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EFFECTS OF HYDROGEN DONOR ADDITIVES ON THE COKING PROPERTIES OF HIGH-TEMPERATURE COAL EXTRACTS

by

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DECLARATION

I, the undersigned, hereby declare that the research in this thesis is my own original work, which has not partly, or fully, been previously submitted by me to any other university in order to obtain a degree.

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ABSTRACT

Refcoal is a carbon precursor obtained by alkali-mediated extraction of coal with aprotic solvents such as DMF. Refcoal can be converted into a graphitic material through appropriate heat treatment. Graphitisable materials require the development of an intermediate liquid crystalline mesophase. Thus formation of a mesophase during the carbonisation of Refcoal is essential for obtaining highly graphitisable anisotropic cokes suitable for nuclear graphite applications. Anisotropic carbons are even more important in other commercial and industrial application because of their distinctive properties. The formation of anisotropic carbon depends on the nature of the parent precursor, temperature and carbonisation conditions, especially the molecular mobility during the mesophase stage. High-temperature extraction of coal produces Refcoal that yield cokes with a low level of anisotropy. Good control of the mesophase stage during carbonisation may lead to the development of anisotropic cokes.

Hydrogen donor additives increase the molecular mobility in the liquid phase by stabilising the free radicals formed by thermal decomposition of coal. Hydrogen donor additives also increase the temperature range over which fluidity occurs, thereby allowing the formation of large sized mosaic structures. Mittal pitches (CTP) and tetralin were examined for their effectiveness as hydrogen donor additives. Refcoal blends containing 10 to 50% by mass additive were prepared by mixing and carbonisation conducted at temperatures ranging form 400 to 1 000 °C.

Samples were analysed using thermogravimetric analysis (TGA), diffuse reflectance infrared Fourier transform (DRIFT), optical microscope techniques, scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD). It was found that addition of at least 10% tetralin improves the optical texture of Refcoal cokes and also increases the carbon yield. In both tetralin and pitch addition, 20% additive gave coarse circular anisotropic cokes after carbonisation at 650°C. However the carbon yield was reduced for the Refcoal coke treated with Mittal pitch. In fact the yield roughly decreases with an increase in pitch content. Although the cokes from pitch treated Refcoals showed a low ratio of d/g (where d indicates the degree of disordering and g the degree of ordering), Raman and XRD results indicate little further improvement in crystallinity but SEM showed development of a smooth morphology with increasing pitch content. Previous literature results suggest that this indicates that the material must have passed through a mesophase stage.

Surprisingly, the addition of tetralin yielded cokes with high ratio of d/g, but improved the carbon yield and optical anisotropy. Increasing tetralin content in the carbonising system increased the size of anisotropic textures but the SEM micrographs show rough morphology with compounds that appear to inhibit mesophase spheres coalescence.

KEYWORDS: Carbonisation, hydrogen donor additive and anisotropic cokes.

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LIST OF ABBREVIATIONS

°C	degrees Celsius
10MP400	Coke from HTRef mixed with 10% pitch after carbonised at 400°C
10MP500	Coke from HTRef mixed with 10% pitch after carbonised at 500°C
10MP650	Coke from HTRef mixed with 10% pitch after carbonised at 650°C
10MPR	Refcoal mixed with 10% Mittal pitch
10TN1000	Coke from HTRef with 10% tetralin after carbonised at 1 000°C
10TN500	Coke from HTRef with 10% tetralin after carbonised at 500°C
10TN650	Coke from HTRef with 10% tetralin after carbonised at 650°C
10TNR	Refcoal mixed with 10% tetralin
20MP1000	Coke from HTRef mixed with 20% pitch after carbonised at 1 000°C
20MP400	Coke from HTRef mixed with 20% pitch after carbonised at 400°C
20MP500	Coke from HTRef mixed with 20% pitch after carbonised at 500°C
20MPR	Refcoal mixed with 20% Mittal pitch
20TN650	Coke from HTRef with 20% tetralin after carbonised at 650°C
20TNR	Refcoal mixed with 20% tetralin
50MP500	Coke from HTRef mixed with 50% pitch after carbonised at 500°C
50MP650	Coke from HTRef with 50% pitch after carbonised at 650°C
50MPR	Refcoal mixed with 50% Mittal pitch
50TN650	Coke from HTRef with 50% tetralin after carbonised at 650°C
50TNR	Refcoal mixed with 50% tetralin
Ar	Aromatic
AR	As received
ASTM	American Society of Testing and Materials
COG	Coke oven gas
CTE	Coefficient of thermal expansion
CTP	Coal tar pitch
DMF	N, N-dimethylformamide
DRIFT	Diffuse reflectance infrared Fourier transformation
DTGS	Deuterised triglycerine sulphate
DTG	Differential Thermogravimetry
FTIR	Fourier transform infrared

HF	Hydrofluoric acid
Hg	Mercury
HT	High temperature (135°C)
HTRef	High-temperature extracted (135°C) Refcoal
KBr	Potassium bromide
kV	Kilovolts
LT	Low temperature (95°C)
M1000	Coke from carbonisation of HTRef at 1 000°C
M400	Coke from carbonisation of HTRef at 400°C
M450	Coke from carbonisation of HTRef at 450°C
M500	Coke from carbonisation of HTRef at 500°C
M550	Coke from carbonisation of HTRef at 550°C
M650	Coke from carbonisation of HTRef at 650°C
MP	Mittal pitch
MP1000	Coke from carbonisation of Mittal pitch at 1 000°C
MP400	Coke from carbonisation of Mittal pitch at 400°C
MP500	Coke from carbonisation of Mittal pitch at 500°C
MP550	Coke from carbonisation of Mittal pitch at 550°C
MP650	Coke from carbonisation of Mittal pitch at 650°C
mW	milliwatts
NaOH	Sodium hydroxide
NMP	N-methylpyrrolidone
NMR	Nuclear magnetic resonance
OM	Optical microscope
PBMR	Pebble Bed Modular Reactor
PPC	Primary coking coal
r/min	Rotations per minute
SABS	South African Bureau of Standards
SEM	Scanning electron microscope
SRC	Solvent-refined coal technology
TBAH	Tetrabutylammonium hydroxide
TCNE	Tetracyanoethelene
TG	Thermogravimetry

TGA	Thermogravimetric analysis
TN	1, 2, 3, 4-tetrahydronaphthalene (tetralin)
UV	Ultraviolet
XRD	X-ray diffraction

CHAPTER 1: LITERATURE SURVEY

1. INTRODUCTION

Eskom is one of the largest power suppliers in the world and South Africa's main electricity supplier. Its older coal-fired power stations will reach the end of their design life by 2025. A total estimated electricity demand of 80 000 MW will be required after 2025. The cost of coal transportation to different power stations and carbon dioxide emissions to the environment are major challenges faced by the electricity supply companies. On the other hand, the large area occupied by the coal-fired power stations could be used for industrial development (Nicholls, 2005 & Koster *et al.,* 2003).

South Africa is now in the process of reviewing and re-establishing nuclear-based power generation through the Pebble Bed Modular Reactor (PBMR) project. This is because of a variety of problems (such as the quality and quantity of coal) experienced with the coal fired electricity power station. The facility (PBMR) is planned to have several reactors and these will generate 165 MW of power per unit. In order to meet the required electricity demand as estimated, about 500 units need to be built if all the electricity is to be supplied through PBMR nuclear technology power generation. This technology is considered to be economically inexpensive and environmentally safe (Nicholls, 2005).

Graphite is the main construction material of the PBMR core reactor and also the main safety feature of the reactor: it has to contain specified levels of impurities, such as metals and minerals. Calcium, strontium and iron are the main catalytically active impurities in graphite, whereas boron, cadmium, gadolinium and europium are high neutron absorbers (Haag *et al.*, 1990). According to the D 7219-05 standard (ASTM) on limits for graphite impurities, the impurities are specified to be calcium < 10 ppm, sodium < 5 ppm, iron < 10 ppm, boron < 10 ppm, cadmium < 0.05 ppm and less than 0.05 ppm for europium. This is normally summarised by an upper limit of about 100 ppm for the ash content of nuclear graphite (Zhao *et al.*, 2006b). Unfortunately, the natural graphite available all over the world is insufficient for use in nuclear power generation.

Needle cokes, produced by delayed coking of petroleum residues, were previously used as the main alternative source of well-graphitisable cokes, but the kind of graphite they produce is undesirable for PBMR purposes (Nicholls, 2005). The graphite required for this application needs to have a high level of isotropy and a low level of anisotropic content. The most desirable coke particle to produce this graphite has a spherical shape, with a high level of a randomly orientated, separate mesophase. Gilsonite used to be the coke that offered such properties and it was obtained from natural bitumen mined in the US. Unfortunately, this material is no longer available from the US and therefore alternative sources are required.

Since graphite is a crystalline form of carbon, the conversion by heat treatment of disordered carbon such as coal and pitches may be required for the manufacture of graphitising cokes. To obtain such cokes, the precursor must pass through a liquid crystalline state, the 'mesophase', during the pyrolysis process. This mesophase has demonstrated the potential to be a good precursor for the manufacture of needle cokes, fibres, binders and fillers (Haag *et al.*, 1990; Dwivedi *et al.*, 1995; Sharma and Singh, 1995; Zondlo *et al.*, 1996 & Choudhury *et al.*, 1997).

In a project undertaken by the CSIR, the development of the so-called Refcoal process, coal from Tshikondeni mine proved to be a possible source of a carbon precursor (i.e. Refcoal) for the manufacture of graphitisable cokes. The Refcoal process was reported to provide a means of pre-purifying coking coals to the level of impurities required for the production of nuclear-grade graphite. The method involves dissolving the organic part of coal in a suitable solvent (e.g. N, N-dimethylformamide (DMF)) and an alkaline medium of sodium hydroxide or potassium hydroxide under an inert atmosphere. Operational temperatures ranging from ambient to just below the boiling point of the extracting solvent (about 135°C) were investigated (Morgan, 2000). The use of alkali solutions such as sodium ethanolate (EtONa) and ammonium hydroxide or carbonate to aid coal solubilisation is documented elsewhere (Onal and Ceylan, 1997).

1.1 Aim of the study

This study was aimed at producing anisotropic cokes from Refcoals obtained through coal extractions at 135°C. Refcoal refers to the kind of coal extract produced from the extraction of coal with a polar aprotic solvent, e.g. DMF, and an alkali medium at operational temperatures below the boiling point of the extracting solvent. A high yield of carbon precursors (Refcoal) is obtained at 135°C compared with those obtained at lower extraction temperatures. There is also no induction period at this extraction temperature, unlike at lower temperatures. On the other hand, the low-viscosity solution obtained at 135°C facilitates the removal of impurities on further purification. However, it was proposed that the extraction of coal at high temperatures would produce Refcoal that would carbonise to entirely isotropic cokes. This hypothesis was made based only on the results obtained from Refcoals produced at ambient temperature and 95°C.

Anisotropic cokes are formed from carbon precursors that pass through the liquid stage (mesophase), whereas isotropic cokes are the products of carbon structures that are cross-linked and are macromolecular in nature. Isotropic cokes are not formed via the mesophase stage. Hydrogen-donor additives facilitate the formation of the mesophase stage during carbonisation. The hydrogen donors investigated in this study are 1, 2, 3, 4-tetrahydronaphthalene (tetralin) and Mittal pitches. Co-carbonisation of these hydroaromatic compounds with Refcoal was expected to modify the coking properties of Refcoal. These compounds were chosen mainly because of their aromatic nature, reactivity and hydrogen-shuttling ability.

Carbonisation of samples was performed in an autoclave using as sample holders aluminium cans for temperatures up to 650°C and graphite cups for higher temperatures. The resultant products, before and after carbonisation, were characterised using thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy (SEM), optical microscopy and X-ray diffraction (XRD).

