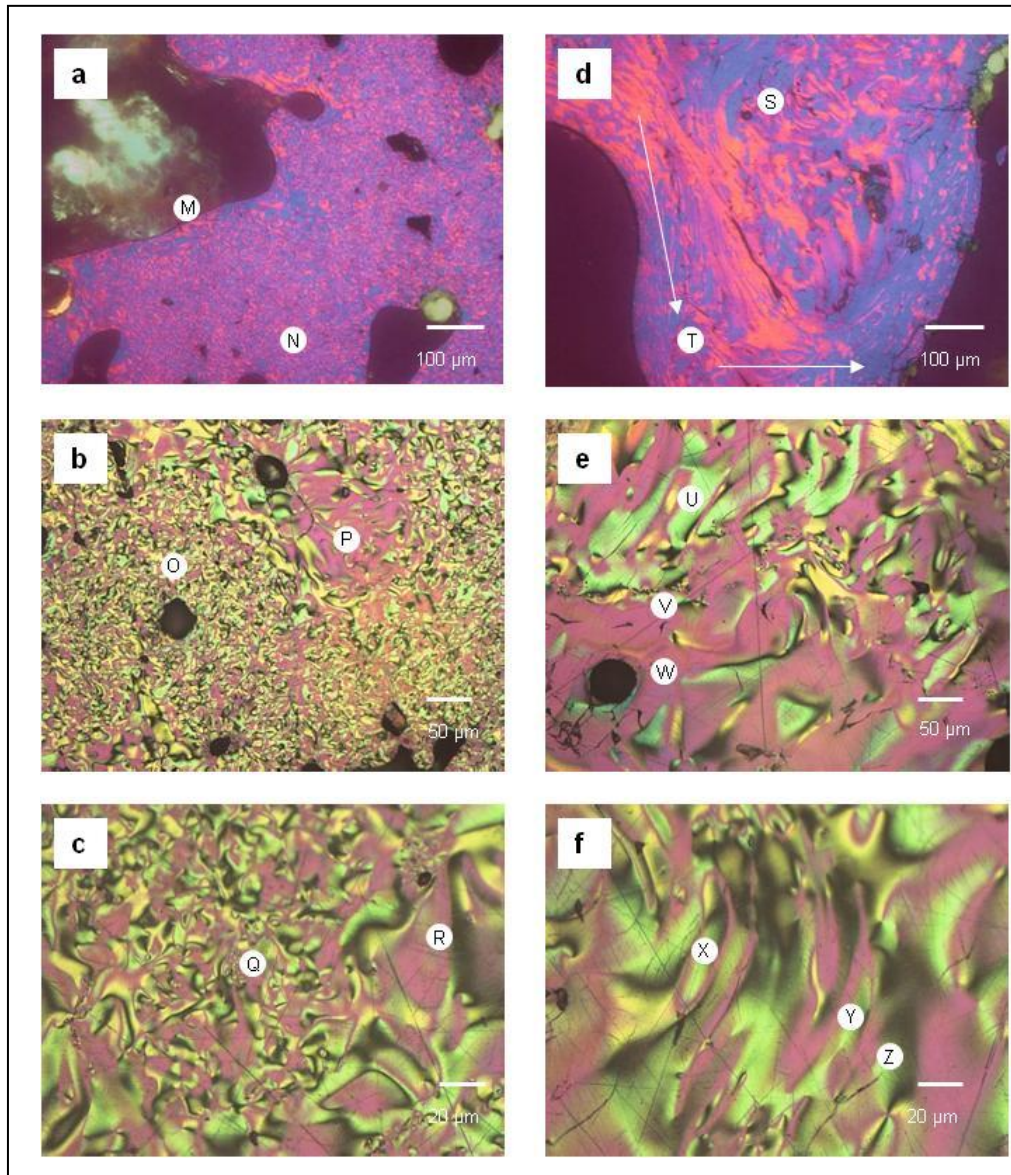


Figure 8-5 Optical micrographs of green coke B at the bottom (a–c) and top (d–f) of the coke section

Whereas the quantitative and qualitative effect of both the catalyst and thermally unstable organics during carbonisation have been established by the microstructure of green coke A, the microstructure of Sample B green coke largely eliminates the effect of the catalyst during carbonisation and therefore its effect on the microstructure.

At the lowest magnification at the bottom of green coke B (Figure 8-5a), the microstructure is a mixture of fine to coarse mosaics (Position N). Independent areas of flow domains (Position M) are evident at the extinction contour of the pores. In comparison with green coke A (Figure 8-4a), there is a notable increase in the frequency of these flow domains around the pores. At higher magnification (Figure 8-5b), the micrograph presents a heterogeneous assembly of microstructural domains of both coarse flow (Position P) and fine to medium mosaics (Position O). At the highest magnification (Figure 8-5c), the most notable omission compared with green coke A (Figure 8-5c) is the catalyst. Again the microstructure shows flow domains (Position R) and more isotropic coarse mosaic microstructures (Position Q).

At the lowest magnification at the top of green coke B (Figure 8-5d), the microstructure is dominated by flow domains of indeterminable length, either straight (Position T) or with a curved geometry (Position S). At higher magnification, the top section of green coke B (Figure 8-5e) shows a general axial flow orientation from the top right to the bottom left of the micrograph (Position U) interspersed with pores which, although possessing a high aspect ratio (Position V), are perpendicular to the flow domain. Of interest is Position W where the domain flow is concentric around a small transverse pore.

The higher reactivity of the molecular composition of Sample B is similar to that reported by Martinez-Escandell *et al.* (1999) who found the formation of very small spheres in the early stages of mesophase development, leading to the formation of coarse mosaics when highly aliphatic vacuum residues were carbonised without prior thermal stabilisation (as seen at the bottom of the coke section).

8.3.4.1 Value of microstructural classification of green cokes A and B

The microstructure of green cokes A and B has been discussed in detail, but their exact classification is perhaps of less importance than the trend that they show. The concept of “reactivity promoters” is defined in this thesis as any compositional characteristic of the Waxy Oil that increases the carbonisation temperature range (by decreasing the temperature at which carbonisation is initiated), increasing the reactivity of the whole system.

Sample A has two reactivity promoters (the iron oxide and the thermal instability of the Waxy Oil organic molecules), while Sample B has one reactivity promoter (the thermal instability of the Waxy Oil organic molecules). However, both Samples A and B are composed of a percentage of thermally stable alkanes which form domains within the higher carbonisation temperature range and are clearly distinguished from the mosaics which form at lower temperatures, falling to the bottom of the test tube due to their increased density. It is this characteristic of Waxy Oil “static” carbonisation that allows the quantitative differentiation of the microstructure based on the height of the green coke section as reported in Table 8-2. The same procedure is used to differentiate between the organic modifications of Waxy Oil, reported in later in Section 8.4.

8.3.5 Analysis of calcined cokes A and B

8.3.5.1 EDX of Waxy Oil Sample A calcined coke

The EDX of Sample A green coke is shown in Figure 8-6.

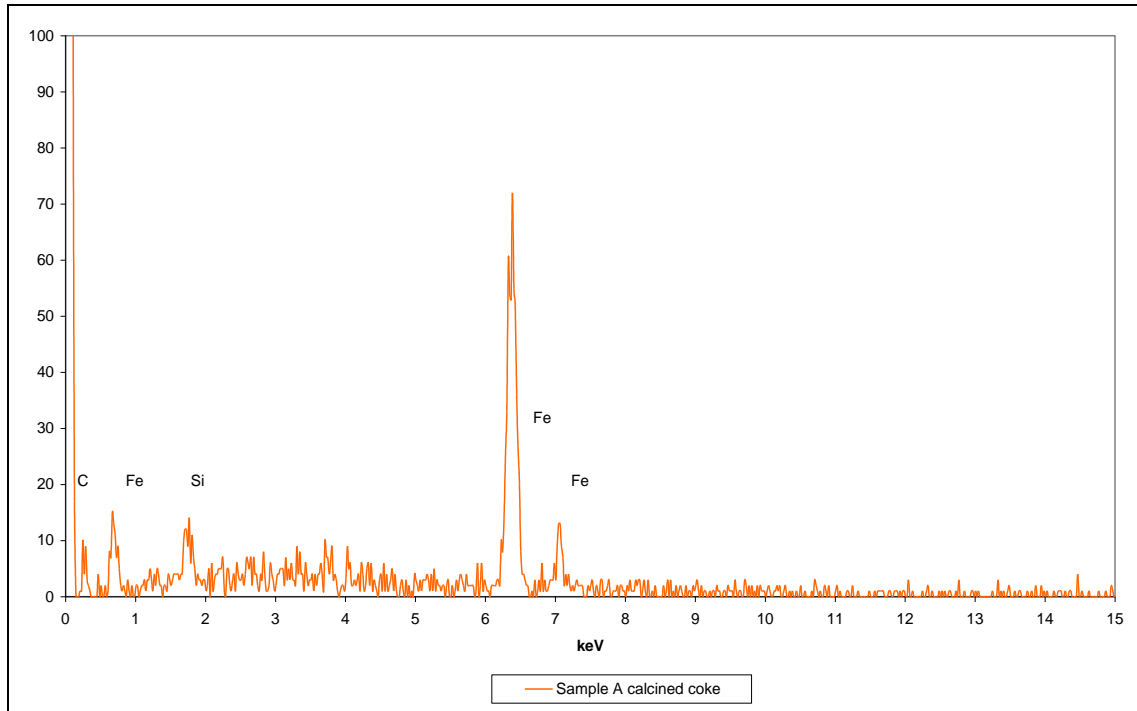


Figure 8-6 EDX of Sample A Waxy Oil calcined coke

Figure 8-6 shows that the mineral composition of the lower portion of calcined coke A is dominated by iron (at approximately 6.5 and 7.1 keV). Another mineral at lower intensity is silicon (approximately 1.7 keV).

