

## CHAPTER 8

### DISCUSSION

#### 8.1 The coals studied

The coals studied were submitted to Coal and Mineral Technologies (Pty) Ltd for proximate, ultimate and major ash analysis and for determination of the major petrographic characteristics. The coal used was kept in nitrogen-purged plastic bags to minimise the intrusion of moisture and oxygen. Moisture is an undesirable component in coal. Its existence in the solvent greatly reduces the solubility effect of the solvent on coal. Existing moisture in the solvent is driven off as the heated reactor attains operating temperature prior to addition of the base. Tables 7.1.1 and 7.1.2 list the results of the proximate analysis and the ultimate analysis (air-dry basis) respectively. Table 7.1.3 lists the major ash components. The major petrographic characteristics of the Tshikondeni and Moatize coals are shown in Table 7.1.4. Tshikondeni coal has the highest vitrinite content of 93 %. However, both types of coal could be classified as meta-bituminous (see Table 7.1.4). Such coals have a hydrogen-rich vitrinite content [16]. The high C/H atomic ratio of 1.65 and the C/O atomic ratio of 0.74 shown by Moatize coal relative to Tshikondeni coal (C/H atomic ratio of 1.54 and C/O atomic of 0.37) suggest better extractability. However, Moatize coal is not readily available since it has been largely worked out. This makes Tshikondeni coal the primary important raw material in this project.

##### 8.1.1 The coal dissolution process

Figure 7.2.1 shows the progress of extraction for various extraction runs at high temperature for 5 h with different amounts of sodium sulphide. The data for the different extraction runs are given in Appendix A2. The standard deviations and variances of the different extraction runs with sodium hydroxide, and with

different amounts of sodium sulphide at various time intervals are 0.1 and 0.004 respectively (see Appendix A3). The marginal deviation and variation order from the data shows reproducibility of the extraction process.

Figure 7.2.2 shows the progress of extraction at high temperature with sodium hydroxide only. The curve appears to be S-shaped with an absorbance of about 1.00 obtained over 5 h. The curve shows an induction period of 15 minutes, suggesting slow interaction of the reagent suit (see data in Appendix A2). The sharp rise in the curve after 15 minutes is thought to result from the coal solvent-base chemical interaction in which bond cleavage occurred to release organics into the solution. The reaction plateau when the maximum absorbance of about 1.00 was reached over 180 minutes. The maximum absorbance obtained corresponds to an 8 % organic content and is consistent with the literature value [54]. This was found to correspond to more than 90 % of the organic part of a 10 % ash flotation product dissolving in dimethylformamide, on addition of 10 % sodium hydroxide (Fig. 7.2.12) [54].

Hydrogen sulphide is known to aid in the metallation of porphyrins. To demineralise the coal further and obtain the very pure coal extracts needed for producing a highly crystalline coke,  $\text{Na}_2\text{S}$  was introduced into the extraction medium to help complex out the heavy metal ions released during chemical comminution. Unlike hydrogen sulphide, which is effective under controlled pH, the activity of sodium sulphide under a strongly basic solution is complex. It releases  $\text{S}^{2-}$  into the medium, which precipitates out certain heavy metals in solution, thereby forming an insoluble metal-sulphide complex [52, 53].

Figure 7.2.3 shows the optimisation results from separate extraction runs with various amounts of  $\text{Na}_2\text{S}$ . The maximum absorbance ( $\lambda_{\text{max}}$ ) decreased with an increase in the dosage of sodium sulphide. The decreasing order of absorbance for the molar ratio mixture of  $\text{NaOH}:\text{Na}_2\text{S}$  (1:0) > (4:1) > (2:1) > (1:1), correspond to absorbances of 1.052 > 0.746 > 0.573 > 0.227 over 5 h respectively. The

addition of sodium sulphide caused a sudden rise in the curve, then a plateau after 60 minutes, suggesting that the maximum extraction is achieved within one hour and that sodium sulphide alone is not desirable in the coal dissolution process, which the author believes is attributable, partly, to the combined strength of the nucleophile. Sodium sulphide is a weaker nucleophile than sodium hydroxide. Its addition to the extraction medium appeared to promote a synergy, which enhanced a faster chemical interaction in which the induction period disappeared. The coal matrix softened and broken bonds instantly allowed organics into the solution. The mineral matters dropping out of the coal structure are thought to have formed insoluble complexes entangled to the insoluble organics in the solution. Coal dissolution in which the combined effects of swelling and bond cleavage weakened the coal matrix has been reported [22]. It is the author's view that some of the minerals released were precipitated out and trapped as insoluble sulphide complexes in the coal residue. However a high dosage of sodium sulphide adversely affected the degree of extraction with subsequent loss in the colour intensity and low yield of the coal extracts (Figure 7.2.4 and Table 7.2.1).

High organic rich coal solution produces coal extracts, which on heat treatment form cokes of high carbon content. Figure 7.2.5 shows a comparison of the optical absorbance of the coal extract solution with its organic solids content at various doses of sodium sulphide. The decrease in absorbance is related to the organic solids content of the coal extract solution. Without sodium sulphide, an absorbance of about 0.95, corresponding to the organic solids content of 8.2 (wt %), was obtained. With the addition of a small dosage<sup>2</sup> of sodium sulphide, the absorbance decreased to 0.64 with a corresponding organic solids content of 6.56 wt %. Further addition<sup>3</sup> of sodium sulphide lowered the absorbance to 0.16 and the organic solids content to 3.89 wt %. It can be generally inferred that

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<sup>2</sup> NaOH:Na<sub>2</sub>S molar ratio of 4:1

<sup>3</sup> NaOH:Na<sub>2</sub>S molar ratio of 1:1

when the amount of sodium sulphide is increased, the organic solids content of the coal extract solution is decreased.

Optimisation of the coal extracts yield appeared to be far too low with the addition of sodium sulphide only. Figure 7.2.6 shows the progress of extraction at various amounts of Na<sub>2</sub>S only (data obtained from Appendix A). The lower absorbance curves observed plateau at 0.30 after one hour suggested an extremely poor extraction yield and that sodium sulphide alone is not desirable for extraction of organics from coal. Sodium sulphide is a weaker nucleophile and its effect in extraction appears to be far less relative to sodium hydroxide. And the loss in colour intensity may be due to moisture released by sodium sulphide reagent, which inhibits the extraction of coal or may be due to chemical reaction or back-precipitation of the dissolved coal as explained in figure 7.2.7.

Figure 7.2.7 shows a curve of the absorbance per gram of coal dissolved over 5 h on addition of Na<sub>2</sub>S and NaOH. The curve illustrates the loss in colour intensity at high dosage of sodium sulphide then a decline to 0.002 absorbance/g of coal dissolved. The addition of sodium sulphide to the extraction medium greatly lowered the absorbance and subsequently the amount of organic solids in the coal extract solution. Table 7.2.1 lists the characteristics of the coal extracts solution at high temperature over 5 h with different amounts of Na<sub>2</sub>S. The loss in colour observed accompanies the decrease in the organic solids content of the coal extract solution. The bulk of the organic solids appear to have back-precipitated to form part of an insoluble ash. The extraction optimisation process was then limited to an hour to obtain high yields of the coal extracts.