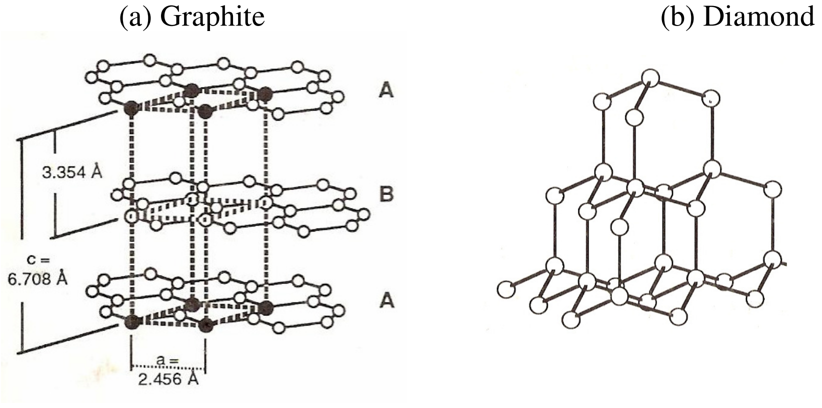
The present study is therefore aimed at investigating most of the assumptions made on the 135°C Refcoal. The following key factors were considered for investigation in this study:

- Is there a correlation between absorbance and concentration of coal extracts during the extraction process?
- What are the structural properties of cokes produced from Refcoals obtained at 135°C?
- What are the effects of co-carbonisation of the 135°C Refcoals with tetralin and Mittal pitches?

1.2 Carbon and its allotropes

The element carbon has an atomic number of six in the periodic table and an atomic weight of 12.011 g/mol. Its electronic configuration is [He] $2s^2\ 2p^2$, indicating that it has four electrons in the outer shell. It is these outer electrons that this element uses during bonding. Its three isotopes are ^{12}C, ^{13}C and ^{14}C, with ^{12}C being the most stable and naturally abundant isotope. ^{14}C is the radioactive carbon isotope generated in the atmosphere through the neutron bombardment of nitrogen. ^{13}C, because of its magnetic moment (spin ½), is used as a probe for nuclear magnetic resonance (NMR) studies. Different forms of carbon result from different orbital hybridisation states, i.e. sp^3, sp^2 and sp (Edwards, 1989).

Carbonaceous materials such as coal and charcoal are examples of the amorphous forms of carbon (Edwards, 1989 & Bourrat, 2000). The two ordered allotropes/forms of carbon are graphite or diamond (see Figure 1.1). Diamond (sp^3 bonded carbon) is observed as an isotropic form and is known to have a face-centred cubic structure with interatomic distances of 0.1545 nm. Each element is covalently bonded to four other carbon atoms in a tetrahedron format. Its stability and hardness result from the regular three-dimensional network of σ-bonds. It also has a higher density (3.51 g/cm^3) than graphite (2.25 g/cm^3).


(a) Graphite

(b) Diamond

Figure 1.1: Crystalline forms of carbon: (a) graphite; (b) diamond (Edwards, 1989)

Graphite has both σ and π bonds holding together the atoms in an infinitely hexagonal order. Graphite (sp^2 bonded carbon) is an anisotropic form of carbon consisting of semi-infinite layers of carbon atoms that are hexagonally distributed in the plane of the sheets. The stacking of layers is ABAB… with atoms aligning with each other in alternating planes. The interlayer spacing between two subsequence layers is 0.3354 nm, with an interatomic distance within sheets of 0.1415 nm. In addition to conventional graphite, a rhombohedral crystal structure exists with an ABCABC…. stacking arrangement. However, this form of carbon is unstable and transforms to a hexagonal structure at temperatures above 1 300^{o}C. Van der Waals-type forces weakly bond the layers in graphite to each other. This makes it a soft material that can be used as a lubricant because the energy needed to slide the layers over one another is low. The strong π-bonding contributes to its high electrical and thermal conductivity (Fiala, 2000).

Other interesting carbon forms include carbon nanotubes and buckminsterfullerene. The latter was discovered in the early 1980s. This carbon form consists of 60-carbon clusters having the shape of a soccer ball. Because of the ball-like curved structure, they are also called ‘bucky balls’ (Jacqualine and Grand, 1992 & Fiala, 2000).

1.2.1 Graphitisable and non-graphitisable carbons

Graphitisable carbons (also referred to as anisotropic carbons) are carbon materials with parallel arrangements of lamellae that have the ability to graphitise on heating to temperatures as high as 2 600°C, whereas isotropic carbons do not graphitise even at temperatures exceeding 3 000°C (Marsh and Walker 1979 & Marsh and Menendez, 1989). Anisotropic carbons resemble a graphite lattice in which carbon atoms are hexagonally linked by sp^2 trigonal bonds. However, there is no three-dimensional ordering in these carbons.

Graphitising carbons are formed from substances (including coking coals) that are inherently rich in hydrogen and relatively poor in oxygen. These materials pass through a fluid stage, the mesophase, during carbonisation. This leads to highly ordered structure (Figure 1.2c); in which neighbouring crystallites align themselves closely parallel to each other. Chaudhuri *et al*. (1997) found that the formation of ordered texture in coke depends on the presence of planar molecules of appropriate size and on the existence of conditions that ensure sufficient mobility of the molecules for the ordering of the lamellae. Conversely, if no fluid phase is present, the carbon that forms will be isotropic (Figure 1.2a). This type of carbon is commonly termed a char (Thrower *et al.,* 1942).

Non-graphitising carbons have the lamellae arranged randomly relative to each other, perhaps with ordering in a short range. These carbons result from carbon structures that do not fuse or melt (e.g. wood and non-fusing coals) during the carbonisation process. They originate from materials such as cellulose, wood and nutshells, which are macromolecular in nature. They may also be the products of cross-linked structures of low-rank coals and non-coking coals. The partially graphitisable carbons (Figure 1.2b) have characteristics intermediate between those of the other two carbons (Mochida *et al*., 1977 & Marsh and Menendez, 1989).

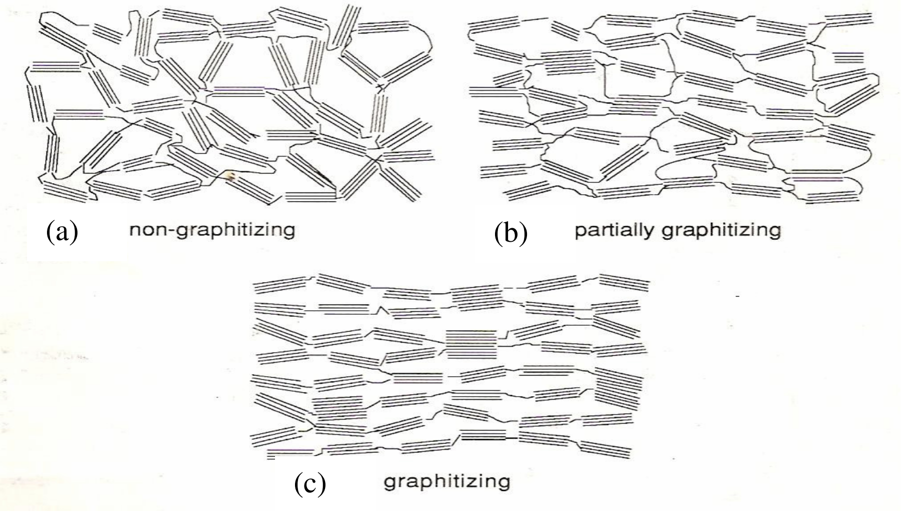


Figure 1.2: Franklin models of carbon structures: (a) non-graphitising carbon (b) partially graphitising carbon and (c) graphitising carbon (Edwards, 1989)

Under favourable conditions (e.g. sufficient residence time and pressure) anisotropic spheres are formed at the expense of the surrounding isotropic materials and coalesce to form large domains of ordered regions. These domains eventually solidify to semicoke. If the growth and coalescence of the mesophase is inhibited, irregularly shaped anisotropic spheres of small scale (0.3-10 µm grain size) are formed (Thrower *et al.,* 1942 & Marsh and Walker, 1979).

1.3 Carbonisation process

Carbonisation, also known as 'coking', is a general phrase referring to the process of converting carbon precursors or carbon-containing compounds in the absence of air to different microstructures, with a degree of structural ordering, through the pyrolysis process. The products of this process are solid carbons, residues, gaseous molecules and volatile hydrocarbons. As with all other pyrolysis processes, carbonisation also involves simultaneously occurring complex reactions, such as condensation, dehydrogenation, isomerisation, hydrogen transfer and polymerisation (Burchell *et al.*, 1999 & Komaki *et al*., 2005).

Carbonisation of coal entails a stepwise heating of the coal to temperatures as high as 1 600°C in the absence of oxygen in order to distil out tars and light oils. A gaseous by-product referred to as 'coke oven gas' (COG) along with ammonia, water and sulphur compounds are also thermally removed from the coal. The coke that remains after this distillation is composed largely of various crystallographic forms of carbon. These carbons may also contain the thermally modified remains of various minerals that were in the original coal. The mineral remains, commonly known as 'coke ash' do not combust and are left as a residue after the coke has been burned in air (Vorres *et al*., 1979).

1.3.1 Low-temperature carbonisation

Low-temperature carbonisation is considered to be effective in the temperature range from ambient to 700°C. In this range, the aim is generally to produce coke with a high-level tar and species of low molecular weight. This coke is marketed as a smokeless domestic fuel that may be produced in lump or powder form, both of which are black and porous, containing 8 to 20% volatile matter. In this case the solid yield is in the range of 70 to 80%, with a tar yield of 7 to 10%.

In the first stage of carbonisation, adsorbed gases such as water vapour, carbon dioxide, oxygen, nitrogen and methane are lost at temperatures below 200°C. With further heat treatment up to 450°C, the structure softens, decomposes into its components and continues to evolve H_2O, CO_2 and CH_4. The development of pores in the coal structure is also noticed at this stage as tar and oils start to be evolved. As oils and tars migrate into the structure through these pores, some structural patterns are induced in the entire coal structure.

In the case of prime coking coals, at temperatures of about 425°C the plasticised reactive macerals of these coals form a mesophase stage, which, at the expense of the isotropic parent liquor, form an anisotropic ordered mosaic structure. Raising the temperature to 500°C evolves gases that are trapped in the plastic phase. This leads to the swelling of coal and eventually a coke is formed. At temperatures above 500°C, additional liquids with a high molecular weight and gases are evolved, but this process ceases above 700°C when the structure solidifies (Vorres, 1979 & Gray, 1989).

1.3.2 High-temperature carbonisation

High-temperature carbonisation is employed for making metallurgical coke at temperatures above 700°C. This type of carbonisation is aimed primarily at manufacturing a hard coke for use in cupolas and blast furnaces. The solid yield on the dry basis is about 70% and the volatile matter of the final coke is less than 1%. This clearly implies that the coke produced in this temperature range is of high quality and rich in carbon. In high-temperature carbonisation, the evolved gases are mainly hydrogen and methane. The solid product obtained at these temperatures has a volatile matter content of 1 to 8%, a carbon content of 55 to 70% and 4.5 to 5.5% tar. It is normally used for domestic fuel and industrial steam-raised equipment. In some industries, the ammonia recovered from the gases and liquor is converted to ammonium sulphite (Gibson and Gregory, 1971). Figure 1.3 summarises the transformation of coal to coke in a single coal particle during carbonisation.