8.3.5.2 Scanning Electron Microscopy of Waxy Oil calcined cokes A and B

Scanning Electron Microscopy (SEM) was conducted down a longitudinal section on both Samples A and B calcined coke. The same numbering system used in Figure 8-1, namely Positions 1, 2 and 3, was utilised.

SEM images of Sample A calcined coke at Position 1 are shown in Figure 8-7.

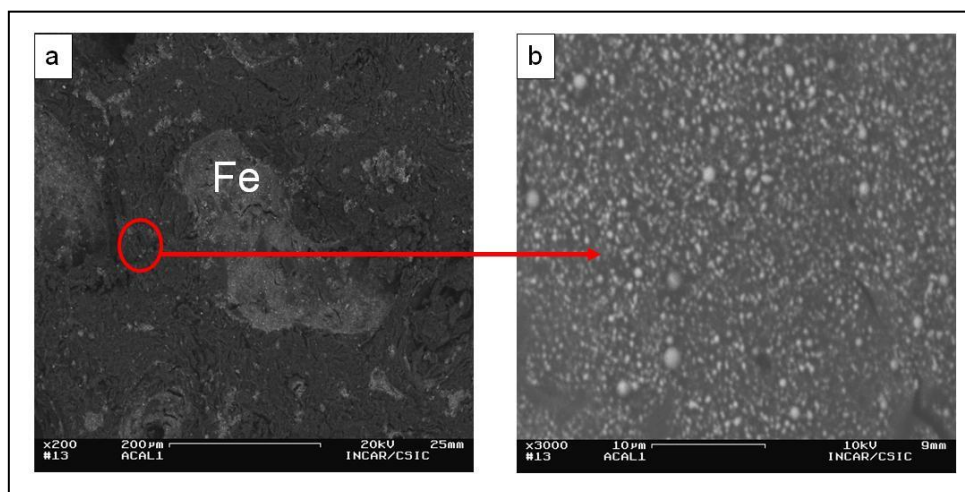


Figure 8-7 Scanning electron micrographs of Sample A calcined coke at Position 1 (bottom) with increasing magnification from (a) to (b)

Figure 8-7 (a) shows agglomerates of catalyst particles of various sizes (the largest being approximately 300 μm in length and 50 μm in width) visible at low magnification in Position 1 (bottom) of Sample A calcined coke, indicated by the lighter shade of grey. However, shown in Figure 8-7b is a region of the coke at higher magnification showing the frequency of smaller catalyst particles (less than 10 μm) embedded in the carbon microstructure.

SEM images of Sample B calcined coke are shown in Figure 8-8 (Position 1) at the bottom of the coke section.

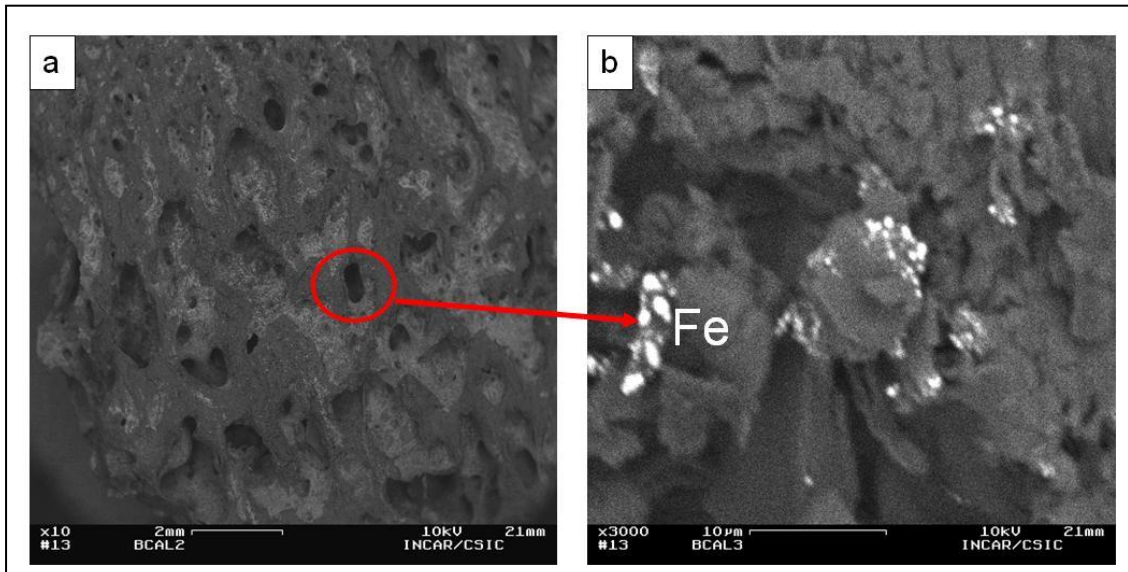


Figure 8-8 Scanning electron micrographs of Sample B calcined coke at Position 1 (a) and (b)

Figure 8-8a shows a substantially lower amount of iron (especially higher PSD particles) with lower agglomeration sizes at lower magnification. At higher magnification, Figure 8-8b shows sparsely populated agglomerates of smaller catalyst particles (appearing as white areas), but far fewer than shown for calcined coke A (Figure 8-7b).

8.3.6 Raman spectroscopy of Waxy Oil calcined cokes

Raman spectroscopy was conducted on samples of calcined coke A and B at various height positions along the longitudinal plane of the piece of coke (as previously defined in Figure 8-1). The degree of disorder was estimated from the relationship $I_D:I_T$, where I_D corresponds to the intensity of the D band (1350 cm^{-1}) and I_T corresponds to the total intensity of all first-order region bands (D, G, D' at 1350 , 1580 and 1620 cm^{-1} respectively). The $I_D:I_T$ ratio is shown as an insert to Figures 8-9, 8-10 and 8-11.

A comparison of the bottom zone of calcined cokes A and B is shown in Figure 8-9.

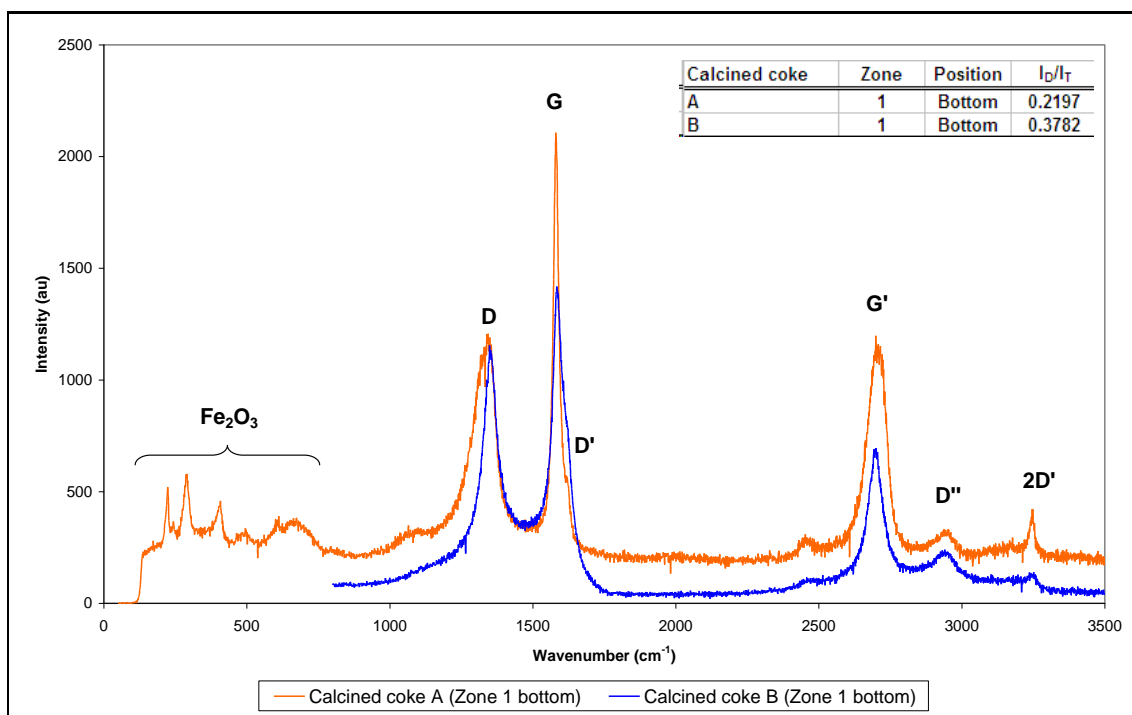


Figure 8-9 Raman spectroscopy trace of calcined coke A (zone 1 bottom) vs. calcined coke B (zone 1 bottom)