#### 8.1.2 The coal extracts or Refcoal

Table 7.2.2 lists the elemental analyses of the high-temperature coal extracts obtained on addition of different amounts of sodium sulphide. The C/H atomic ratio of coal extracts with no S<sup>-2</sup> additives is high. The addition of sulphide lowers

the ratio. Such behaviour is believed to favour hydrogenation of the coal extracts. Coal being rich in aromatics, it is surely hydrogen-deficient. Hydrogenation of the coal extracts is reported to stabilise the free radicals generated in situ, thus favouring its dissolution [180]. It is pointed out in the literature that a solvent should have a hydrogen donor capability to stabilise the free radicals generated and thereby reduce the undesirable re-polymerisation process [39]. However, the solvent used in this project is N, N-dimethylformamide, a hydrogen donor. The increase in hydrogen could have been generated in situ by complex mechanisms and these could have accounted for the observed instant dissolution of the coal on the addition of  $S^{-2}$ , which resulted in the elimination of an induction period.

The oxygen content of the coal extracts decreases with increasing dosage of  $S^{-2}$  relative to the coal extracts without  $S^{-2}$  (Table 7.2.2). The decreasing order in oxygen content of the coal extracts is  $7.49 > 5.78 > 5.72 > 5.04$  wt %, corresponding to NaOH:Na<sub>2</sub>S molar ratios of (1;0) > (4:1) > (2:1) > (1:1) respectively. The results suggest the removal of insoluble carbon containing oxygen. This behaviour favours the development of the mesophase.

The amount of ash in the coal extracts greatly affects the foaming and swelling during pyrolysis. The gradual decrease in the ash content following an increase in the dosage of  $S^{-2}$  provides the coal extracts with the purity favourable for producing the required graphitisable carbon. The decreasing order in the ash content of  $1.30 > 1.00 > 0.70$  wt % corresponds to the addition of NaOH:Na<sub>2</sub>S molar ratio of (4:1) > (2:1) > (1:1) respectively. Without sodium sulphide, the coal extracts showed the ash content of 1.60 wt %.

Figure 7.2.8 shows the extent of purification of the Tshikondeni coal extracts. The total ash has been lowered from 6 651 ppm in the coal, to 71 ppm in the coal extracts on extraction with sodium hydroxide only. The addition of sodium sulphide to the extraction medium lowered the total ash further to 52 ppm, suggesting the effectiveness of sodium sulphide in coal purification. The removal

of complexed ash, such as kaolin with free silica entangled in a macromolecular structure ( $\text{SiO}_2$  constitutes the highest ash content of the coal, see Table 7.1.3) of condensed aromatics rings, insoluble carbon, other inorganic elements and sulphide-metal complexes during the organic solids recovery process forms the basis for the high fluidity in the  $\text{S}^{-2}$  derived coal extracts [22, 24]. The result is differential swelling of the coal macerals and stresses that contribute to chemical comminution. The destruction of cross-linkages in a well-purified coal by cleavage of hydrogen bonds facilitates the reorganisation of aromatic units into a graphite-like structure during pyrolysis of the extracts [23, 24]. It is the purity of the coal extracts that determines the degree and graphitisability of carbon on heat treatment.

However, the method of recovering the coal extract remains important in lowering the ash content. Solvent evaporation produced extremely poor foaming of the coal extracts on pyrolysis, partly because of the high ash content still entangled within the coal matrix. Recovery of the coal extracts by water precipitation with a washing efficiency of 33 % produced well-foamed cokes. The washing efficiency of > 33 % could even provide the purity needed to promote foaming of the coal extracts, but there is a risk of the intrusion of oxygen during the solids recovery process. The resident time of water in the coal gel greatly affects the foaming of the coal extracts. An estimated amount of 86 % water was lost from the wet cake (formed after the filtration process) on heat drying in an oven at 60 °C under nitrogen flow. This huge loss of water could severely oxidise the coal extracts if drying is allowed at room temperature under nitrogen.

Table 7.2.3 lists the elemental analyses of the coal extract residue obtained at room temperature with different amounts of sodium sulphide. The degree of extraction on the addition of different doses of sodium sulphide and without the  $\text{S}^{-2}$  additives are listed. Without sodium sulphide, over 90 % of the organics are extracted. The addition of sodium sulphide to the extraction medium severely decreased the organic yields. The decreasing order of organics extracted is

90 > 89 > 85 > 71 wt % corresponding to NaOH/Na<sub>2</sub>S molar ratio of 1:0, 2:1, 4:1 and 1:1 respectively. The intensity of the colour corresponds to the organic solids content of the coal extract solution.

Figure 7.2.9 shows the absorbance of the coal extract solution obtained at room temperature against its organic solids content. An absorbance of about 1.00, corresponding to an organic solids content of 82 %, is obtained. The addition of sodium sulphide reduced the absorbance to 0.58, corresponding to an organic solids content of about 6 %. However, the absorbance obtained at room temperature on the addition of sodium sulphide is higher relative to absorbance obtained from a high-temperature-derived coal extract solution (Fig. 7.2.5).

The (C/H) and (C/O) atomic ratios decrease with an increase in the dosage of sodium sulphide. Such systems are known to increase the solubility of the coal in different solvents, and the results are similar to those obtained in petroleum pitches in which a low C/H ratio favoured solubility in different solvents and reduced condensation of the hydrogen-rich aromatic molecules [34]. The residue without sodium sulphide showed lower hydrogen, oxygen and sulphur contents. The elemental composition of the coal shows (C/H) and (C/O) atomic ratios of 1.54 and 0.37 respectively (Table 7.1.2). These ratios are higher than in the sulphide-derived coal extract residues (Table 7.2.3). Such a pronounced decrease in hydrogen and oxygen could result from the induced dehydrogenation process, either from the coal or from the formation of water molecules [52].

The sulphur content is reduced from 0.81 % in the coal to 0.75 % in the coal extracts (Table 7.2.2). The decrease in sulphur content of the coal on the addition of the sodium sulphide, suggests efficient washing during the organics recovery process. The removal of minerals as a metal sulphide complex, together with insoluble carbon, cannot be ignored. The improvement in the purity of the coal observed on addition of sodium sulphide is a recipe for a better foaming of the extracts on heat treatment [150].

High sulphur content is commercially undesirable since it causes puffing of the graphite during heat treatment. Its existence in the coal extracts suggests the possibility of dehydrogenation during heat treatment. Polycyclic aromatic hydrocarbons, aliphatic materials and their derivatives result from the dehydrogenation process. Incorporation into the aromatic rings as thiophenic rings through radicalisation of the aliphatic chains, formation of conjugated chains, then cyclisation in which sulphur becomes part of the aromatic ring can occur. Research has shown that above 200 °C, sulphur extracts hydrogen from aromatic compounds, during which the thioether, C-S bonds are broken to release active fragments that participate in radical polymerisation, addition and substitution reactions [17, 95].

The effects of different nucleophiles in extraction viz. cyanide and thiosulphate did not make substantial difference to the degree of extraction. Table 7.2.4 and Table 7.2.5 show the elemental analyses of the coal extract residue obtained at room temperature with different amounts of potassium cyanide and sodium sulphate respectively. The degree of carbon extraction remains marginally the same, with no clear-cut difference in the percentage of carbon extraction. An absorbance of approximately 1.00 is observed.

However, the inconsistent low carbon-hydrogen and carbon-oxygen atomic ratios obtained favoured hydrogenation and formation of the mesophase. The inconsistency is thought to come from the sample homogeneity. The trend observed is that the (C/H) and (C/O) atomic ratios decrease with increasing dosage of the nucleophiles. The sulphur content in the extract residue is lower than in the original coal extract residue.