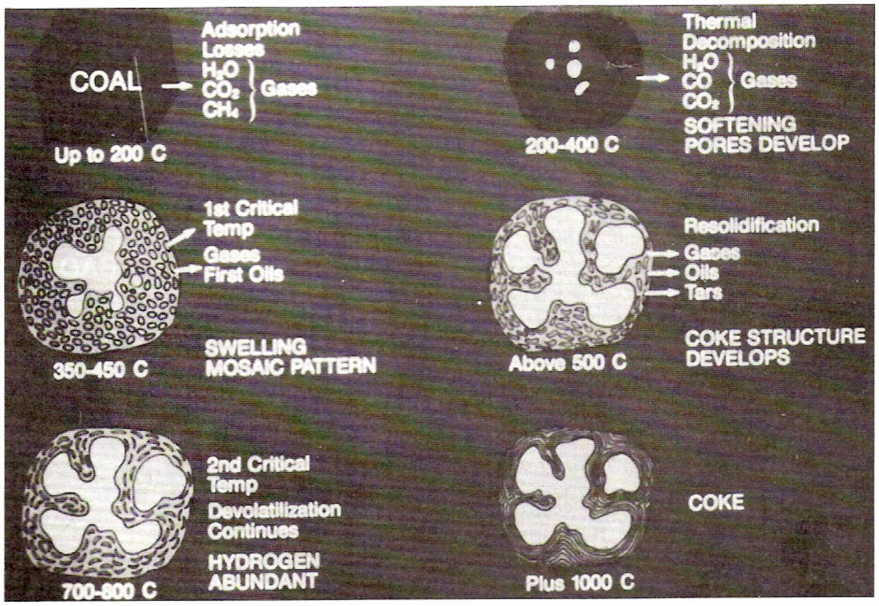


Figure 1.3: The process of coal transformation to coke in a single coal particle during carbonisation (Gray, 1989)

1.3.3 Mesophase stage

The word ‘mesophase’ is derived from the Greek word *mesos*, meaning intermediate species. Brooks and Taylor (1968) first described mesophase as a discotic nematic liquid crystal that consists of aromatic oligomers in which the aromatic planes are stacked approximately parallel to each other. It forms during the liquid-phase pyrolysis of many aromatic hydrocarbons such as prime coking coals, coal tar and petroleum pitch in the temperature range 350 to 450°C (Marsh and Walker, 1979) and results from aromatic polymerisation, as well as the vaporisation of volatile species. Both the concentration and the size of flat aromatic molecules are increased in this stage. The carbonaceous mesophase contains molecules that are aligned parallel to each other, similar to a batch of discs. This mesophase is required during carbonisation to promote the crystallographic alignment of the carbon atoms into locally oriented regions known as a ‘mosaic structure’. It is therefore considered as the first step in the formation of graphitic materials (Brooks and Taylor, 1968; Zimmer and White, 1978 & Dubois *et al.,* 1970).

The progress of the mesophase during carbonisation was first studied by Lewis and Kovac (1978) and White and Buechler (1986). The studies proposed that the mesophase proceeds through several successive steps of nucleation, growth and coalescence of anisotropic spheres into a final bulk mesophase. Greinke *et al.* (1988) reported that the mesophase could be due to the macroscopic changes experienced during the softening stage, accompanied by microstructural rearrangements within the fluid phase.

Mesophase formation may also result from the extremely complex and interdependent physical and chemical processes occurring during carbonisation. The first chemical changes during this stage are the rupture of weak bonds, the breaking down of molecular networks and the formation of free radicals (Scaroni *et al.,* 2003). Mochida *et al.* (1977) first extracted the mesophase as a quinoline-insoluble fraction in carbonised pitch. Santamaria-Ramirez *et al.,* (1999) were the first to report the chemistry of the mesophase using petroleum residue in a pressurised autoclave.

According to the Spider Wedge model, the mesophase consists of aromatic units 0.6–1.5 nm in diameter, linked by phenyl-phenyl or methylene bridges to give a molecular weight in the range 400–4000. These aromatic planes consist of some alkyl and naphthenic groups. A computational modelling study (Monte Carlo simulation) of the mesophase suggested that a minimum molecular weight of about 600 Dalton is required for the formation of the carbonaceous mesophase (Khanna *et al.,* 2005). This method also indicated that a mixture of both large and irregular molecular sizes is required for the development of the mesophase. Although the maximum coal fluidity development during pyrolysis and the molecular weight distribution of the mesophase system are regarded as vital for controlling mesophase growth (Carreira *et al.,* 2001), it is still difficult to determine the major factors affecting mesophase formation, since several of the factors mentioned above occur simultaneously (Sanada *et al.*, 1973).

1.3.4 Effects of additives during carbonisation

The coking properties of coals considered to be poor coking coal can be improved by the incorporation of non coking coals with different small amounts of additives, depending on the desired coke properties. The process of modifying the carbonising species with an additive to change its coking properties is called the ‘co-carbonisation processes'. This process was first developed for economic reasons, the aim being to improve the properties of the coke such as mechanical strength, reactivity, thermal properties and fluidity development of the carbonising system. The two categories of additives known to have this effect are inert diluents and reactive additives (Loison, *et al.*, 1963 & Yokono *et al.*, 1981).

Inert additives may provide sites for complex reactions of coal and some may reduce the fluidity of the carbonising system by absorbing primary decomposition products (e.g. hydrogen donor additives). On the other hand, reactive additives may react chemically with the pyrolytic products (Gibson and Gregory, 1971). The most commonly investigated additives are oxygen, metal catalysts and organic (hyrdogen-donor) additives.

1.3.4.1 Oxygen

Oxygen is the most studied additive in coal utilisation processes. Similar to other heteroatoms such as sulphur, oxygen is known to severely retard mesophase development by increasing the viscosity of the carbonising system. For example, the presence of oxygen during carbonisation destroys the plasticity of coal by the formation of ether and ester cross-links. These cross-linkages lead to the reduction of the aliphatic hydrogen and carbon content of coal (Schmidt, 1945 & Clemens *et al.*, 1989). The products of oxidation are mainly water and carbon dioxide, which are also undesirable in carbonisation. In addition, oxidation increases the softening temperature and reduces the resolidification temperature of coal. This shortens the temperature interval of the fluid stage (Barr and Lewis, 1978).

Although coal oxidation is harmful under normal coking practices, it may be viewed as useful in some other applications. For example, oxidative stabilisation treatment of coal is a good technique for reducing swelling of the coke structure (Tzeng and Wang, 2001). Oxidation of a Refcoal sample followed by hydrogenation with diabietic acid was reported to prevent the development of cracks during carbonisation (Ludere, 2006). Oxygen-containing groups behave as acids or bases, which possess ion-exchange properties for use in the preparation of carbon-supported noble catalysts by exchange with cationic metal complexes (Shim *et al.*, 2001). Marsh *et al.,* (1973) proposed that the presence of some oxygen-containing compounds (except for phenol which retards mesophase growth) improves mesophase growth during carbonisation.

1.3.4.2 Metal catalysts

Metal catalysts such as iron oxide are commonly used during graphitisation as puffing inhibitors, although their effectiveness begins just within the carbonisation temperature region. During heat treatment of coke from 1 400 to 1 800°C, sulphur is the main cause of puffing when it evolves. Puffing of coke causes cracks and shutting of the carbon structure. It was reported that iron (III) oxide reacts with sulphur in the coke, delaying the time of sulphur release. Other inhibitors that were previously investigated are boric acid, aluminium chloride and iron (II) sulphate (Letizia, 1977a & 1977b). The addition of puffing inhibitors during carbonisation and graphitisation also improves the optical texture size and crystallographic parameters of the resulting carbon material (Kawano *et al.*, 2000).

1.3.4.3 Hydrogen donor additives

Hydrogen donor additives are basically used to stabilise the free radicals formed by the thermal rupture of bonds in reactive species during the carbonisation process. This prevents extensive cross-linking at the early stage of carbonisation. Hydrogen donor additives suppress the intermolecular reactivity of the constituent molecules of the mesophase, thereby facilitating the growth, coalescence and mobility of the liquid crystal system (Marsh and Menendez, 1988). They may also lower the temperature of mesophase formation and also enhance the coalescence of mesophase (Yokono *et al.,* 1981).

Several authors (Lewis, 1982; Diez. *et al*., 1999 & Swietlik *et al*., 1999) have reported that hydrogen donor additives provide enough mobility for aromatic molecular systems to stack parallel to each other by delaying the formation of coke. This leads to the development of anisotropic texture in coke. The plastic phase of carbonisation is also extended and the fluidity of the carbonising system is lowered. However, a very low viscosity of the plastic phase leads to a highly porous coke (Kolar-Legin *et al*., 1999 & Swietlik *et al*., 1999). The process of stablisation of free radicals by hydrogen transfer during carbonisation is illustrated in Figure 2.4. Note the sizes and types of molecules formed in the system with a hydrogen donor additive (**I** in Figure 2.4) and the cross-linkages shown by the system carbonising in the absence of a hydrogen donor additive.

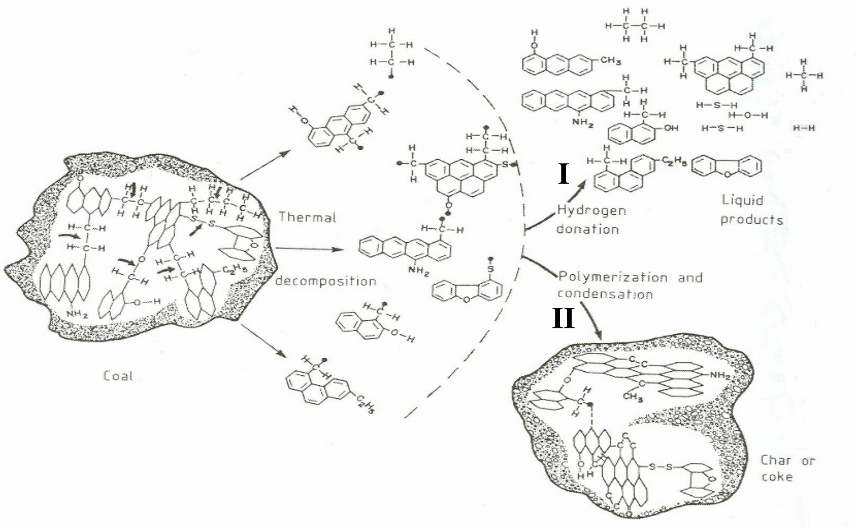


Figure 1.4: Stabilisation of free radicals by hydrogen transfer during carbonisation (Scaroni *et al*., 2003)

Hydroaromatic compounds such as coal tar pitch (CTP) and 9, 10-dihydroanthracene have the potential to carbonise when singly coked. They also have good reactivity with coal. These compounds are therefore considered as successful hydrogen donor additives and modifying agents for weakly coking coals. Hydroaromatic compounds may also serve as solvating vehicles, thereby maintaining the fluidity of the carbonising system (Yokono *et al.*, 1981).

Marsh and Neavel (1980) were the first to report the ability of coal tar pitch to transfer hydrogen when co-carbonised with coal. Kolar-Legin *et al*. (1999) examined the ability of CTP to aid the development of globular and lamellar structural components in coke. The use of CTP as a modifying agent also decreases the interlayer spacing (d_{002}) during graphitisation. Swietlik *et al*. (1999) found that CTP acts as a suspension medium (delaying agent) during mesophase arrangement and also improves the mode of arrangement of aromatic layers in the final coke structure. CTPs allow an increase in the aromatic content of the carbonising system and hence a better structural development. They are also capable of supplying and consuming hydrogen when co-carbonised respectively with good hydrogen acceptors (e.g. anthracene) and hydrogen donor agents such as 9, 10-dihydroanthracene (Diez *et al*., 1999).

Other hydroaromatic organic additives that may be used as hydrogen donor additives include acenaphthylene, chrysene, phthalimide, anthracene and pyrene. Unlike decacyclene and CTP, pyrene and chrysene provide a poor interaction with oxidised coals and do not penetrate easily into coal. But when an un-oxidised coal is used, chrysene is an effective modifier of the optical texture size because of its lowest free valence as compared with pyrene and decacyclene (Yokono *et al.,* 1981). Mastral *et al*. (2001) and Sugano *et al*. (2005) investigated the use of tyres as hydrogen donor additives during coal conversion processes. In this case it was found that the aliphatic compounds in the aromatic rubber composition of tyres make them promising hydrogen donors. Unfortunately, their carbon black content inhibits coalescence of spheres in the fluid stage.