The bottom part of calcined coke A shows evidence of the iron catalyst at lower wave numbers ($100\text{--}750\text{ cm}^{-1}$) which is absent in calcined coke B. Furthermore, calcined coke A shows well-defined first- and second-order spectra with a high degree of order. The second-order spectrum for calcined coke B is less defined. In terms of the degree of order (shown as an insert to Figure 8-9), calcined coke A is substantially more ordered than calcined coke B. Although both samples possess a mosaic microstructure at the bottom of the coke, calcined coke A has a high iron concentration. The graphitisation mechanism is consequently dominated by catalysis forming relatively pure graphite, therefore on average increasing the order compared with calcined coke B with little or no catalyst.

In order to evaluate the structural order through the height of **calcined coke A**, the spectra obtained from the bottom, middle and top zones of the coke are shown in Figure 8-10.

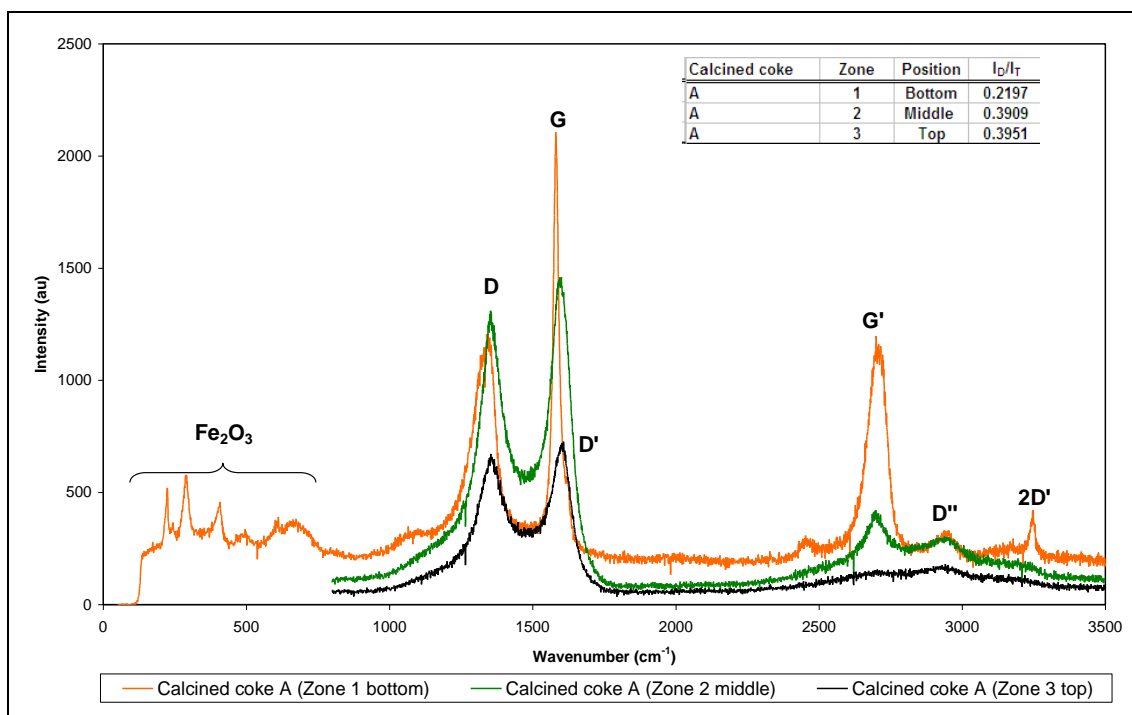


Figure 8-10 Raman spectroscopy trace of calcined coke A (zone 1 bottom), zone 2 (middle) and zone 3 (top)

The second-order spectrum of the middle (zone 2) and top (zone 3) of calcined coke A is less well defined as the catalyst concentration within these zones is lower than in the bottom of the coke (zone 1). The degree of order (shown as an insert to Figure 8-10) shows that the effect of catalytic graphitisation is severely diminished in zones 2 and 3 due to the catalyst gravitating towards the bottom of the test tube (zone 1) during the initial heating phase of carbonisation. A comparison between zones 2 and 3 is perhaps confusing as the effects of both catalytic graphitisation and crystal order development as a function of thermal treatment (and depending on the anisotropy of the microstructure) need to be considered. From the micrographs (Figure 8-4d–f) and the quantitative analysis of microstructural anisotropy (Table 8-2) it is clear that flow domains preside at the top of calcined coke A, while in the middle the microstructure is more isotropic. However, in the middle there is more likely to be fine catalyst which influences the degree of order. Thus it is more correct to make a comparison only between zone (1) and zones (2 and 3).

In order to evaluate the structural order through the height of calcined coke B, the spectra obtained from the bottom, middle and top zones of the coke are shown in Figure 8-11.

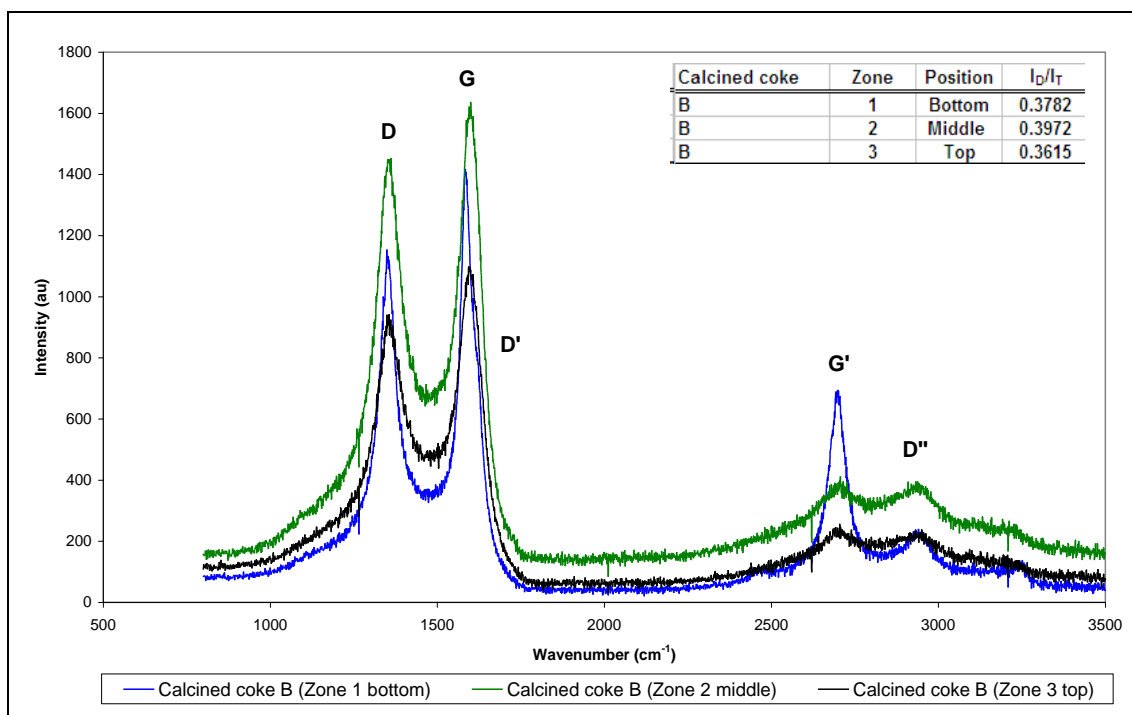


Figure 8-11 Raman spectroscopy trace of calcined coke A (zone 1 bottom), zone 2 (middle) and zone 3 (top)

Within the bottom section (zone 1) of calcined coke B there is SEM evidence of a miniscule amount of catalyst (Figure 8-8b), at least when compared with calcined coke A (Figure 8-7b). While microstructurally both the bottom (zone 1) and middle (zone 2) have a mosaic microstructure, based on a comparison of the micrographs there do appear to be isolated areas of domain flow within the middle section. So although from a microstructural analysis the Raman order should be higher in the middle section, it is not. Even the miniscule amount of catalyst in the bottom section, which from the SEM would appear insignificant, promotes catalytic graphitisation and therefore, on average, the order is higher. Comparison of zone 2 (middle) with zone 3 (top) is the only comparison where the effect of the catalyst can be discounted; the higher order reported for zone 3 (top) is based on its greater anisotropy and hence the higher Raman order due to thermal graphitisation.