Figure 7.2.10 shows a comparison of the solubility of coal at different amounts of the nucleophiles. The addition of cyanide and thiosulphate separately to the extraction medium slightly decreases the absorbance, suggesting ineffective chemical interaction of the nucleophiles with the sodium hydroxide and coal



particles in the solution. However, the addition of sodium sulphide decreases the absorbance. The decrease is consistent with the previously discussed results and suggests a strong chemical interaction between species in the solution.

Figure 7.2.11 shows the organic solids content of the coal extract obtained on the addition of different amounts of nucleophiles. The organic solid content (%) decreases slightly with increasing dosage of cyanide and thiosulphate. The decrease is abrupt on the addition of sulphide. The purification of coal with the addition of cyanide and thiosulphate was discontinued because of not only safety reasons but also availability of the reagents.

## 8.2 Pyrolysis of the coal extracts or Refcoal

Figure 7.2.12 shows the average weight loss (%) of the heat-treated coal extracts obtained on the addition of different amounts of cyanide, thiosulphate and sulphide. The highest amount of wt % loss was obtained on the addition of sulphide. However, the carbon yield was relatively low. High carbon yield in the coke is desirable for the density and tensile strength of the graphite. The coal extracts obtained from the addition of sodium sulphide swells better than the coal extracts with sodium hydroxide only. The better swelling implies that the coal extracts with both NaOH and Na<sub>2</sub>S goes through a more liquid phase. This suggests the formation of a better size of the mesophase region.

The swelling was determined at Coal and Mineral Technologies (Pty) Ltd by measuring the change in volume as the sample is taken from a low temperature to about 500 °C in an inert atmosphere. The swelling number for the coal extracts with sodium hydroxide only is 4.5, while a mixture of NaOH and Na<sub>2</sub>S (molar ratio 1:1) gave swelling numbers of 9 and 9.5 (Table 7.2.1).

Swelling is thought to put a strain on the coal matrix, leading to the rupture of the hydrogen bonds, and the reorientation of the coal matrix allows reorientation of the hydrogen bonding structure [33]. It is believed that an appropriate hydrogen-

bonding agent, if allowed to penetrate the swollen coal structure, would be capable of “tying up” hydrogen bonding sites in the coal. The swelling index is related to the fluidity and is also used in this context to estimate the size of the mesophase. The higher the fluidity, the higher the swelling index, the larger is the size of the mesophase.

The addition of sulphide to the extraction medium greatly increases the fluidity of the coal extracts. Table 7.2.6 lists the fluidity data of the coal extract as a function of temperature. The S<sup>-2</sup> derived coal extracts at room temperature show a fluidity of > 30 716 ddpm at 466 °C relative to the coal with fluidity of 13 550 (ddpm) at 464 °C. The high-temperature coal extracts show inconsistent fluidity at a slightly higher temperature of 480 °C. The observed inconsistency in fluidity on the addition of various dosages of sulphide is thought to come from oxygen intrusion during extraction or during the organic solids recovery process. Oxygen inhibits the extraction and foaming of the coal extracts during pyrolysis.

Figure 7.2.13 shows the foamed coke obtained on carbonisation of the room temperature prepared coal extracts. Without S<sup>-2</sup>, the average foaming volume of +17 cm<sup>3</sup>/g of Refcoal pyrolysed was obtained. However the room temperature prepared coal extracts<sup>4</sup> produced a coke with an average estimated volume of > 45 cm<sup>3</sup>/g of Refcoal carbonised and far higher than the raw coal<sup>5</sup> at 27 cm<sup>3</sup>/g coal pyrolysed. The high foaming volume is used as a measure of estimating the size of the mesophase region and is favourable for the formation of a crystalline anisotropic coke with intensive flow texture domains. The high temperature prepared coal extracts produced an estimated foaming volume of 13.2 cm<sup>3</sup>/g of coal carbonised.

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<sup>4</sup> NaOH/Na<sub>2</sub>S molar ratio of 1:1

<sup>5</sup> Unpurified coal

Foaming of the coke depends on the pressure build-up within the melted coal. There is a minimum fluidity of the coal needed to entrap the volatiles to permit a high degree of foaming. A very fluidised coal allows the volatile matter to escape easily, thus reducing the foaming. Poor devolatilisation pores suggest that pressure built up within the coal mass to enhance foaming. Pyrolysis of the S<sup>-2</sup> derived coal extracts produced a coke with far fewer devolatilised pores and improved foaming. However, sulphur in the coal extract is a problem as it causes puffing of the graphite on further heat treatment [53].

### 8.3 Optical texture of the cokes

Isotropy in this context is distinguished from anisotropy on the basis of changes in the surface characteristics of the resin-mounted polished sample when observed through an optical microscope rotated by 90°. The dark purple or black colour changed to light yellow or white on rotation of the stage, which is indicative of anisotropic domains textures. However, when the colour remains unchanged on rotation of the stage it suggests isotropic texture. Figure 7.2.14 shows a micrograph of the polished coke, CSF-0RT. Microscopic examination of the resin-mounted polished sample under polarised light showed that the coke is essentially isotropic with isolated low levels of anisotropic domain, and poorly developed pores with thickened walls. The high plasticity of the coal extracts suggests a larger size of the mesophase. The black spherical bodies typical of pores in the coke suggest that the plastic mass formed was too fluid and is consistent with the observed swelling index.

Figure 7.2.15 shows a micrograph of the polished coke, CSF-0HT. The coke is essentially isotropic with poor devolatilisation pores. The limited coke porosity observed is thought to provide a coke density suitable for blast furnace operations and with the tensile strength required for nuclear carbon. The high

plasticity of the coal extracts in the sample RSF-0RT is suggestive of a large mesophase size, leading to the formation of anisotropic coke.

The number of pores observed in the coke suggested that a plastic mass formed, allowing gas bubbles to escape at relatively low pressure and thus forming microspores as suggested by the swelling index of 4.5. It is important to note that not all the domains of the sample show a change in their characteristic tints while the stage is being rotated, suggesting the less anisotropic character of the CSF-0RT. The measured bi-reflectance of 1.75 % is consistent with the texture of the coke. The coke yield is averaged at 76 %. However the related swelling index and foaming volume were low. The addition of  $S^{-2}$  to the extraction medium and the subsequent pyrolysis of the coal extracts changed the texture of the resultant coke.

Figure 7.2.16 shows a micrograph of the coke obtained on the addition of  $S^{-2}$ , CSF-25RT. The optical character of the coke showed thickened walls, poor devolatilisation pores with stacks of parallel lamellae and extensive flow texture pattern, and coarse flow-grained anisotropy of  $> 60 \mu\text{m}$  (scale  $\sim 50 \mu\text{m}$ ). Rotation of the polished resin-mounted sample of coke on the microscopic stage resulted in a change in characteristic tints. The dark purple tints turned to yellow when the stage-mounted sample was rotated to an angle of  $90^\circ$  [4, 5]. All the domains of the sample show a change in their characteristic tints when the stage is rotated, suggesting the 100 % anisotropic character of the CSF-25RT. The measured bi-reflectance of 5.45 % suggests a relatively high degree of ordered coke. The coke produced was anisotropic and the average carbon yield was 75 % – slightly lower than the coke without sulphide.