The proportion of the additive in the carbonising system is critical for effective use of the additive. Mochida *et al*. (1979b) reported an optimum coal:additive ratio of 7:3 (30% additive). In this case the least and the most hydrogenated coals resulted in an optically isotropic texture, whereas the averagely hydrogenated coals produced coarse (for the highest moderate) and fine mosaic textures (for the lowest moderate) (McMillen *et al.*, 1987 & Shibaoka*,* 1982b).

1.3.5 Temperature

During the initial stage of carbonisation, temperature is the main cause of decomposition of the coal structure and the evolution of gases. When carbonisation proceeds under elevated temperatures, the mobility of molecules and the formation of volatile matter are increased (Shibaoka, 1982a). Increasing the temperature further improves the rearrangement of the mesophase liquid crystals.

Marsh *et al.* (1973) reported an increase in the size of the mesophase domain spheres with an increase in temperature. On the other hand, a low carbonising temperature and a slow heating rate favour an increased coke yield. This is mainly because the volatile matter remains for longer in the carbonising mass, thereby promoting secondary cracking of the volatiles. The development of anisotropic spheres increases with increased carbonisation temperature (Mochida *et al.*, 1987 & Man *et al.,* 1997).

1.3.6 Pressure

Most petroleum and coal processes are operated under atmospheric pressure conditions. But for commercial considerations, the use of high pressure has become a point for discussion among most researchers (Tzeng *et al.*, 2002 & Man *et al.*, 1994). Laboratory-scale pressure carbonisation is normally carried out in a 'tube bomb' at rapid heating under conditions similar to those employed in a commercial, delayed coking process. However, very little information is available on the effect of pressure on the properties of the mesophase at low heating rates.

When carbonisation is performed under high pressure, coke properties such as anisotropic texture, bulk density, the coefficient of thermal expansion (CTE), the release of volatile matter, coke yield and the viscosity of the plastic phase are either directly or indirectly affected (Mochida *et al.*, 1986, Mochida *et al.,* 1988, Tzeng *et al.*, 2002 & Man *et al.*, 1997). Marsh (1973) used pressure to isolate the liquid crystals and other shapes of the mesophase during the carbonisation of models of heterocyclic compounds.

Pressure carbonisation lowers the viscosity of the carbonising system by delaying the evolution of volatile matter. The delay maximises the thermal cracking of volatiles. This allows the production of more radicals and also extends the interaction between hydrogen and radicals (Rodriguez-Reinoso *et al.*, 1998a). Man *et al.* (1997) explored the technique of pressure carbonisation to increase the development of fluidity in the mesophase stage and also to enhance the secondary cracking of volatiles.

1.3.7 Coke and its applications

Coke is a carbonaceous product of the pyrolysis of organic materials, at least part of which has passed through the liquid phase. It is derived from the destructive distillation of organic matter, particularly coal and petroleum residuals. The resulting carbon structure is a mixture of various optical texture sizes, ranging from optically isotropic texture to domain and flow texture, depending on the carbonisation condition (Gray *et al.*, 1989 & Stansberry *et al.*, 1999). Most cokes are produced as by-products in the delayed coking industries. The different types of coke include green coke, calcined coke, petroleum coke, coal-derived pitch coke, metallurgical coke, delayed or needle coke and hybrid coke. Their applications range from fuels, supporting materials in the blast furnace and fillers to electrodes in metallurgical industries (Rodriguez-Reinoso, 1998b & Gray *et al.*, 1989).

Green coke is a primary solid carbonisation product obtained from high-boiling carbon fractions at temperatures below 900°C, whereas calcined coke is a petroleum- or coal-derived pitch-like coke with a mass fraction of hydrogen of less than 0.1 wt%. Petroleum cokes, which are commonly used as fuels, are the carbonisation products of high-boiling carbon fractions obtained in petroleum processing. Coal-derived pitch cokes, on the other hand, are the primary industrial solid carbonisation products from coal-tar pitch. Metallurgical coke and delayed coke are the most-used cokes due to their distinctive properties. Metallurgical coke and needle coke are normally produced in a delayed coking process by the carbonisation of coal or coal blends at a temperature of 1 400 K to produce a macroporous carbon material of high strength (Gray *et al.*, 1989).

1.4 Coal

Coal is a solid, flammable, brownish-black rock formed in wetland ecosystems where plant debris was saved by water and mud from oxidation and biodegradation. When plant debris is buried in the presence of pressure and temperature for a long period, it undergoes first peatification and then coalification. This results in the formation of different kinds of coal. The degree of coalification, referred to as the 'rank', depends on factors such as pressure, temperature and the period that the debris has been buried. This complex is composed principally of organic entities called 'macerals' (Suarez-Ruiz, 2000) and to a lesser extent of inorganic entities called 'minerals'. The three major groups of macerals are: vitrinite, liptinite (exinite) and inertinite. The vitrinites are derived from various decompositions of woody tissues and the liptinites are derived from spores and pollen coats, cuticles, resins, and other fatty secretions. Inertinites, on the other hand, are derived from the intensive chemical degradation induced by micro-organisms. Water and gases are also trapped in sub-microscopic pores. The organic entities comprise mainly carbon, along with other elements such as hydrogen, sulphur and nitrogen (Ting, 1982 & Wilson and Wells, 1950).

Coal is mined from the ground by either underground mining or open-pit mining (Van Krevelen, 1961 & Kabe *et al.*, 2004). Worldwide, it is the fuel most widely used for the generation of electricity, as well as the largest source of carbon dioxide emissions which are considered to be the largest cause of global warming. It is also used for the manufacture of various carbon products such as chemicals, plastics, cokes, pitches and other carbonaceous materials, such as high-performance carbon-carbon composites, fibres and nuclear-grade graphite (Pitt *et al.*, 1979 & Stansberry *et al.*, 1999).

1.4.1 Coalification

Coalification is a general phrase referring to the formation of coals of different ranks, i.e. peat, lignite, sub-bituminous, bituminous and anthracite. Coalification is geologically defined as a range of chemical changes, some microbiological changes and thermal changes acting on plant debris. These changes include the naturally occurring photosynthesis process in which CO_2 is changed into cellulose and protein in the presence of water. The process can therefore be considered as reverse combustion process (Pitt *et al.,* 1979 & Scaroni *et al.*, 2003). The properties of coal are characterised in terms of rank, type and grade. The rank and type refer to the level of the coal's maturity and the kinds of plant from which it formed, whereas the grade is the purity. Most coal classification standards use volatile matter, fixed carbon, calorific value, and moisture content and vitrinite reflectance. However, these standards may differ between individual countries (Kabe *et al.*, 2004).

As a coal matures, its rank increases. Consequently, the moisture, volatile matter and ultimately the oxygen and hydrogen contents decrease, whereas the fixed and ultimate carbon, the calorific value and the vitrinite reflectance increase. All these measurements are therefore used to classify coal (Tsai, 1982; Crelling, 1989; Suarez-Ruiz, 2000 & Kabe *et al.*, 2004).

1.4.2 Coal classification

Coals are classified by rank according to the ASTM D388-05 method (American Society for Testing and Materials), into four classes: lignite, sub-bituminous, bituminous or anthracite (Gray, 1989). These ranks are also specified by the proximate analysis (moisture, volatile matter, fixed carbon and ash contents), the fuel ratio and the heating value. The heating value is the ratio of the percentage of fixed carbon to volatile matter. The petrographic classification of coals, on the other hand, is concerned with the textural components of coal as analysed by microscope. The coal texture includes microlithotype and macerals, the macerals being the most used texture for petrographic classification (Kabe *et al.*, 2004).

1.4.2.1 Rank classification

Rank classification is concerned with the level of maturity reached by a coal through the coalification process, which changes both the physical and chemical properties of coal. The rank classification based on the ASTM D388-05 method is a measure of the continuous development of the parent plant material towards a pure carbon or graphite structure. Thus the composition of carbon in coal increases as the rank increases from lignite, via bituminous to anthracite. There is also a decrease in the oxygen and hydrogen contents. The reactivity also decreases in this order.

According to ASTM D388-05, the different ranks are specified through the standard heating technique, proximate analysis, in which the moisture, volatile matter, fixed carbon, ash and fuel ratio (heating value of a coal) are measured. This technique involves heating a weighed coal at the rate of 100°C/min in a covered crucible to temperatures as high as 950°C and maintaining it at this temperature for 6 minutes. Lignite contains the most moisture and volatile matter and also has a low heating value. The volatile matter and the moisture content decrease from 52% and 69% to less than 1% and 2% for anthracite and lignite respectively. The fixed and ultimate carbon, colorific value, as well as the vitrinite reflectance, increases with rank. Thus anthracite contains a low level of volatile matter and has the highest carbon content (94%) (Tsai, 1982 & Crelling, 1989). The proximate analysis for the coal used in this study is given in Table 1.1.

Table 1.1: Proximate analyses of Tshikondeni coal (Mthembi, 2003)

Parameter	Content (%wt)
Moisture[b]	0.9
Volatile matter[a]	23.3
Fixed carbon[a]	66.4
Ash[a]	9.4

a = analysis on a moisture-free basis
b = analysis on a moisture to air-free basis (maf)

1.4.2.2 Petrographic classification

Petrographic classification entails the physical composition of coal, i.e. macerals, pores and minerals. Thus this classification method is based on the variation of the physical properties (e.g. colour and appearance) resulting from the degradation of different parts of the parent material. The method is mainly concerned with the reflectance of light by the organic entities called macerals. Macerals are petrograhically classified by their physical and chemical properties as liptinites (or exinites), vitrinites and inertinites, depending on the structure of the fossilised plant tissue and its constituents. In terms of appearance and colour, liptinites are leaf-like and greyish in colour; vitrinites are smooth and appear whitish-grey, whereas inertinites are white in colour. The white colour indicates the dominance of carbon, whereas grey signifies a hydrogen-rich coal particle (Falcon and Snyman, 1986 & Suarez-Ruiz, 2000).

Macerals consist primarily of carbon, hydrogen, oxygen, nitrogen and sulphur. Within the same rank, say bituminous coal, the percentage H/C ratio on an atomic basis decreases from 1.18 to 0.47% as one move from exinite to inertinite. There is also an increasing order of the carbon content from 43% to 67%. Thus exinite has the highest H/C ratio and is the most volatile maceral (79%). Vitrinite is intermediate in volatility and H/C ratio (Tsai, 1982 & Saurez-Ruiz, 2000).

Each of the macerals can be further classified in terms of rank as lignite (commonly known as brown coal), sub-bituminous, bituminous and anthracite respectively in increasing order of aromaticity of the constituent carbon atoms within the coal (Tsai, 1982 & Harris, 2001). Macerals are classified in terms of the degree of vitrinite reflectance since vitrinite is the most abundant maceral group in coals. The amount of light reflected is calculated from the following formula:

$$R = R_s \times \frac{A}{A_s} \qquad (1.1)$$

Where

R = the reflectance of the vitrinite particles (%)

R_s = the reflectance calibration standard (%)

A = the deflection of the photomultiplier system from vitrinite

A_s = the deflection of the photomultiplier for the calibration standard

In this case the reflectance, R, is determined from the optical properties of other materials and immersion medium by the following Beer's equation:

$$R = \frac{(n-n_1)^2 + n^2k^2}{(n-n_1{}^2) + n^2k^2} \qquad (1.2)$$

Where
n = reflective index of reflecting material
k = absorption index of reflecting material
n_1 = refractive index of medium in which measurement are made

A newer method for the classification of coal is based on the vitrinite reflectance class (RoV %) or the V-type. The vitrinite maceral is contained in all coal maceral and its content differs from one coal to another. According to RoV % classification method, the RoV % range 0–0.4 is associated with lignite, 0.4–2.0 is associated with vitrinite, and 2.0 to 10.00 is associated with anthracite. These V-classes can also give an indication of the type of coke texture that will be produced. For example, isotropic carbons are derived from V-7 type, whereas anisotropic cokes are produced from V-8 class or higher as summarised in Table A.4 (Gray and Devanney, 1986 & Suarez-Ruiz, 2000).