8.3.7 Carboxy (CO₂) reactivity of Waxy Oil calcined cokes

Samples of Waxy Oil calcined coke (-200 μm) were heated in a thermogravimetric analyser to 1 000 °C (10 °C.min⁻¹) with continued isothermal conditions for 1 h in the presence of carbon dioxide (150 ml.min⁻¹) and nitrogen (150 ml.min⁻¹). The carboxy reactivity profile was determined for calcined cokes A and B. The graph of the TGA reactivity profiles is shown in Figure 8-12 and the DTG reactivity profiles in Figure 8-13.

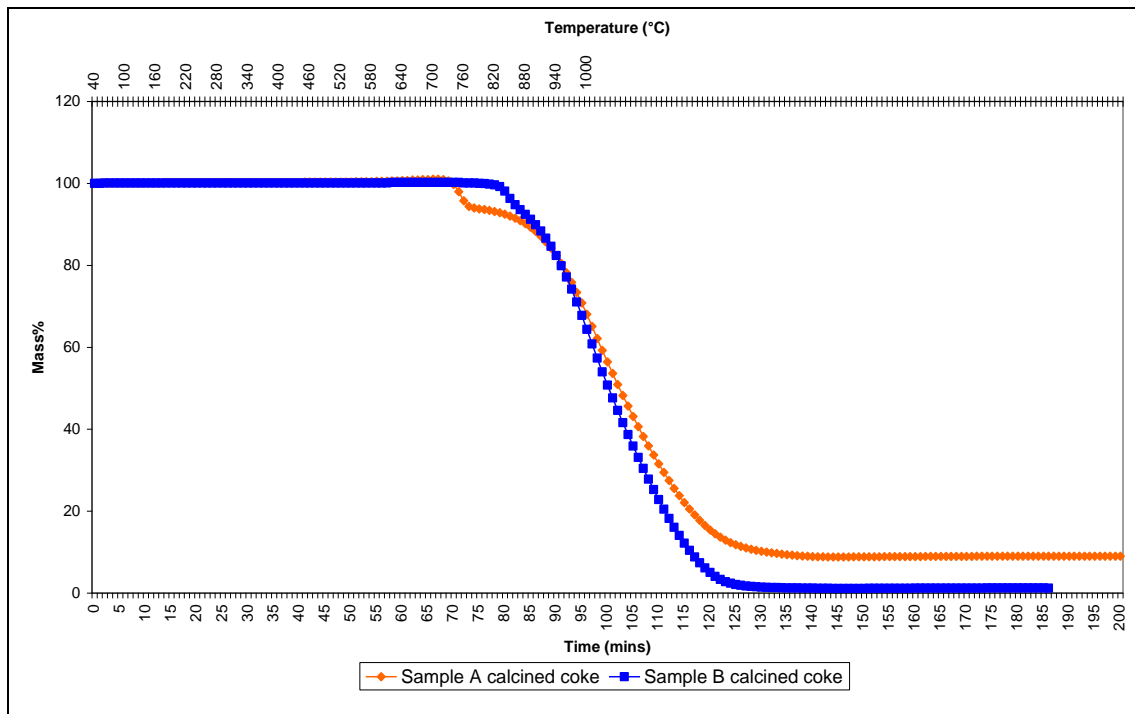


Figure 8-12 TGA carboxy (CO₂) reactivity profile of calcined cokes A and B

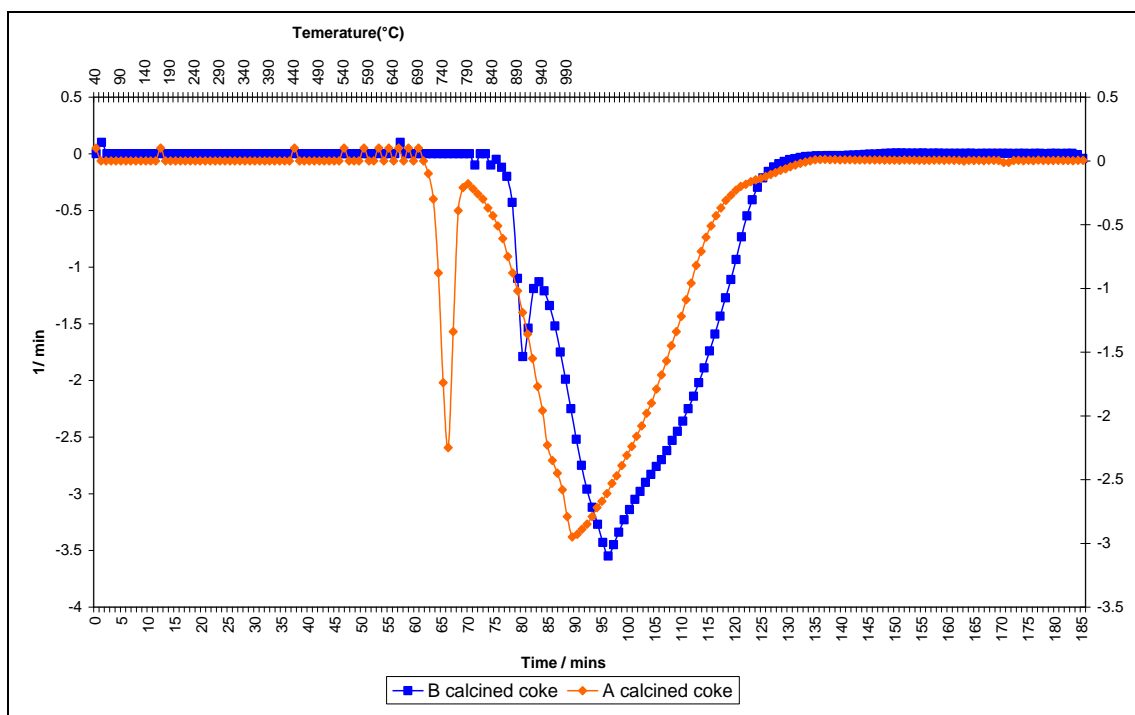


Figure 8-13 DTG carboxy (CO₂) reactivity profile of calcined cokes A and B

In general, Sample A shows a mass loss of approximately 10% initiated at a temperature of 730 °C (Figure 8-12). Further substantial mass loss is then only evident at 860 °C. The residuum of calcined coke A is approximately 10%. The initial mass loss for Sample B (Figure 8-12) occurs at a higher temperature (850 °C). However, the next gradient of mass loss is steeper than for calcined coke A. The residuum of calcined coked B is negligible.

It is convenient to calculate the reactivity in two ranges, i.e. **before 1 000 °C** and **after 1 000 °C under isothermal conditions**.

As shown in Figure 8-12, the mass loss from calcined coke A is in a window of 270 °C (between 730 and 1 000 °C; 32.6% mass loss), while the mass loss window for calcined coke B is 210 °C (between 790 and 1 000 °C; 36.0% mass loss).

As shown in Figure 8-12, the second mass loss range of calcined coke A at isothermal conditions is in a time window of 43 min (between 96 and 143 min; 59.05%) until a stable residuum mass is attained, while that of calcined coke B is in a time window of 47 min (between 96 and 143 min; 63.2%) until a stable residuum mass is attained. The mass loss rates for calcined cokes A and B are similar (1.37 and 1.34%.min⁻¹ respectively). In summary, the initial DTG reactivity peak for calcined coke A (Figure 9-13) is probably enhanced by iron catalysis compared with the lower-intensity initial peak at a higher temperature for calcined coke B.