Additives alone do not determine foaming of the coal extracts during coking. The heating rate, which can be explained in terms of a competition between the evolution of volatile matter and thermal decomposition, is important in determining swelling [179]. The rate of heating of  $10 \text{ }^\circ\text{C}/\text{min}$  to  $480 \text{ }^\circ\text{C}$  for 1 h,

then to 900 °C for 2 h allows pressure built up within the fluidised coal mass and enhance foaming with formation of few microns. The accumulated volatiles escape to reduce the pressure built up. The soaking period allow maximum formation and coalescence of the mesophase spheres [179]. The high-temperature coal extracts with  $S^{2-}$ , CSF-25HT showed a medium-grained anisotropic domain with some flow texture. Devolatilisation of CSF-25RT is a factor of the rate (of carbonisation) and the amount of  $S^{2-}$  added.

Figure 7.2.17 shows a photomicrograph of the coke derived from the coal extracts prepared on the addition of  $S^{2-}$  at high temperature. The optical character of the coke showed a thinner wall, well-marked devolatilisation pores, and fine to coarse-grained anisotropy with some flow structure. The weight loss of the coal extracts prepared at various conditions is consistent with the formation of pores in the resultant cokes. Figure 7.2.18 shows a comparison of an average weight loss (%) of the heat treated coal extracts prepared at high temperature as a function of the amounts of sulphide added, with the room temperature prepared heat-treated coal extraction. Higher weight loss is obtained in the high-temperature coal extracts than in the room-temperature coal extracts. This favours the formation of coke with less carbon content than the cokes produced from pyrolysis of the coal extracts prepared at room temperature.

#### 8.4 The graphitised cokes

Figure 7.2.19 shows an X-ray diffractogram of the graphitised cokes. For the same amount of  $S^{2-}$  but at different extraction temperatures, the  $d_{002}$  values of the graphites changed slightly. The  $d_{002}$  value of the graphite GSF-25RT is 3.37Å, while the  $d_{002}$  value of the graphitised cokes obtained from the coal extracts prepared at high temperature is slightly higher at 3.38 Å. Without sodium sulphide, the degree of graphitisation is low. However, with the addition of sodium sulphide to the extraction medium, the graphitised cokes showed improved degrees of graphitisation.

Figure 7.2.20 shows the Raman spectra of the graphitised carbons with a pair of bands at around  $1350.5\text{ cm}^{-1}$  and  $1579.1\text{ cm}^{-1}$  corresponding to the d-peak and g-peak respectively. Such Raman absorption frequency bands are very close to natural graphite. The difference in frequency is thought to come from the defects within the graphite structure. In natural graphite, the d-peak and g-peak are at  $1350\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$  respectively. Such peaks are associated with well-ordered graphite lamellae [189].

Table 7.2.7 lists the ratio of g to d peaks, the interlayer spacing  $d_{(002)}$  and the graphitisation factor, g. The ratio of the d-peak to the g-peak in the order GSF-0HT < GSF-0RT and GSF-25HT < GSF-25RT corresponds to  $1.26 < 1.75$  and  $6.7 < 7.0$  respectively. It appears that, for the same amount of sulphide added, the graphitised coal extracts prepared at room temperature showed a decrease in the area of the defect peak (d-peak) relative to the g-peak. The broad d-peak is indicative of the existence of disordered carbon in the distorted carbon network. This could be associated with the presence of hydrogen and alkyl groups at the edge of the planes thus decreasing the interactions between each molecule, which is thought to give rise to poor vibrational modes [188]. When these alkyl groups are between the planes, distortion of the carbon network occurs, resulting in some first-order bands as seen in Raman spectroscopy. In natural graphite, only a Raman band at  $1580\text{ cm}^{-1}$  ( $E_{2g}$  mode) appears. However, in synthetic graphite, Raman bands appear at  $1580\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$ . These bands have been used to measure the crystal size,  $L_a$ , of the graphite sheets [164].

In addition, this graphitised cokes showed a different degree of graphitisation. The graphites produced from the coal extracts prepared at room temperature showed the highest degree of graphitisation, as opposed to the graphites produced from the coal extracts prepared at high temperature. The order of graphitisation is GSF-0HT (25 %) < GSF-0RT (64 %) and GSF-25HT (74 %) <

GSF-25RT (79 %). High temperature of extraction appears to produce poorly graphitised cokes. Graphitised high-temperature-derived coal extracts showed low intensity ratio value ( $R = I_g/I_d$ ) suggestive of a turbostratic structure. The highest intensity ratio values ( $R$ ) were observed in graphites prepared from room-temperature prepared coal extracts suggesting a more ordered graphite structure.

Figure 7.2.21 shows a plot of average full width at half maximum (FWHM) of the  $E_{2g}$  mode ( $1580\text{ cm}^{-1}$ ) versus  $L_a$  for the graphites and their blends of sodium sulphide under various conditions. The  $E_{2g}$  mode corresponds to the stretching vibration in the aromatic layers. Because the aromatic bond involves high energy, this mode occurred at a high frequency ( $1580\text{ cm}^{-1}$ ). In perfect crystalline graphite, there is only the g-band in the first-order region. In poorly organised crystalline graphite, additional bands appear in the first-order region around  $1150$ ,  $1350$ ,  $1500$  and  $1620\text{ cm}^{-1}$ . The  $A_{1g}$  mode is called the defect band [150]. The crystallite size along the a-axis,  $L_a$ , was obtained by fitting the Raman intensity ratio ( $R$ ) data into the equation [10]. The area ratio is used to estimate the crystallite size,  $L_a = 4.3/R$  where  $R$  is the ratio of the  $E_{2g}$  mode ( $1580\text{ cm}^{-1}$ ) to the  $A_{1g}$  mode ( $1350\text{ cm}^{-1}$ ) in the Raman spectra (Fig. 7.2.20). From the equation  $L_a = 4.3/R$  and  $R = g/d$ , it can be inferred that when the area of the degenerate peak (d-peak) becomes smaller, the area of the graphitic peak (g-peak) becomes larger, and the result is a bigger ratio ( $R$ ) and a smaller crystal size,  $L_a$  in the a-axis. The g-peak becomes sharper and narrower in graphitised carbon obtained from room temperature prepared coal extracts. The addition of same dosage of  $S^{-2}$  improves further the intensity of the g-peak. Such inference is consistent with the increasing degree of graphitisation.

Extremely disorganised crystalline graphite may show a peak at  $1350\text{ cm}^{-1}$ . Since graphitic material has a crystal structure consisting of flat layers in which the trivalent carbon atoms are connected with  $\sigma$ -bonds in  $sp^2$  hybridised orbit in the plane containing the a – b axes, the layers are held by  $\pi$ -bond along the c-

axis. The presence of impurities material or heteroatom such as sulphur on the surface of the aromatic plane greatly affected the electronic environment and thus created defects within the crystal structure of the graphite, which is presumed to account for the existence of additional bands in the first-order region. A heteroatom such as sulphur, if it were attached to an alkyl carbon skeleton in the coal extract, would be released together with the volatiles during heat treatment. But if the sulphur is incorporated into the aromatic rings, it is difficult for it to be released with the volatiles at a coking temperature of about 500 °C. This may cause puffing of the graphite during further heat treatment and thus affect the quality of the resultant graphite.

Without the addition of sulphide, the graphite sample GSF-0RT showed the crystallite size,  $L_a$ , of 1.22 nm, corresponding to the FWHM of the  $E_{2g}$  peak at  $37.39\text{ cm}^{-1}$ , while the graphite, GSF-0HT obtained from the high-temperature-derived coal extracts showed a larger crystallite size,  $L_a$ , of 5.41 nm, corresponding to a FWHM of  $43.65\text{ cm}^{-1}$ . This suggests that the room-temperature-derived graphites are more ordered than the high-temperature-derived graphites. With the addition of sulphide, the FWHM of the  $E_{2g}$  peak in the Raman spectra of the sample GSF-25HT is bigger at  $36.67\text{ cm}^{-1}$  corresponding to a crystallite size of 1.70 nm while the sample of graphite GSF-25RT showed FWHM of  $34.37\text{ cm}^{-1}$  corresponding to a crystallite size of 0.92 nm. The smaller FWHM value suggests a sharp and narrower intensity of the g-peak (Table 7.2.7 and Appendix G1).