Liptinite group

Liptinites are the types of maceral that dominate only in some unusual coal types such as 'cannel' and 'boghead'. The liptinite macerals are derived from the waxy and pitch-like parts of plants, such as spores, cuticles and resin. In any given coal, the ultimate analysis of the liptinites shows a higher hydrogen content than the vitrinites. They can also have higher carbon contents. For example, in bituminous coal their hydrogen content ranges from 7 to 10%, carbon from 75 to 85% and oxygen from 5 to 18%. However, liptinites are the most resistant to alteration during coalification. Their reflectance change is slight up to a medium volatile matter (moisture ash-free) coal. They have the lowest density amongst the other groups that is ranging from 1.0 to 1.25 g/cm^3. Their optical reflectance is the lowest of the other maceral groups (Pitt *et al*. 1979; Crelling, 1989 & Clarke, 2000).

Vitrinite group

Vitrinite is the predominant maceral group in most coals. Vitrinites are mainly the derivatives of the cell-wall material (i.e. woody tissue) of plants, which is chemically composed of the polymers, cellulose and lignin. Vitrinites are the most frequently studied and most important maceral group occurring in bituminous coal. Their carbon, oxygen and hydrogen contents and their optical reflectance within a given rank are intermediate between those of liptinite and inertinite. The optical reflectance is found to increase uniformly with coal rank. In bituminous coal the hydrogen content ranges from 4.5 to 5.5%, the oxygen content from 5 to 20%, and the carbon content from 25 to 96%. The density of vitrinites varies with coal rank and is estimated to be in the range of 1.2 to 1.8 g/ml (Tsai, 1982; Falcon and Snyman, 1986 & Crelling, 1989).

Inertinite group

Inertinite macerals are also derived from plant material, usually woody tissue (like vitrinites). Unlike liptinite macerals, which make up 5 to 15% of the North American coals, inertinite macerals contribute up to 40% of a given coal. They have the lowest hydrogen content, along with high carbon content. The values range from 2.75 to 4.25% for hydrogen content, 73 to 85% for carbon content and 13 to 25% for oxygen content. However, the optical reflectance of inertinites is the highest of all the macerals with the density ranging from 1.36 to 1.60 g/ml (Van Krevelen, 1961 & Crelling, 1989). The petrographic data of the coal used in this study are shown in Table 1.2.

Table 1.2: Petrographic analysis of Tshikondeni coal (Mthembi, 2003)

Rank	Bituminous
Seam classification	Medium rank B
Mean Random Reflectance	1.42%
Vitrinite class distribution	V15-16
Vitrinite content	95%
Liptinite content	<1%
Inertinite content	6%

1.4.3 Mineral matter

Mineral matter refers to the inorganic material contained in coal. This includes the complex metals and anions. The major mineral constituents in coal are clays, carbonates, sulphides and silica. Other groups may be oxides, hydroxides and phosphates. Microscopic identification of minerals is commonly based on their morphology and colours. For example, pyrite reflects yellow to bronze colours, whereas quartz shows dark grey to black colours (Huggin and Huffman, 1996; Mukherjee and Borthakur, 2001 & Saurez-Ruiz, 2000). The most dominant mineral matters are those formed from elements such as silicon, calcium, iron, aluminium, sodium and sulphur. These mineral matters originate from processes such as coalification and peatifcation of the parent plant (Xu *et al.*, 2003).

1.4.4 Coal structure

Since the 1950s different instrumental analyses of coal structure have received considerable attention among coal scientists in order to determine exactly what the structure of coal is. A variety of analytical methods, such as X-ray analysis, optical microscopy, nuclear magnetic resonance spectroscopy, infrared (IR) spectroscopy and chemical analyses have been investigated. X-ray diffraction (XRD) analyses have been carried out to estimate the skeletal arrangement of carbon atoms through the d_{002} values, whereas IR spectroscopy is used mainly to estimate the functional groups in the coal. Some chemical analyses, such as solvent extraction and proximate and ultimate analyses have also been used to study coal structure. Proximate analysis provides the moisture content, volatile matter, fixed carbon and ash contents, whereas ultimate analysis gives the constituent elements (Zhang *et al.,* 2002 & Marzec *et al.*, 2002) However, there is no true standard organic chemical test for coal (Crelling, 1989).

Coal is a heterogeneous substance containing several different macerals, as discussed above. It is also considered to be a three-dimensional macromolecular network composed of aromatic and hydroaromatic units cross-linked by ether bonds, methylenic groups, hydrogen bonds and van der Waals interactions. The characteristic organic part of coal structure can be schematically represented as shown in Figure 1.5 (Loison *et al.,* 1989 & Scaroni *et al.*, 2003).

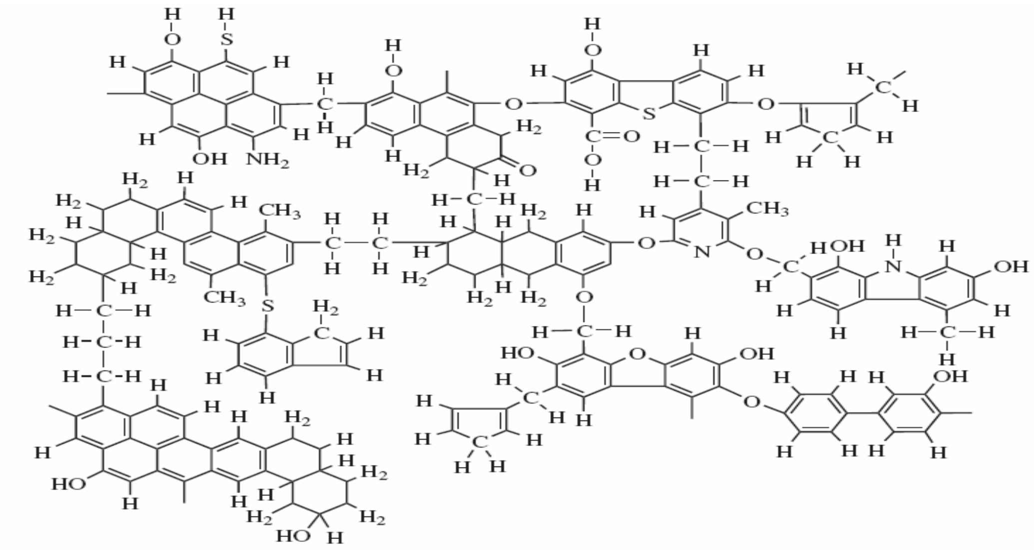


Figure 1.5: Wiser models of the structural groups and connecting bridges in bituminous coal (Scaroni *et al.*, 2003)

Figure 1.5 shows the possible structural groups and connecting bridges that are present in a typical bituminous coal. The principal types of bridging linkages between clusters are short aliphatic groups $(CH_2)_n$ (where n = 1-4), different types of ether linkages, and sulphide and biphenyl bonds. All except the latter are considered to undergo bond cleavage readily due to their ability to undergo thermal cleavage reactions (Van Krevelen, 1961 & Scaroni *et al.*, 2003).

The molecular weight distribution of coal consists of about 130–600 small molecules and 1 300–3 500 large molecules, with about 20–40% soluble portion as determined using MALDI-TOF analyses (Marzec *et al.,* 2002). It is mainly these molecules that are found reactive during coal utilisation processes such as liquefaction, pyrolysis and coking (Miura *et al.*, 2001). However, the molecules are tightly held within the coal structure and therefore making those difficult to be extracted at very low temperature (Morgan, 1991).

1.4.5 Coal extraction

Solvent extraction is a unique technique applied in coal utilisation processes for the separation of components in order to study the structure of a coal. This process provides a means of coal purification required in clean coal technology (Iino, 2000). Several factors have been identified as affecting the extraction of coal in an extracting solvent. These include the nature of the coal and the solvent itself, the solvent-to-coal ratio, the extraction temperature and the treatment time (Renganathan and Zondlo, 1993). Other factors such as coal particle size, pressure, catalysts and the extraction environment (either a reduced atmosphere or mild conditions) may also be considered for their effects on coal extraction. The most important parameters are the nature of the coal, the solvent and the extraction temperature (Rodriquez *et al.,* 1998a).

1.4.5.1 Nature of coal

High functionalities, cross-links and the low content of condensed aromatic clusters in low-rank coals make them very reactive. They undergo fast and extensive bond breaking during utilisation processes such as extraction and liquefaction. Sharma and Singh (1995) and Rodriquez *et al.* (1998b) separately reported that when lignite is dissolved in a non-hydrogen bonding solvent, a very low extraction yield is observed, indicating low or no dissolution or bond cleavage taking place. When this coal was pre-treated with HCl, EtOH, EtONa or tetrabutylammonium hydroxide (TBAH), some cations were removed in the chelate structure and some of the esters and ether bonds were broken, thereby increasing the amount of extractable coal units (Sharma and Singh, 1995 & Onal and Ceylan, 1997). Renganathan and Zondlo (1993) reported that the extent of coal extraction was slightly dependent on by the coal particle size.

1.4.5.2 Solvents

A solvent is basically used to dissolve and transport the required coal components (minerals or macerals) in most coal utilisation processes. It can also serve as a heat transfer medium and can even act as a source of hydrogen. An effective solvent for coal dissolution must be able to swell the coal during utilisation. This enables the coal structure to expand, thereby facilitating the diffusion of solvent or dissolved substances through the coal particles. The electron donor-acceptor number is the key parameters interconnecting swelling and extraction. Thus, the electron donor-acceptor bonds are responsible for binding together the coal macromolecular network and extractable molecules. The molecules are freed by the action of solvent on these bonds. The extraction yield increases with an increase in the swelling ratio; it also depends on the presence of guest molecules, the amount of solvent and the composition of the coal (Onal and Ceylan, 1997).

Conventional solvents for coal extraction are categorised as specific solvents, non-specific solvents, degrading solvents and reactive solvents. The specific solvents (e.g. pyridine) extract only up to 40% of coal at low temperatures and most of these solvents are nucleophilic. The non-specific solvents, such as ethanol, chloroform and acetone, extract a very low percentage of coal at temperatures below 200°C. Degrading solvents (e.g. dimethylformamide – DMF), which are easily recovered from the solution after extraction, extract a considerable amount of coal. Reactive solvents, most of which are hydrogen donor solvents (e.g. tetralin), also extract most of the coal but their chemical composition is changed during the process, making their action different from that of degrading solvents (Crelling, 1989; Onal and Ceylan, 1997 & Scaroni *et al.*, 2003). Most of the effective coal extraction solvents are organic solvents, but a few inorganic solvents are known. Acids, such as sulphuric acids and hydroflouric acid (HF), are amongst those that were investigated for this application (Mukherjee & Borthakur, 2001).

1.4.5.3 Solvent-refined coal technology

'Solvent-refined coal technology' refers to the method of purifying coal with organic solvents as a means of producing low-ash coal extracts. Recent studies on this technology include those reported by Dwivedi *et al.* (1995), Sharma and Singh (1995) and Choudhury *et al.* (1997); the 'HyperCoal' production technology using polar solvents (Okuyama *et al.*, 2004 & Yoshida *et al*., 2004); low-temperature 'solvent skimming' of coal, which minimises the amount of solvent used (Miura *et al*., 2001); the Refcoal process (Morgan, 2000), which minimises both the amount of solvent and the extraction temperature; and the mixed solvent technique (Iino *et al.,* 1988 & Dyrkacz*,* 2001). The latter technique was developed to overcome the limitations of different solvents when used singly for coal extraction.

Solvent-refined coal (SRC) technology was first developed by the Germans in the Second World War with the aim of producing low-ash electrode-grade coke. Other countries such as Japan and the US then inherited the technology for making low-ash, sulphur-free boiler fuels, ash-free carbon electrodes and binders for making briquettes, etc. Attempts were also made to produce SRC from high-ash, non-coking coal. SRC was found suitable for use as a substitute for primary coking coal (PPC). This technology was also used for the production of coking additives for use in steel-making industries in order to improve blast-furnace-grade coke since the technique is capable of producing high-quality metallurgical coke (Dwivedi *et al.*, 1995; Sharma and Singh, 1995 & Choudhury *et al.*, 1997).