8.3.8 Air reactivity of Waxy Oil calcined cokes

Samples of Waxy Oil calcined coke (-200 µm) were heated in a thermogravimetric analyser to 1 000 °C with an air flow of 150 ml.min⁻¹ and a nitrogen flow of 150 ml.min⁻¹. The air reactivity profile was determined for the calcined cokes A and B. The graph of the TGA reactivity profiles is shown in Figure 8-14 and the DTG reactivity profiles in Figure 8-15.

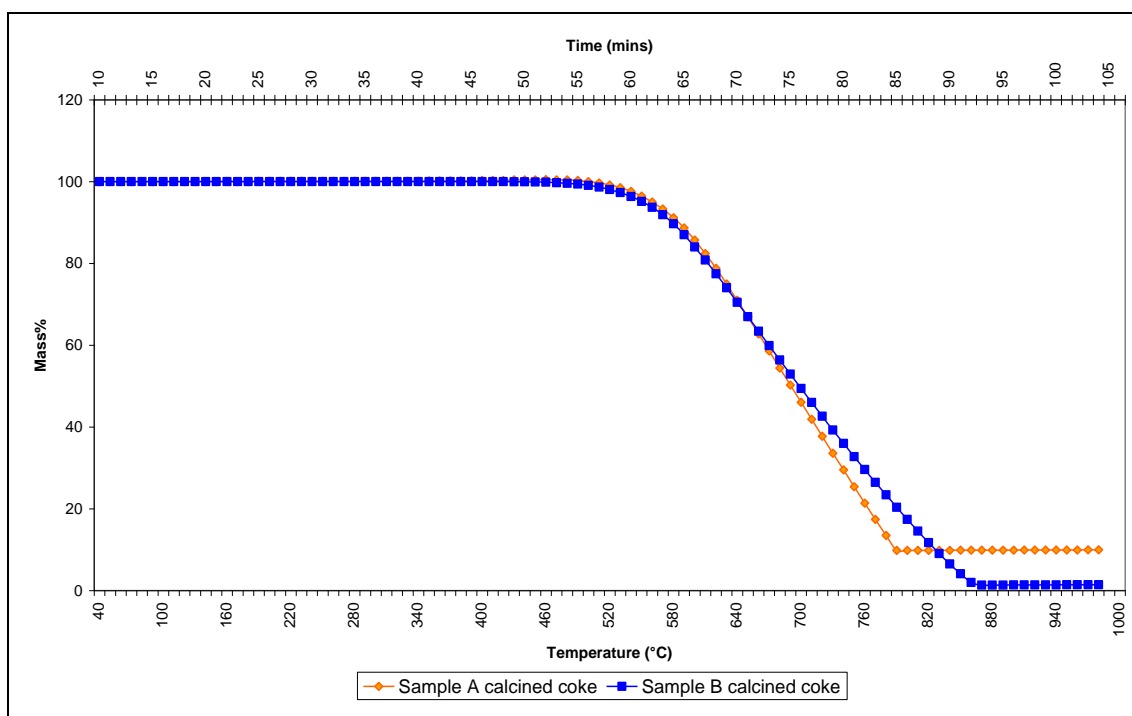


Figure 8-14 TGA air reactivity profile of calcined cokes A and B

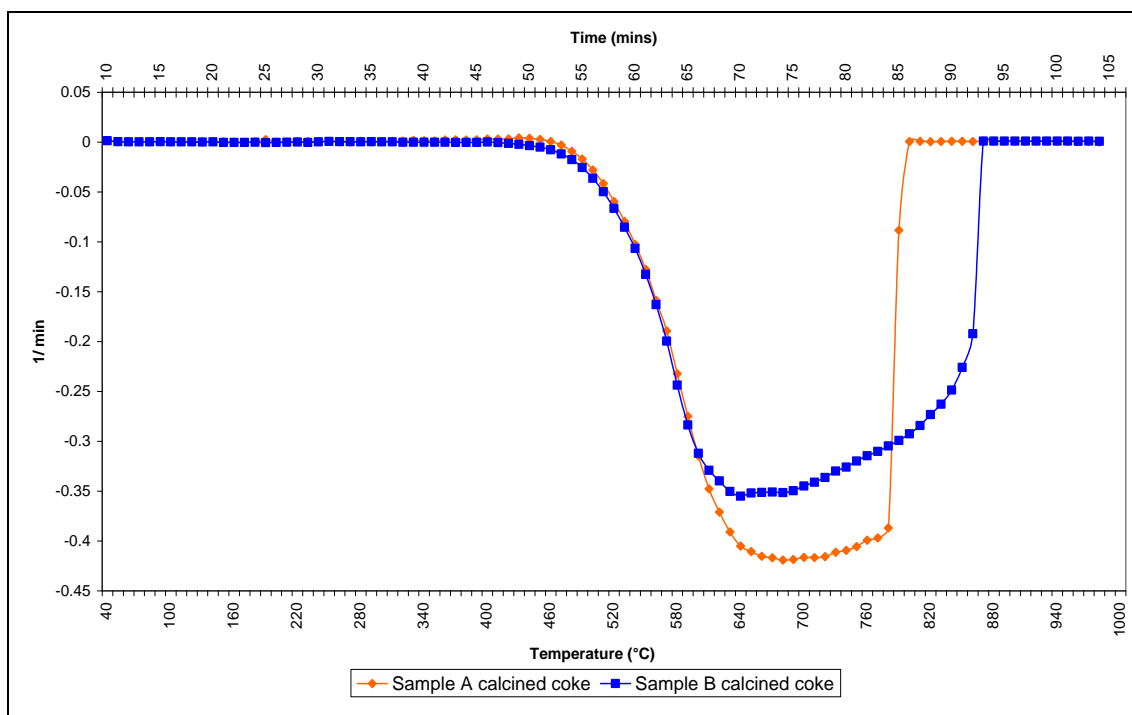


Figure 8-15 DTG air reactivity profile of calcined cokes A and B

As shown in Figure 8-14, calcined coke A shows an initial slight mass increase between 400 and 490 °C, which is probably due to the oxidation of iron. Calcined coke A shows an oxidation window of 290 °C (between 500 and 790 °C), whereas calcined coke B has a larger oxidation temperature window of 460 °C (between 410 and 870 °C). The reactivity profile of both samples (from onset of mass loss to equilibrium) indicates that the reactivity of calcined coke A ($0.31\% \cdot ^\circ\text{C}^{-1}$) is slightly higher than of calcined coke B ($0.21\% \cdot ^\circ\text{C}^{-1}$). The higher stable residual mass of calcined coke A is accounted for mainly by the higher catalyst content.

The DTG analysis of the reactivity profiles shown in Figure 8-15 indicates a similar initial reaction rate for both calcined cokes A and B, between 450 and 600 °C, which indicates that the iron does not catalyse an increase in the reactivity of calcined coke A in this temperature range.

8.3.9 The difference in the profiles of air and carboxy reactivity

As determined in Chapter 6, calcination induces a substantial reduction of iron oxide to elemental iron, which has previously been described as a good catalyst for both carboxy and air reactivity.

In carbon dioxide, minimal oxidation of the catalyst would occur so the sharp mass loss peak is attributed to iron catalysis. In air, the elemental iron portion of the catalyst is slowly re-oxidised as the temperature increases, which may account for the absence of a sharp peak as seen for the carboxy reactivity since iron oxide is a poor catalyst for both reactivities.

8.4 The effect of molecular modification of Waxy Oil on green coke microstructure and yield

8.4.1 Waxy Oil green coke yield and quantitative optical microscopy

The green coke yield and quantitative microscopic analysis of the carbonisation of Samples C1, C2, D1, D3, D4, E2 and E1b are shown in Table 8-3.

Table 8-3 Green coke yield and quantitative optical microscopic analysis of carbonised samples of distilled and thermally treated, filtered Waxy Oil

Sample	Waxy Oil modification	Residue yield (%) ²	Green coke			
			Yield ¹ (%)	Yield ² (%)	Microstructure ³	
					Mosaic (%)	Domain (%)
C1	Sample B distilled (480 °C at -0.9 kPa)	87.0	21.9	26.0	41	59
C2	Sample B distilled (440 °C at -0.9 kPa)	94.3	20.8	22.0	50	50
D1	Sample B thermally treated (400 °C, 5 bar, 2 h)	73.1	19.7	27.0	38	62
D3	Sample B thermally treated (410 °C, 5 bar, 2 h)	58.7	17.5	29.8	36	64
D4	Sample B thermally treated (420 °C, 5 bar, 2 h)	49.6	15.2	30.6	36	64
E2	Sample B thermally treated (410 °C, 5 bar, 1 h at 5 bar and 1 h at 1 bar)	45.2	14.9	32.9	22	78
E1b	Sample B thermally treated (410 °C, 5 bar, 2 h, distilled to 325 °C under nitrogen)	43.0	15.5	36.3	0	100

1 Based on carbonisation residue feed

2 Based on fresh Waxy Oil feed

3 The percentage of the flow domain and isotropic areas of the micrographs are representative of the middle of the coke section and the left and right adjacent to the Pyrex glass tube

Before the effect of the modifications on the green coke yield **based on the residue** is determined, it is important that it is initially determined **based on the fresh Waxy Oil feed** (iron free). The green coke yield of the carbonisation of the two distilled samples (C1 and C2) is similar to that of Sample B. Thereafter there is a decreasing green coke yield (based on fresh Waxy Oil feed) as the temperature increases and the pressure of the modification temperatures is reduced. This is not unexpected as when the thermal treatment temperature increases and the pressure drops, lighter molecules are produced and, secondly, report to the

distillate fraction. The discussion of the effect of Waxy Oil pre-carbonisation modification on the green coke yield (discussed below) is **based on the residue and not the fresh feed**.