In general, the decrease in crystal size,  $L_a$ , of the graphite favours extraction at room temperature relative to high temperature. This favours the formation of a well-ordered graphitised carbon. High FWHM value of the  $E_{2g}$  peak may suggest various boundary conditions of the layer planes or a large number of defective structures introduced into the graphitic lattice within the layer planes, creating an environment that distorts the structure of the graphite.



## 8.5 Control of the coke texture

In carbonisation, bonds are broken and the active fragments formed participate in reactions of addition and substitution. The process of interstructural plastification takes place. The viscosity of the heat-treated coal extract and the high lability of the macromolecular fragments are determined by specific characteristics of the parent coal. Additives can influence the coal's thermoplastic properties but the effect depends on the nature of the additive used, the amount added and also the structure of the parent coal. The additives used in this work were carbonaceous.

### 8.5.1 The coal extracts prepared on the addition of S<sup>-2</sup>

The coal extracts used were prepared at room temperature on the addition of sodium sulphide. The carbon additives used in blending the coal extracts were acetylene and carbon black, the properties of which are given in Appendix H. Mixing and dispersion of the carbon additives were described in Section 6.7.

Figure 7.3.1 shows SEM photomicrographs of a carbon additive and its surface characteristics. Carbon black is more spherical, while acetylene black is flat in shape. The carbon additives showed chains of aggregates that made it difficult to disperse uniformly in the viscous coal solution. As opposed to acetylene black, carbon black is relatively easier to disperse because of its structure (Appendix H).

Figure 7.3.2 shows SEM photomicrographs of the carbon black dispersed in the heat-treated coal extracts. The surface texture observed shows some ridges that become smaller with increasing amounts of carbon black. The fine surface texture is more visible with 0.88 % (by wt) of carbon black.

Figure 7.3.3 shows SEM photomicrographs of acetylene black dispersed in the heat-treated coal extracts. The surface texture observed remains coarse with increasing amounts of acetylene black. However, a fine texture was observed on the addition of 0.88 % (by wt) of carbon black. Such inconsistency could be attributable to the ease of dispersion.

Table 7.3.1 shows the elemental analysis of the coal extracts blended with carbon additives. The unblended coal extracts show lower C/H ratios relative to the extracts with carbon additives, suggesting the existence of hydrogen-rich molecules such as saturated hydrocarbons etc. With the addition of a carbon additive, the C/H ratio, however inconsistent, increases, suggesting the formation of hydrogen-deficient molecules. This favoured formation of radicals, which are important in dehydrogenative polymerisation [96]. However, the low C/O ratio observed in the blended coal extracts suggest poor formation of the mesophase on pyrolysis and formation of oxygen substituted aromatic hydrocarbons [14]

Pyrolysis of the sulphide-derived coal extracts produced an average of 64 wt % carbon yield. The addition of 0.44, 0.88, and 1.60 wt % of acetylene black produced on average 67, 67, and 68 % wt carbon yield respectively. A similar trend was observed with the addition of carbon black. The addition of about 0.44, 0.88, and 1.60 wt % carbon black produced 70, 71 and 69 % carbon yield respectively. The increasing trend in carbon yield of the cokes appears to happen albeit discounting the amount of carbon additives used prior heat treatment.

Figures 7.3.4 and 7.3.5 show TGA analysis of the coal extracts and their blends of carbon additives. The curves show significant weight loss (%) between 425 °C and 525 °C. The weight loss produced resulted from the physicochemical changes occurring in the thermoplastic stage during carbonisation and includes water, oxides of carbon and hydrogen, sulphide from thermally labile substituents or facile condensation reactions, breaking of cross-linkages comprising oxygen or non-aromatic carbon bridges between adjoining aromatic groups, etc. [135,

136]. The effect is more pronounced at a low dosage of the carbon additives. The difference in the amount of weight loss is more pronounced at 500 °C on the addition of carbon black relative to acetylene black, which shows sudden weight loss from 420 to 500 °C. Carbon black is more effective in suppressing the volatiles released during carbonisation relative to acetylene black. Such results complement the observed surface characteristics of the dispersed carbon additives in the coal extracts.

Figure 7.3.6 shows the curves of the maximum weight loss in the temperature region of 300 – 550 °C (obtained from Thermal analysis of the coal extracts) with the addition of acetylene black. The maximum weight loss excludes regions in which moisture and other light volatiles were released in the regions of < 300 °C and includes all volatiles released at the temperature of < 900 °C. Only the points on the TGA curves within these regions and up to 900 °C were used to produce curves. This is because the effect of carbon additive was reported to be more pronounced at the mesophase region of the pyrolysed coal extracts [114]. Without carbon black, the maximum weight loss of 27 % appears at a temperature of  $471 \pm 01$  °C. The addition of 0.44 % carbon black slightly shifted the weight loss of 24 % to a temperature of  $491 \pm 01$  °C. Further addition of 0.88 and 1.60 wt % acetylene black shifted the weight loss of 23 % and 21 % to temperatures of  $592 \pm 01$  °C and  $535 \pm 01$  °C respectively. Similar behaviour is observed with carbon black.

Figure 7.3.7 shows the curves of the maximum weight loss in the temperature region of 300 – 550 °C (obtained from Thermal analysis of the coal extracts, i.e. TGA curves) with the addition of carbon black. Without carbon black, the weight loss of 27 % appears at a temperature of  $471 \pm 01$  °C. The addition of 0.44 % carbon black slightly shifted the weight loss of 24 % to a temperature of  $479 \pm 01$  °C. Further addition of 0.88 and 1.60 wt % of carbon black shifted the maximum weight loss of 23 % and 22 % to the temperatures of  $492 \pm 01$  °C and  $495 \pm 01$  °C respectively. It appears that in the presence of carbon additives, the

start of the weight loss (temperature range 450 – 550 °C of the mesophase region) is delayed up to a slightly higher temperature during the heating process. This behaviour is similar in carbonisation systems of pitches in which carbon black delays the appearance of liquid crystals and causes the supersaturated mesogens not to precipitate. Supersaturated mesogens lead to a large number of smaller-sized spheres [113].

Figure 7.3.8 shows the total weight loss of pyrolysed coal extracts at different dosages of the carbon additives. The original coal extracts showed the highest weight loss (%) during pyrolysis. The addition of carbon black to the coal extract solution affected the weight loss (%). The decreasing order of weight loss (%) with dosage of carbon black is 35.50 > 32.34 > 31.48 > 31.56 (by wt %), corresponding to RSF-0, RSF-0.44, RSF-0.88 and RSF-1.60 respectively. For acetylene black, the decreasing order of the total weight loss (by wt %) is 35.50 > 32.87 > 32.07 > 31.52 corresponding to RSF-0, RSF-0.44, RSF-0.88 and RSF-1.60 respectively. Both carbon additives are effective in reducing the amount of weight loss (%) during thermal analysis. However, the effectiveness of suppressing the weight loss (%) is more pronounced with the addition of carbon black relative to acetylene black. The results compare favourably with the observations made by Kanno *et al.* in which 5 % of carbon black addition in pitch was found to suppress the swelling of mesophase pitch sufficiently by initiating pyrolysis at lower temperatures, thus avoiding the intense evolution that may lead to severe swelling and increased size of the optical units [18, 127].