HyperCoal technology

In the HyperCoal process, which is a cost-effective solid-liquid separation process, solvent de-ashing technology is employed. Solvents such as 1-methylnaphthalene, dimethylnaphthalene and light oil cycles have been investigated mostly at temperatures between 200 and 380°C. This process has advantages such as the production of low-ash (i.e. 0.1%) extracts known as 'HyperCoal', a high yield (up to 80%) and solvent recycling under mild conditions (Okuyama *et al.*, 2004 & Yoshita *et al.*, 2004).

Extraction of coal with mixed solvents

When certain solvents are used singly during coal extraction at room temperature or even higher, the extraction yield is extremely low. Previous studies have shown that the extraction of coal in a single solvent is limited with regard to factors such as extraction yield and swelling. In attempting to enhance the extractability of coal in organic solvents, Larsen *et al.* (1985) investigated the use of mixtures of different solvents. Iino *et al.* (1984) first reported the effect of binary solvents such as CS_2-pyridine, CS_2-dimethylformamide, CS_2-methylpyrrolidone, etc. on extraction yield. It was found that the yield can be increased to as high as 60% with solvents that give a high yield when used alone. For example, when pyridine, DMF and N-methylpyrrolidone (NMP) were used alone for the extraction of Shin-Yubari coal, the yields were 3.0, 2.6 and 9.3 wt % (dry ash-free) respectively. But when these solvents were blended with CS_2, the yields increased to as high as 55.9 wt % (Iino *et al.,* 1988).

After Iino and co-wrokers had established the efficicacy of mixed solvent technology; other aspects of enhancing the extraction yield with mixed solvents were investigated for the extraction of coal. Takanohashi *et al.* (1993) and Dyrkacz (2001) respectively investigated the dissolution efficiency of the vitrinite and inertinite maceral groups in CS_2/NMP. These studies found that with CS_2/NMP, vitrinites are more soluble than inertinites and liptinites. Chen *et al.* (1999) established that the addition of tetracyanoethelene (TCNE) increases the solubility of bituminous coal from 60 to

80% in CS_2/NMP mixed solvents. Pande and Sharma (2002) revealed that adding a small amount of ethylene diamine increases the yield of coal extraction in NMP from 50.9% (Renganathan and Zondlo, 1993) to about 70%. Li *et al.* (2000) studied the effect of lithium halides (LiCl, LiBr and LiI) as additives to enhance the extraction yield of coal in CS_2/NMP at room temperature.

Hydrogen donor solvents

Most of the coal extraction processes are performed at temperatures near the boiling temperature of the extracting solvent. At these temperatures low-rank coals undergo extensive bond cleavages owing to their high reactivity. In this case the availability of transferable hydrogen is required to stabilise the free radicals formed from the rupture of the coal structure. If hydrogen is not transferred to the free radicals, these radicals recombine to form a solid stable residue, thereby making further processing of the resulting extracts more difficult. Hydrogen donor solvents may also destroy the internal interactions in the coal network by replacing C-C bonds or hydrogen bonds with stronger coal-solvent hydrogen bonds. This releases most of the extractable part of the coal (Derbyshire *et al.,* 1982, Onal and Ceylan, 1997, Miura *et al.,* 2001 & Sato *et al.,* 2004).

Decacyclene and 1, 2, 3, 4-tetrahydronaphthalene (tetralin) are the most investigated hydrogen donor solvents. Tetralin is the most effective solvent at high temperatures due to its high thermal stability. It forms naphthalene, 1-methylindane and n-butylbenzene as major dehydrogenated products (Shibaoka, 1981; 1982 and 1984; Grigorieva *et al.*, 1994 & Kabe *et al.*, 1991). However, tetralin is a poor physical solvent since it causes some liquefied coal products to precipitate when the coal and solvent solution is cooled. This failure can be mitigated by incorporating high-boiling solvents such as pyrene and fluoranthene (Franz *et al.*, 1979). Other solvents, such as phenol, can be used as hydrogen donor solvents although their extraction efficiency is less pronounced than that of tetralin and decacyclene (Sharma and Singh, 1995 & Onal and Ceylan, 1997).

Hydrogenation catalysts such as $CoMo/Al_2O_3$ and stabilised nickel may enhance the effectiveness of hydrogen donor solvents. These catalysts lower the extraction temperature and the proportion of solvent used for coal extraction (Mondragon *et al.*, 1984 & Rodriquez *et al.*, 1999). Andresen *et al.* (2004) highlighted the effectiveness and hydrogen donor ability of tetralin under ammonium tetrathiomolybdate (ATTM) catalyst using anthracene as a model hydrogen acceptor. The study indicated that tetralin functions better in the presence of the hydrogen donor catalyst than without the catalyst.

In the present work, coal extraction was performed at a temperature (135°C) far below the decomposition temperature of coal and therefore a non-hydrogen donor solvent (DMF) was used.

1.4.6 The 'Refcoal process'

The Refcoal process was first developed at the CSIR in a coal solubilisation project aimed at producing clean and low-ash coal. The process entails soaking a medium-rank bituminous coal with DMF and NaOH in an alkaline medium under an inert N_2 atmosphere. Sodium hydroxide is employed during coal dissolution as it is thought to aid the decomposition of the coal matrix and release the soluble coal components. The method was also aimed at releasing macerals and minerals from the entire coal structure without degrading the structure. The proportion of carbon removed from the coal through extraction describes the extraction efficiency, as in equation (1.3).

$$\%\ \text{Carbon extraction} = \frac{\text{mass of carbon in coal - mass of C in residue}}{\text{mass of carbon in coal}} \times 100 \qquad (1.3)$$

The extraction yield was found to be over 92% (Morgan, 1991). This is comparable to the 90.2% yield when coal was extracted with pyridine in the presence of a transfer catalyst. A yield of as high as 90.3% was also obtained when coal was extracted using N-methylpyrrolidone in the presence of KOH. About 70% of coal was extracted through consecutive steps of alkaline treatment of coal in tetralin, followed by hot phenol (Zondlo *et al.,* 1996). However, it is difficult to recover pyridine and N-methylpyrrolidone after the extraction process is complete. This makes these solvents unsuitable for this purpose and difficult to use for studying the structure of coal. On the other hand, the extraction temperature and period are somewhat higher than those used in the Refcoal process.

Work has been done by the University of Pretoria's Carbon Technology Laboratory on the Refcoal process to investigate the proposition that the kinds of coal extracts produced through this process have the potential to graphitise to nuclear-grade graphite. Pre-treatment of the coal extracts produced through the Refcoal process may also be important to modify their coking properties and also to improve the molecular ordering in the coke structure. Several studies have been conducted on the modification of Refcoals in order to prepare them to a level suitable for use as coke precursors (Mthembi, 2003 & Phupheli, 2006). Mthembi (2003) determined the types of minerals present in Tshikondeni coal, whereas Phupheli (2006) investigated suitable methods for the removal of silicates from this coal.

1.5 Temperature

Temperature is the key factor for the extraction behaviour of coal and for the ability of a solvent to release the insoluble portion of the coal structure. Iino *et al.* (1988) reported the extraction of coal at room temperature in a single solvent and obtained only up to 9.4% extraction yield with NMP as an extracting solvent. The degree of coal dissolution depends on the boiling point of the extracting solvent. Thus some solvents dissolve more coal when used at higher temperature than at lower temperature. High-temperature extraction allows the diffusion of solvent vapour into the intermolecular coal structure, causing the rupture of weak bonds. High-temperature extraction also allows sufficient interaction between solvent and coal for the coal to release its insoluble portion (Derbyshire *et al.*, 1982; Morgan, 1991; Kaegi *et al.*, 1993; Sharma and Singh, 1995 & Liu *et al.,* 1993). According to Renganathan and Zondlo (1993), the treatment temperature of coal has a more significant effect on the extent of extraction than other factors such as solvent ratio and coal particle size.

1.5.1 Low-temperature coal extraction

Low-temperature coal extraction refers to temperatures below the boiling points of most organic solvents used for coal extraction. These temperatures range mainly from ambient to 350°C for most organic solvents. Low-temperature extractions only cause small changes in the coal structure and therefore may be used to study effectively the structure of coal without decomposing it into its components (Onal and Ceylan, 1997 & Miura *et al.,* 2001). The swelling behaviour of solvents is also studied at low temperatures. However, the yield of coal extraction at low temperature has been found to be very low, even with mixed solvents (Iino *et al.*, 1988). In the Refcoal process, in which coal was extracted with DMF and alkaline medium, the extraction yield was also reported to increase slightly as the extraction temperature increased from ambient to 135°C (Kgobane, 2005).

1.5.2 High-temperature coal extraction

The main aim of extracting coal at high temperature is to study the liquefaction behaviour of coal. This process is normally carried out either in a batch reactor or using Soxhlet extraction at temperatures near or above the boiling point of the extracting solvent. The advantages of high-temperature extraction include a high extraction yield, a reduced period for extraction and lower viscosity of the extraction solution. However, high-temperature extraction makes it difficult to separate the fraction of coal that is soluble at high temperature but precipitates at low temperature. In addition, the coal structure undergoes thermal cleavages, thereby making it difficult to study the macromolecular structure (Sharma and Singh, 1995 & Miura *et al.*, 2001). High-temperature extraction may also induce secondary reactions, such as the oxidation and depolymerisation of coal (Morgan, 1991).

1.6 Oxidation

Coal oxidation with molecular oxygen at low temperature is a process that can lead to spontaneous combustion. The presence of oxygen and moisture during coal extraction was previously reported to reduce the extraction yield in most organic solvents and to severely decrease the fluidity of coal. Oxidation also depletes the supply of hydrogen donors and diminishes the amount of the soluble fraction of coal. The presence of moisture during extraction is detrimental for water-insoluble solvents since water is also known as a poor solvent for coal extraction (Lopez *et al.*, 1998 & McCutcheon and Wilson 2003).

Coal oxidation at temperatures below 100°C involves the attack of certain aliphatic bonds (methylene (CH_2) or –OR) by the molecular oxygen (Wang *et al.*, 2002). This is commonly recognised by an increase in the O/C ratio and a reduction in the H/C ratio, indicating an increase in the oxygen content and a reduction in the hydrogen content of coal respectively. The presence of oxygenated products such as carbonyls, phenolic groups, esters and acids is undesirable for further coal processing (Hayashi *et al.*, 1997 & Lopez *et al.*, 1998).

1.7 Summary of the 'Refcoal process'

Several studies (Kgobane, 2005, Shoko, 2006, Ludere, 2006 and others) have been carried out on the Refcoal process and the cokes obtained after carbonisation of these Refcoals. The studies proposed that the action of solvent reduces the coking properties of the original coal as indicated by the reduced anisotropy in the cokes from Refcoals as compared to the cokes from the parent coal. Fortunately, appropriate modification of these Refcoals with sodium sulphide (Kgobane, 2005) and organic additives (Ludere, 2006) was reported to give cokes with improved optical anisotropy (Figure 2.6) and reduced ash content. These optical textures are taken from the polished sections of cokes obtained 95°C extracted Refcoals.

The coke produced from the Refcoal treated with sulphur shows a mixture of fine lenticular and flow anisotropy, with extensive pore development and thin walls, as shown in Figure 2.6(a). The red-pink area shows the presence of isotropic regions. When acetylene black was used as an aromatic additive to investigate its effect on the degree of anisotropy, the optical texture of Refcoal cokes was improved by the addition of only a small amount. Figure 2.6 (b) shows that increasing the composition of this additive in the carbonising system lower the optical anisotropy of the resulting cokes. Ludere (2006) reported that co-carbonisation of oxidised Refcoals with diabietic acid restored the coking behaviour of these Refcoals. The cokes produced after the Refcoal had been blended with 10% diabietic acid (Figure 2.6 (c)) exhibited a mixture of coarse anisotropy and flowing anisotropic textures for non-oxidised Refcoal and incipient anisotropy for fully (429 mg O_2) oxidised Refcoal (Figure 2.6(d)). Thus diabietic acid does not fully restore the coking behaviour of oxidised Refcoals, but it singly carbonises to flow anisotropic texture. Other available raw materials and organic additives need to be investigated for the modification of the coking properties of Refcoal.