The distillation of filtered Waxy Oil to 440 °C (Sample C2) produced a green coke with approximately the same yield as that of the filtered Waxy Oil (Sample B). This is not unexpected as only 5% of the mass was removed. Sample C1 produced a green coke with a slightly higher yield, which can be ascribed to the mild thermal treatment conditions and removal of lighter cracked hydrocarbons. This is evident in the lower residue mass. The green coke yield for the thermal treatments at 5 bar indicates that as the temperature is increased (producing lighter distillates), the residue is reduced and so the carbon residuum yield increases.

The experiment aimed at removing lighter cracked hydrocarbons from the residue (Sample E2) by reducing the pressure during thermal treatment resulted in an increase in the green coke yield.

Sample E1a was not subjected to “static” carbonisation but rather was distilled under nitrogen to effect complete removal of the lighter cracked hydrocarbons in the residue. Thus it is not surprising that the residue percentage relative to the Waxy Oil is reduced whereas the green coke yield of Sample E1b increases to 36.3%. The yield of Sample E1b is similar to those obtained from the pyrolysis and distillation of a highly aliphatic vacuum residue, as reported by Martinez-Escandell *et al.* (1999) who determined coke yields of between 30 and 40%.

Thus, while it is possible to increase the green coke yield of filtered Waxy Oil from 22.0% to 36.3%, the yield is still comparatively low compared with residues with a greater aromaticity, as described by Mochida *et al.* (1989) and Marsh *et al.* (1999). Although Fanjul *et al.* (2002) used air blowing to increase the carbonisation yield and Wang *et al.* (2001) achieved the same by the addition of iron oxide, both of these methods also decrease the anisotropy of the coke and are thus not viable for this study.

Another possible method would be to conduct the carbonisation at a lower temperature, as previously reported by Eser *et al.* (1989). However, all the cited literature refers to highly aromatic feeds. Waxy Oil, being a highly aliphatic feedstock, is subject to cracking reactions (even of thermally stable molecules) at carbonisation temperatures. Historically, the cited literature (Sangrama *et al.*, 2010; He *et al.*, 2003) using long-chain paraffins as a feed has been dedicated to the formation of lower molecular weight alkenes from higher molecular weight normal alkanes. It is therefore suggested that lower carbonisation temperatures may not completely effect aromatisation of the normal alkanes and thus promote polymerisation of the alkenes.

Samples C1 and C2 modified Waxy Oils are clearly very different (in terms of their respective concentrations of both alkylated and pure aliphatic/aromatic molecules, as described in Chapter 7, Section 7.2). The quantitative comparison of their microstructure (Table 8-3) indicates that while C1 green coke does show a marginal improvement in the height percentage of domain flow (59 vs. 50% for C1 and C2 green cokes respectively), there is still a substantial percentage of carbon at the bottom of the coke section with a mosaic microstructure. One similar characteristic both these modified Waxy Oils share is the relatively high concentration of oxygenates [Sample C1 (10.34%) and Sample C2 (11.05%)], which may explain the height percentage of mosaic microstructures (41–50%).

Thermal treatment at 5 bar pressure between 400 and 420 °C did increase the relative percentage of domain microstructures [D1, D3 and D4 (62–64%) respectively] in comparison with the distillation experiments. However, there was no specific conclusive evidence to suggest a substantial influence of thermal treatment temperature (within this group of samples) on the microstructure. As discussed in Chapter 7, Section 7.2.4, thermal treatment does substantially reduce the effect of two of the reactivity promoters, namely oxygenates and multi-alkylated alkanes, and thus the increase in the overall anisotropy of the green coke is validated. As there is still a substantial percentage of mosaic microstructures (36–38%) within these three cokes, it is concluded that the lighter hydrocarbons remaining in Samples D1–D4 act as reactivity promoters, as discussed in Chapter 7, Section 7.2.4.

Reducing the pressure during thermal treatment removes much of the lighter hydrocarbons from the residue (Sample E2). This increases the degree of anisotropy to 78%. Distillation of the residue after thermal treatment at 410 °C removes the great majority of lighter hydrocarbons from the pre-carbonisation residue. The microstructural anisotropy of green coke E1b consequently increases to 100% domain flow. The microstructural analysis of green coke E1b is discussed in greater detail below.

8.4.2 Optical microscopy of Waxy Oil green coke E1b

Although a microstructural classification of all the green cokes was conducted (in order to determine the relative quantitative anisotropy listed in Table 8-3), it would be of little benefit to describe the micrographs in detail (as was done for green cokes A and B) as they all show similar isotropic microstructures towards the bottom of the coke section and anisotropic microstructures towards the top of the coke section. The only variance is the height percentage at which there is a change in the morphology of the microstructure.

However, as the aim of this study is to increase the anisotropy of the green coke and it is reported that green coke E1b is composed solely of flow domains, a comparative microstructural description between the bottom and top of the coke section is provided in Figure 8-16. Figure 8-16 (a) shows the microstructure of green coke E1b at the bottom of the coke section, while Figure 8-16 (b) is also a micrograph of the bottom section of green coke E1b, just at a higher magnification. Figures 8-16 (c and d) show micrographs of the top section of green coke E1b.

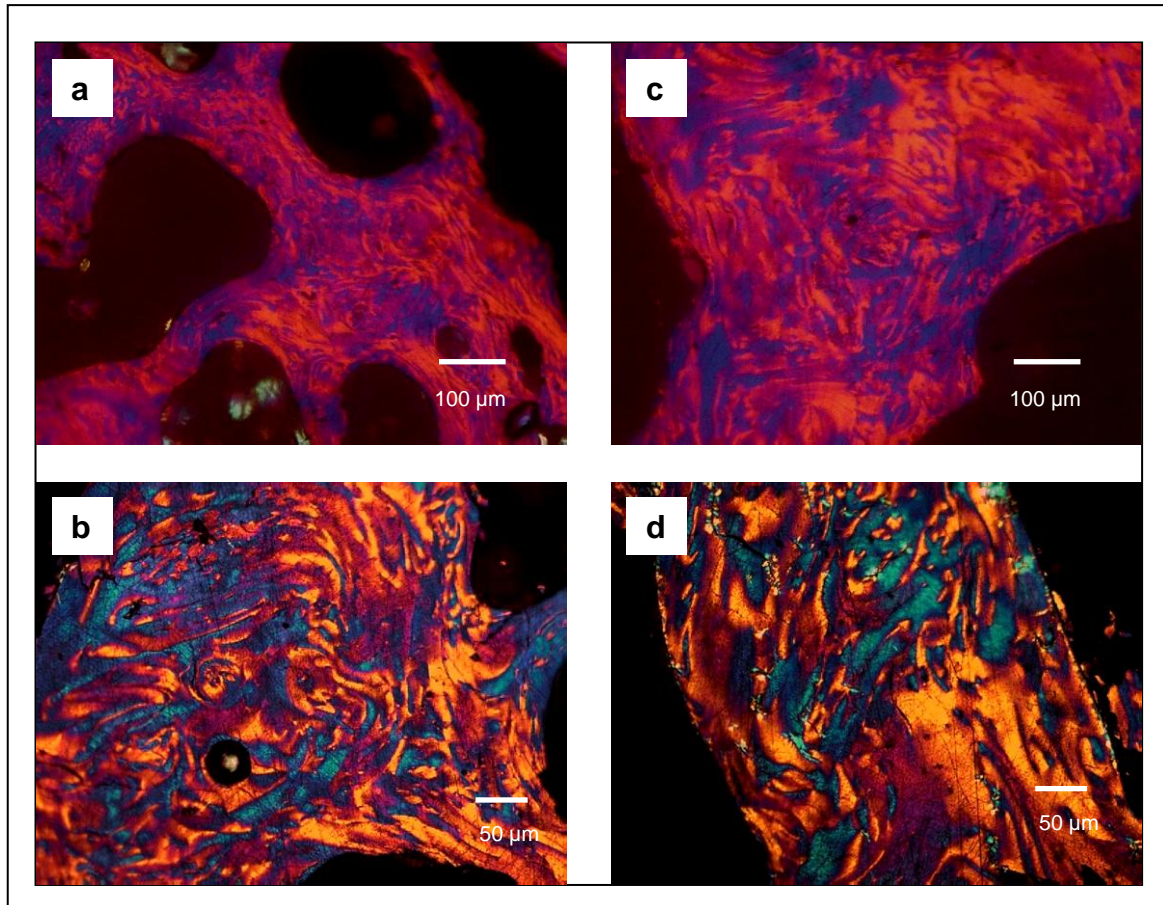


Figure 8-16 Optical micrographs of the bottom (a–b) and top (c–d) sections of green coke E1b

As has been observed in the preceding micrographs of green cokes A and B (Figures 8-4 and 8-5 respectively), the more reactive species form mosaic coke at the bottom of the coke section and with an increase in height the microstructure becomes all the more anisotropic.