The slight increase in the maximum temperature at which the mesophase occurs is associated with the addition of carbon additives. Such a shift or delay in the maximum temperature corresponds to a gradual decline in the amount of weight loss and subsequently a reduction in the size of the crystalline domain of the coke. This is not favourable for graphitisation.

Figure 7.3.9 shows the optical micrographs of the cokes obtained from the coal extract blends of carbon black. The coal extracts alone show an extensive flow domain texture, as shown by the darkened parallel lamellae and the large crystalline domain units of about >10 microns. The extensive flow texture and high crystallinity of the coke result from severe expansion of the mesophase region within the temperature range of 470 – 520 °C, and characterise the size of the plasticity region formed during carbonisation. The addition of carbon additives significantly reduces the size of the optical units and provides mosaic domain texture. Perez *et al.* attributed this observation to insoluble solids offsetting the ability of petroleum pitch to generate large regions of the mesophase. The mesophase development is modified and affects the formation of new spheres, the growth of existing spheres and mesophase coalescence [126]. The size of the mosaic texture is influenced by the amount of the carbon additive present. Unlike acetylene black, a high dosage of carbon black produces a homogeneous fine mosaic coke texture, the reason being the effective dispersal of carbon black in the coal extract slurry. Dispersion of acetylene black has proved to be difficult. Chain-like aggregates that possess a cage structure have been observed (Fig. 7.3.1) and this structure has been reported to hinder the growth and stacking of mesophase molecules, leading to reduced size of the optical units to provide a fine-grained mosaic texture [120]. The disappearance of the flow texture domain is observed on the addition of the carbon additive and suggests interaction between the functionality of the carbon additive and the surface of the coal extract. Such interaction takes place within the temperature range of 470–520 °C in the early stage of carbonisation. The observation complements the weight loss (%) observed in the region of the plastic region formed during thermal analysis of the coal extracts and their blends of carbon additives.

Figure 7.3.10 shows the optical micrographs of the cokes obtained from the coal extract blends with acetylene black. A similar behavioural trend is observed with acetylene black. However, the poor dispersion of acetylene black in the coal extract slurry affected the homogeneity of the mosaic texture in the cokes

(Figs 7.3.2 and 7.3.3). There is inconsistency in the size of the domain texture. Reduced size of the optical units is also observed.

It can be concluded that the expansion (and subsequent flow texture) of the coke formed during carbonisation takes place as a result of gas evolution from the viscous liquid of the mesophase coal extracts during carbonisation and just before the solidification. The addition of carbon additives modifies the carbonisation properties of the mesophase coal extracts through chemical and physical interaction on their surface. Smaller size and larger number of crystalline domains in the coke were formed. The end result was the formation of a carbon with less flow texture and smaller domain texture units.

Figure 7.3.11 shows the Raman spectra of the graphitised cokes prepared with the addition of carbon black. The intensity ratio of the peak height,  $R = I_G/I_D$ , is a measure of the crystallinity of the graphitised coke (1). The unblended graphitised coke (1) shows a d-peak at  $1351 \text{ cm}^{-1}$  and a split of the g-peak into  $1580 \text{ cm}^{-1}$  and  $1612 \text{ cm}^{-1}$ . The largest intensity ratio ( $R$ ) of 5.432 suggests a highly ordered graphite structure. The graphitised coke blend (2) shows a d-peak at  $1355 \text{ cm}^{-1}$  and a g-peak that has split into  $1581 \text{ cm}^{-1}$  and  $1618 \text{ cm}^{-1}$  with an intensity ratio of 4.430. The ratio of the g-peak to d-peak decreases in the order  $(1)^6 > (2)^7 > (3)^8 > (4)^9$ , corresponding to the intensity ratios of  $5.432 > 4.430 > 4.176 > 3.463$  respectively. This decrease in intensity ratio suggests the formation of a turbostratic graphite structure. In the graphitised coke blend (3) the d-peak has a frequency of  $1350 \text{ cm}^{-1}$  and the g-peak splits into  $1580 \text{ cm}^{-1}$  and  $1618 \text{ cm}^{-1}$ . Similarly, the graphitised coke blend (4) shows a d-peak at  $1349 \text{ cm}^{-1}$  and g-peak slightly lowered to  $1582 \text{ cm}^{-1}$ . The same observation holds for

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<sup>6</sup> GSF-0    <sup>4</sup> GSF-0.44    <sup>5</sup> GSF-0.88    <sup>6</sup> GSF-1.60

graphitised coke blends of acetylene black. Such a split in the g-peak comes from some intrusions in the graphite structure.

Figure 7.3.12 shows the Raman spectra of the graphitised cokes prepared with the addition of acetylene black. Similarly, graphitised coke blends of acetylene black show decreasing order in the intensity ratio ( $I_D/I_G$ ) of the peak height, i.e.  $5.432 > 5.267 > 4.475 > 4.675$ , corresponding to graphite samples (1) > (2) > (3) > (4) respectively. The inconsistency in the intensity ratio of sample GSF-0.44 arises from the difficulty with which acetylene black disperses in the coal extract solution. The results obtained suggest a decrease in crystallinity with increasing dosage of carbon additives, leading to poor graphite formation. The graphites with less flow texture favoured a dosage below 0.22 % of carbon additives.

The relative intensity of the g-band increases from  $1580\text{ cm}^{-1}$  to  $1582\text{ cm}^{-1}$  as the graphitisation temperature decreases from 2976 to 2949 °C. In addition to the decreasing intensity ratio of the peak height in the coke blends, a second-order band occurring at approximately  $1580\text{ cm}^{-1}$  tends to split into a double g-peak at  $\sim 1580\text{ cm}^{-1}$  and  $g'$  at  $1617\text{ cm}^{-1}$ , suggesting structural disorder in the graphite. The subsequent doubling in the dosage of the carbon black to 0.88 wt % resulted in a similar split of the g-peak, indicating the occurrence of the triperiodic order.

The presence of carbon additives causes the qualitative differences in the Raman spectra of the materials. Since the properties of the graphite are determined largely by the quality of the starting material, the carbon additives present appear to be coating the mesophase spheres and affecting the crystal domain size and anisotropy of the graphites. The result is a decrease in the crystalline domain, which favours the formation of turbostratic carbon. The carbon additives decrease the graphitisability of the coke blends. The degree of graphitisability of the coke blends decreases with an increase in the dosage of carbon additives. The crystallite size,  $L_a$  (along the a-axis), is an important parameter in determining the spacing between the graphite layers.

The ratio of the peak area may be related to the crystalline size of the graphite along the a-axis. The crystallite size  $L_a$  was calculated from the calibration equation,  $L_a = 4.3/R$  where  $R$  is the ratio of the g to the d peaks. It can be inferred that when the area of the degenerate peak (d) becomes bigger, the area of the graphitic peak (g) becomes smaller, and the result is a smaller ratio,  $R$ , and a bigger crystal size,  $L_a$ , in the a-axis. The area ratio is used to estimate the crystallite size,  $L_a$ . The crystallite size,  $L_a$ , is related to the FWHM (full width at half maximum) and its determination helps in the assessment of crystallinity.