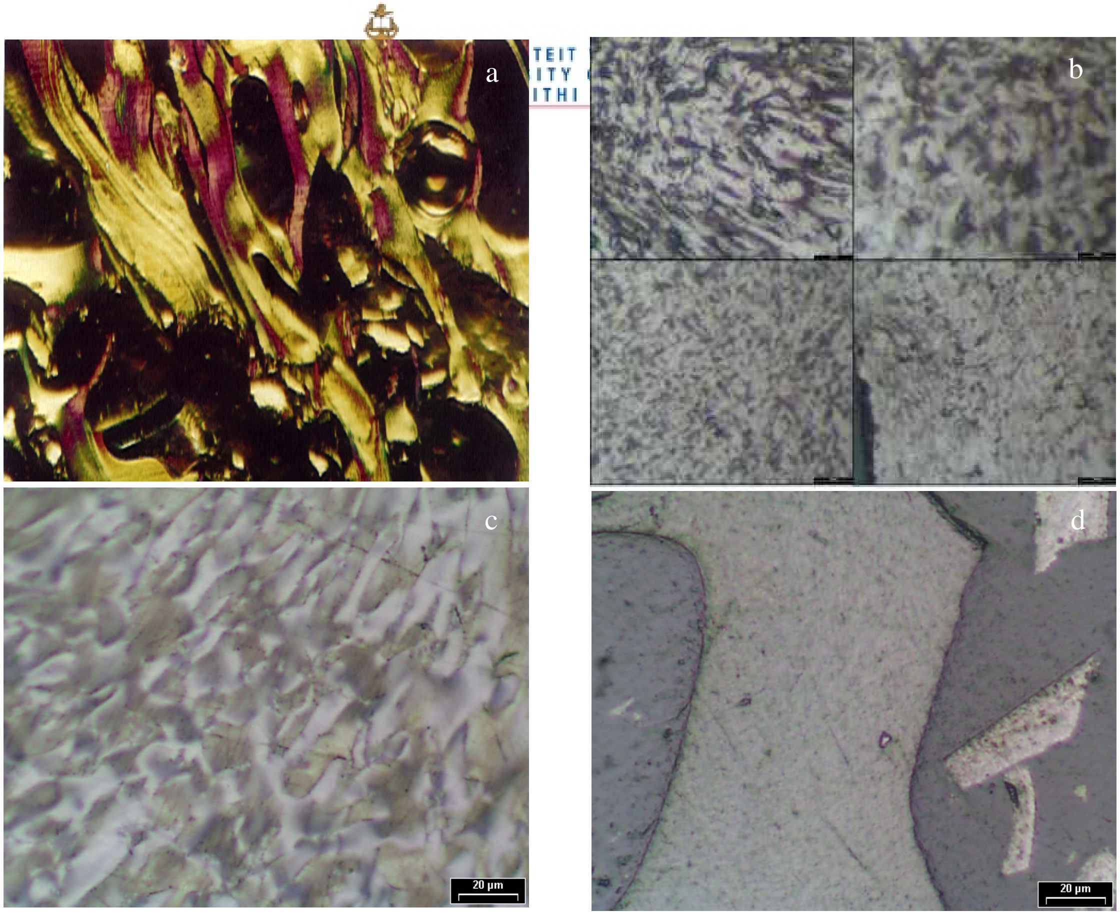


Figure 1.6: Optical micrographs of cokes from 95°C Refcoals treated with: (a) sulphur, (b) 0.0-1.6 acetylene black (Kgobane, 2005), (c) 10 % diabietic acid and (d) 429 mg oxygen and 10% diabietic acid (Ludere, 2006)

Sulphur is the main cause of puffing in cokes when exposed to high temperature and therefore the presence of this element in the coke structure should be minimised. In the work reported by Kgobane (2005), the use of sulphur as a modifying agent for the coking properties Refcoals was reported to produce highly porous cokes and a mixture of coarse and flowing anisotropic textures (see Figure 1.6 (b)). Sulfur is know as a good dehydrogenating agent for organic compounds and coal. The major product of this reaction is a carboneceous material with hydrogen sulfide been evolved. Such reactions are possible at considerably low temperatures of about 250-250°C (Jusino and Schobert, 2006). Thus the formation of coke in the present of sulfur is through dehydrogenaton of the coal structure to form hydrogen sulfide and therefore inhibiting mesophase formation during coking.

In Kgobane's (2005) study, other aspects such as the effects of extraction temperature on the properties of the resulting Refcoals and the use of organic compounds were also investigated. This study proposed that increasing the extraction temperature would provide advantages such as low-viscosity Refcoal solution and high extraction yield. It was further suggested that increasing the extraction temperature lowers the development of anisotropy in the resulting cokes after carbonisation. However, these assumptions were made based on the results obtained on the extraction of coal at ambient temperature and 95°C. The only work done on the extraction of Refcoals at temperatures exceeding 95°C was regarding the relationship between absorbance and the extraction time at an extraction temperature of 135°C. Absorbance of as high as 2.8 was reported in this case and it was assumed that the absorbance is directly related to the concentration of coal extracts in the Refcoal solution after recovery.

1.8 Strategic planning and methodology

The extraction of coal was carried out in an autoclave according to the method used in the "Refcoal process". However, in this study the progress of extraction was monitored for the correlation between absorbance and the concentration of coal extracts in the Refcoal solution instead of for time. The operational temperature was 135°C and the ratio 100:30:3 was used for the reactants, DMF: Coal: NaOH respectively, as previously optimised in the study reported by Shoko (2006).

Co-carbonisation of Recoals with tetralin was preceded by boiling the Refcoal solution with different proportions of tetralin under a flow of nitrogen for a period of 30 minutes. The solutions after treatment were washed and treated according to the Refcoal process. In the case where pitches were used as additives, the required proportion of pitch was ground with the Refcoal. The resulting hydro-Refcoals were carbonised and compared with the carbonised neat Refcoals. Carbonisation was performed mainly in the mesophase temperature region. Various analytical techniques were used to elucidate the properties of the Refcoals before and after carbonisation.

CHAPTER 2: EXPERIMENTAL

2.1 MATERIALS USED

2.1.1 Chemicals

All the chemicals used were of chemically pure grade and used without further upgrading. The chemicals used were N, N-dimethylformamide (DMF): 99.9% AR; NaOH: in pearl form; and 1, 2, 3, 4-tetrahydronaphthalene (tetralin).

2.1.2 Coal and pitches studied

Medium-rank bituminous coal from Tshikondeni mine was used for this study. The coal was supplied by Kumba Resources based in South Africa. The petrographic analyses of the coals were performed according to the coal petrography standards of the South African Bureau of Standards (SABS) (see Tables 3.1 and 3.2). Mittal 110 pitches were used as hydrogen donor additives and as a coking modifying agent. These pitches were used without prior treatment.

2.1.3 Apparatus

1. Reactors: The reactors used had capacities of 500 ml and 1 000 ml, and were both made of stainless steel. The 1-litre reactor was used for coal extraction and the 500 ml reactor was used for the treatment of Refcoal with tetralin. The reactors incorporated inlet and outlet pipes, a stirring rod and a stainless steel lid. The lid used for the 1-litre extraction reactor was designed to condense the extracting solvent in order to minimise its vaporisation. The reactor was attached to an automated Haake F3 oil bath operating at 135°C.
2. An PFE prestige furnace was used for carbonisation of the samples. The furnace was equipped with an automated temperature programme and an autoclave with pressure-gauging system attached to a nitrogen cylinder.
3. An IEC Model K centrifuge operating at a maximum speed of 5 000 r/min and a Hettich EBA 35 midi centrifuge (supplied by Labotech (Pty) Ltd) operating at maximum speed of 6 000 r/min were used for centrifugation.

4. A Sartorius analytical balance with a maximum capacity of 2 100 g and a resolution of 0.0001 g, and a Mettler Toledo analytical balance with 0.1 g resolution were used to weigh the samples.
5. The stirrer used was a Heildph-Labortech stirrer operating at a maximum speed of 1100 r/min.
6. 500 ml Polytop centrifuge bottles were used.
7. An LKB Biochrom Ultrospec 4051 visible spectrophotometer was used.

2.2 Coal extraction

2.2.1 Extraction of organic coal with DMF

Coal extraction was performed according to the method developed by Morgan (1991). In a 1-litre steel reactor mounted in an oil jacket, a mixture of DMF: coal: NaOH was carefully placed in the ratio 100:30:3. Tshikondeni medium-rank coal was used. The reactor was carefully sealed with silicon gel and purged with a flow of nitrogen to maintain an absolutely inert atmosphere. The reaction was carried out under continuous stirring of 700 r/min. The extraction process was allowed to run for 4–5 hours, after which the extraction solution was transferred into 500-ml centrifuge bottles to separate the impurities from the dissolved organic components through high-speed centrifugation. The solutions were divided into 200 g portions and placed in the centrifuge bottles, after which they were centrifuged for 1 hour at 4 500 r/min using an IEC Model K centrifuge to precipitate the minerals from the macerals.

2.2.2 Monitoring of the extraction process

The progress of extraction was monitored by carefully sampling about 10 ml of extraction solution at set time intervals. The samples were centrifuged for 5 minutes at 3 000 r/min using the Hettich EBA 35 midi centrifuge. The efficiency of extraction was determined by accurately weighing ca. 0.1 g of the supernatant after centrifugation into a 50-ml volumetric flask. The samples were taken at intervals of 15 minutes for the first hour, at 30-minute intervals for the next 2 hours and finally each hour for the last 1–2 hours. The flask was filled to the mark with DMF and the absorbance of each solution was measured at 600 nm using the LKB Biochrom UV/visible spectrophotometer. The mass of coal dissolved in the solvent was also determined by transferring 4 g of each supernatant into a clearly marked test tube. The solutions were washed and dried as detailed in the recovery process to remove the solvent (see Section 2.2.3). The washed samples were then weighed and plotted against the corresponding absorbance (Table A.1 in the Appendix). Medium-temperature (95°C) coal extraction was also carried out as for the 135°C extractions to enable comparison of the results. However, in this case the ratio of DMF:coal:NaOH was 100:10:1.

2.2.3 Refcoal recovery

The Refcoal recovery process includes the removal of impurities and the undissolved coal from the organic entities. In this step Refcoals were recovered from the solvent and other insolubles through centrifugation of the extraction solution (Refcoal solution) in Polytop centrifuge bottles using IEC Model K centrifuge. After extraction, the solution was divided into equal portions and centrifuged for one hour at a speed of 4 500 r/min. After centrifugation, the Refcoal solutions were further divided into 200g portions. *It was after this stage that the treatment of Refcoals with tetralin was performed.* Each portion was washed five times with fresh distilled water in the centrifugation bottle by shaking the Refcoal/water mixture for 5 minutes to precipitate the organic solid products. The resulting solid, black-grey, shiny gel (HTRef) was filtered under vacuum and finally dried in an oven under nitrogen atmosphere at 110°C for 18 hours. After it had been dried, the neat Refcoal was analysed using DRIFT and TGA to elucidate its properties before further processing.

2.3 Hydrogenation of Refcoals

Hydrogenation of Refcoal solutions was carried out during the Refcoal-recovery stage for the Refcoals treated with tetralin and after the Refcoal gel had dried for those treated with the Mittal pitch (described in Section 2.1.2). The hydrogenation of Refcoal solutions with tetralin was carried out by boiling 200 g of the supernatant after 1 hour of centrifugation in the 500 ml reactor with the desired portion (10 to 50% on dry Refcoal solids from each 200 g solution) of tetralin. The reaction was performed for 30 minutes under a flow of nitrogen. After the reaction was complete, the mixture was immediately washed with distilled water as in the recovery process. The resulting hydroRefcoals were designated according to the percentage of additive (number) and the name of the additive (second two letters), e.g. 10TNR refers to the

Refcoal with 10% tetralin, 20TNR to the Refcoal with 20% tetralin, and 50TNR to the Refcoal with 50% tetralin.