Thus it is interesting to note that micrographs taken of the bottom (Figure 8-16a) and top (Figure 8-16c) of E1b green coke have a similar domain flow microstructure. One notable difference is that at the bottom of E1b there appears to be a greater porosity, which dictates the flow vector of the domains. The similarity in the microstructure is also evident when micrographs of the top (Figure 8-16b) and bottom (Figure 8-16 (d)) of green coke E1b are compared at higher magnification.

The micrographs of green coke E1b at the bottom of the coke section (0%) and at the top (100%) shown above in Figure 8-16a–d have flow domain microstructures. A series of micrographs showing the microstructure of green coke E1b through the longitudinal height section of the coke is shown in Figure 8-17a–d, in accordance with a similar procedure described by Mochida *et al.* (1989) when examining the effect of co-carbonising blends of LSVR and FCCDO.

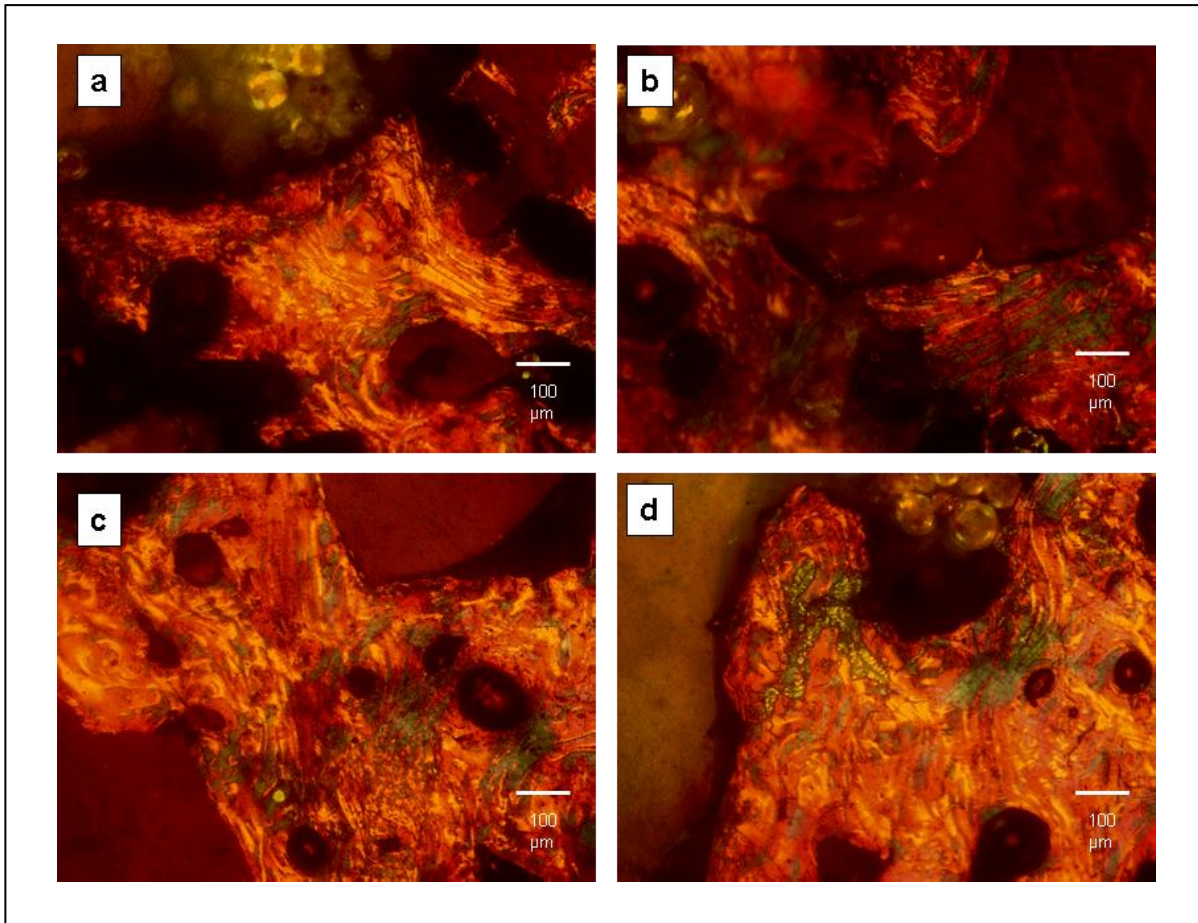


Figure 8-17 Series of micrographs of green coke E1b with increasing height percentage: (a) 13%; (b) 30%; (c) 60%; and (d) 80%

Throughout the height percentage of green coke E1b, the dominating microstructure is one of flow domains. However, what is evident is the substantial porosity in all of the micrographs (Figure 8-17a–d).

The necessity for stabilising Waxy Oil for the production of anisotropic coke has been demonstrated above. However, it must be realised that not all residues need to undergo this intermediate reaction. Generally, the more aromatic a residue (without asphaltenes), the greater the ease with which the self-assembly of mesogens occurs, leading to an anisotropic mesophase. This is substantiated by the difference in the carbonisation mechanisms of aromatic and aliphatic feeds described by Torregrosa-Rodriguez *et al.* (2000).

8.4.3 Macrostructure of Waxy Oil green cokes B and E1b

The macromorphology of green coke E1b at the top, middle and bottom of the coke bed is shown in Figure 8-18a–c respectively. The macromorphology of green coke B at the top, middle and bottom of the coke bed is shown in Figure 8-18e–f respectively. Green coke B is shown for comparison.

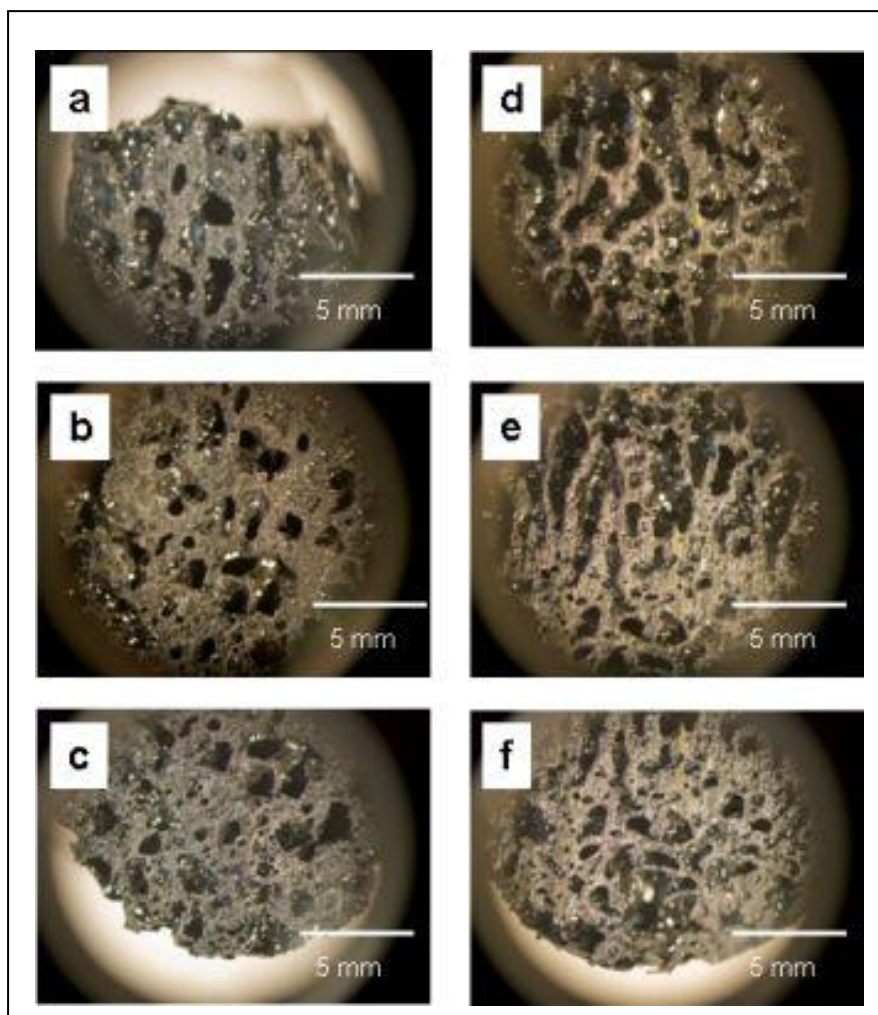


Figure 8-18 Macromorphology of green coke E1b at the top, middle and bottom of the coke bed (a–c) respectively and macro-morphology of green coke B at the top, middle and bottom of the coke bed (e–f) respectively