Figure 7.3.13 shows the FWHM of the  $E_{2g}$  mode versus  $L_a$  over a temperature range from 2952 °C to 2976 °C. The FWHM is related to the crystallite size to allow a further assessment of the degree of crystallinity in each of the graphites. The FWHM of the  $E_{2g}$  peak in the coal extract blends becomes narrower and decreases with an increase in the dosage of carbon additives. Corresponding to the decrease in the FWHM, an increase in the  $L_a$  value is observed. These increase in graphite crystal size,  $L_a$  occurs when the dosage of the carbon additive is increased from 0.44 % to 1.60 %. The  $E_{2g}$  ( $1380 \text{ cm}^{-1}$ ) vibrational mode is affected by the distortion of the hexagonal graphite lattice near the crystal boundary; this originates from the reduced size of the crystalline domains within the coke blends. The carbon atoms at the crystal boundary are usually attached to chemical groups, such as a carbonyl group, hydroxyl group or carboxyl group, or to a hydrogen atom [11]. A rise in the FWHM of the  $E_{2g}$  peak with an increase in carbon black dosage may suggest various boundary conditions of the layer planes or a large number of defective structures introduced into the graphitic lattice within the layer planes.

Figures 7.3.14 and 7.3.15 show the XRD spectra of the graphitised coke blends with acetylene black and carbon black respectively. The degree of graphitisation ( $g$ ), the interlayer spacing ( $d_{002}$  value) and the Raman intensity ratio ( $R$ ) of the graphitic/degenerate peak are listed in Table 7.3.2. The crystallite size  $L_a$



increases with the addition of the carbon additives while the d-spacing decreases accordingly. And the incipient asymmetry of the  $d_{002}$  peak was observed in the Raman spectroscopy of the graphitised samples, which gradually increased with increasing dosage of the carbon additive. This is thought to come from the introduction of defects into the lattice structure of the graphite, a similar result was reported by Wakayama *et al.* [188].

Table 7.3.2 lists the Raman spectrometry and XRD data on the graphitised carbons. The graphite produced without carbon additives shows the highest degree of graphitisability of 58 % to 66 %. The addition of carbon additive to the coal extracts decreases the degree of graphitisation. With increasing dosage of acetylene black from 0.05 through 0.88 to 1.60 wt %, the decreasing order in the degree of graphitisation is 69 %, 61 % and 62 % respectively. Similarly, carbon black shows the same trend and the decreasing order of graphitisability is 57.7 %, 56.5 % and 51.5 % respectively. Corresponding to this, the interlayer spacing,  $d_{002}$ , which decreases accordingly. The Raman intensity ratio of the g to the d peaks decrease with increasing dosage of the carbon additive. This suggests a broadening of the defect peak (d) resulting from induced defects within the crystal structure of the graphite.

Figures 7.3.16 and 7.3.17 show optical micrographs of the cokes graphitised with acetylene black and carbon black respectively. The effectiveness of the carbon additives hindered the graphitisability of the cokes as indicated by the char on the observed graphites' morphology.

Figure 7.3.18 shows the behaviour of the cokes with respect to weight loss during graphitisation. The temperature of graphitisation decreases with increasing dosage of the carbon additives and the weight loss (%) decreases accordingly. Figure 7.4.1 shows the behaviour of the graphitised coke blended with carbon additives at 2 000 °C for 2 h, and the relationship between the weight loss (%) and the temperature of graphitisation for the coal extracts and their

blends. Graphitisation of the coke labelled CSF-0 results in a weight loss of 26 % at 2 976 °C. The coke blends graphitised with carbon black, CSF-0.44, CSF-0.88 and CSF-1.60, show graphitisation weight losses of 24.2 % at 2976 °C, 15.9 % at 2952 °C, and 13.8 % at 2949 °C respectively. The same dosage of acetylene black gave 10.1 % at 2974 °C, 8.80 % at 2 972 °C, and 10.5 % at 2 964 °C respectively. The results indicate that the amount of weight loss (%) and consequently the graphitisation temperature (°C) decrease with increasing dosage of the carbon additives. For the same period of graphitisation (2 h) and dosage of carbon additive, the cokes show similar behavioural trends during graphitisation. However, the main differences are those between the two carbon additives, the decreases in the graphitisation temperature and the weight losses, complementing the declining intensity ratio of the peak height, and these differences account, to a great extent, for the decrease in the graphite crystal size, and subsequently for the increase in induced defects within the graphite structure.

It could be inferred from this study that the reduction in the flow texture of the carbon favoured the formation of isotropic carbon. However, at large dosages of the carbon additives, graphitisation is severely hindered. Induced defects within the crystal structure of the graphite were observed on the addition of the carbon additives. It can be concluded that the addition of the carbon additives decreases the amount of the weight loss, and consequently the graphitisability of carbon.

#### 8.5.2 The coal extracts prepared without S<sup>-2</sup> additives

Figure 7.4.1 shows the optical texture of the cokes obtained from the coal extracts on the addition of carbon black. The coal extracts without additives show extensive flow texture domains. The addition of the carbon additives significantly reduces the size of the optical units and provides reduced mosaic texture domain. The size of the mosaic texture is determined by the amount of the carbon additive present. Higher dosages of carbon black produced

homogeneous fine mosaic texture cokes, which are essentially isotropic. The order of decreasing size of the optical units is CCB-0.0 > CCB-0.15 > CCB-0.22 > CCB-1.60. However, the degree of graphitisation is decreased. At very high dosages of carbon additive, graphitisation ceased altogether. Carbon black hinders the growth and stacking of mesophase molecules, leading to reduced size of the optical units providing a fine-grained mosaic texture [112, 113]. The size of the optical units is determined by the modification of the domain anisotropy of the blend's mesophase during the carbonisation process.

Table 7.4.1 lists the Raman spectroscopy and XRD data on the graphitised cokes containing carbon black and iron. The graphitised cokes without carbon black show the highest degree of graphitisation relative to the graphitised cokes with carbon black. The degree of graphitisation decreases in the order GCB > GCB-0.15 < GCB-0.22 > GCB-0.44, corresponding to 60 > 20 < 50 > 20 %. The inconsistency observed is thought to be associated with the effectiveness of dispersal of carbon black in the coal solution, as observed in GCB-0.15. The minimum amount of carbon black required to reduce the flow texture and produce an isotropic coke with a crystalline domain texture is < 0.22 % (by wt). Above this dosage of carbon black, the coke becomes essentially isotropic.

Figure 7.4.5 shows the average full width at half maximum (FWHM) of the  $E_{2g}$  mode ( $1580\text{ cm}^{-1}$ ) as a function of the graphite crystallite size,  $L_a$ . The crystallite size,  $L_a$ , increases with increasing amount of carbon black. Additives such as carbon black and  $Al_4C_3$  have been reported to lead to an increase in the crystallite dimension,  $L_c$ . These are thought to increase the density of the graphite and improve its neutron radiation stability [63, 72, 178].

## 8.6 The coal extracts on the addition of iron (III) compound

Figure 7.4.2 shows the optical micrographs of the coke containing iron (III) compound. The coke without iron (a and b) shows a small crystalline domain

texture. The addition of a small amount of iron (III) compound (c, 1 % by wt) produced changes in the appearance of the crystalline domain to a concentric flow pattern. This is thought to emanate from dispersion of the iron (III) gel in the coal extract solution during mixing. A high dosage of iron (III) compound (d, 3 % by wt) produced an essentially isotropic coke. The degree of graphitisation was consequently decreased.

Figure 7.4.3 shows the XRD spectra of the graphitised cokes containing iron. Without iron (III) compound, the degree of graphitisation appeared to be relatively high compared with the graphite with iron (III) compound. However, the graphite Gfe-3 containing 3 % by wt of iron (III) compound showed a slight improvement in the degree of graphitisation relative to Gfe-1.

Figure 7.4.4 shows the XRD spectra of the graphitised cokes containing carbon black. The calibration peak of ZnO is clearly visible. The  $d_{002}$  value appeared to be higher on the addition of carbon black, suggesting movement towards disordered graphites. In addition, the crystallite size and degree of graphitisation decreased with an increase in the dosage of carbon black (Table 7.4.1). Evidently, the addition of a high dosage of carbon additive hinders the formation of graphites.

Table 7.4.1 lists the data on the degree of graphitisation for each of the graphites. The coke with the highest dose of iron (III) compound showed 27 % graphitisation relative to the coke with the lowest amount of iron (III) compound, which is at 21 %. This is a promising step towards catalytic graphitisation and is a subject of interest for future research work. Oxygen intrusion during mixing could be a problem. Previous research work on oxygen-containing aromatics showed that oxygen substitution could result in both well-ordered and poorly ordered graphite [48, 49, 56, 103]. Poor graphitisation could be the result of the formation of quinines, which lost carbon monoxide (CO) on pyrolysis to give non-planar

radicals, leading to a dramatic decrease in the final graphitisability of the starting material.

The corresponding  $d_{(002)}$  spacing increases accordingly and is consistent with the Raman spectroscopy results (Table 7.4.1). The intensity ratios ( $R = g/d$ ) of the graphites Gfe-3 and Gfe-1 are 0.76 and 0.54 respectively. The intensity ratio of the degenerate peak (d) decreases with increasing amounts of iron. Subsequent to that, the  $d_{(002)}$  value decreases with increasing amounts of iron.

Previous work showed that heat treatment of iron or iron compounds with amorphous carbon led to the formation of the carbide, cementite ( $Fe_3C$ ) that decomposed on further heating to give graphite [169]. The formation of cementite was further reported to yield even better graphite when used in conjunction with silicon as ferrosilicon [169]. The effect of iron is consistent with the literature study in which iron was found to improve the graphitisability of hard carbons through the formation of cementite, as intermediate carbide, which decomposed on further heating to give graphite [67].

Further work on catalytic graphitisation needs to be done to improve the degree of graphitisation. However, it appears conclusively that iron or iron compounds catalyse the conversion of hard carbon into graphitisable carbon by firstly dissolving the intercellular hard carbon to form graphite via one of the mechanisms documented in the literature [168, 169].

It can be concluded that the thermal reactions during carbonisation can be altered considerably through the use of certain additives. These are chemical substances that influence the thermoplastic properties of coal. Their effect on the coal structure occurs via active centres of the coal macromolecules (functional groups, labile hydrogen) and they influence the condensation reactions at pre-coking temperatures with the evolution of free radicals at increasing

carbonisation temperatures. This effect depends on the nature of the additive used, the amount added and also the structure of the parent coal.

## CHAPTER 9

### CONCLUSIONS

High-ash coals are not suitable for efficient use in carbonisation. The Tshikondeni coal, like any other coal in South Africa, is ashed and contains polynuclear aromatic (hydrogen-deficient) structures bound to inorganic elements. The CSIR coal solubilisation process unlocked the elements by disrupting the bonds and allowed the bulk of the organic part of the coal into the solution. This lowered the ash content. The relatively pure coal extracts obtained through centrifugation and water precipitation provided a starting material suitable for carbonisation and graphitisation. The washing efficiency in the recovery of organic solids produced coal extracts with the desired purity. In addition, this method of carbon recovery offers advantages over other known coal purification processes used elsewhere. The solvent is relatively inexpensive and the coal extract solution produced can be beneficiated into numerous carbon end products. The addition of sodium sulphide lowered the ash level further with subsequent improvement in the coke texture. The well-purified coal extracts used in this project produced graphitisable and isotropic carbon, which is currently made from petroleum pitch. However, the carbon yield of the resultant coke was low. Coal being an abundant raw material in South Africa, it has the potential to be the future source of coke and graphitisable carbon needed in the pebble bed modular reactor (PBMR).

The low C/H atomic ratio observed in the coal extracts prepared at room temperature on the addition of  $S^{-2}$  enhanced hydrogenation of the coal extracts and increased the solubility of the coal in DMF. This was observed by the decrease in the delay time and the appearance of instant colour within a few minutes of extraction starting. Heat treatment of the purified coal extracts resulted in a high swelling index, extensive foaming and a highly plastic carbon material.

The coke formed was produced from the heat-treated coal extracts, which liquefied and formed domains of discoidal liquid crystal prior to cross-linking, with loss of volatile material. When polished specimens of the cokes were observed by reflectance microscopy, flow textures with domain sizes of a few to many microns were observed. Isotropic, poorly graphitising cokes showed little or no structure. Anisotropic cokes were produced when these domains of liquid crystal grew and coalesced. The cokes were found to be highly graphitisable. However, in the heat-treated coal extracts prepared at high temperature, the liquid crystal domains were graphitisable but appeared not to have coalesced. Nevertheless, the random orientation of the domains allowed isotropic blocks to be formed with extremely low crystallinity. The precursors that form these liquid crystals are generally materials known to have a high aromatic carbon content.

Extensive flow textures in the cokes obtained on the addition of sodium sulphide to the starting material produced coarse-grained, anisotropic graphites. The cokes produced were highly ordered, as suggested by the measured bireflectance. Such cokes were better when produced from the room-temperature-derived coal extracts than from the high-temperature-derived coal extracts. The degree of graphitisation increased on the addition of sodium sulphide. The highly anisotropic crystalline domains and the relatively high swelling index observed in the heat-treated room-temperature coal extracts complemented the measured foaming and fluidity, which was used as a measure for estimating the size of the mesophase.

The temperature at which the coal extract is prepared and the amount of sodium sulphide added determine the level of anisotropy. The highest degree of graphitisation was obtained in the coal extracts prepared at room temperature on the addition of sodium sulphide. The increase in the interlayer spacing ( $d_{002}$  value) of the graphites suggested the development of defects within the crystal lattice. This is a function of the method used to prepare the coal extracts.



Heat treatment of the coal extracts prepared at room temperature without the addition of sodium sulphide resulted in a low level of anisotropy and coarse flow texture. The addition of carbon black substantially reduced the coarseness of the flow texture. However, the effect of carbon black compromised the graphitisability of the carbon produced.

The carbon additives stimulated nucleation and restricted the growth and coalescence of spheres, resulting in the formation of smaller texture domains. Moreover, the carbon additives, especially acetylene black, agglomerated to restrict the diffusion of the mesogen molecules within the coal extracts. Such a hindrance reduced the size of the crystalline carbon domains and produced a large number of smaller spheres. The trend established was that when the amount of carbon additive increased, the sizes of the carbon domains tended to become smaller with uniform size distribution. The minimum threshold dosage of carbon additive required to reduce the flow texture without reducing the graphitisability of carbon was found to be very low. This is a significant step towards producing isotropic and crystalline graphite from coal.

Iron (III) compound was also used with the purpose of influencing transition from liquid to solid reactions. The intention was to convert the intracellular hard carbons into soft carbons, thereby increasing the size of the mesophase around the mesophase temperature region. Iron (III) compound showed insignificant but promising improvement in the degree of graphitisation. More attention is needed in future to improve the preparation methodology in order to improve the degree of graphitisation substantially.