Green coke B is compared with green coke E1b to determine the difference of the most effective Waxy Oil modification (Sample E1b) against no molecular modification (Sample B).

In comparison with green coke B (Figure 8-18d–f), all the height sections of E1b (Figure 8-18a–c) contain similar visible porosity.

In Chapter 6 (Figures 6-1 to 6-4) the macromorphology of the pores (at least in one of the planes) did show a greater aspect ratio than Sample E1b. The aforementioned cokes were, however, produced by “dynamic” or delayed coking and there was a continual supply of gas

(and thus larger shear forces), which has the effect of “dragging” the mesophase at the solidification stage, thus increasing the aspect ratio.

8.5 Maximising the value of Waxy Oil modification

Maximising the value of Waxy Oil feed modification (in terms of needle coke) can be measured against:

- the residue yield (from modification of virgin Waxy Oil)
- the green coke yield (from the residue)
- the green coke anisotropy

A comparative histogram of these variables is plotted for each of the modifications conducted and shown in Figure 8-19.

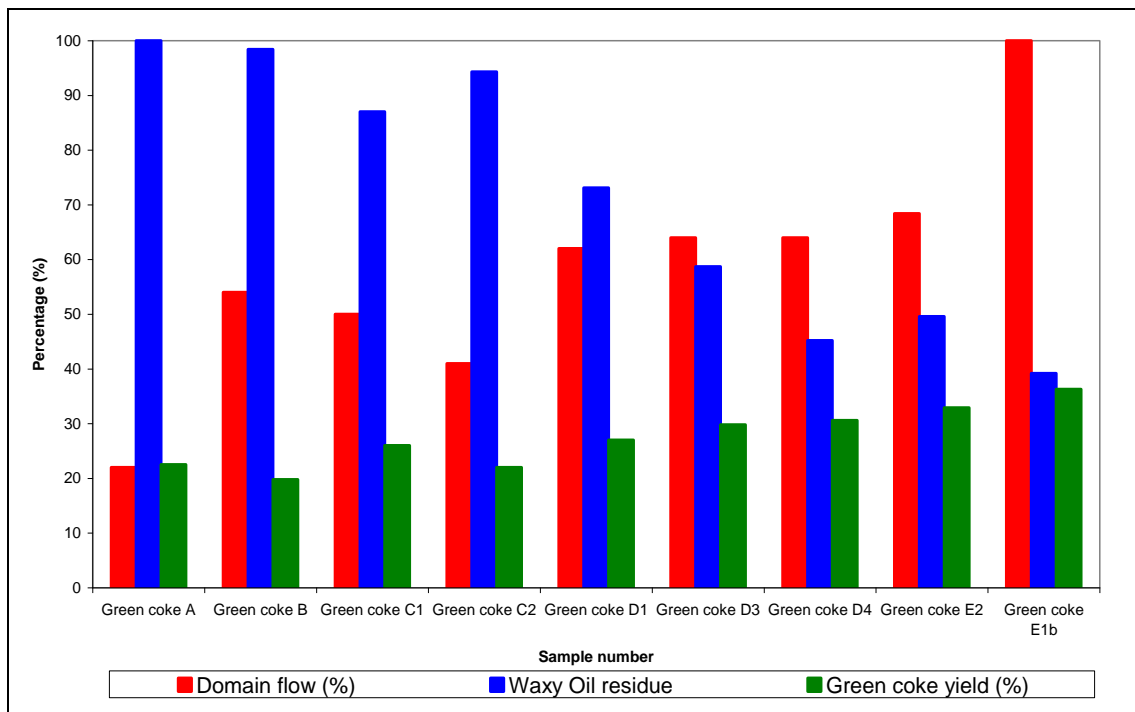


Figure 8-19 Histogram showing the influence of Waxy Oil modification on the residue yield, green coke yield and degree of green coke anisotropy (as measured by the percentage of flow domains)

In terms of the optimal Waxy Oil modification for needle coke production, it is clear that thermal treatment followed by distillation (Sample E1b) gives the maximum value.

It is possible to decrease the residue yield to 43% (Sample E1b) and by so doing maximise the green coke yield from approximately 20% (Sample B) to 36% (Sample E1b). The advantages thereof include:

- Maximising the green coke produced
- Maximising the green coke yield, which reduces porosity and increases the apparent density
- Increasing the capacity of the delayed coker to process feed

- Reducing the amount of cracked hydrocarbon distillates from the coker; it is more beneficial to remove the cracked hydrocarbons prior to carbonisation to limit dehydrogenation

In terms of importance, the microstructure of the coke produced defines the market to which the product can be allocated. The ability to remove the ash content to needle coke specifications has been shown and thus Sample A is automatically discounted as a possible feed. The microstructure domain flow can be increased to 100% (Sample E1b). Increasing the anisotropy of the coke would be expected to decrease the Coefficient of Thermal Expansion (CTE) of extruded artefacts, as previously established by Mochida *et al.* (1989).

In all aspects mentioned, Sample E1b is considered the optimum feedstock. The results of Chapter 8 do not include parameters such as CTE, VBD, etc. as delayed coking will influence the characteristics of the coke.

8.6 Is the low green coke yield of Waxy Oil carbonisation a potential problem?

The very simple answer is that the low green coke yield, even of Sample E1b (36%), is a cause for great concern and cannot be ignored.

Although stabilisation treatments accompanied by distillation do increase the green coke yield, the fact still remains that the residue is composed of long-chain normal alkanes which are more reactive than aromatic residues and thus will always produce a lower green coke yield. Thus all reasonable measures need to be considered to reduce further mass loss during calcination. Inert calcination of the green coke is strongly recommended to reduce the effect of air and carboxy reactivities. It should be possible to produce a calcined coke yield of approximately 32% (based on fresh Waxy Oil feed).

8.7 Conclusions – “Static carbonisation” of Waxy Oils

This chapter presents data showing the effect of Waxy Oil modification on the characteristics and yield of green coke produced by “static” test tube carbonisation.

The conclusions drawn are as follows:

- A reduction in the ash content of the Waxy Oil feed prior to carbonisation has the following effects on the coke quality:
 - There is only a slight decrease in the green and calcined coke yield.
 - There is a substantial decrease in the height percentage of mosaic microstructures in the green coke.
 - The oxidative consumption catalytic activity of the iron is only evident after 600 °C.
 - The carboxy reactivity mass loss is initially catalysed by the iron catalyst as it is in the form of the element (Fe) rather than the less reactive oxide.
 - The crystal structure is less dependent on multiphase graphitisation.

- The crystal structure is less ordered due to the reduction of multi-phase graphitisation.
- The more reactive Waxy Oils have a higher percentage of mosaic microstructures than the less reactive Waxy Oils. The importance to the microstructure of removing cracked lighter material from the residue after thermal treatment has also been established.
- It is possible to produce a green coke with a domain flow structure through the length of the longitudinal section using thermal treatment followed by distillation.
- Thermal treatment followed by distillation provides the largest green coke yield.

8.8 Recommendations – “Static carbonisation” of Waxy Oils

Based on the evidence provided in this chapter, the following recommendation is made:

Although it has been established that the anisotropy of green coke can be substantially influenced by modification of the carbonisation precursor, the mechanism involved is not understood. It is therefore recommended that the carbonisation mechanism of Waxy Oil be studied to provide a reasonable answer and this is studied in Chapter 9.