Hydrogenation of Refcoals with Mittal pitch was performed by finely grinding an appropriate amount of pitch with HTRef prepared as described in Section 2.2.3. The samples were then designated as for the tetralin-treated Refcoals as 10MPR, 20MPR and 50MPR. All the treated samples were also analysed using DRIFT and TGA to estimate their coking properties.

2.4 Carbonisation of samples

Carbonisation of the samples was performed in an autoclave under a flow of nitrogen gas using the PFE prestige furnace. Aluminium cans were used as sample holders for the samples carbonised at temperatures up to 650°C. The dimensions of the cans that were used are ca. 14.6 cm in height and 3.7 cm in diameter. Carbonisation was preceded by accurately weighing 10 g of the sample into a new can. The can was placed in the autoclave after it had been sprayed with graphite spray to minimise friction between the can and the walls of the autoclave. After the autoclave had been tightly closed, it was placed in the furnace. The content was then heated from room temperature to the required temperature at the rate of 10°C/min under an inert nitrogen atmosphere as follows:

- Room temperature to 400°C in 40 minutes and kept constant for 2 hours at this temperature (samples M400 and MP400)
- Room temperature to 450°C in 45 minutes and kept constant for 2 hours at this temperature (samples M450 and MP400)
- Room temperature to 500°C in 50 minutes and kept constant for 2 hours at this temperature (samples M500 and MP500)
- Room temperature to 550°C in 55 minutes and kept constant for 2 hours at this temperature (samples M550 and MP550).

Carbonisation of the samples at 650°C was performed by heating the samples from room temperature to 500°C in 50 minutes, keeping this temperature constant for 2 hours and finally raising it to 650°C. The temperature was then kept at 650°C for 1 hour and such samples were designated M650

For the samples carbonised at 1 000°C, graphite cups were used as sample holders instead of the aluminium cans. In this case the samples were carbonised from room temperature to 500°C, kept at this temperature for 2 hours and finally raised to 1 000°C. The system was kept at the carbonisation temperature for 1 hour and the resulting carbonaceous product, after cooling under nitrogen, was designated M1000. In this case the number indicates the final carbonisation temperature of the sample.

For the samples that were treated with tetralin and pitches, the carbonising system was first allowed to remain at 300°C for 1 hour before being raised to the desired carbonisation temperature. This was done to allow interaction of the additive with the Refcoal since these additives start being reactive at lower temperatures. After carbonisation, all the carbon materials were analysed using DRIFT, optical microscopy, SEM, Raman spectroscopy and XRD to investigate the changes caused by thermal treatment and the additives.

2.5 Characterisation of samples

2.5.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to estimate the pyrolysis behaviour and the weight loss incurred during the heat treatment of the material. This technique can also be used to estimate other changes such as melting, decomposition, phase transition, sublimation and thermal stability of the material as the temperature increases. The analysis of the thermal behaviour of samples is carried out under an inert nitrogen and oxygen atmosphere to observe the combustion of the material. The combustion products of the samples are analysed to determine the fixed carbon and ash contents. When coupled with techniques such as mass spectroscopy, infrared spectroscopy and gas chromatography, qualitative and quantitative analyses can be made. For example, when TGA is coupled with IR, the evolution of gases at different temperatures can be quantified (Bermejo, 2001).

Information on the nature of the thermal decomposition of coal can be obtained when coal is heated under a nitrogen atmosphere at a constant temperature and a controlled heating rate. The decomposition of coal varies with the particular coal being studied. The maximum weight loss appears at higher temperatures for high-rank coals. Thus the maximum weight loss is 440°C for coking coals and 400°C for low-rank coals. The temperature range of decomposition for high-rank coals is smaller than that for low-rank coals. The temperature at which coals start decomposing is higher (~400°C) for high-rank coal than for low-rank coals. Sub-bituminous coal starts decomposing at 350°C, whereas lignite starts at 300°C and all coals cease decomposing at 500 to 550°C (Tsai, 1982 & Haines, 1995).

Thermogravimetric analysis (TGA) was used to estimate the thermal behaviour of the samples. In this study a Mettler Toledo TGA/SDTA 871^{e} thermal analyser was used to investigate the thermal behaviour of the materials. Proximate analysis is the method of choice for the measurement of moisture, volatile matter, carbon and ash contents of samples. Proximate analysis was performed by first weighing about 10 mg of each sample in a 70 μl alumina crucible. The crucible, together with the sample, was then heated stepwise under a constant flow (50 ml/min) of nitrogen gas and at a heating rate of 10°C/min from 40 to 900°C, followed by heating in air in order to separate the fixed carbon from the ash. Table A2 in the Appendix summarises the results of the proximate analysis.

2.5.2 Fourier transform infrared analysis

Infrared (IR) spectroscopic techniques such as Fourier transform infrared (FTIR) and diffuse reflectance infrared Fourier transformation (DRIFT) are the most powerful techniques for directly analysing the functional groups in coal and coal-related compounds (Sobkbiak and Painter, 1995; Miura *et. al*, 2001 & Chen *et al.*, 1998). These are non-destructive techniques used to determine the nature of the functional groups. From a study of coal by FTIR, Solomon and Carangelo (1982) assigned the peaks at 3400, 3030, 2940, 1700, 1600 and 1200 cm^{-1} to hydroxyl groups, aromatic hydrogen, aliphatic hydrogen, carbonyl, aromatic rings C=C (enhanced by enhanced by oxygen groups) and ether, respectively. Other important bands include the condensed aromatic band at 1575cm^{-1}, the aliphatic CH_2 at 1460 cm^{-1}, the aromatic CH_2 at 1375 cm^{-1} and the aromatic out-of-plane C-H band positioned at 870 cm^{-1} (Kabe *et al.*, 2004).

In IR measurements, several problems are encountered when using the KBr pellet method. These include the absorption of water by the KBr and a sloping baseline. The in situ diffuse reflectance infrared Fourier transformation (DRIFT) technique is used to overcome these problems. This technique uses neat undiluted coal samples to minimise in situ reactions such as oxidation, dehydration and other reactions involving oxygen (Painter *et al.,* 1987). In this study the DRIFT method of sample preparation was used to examine changes in the functional groups.

Fourier transform infrared analysis (FTIR) is used to study the chemical composition of samples in order to examine the effects of extraction, additives and carbonisation. FTIR was preceded by observing the changes in the characteristic bending, vibration and stretching frequencies using a Perkin-Elmer Spectrum GX FTIR spectrometer, with a room-temperature, deuterated triglycerine sulphate (DTGS) detector. The instrument was equipped with an auto-image microscope system and computerised Spectrum Version 5.3.1 software. The KBr method was used to prepare the samples, in which a ratio of sample to KBr of 100 mg per 5 mg was used. A DRIFT sampling accessory was used for the evaluation of the samples. The samples were scanned over the wave numbers 4000 cm^{-1} to 400 cm^{-1} at 4 cm^{-1} resolution.

2.5.3 Optical microscopy

When applied to coal and carbon, the optical microscopic technique provides necessary information to explain the changes that chemical tests may not explain or can differentiate between coals that react similarly during utilisation. Optical microscopy permits virtual observation of the changes caused by heat treatment of the material. The shape and size of the spheres, as well as qualitative measurements of reflectance, explain the anisotropy in polarised light. This information is obtained by mounting a finely ground sample in a resin block that is polished to an optical flatness using diamond. When the surface of the resulting disk is examined using reflected polarised light, the interferences of colours is observed due to the different orientations of the graphitic lamellae. The appearance of the surface is then called the ‘optical texture’ (Edwards, 1989 & Marsh and Menendez, 1989). This technique was used in this study to determine the type of optical textures produced by the cokes from the Refcoal samples.

Optical micrographs were obtained by using a Leica DM2500 version 3.61 optical microscopes equipped with a computerised digital camera. The software used for the analysis of micrographs is Leica materials workshop (MW) version V 3.6.1. The specimens were prepared by mounting a finely ground sample in a 21× 25× round Perspex tube. The surface of the block, after grinding with 120, 600, 1 200 and 4 000 grids, was polished to an optical flatness using successive grades of diamond. The machines used for grinding and polishing were a Struers Rotopol and an ATM Saphir 550 respectively. The polishing process was carried out under a continuous flow of water. After the samples had been successfully polished, the polished blocks were washed with methanol.

Sample analysis was preceded by mounting the sample with plasticine and pressing it with a hand mounting press. The surface of the resulting disk was examined using reflected polarised light with a retarder plate, a polariser, an analyser and a filter. The microscope is also equipped with an analyzer giving the same information as a rotating stage when rotated 180°C. Thus yellow and blue colours are interchanging for anisotropic cokes and the texture remaining purple or grey in teams of isotropic cokes on rotation of the analyzer 180°C. The micrographs of repeated units were taken at 100 × magnifications under an oil immersed lenses. The interferences of colours were then observed; these are due to the orientation of the graphitic lamellae. Interpretation of the textures was done based on the method reported by Gray and Devanney (1986).

2.5.4 Scanning electron microscopy

Scanning electron microscopy (SEM) was employed in this study to examine the fractured surfaces of samples. SEM is an excellent technique for monitoring changes in the morphology of carbon precursors resulting from various treatments such as gasification and carbonisation. Analysis of the SEM images provided useful information, such as particle size, swelling of particles during treatment, and the structure and composition of the carbon material formed, which can be correlated with the properties of the parent material and the changes it has undergone. Unlike optical microscopy which uses light for image formation, SEM uses the scattering of electrons from the surface of the sample to reveal the topology of the material. This technique also allows a three-dimensional study of the sample. Because of the gold coating on the specimen, SEM provides higher resolution and magnification than optical microscopy and therefore can identify changes that optical microscopy may not detect. However, the technique is limited to elements of higher atomic weight than fluorine (Markovic and Marsh, 1983, Marsh and Crawford, 1984 & Bourrat *et al.*, 1986).

The morphology of the samples was examined using a JEOL JSM-840 scanning electron microscope (SEM) connected to Orion 6.53 computer software. The microscope was operated at 5.0 kV. The photographs of repeatable units were taken at 2 000× magnifications.

Sample preparation consisted of mounting a ground sample on a strip of adhesive double-sided carbon tape by dipping a stub of the tape into the powdered sample. Excess sample material was removed by tapping the stub on a solid surface. The stubs were then mounted on an aluminium slide covered with double-sided sellotape. Finally, the aluminium slides were sputter-coated with gold using SEM auto-coating unit E5200 supplied by Polaron Equipment Ltd, Watford, England. Some SEM photomicrographs of the samples are shown in Figures 3.5, Figure 3.9 and Figures 3.15 (a) to (g).

2.5.5 Raman spectroscopy

Raman spectroscopy is a non-destructive, light-scattering technique yielding information about the atomic ordering in a material. It provides the characteristic vibration frequencies of the carbonaceous materials. This analytical technique makes it possible to differentiate between the ordered graphitic and disordered amorphous regions of the material. Raman spectra for all carbon materials show several identical features in the region 800 to 2000 cm^{-1} (Tuinstra *et al.,* 1970 & Cottinet *et al.,* 1988).

The ordered graphitic layers show resonance between 1580 cm^{-1} and 1600 cm^{-1} and the band is called the G-peak. The G-peak is associated with the E_{2g} vibrational mode, i.e. vibration of the carbon atoms within the hexagonal sp^2 network of graphene layers. This band narrows and shifts to 1580 cm^{-1} with the development of more ordered layers. For highly disordered carbon materials, a resonance is identified between 1350 cm^{-1} and 1380 cm^{-1} assigned to the D-peak, and it disappears with graphitisation. Amorphous carbon, such as coal and soot does not contain graphene layers. In this case the sp^2 pair of atoms in the rings has experienced bond stretching or disruption of the carbon atoms' symmetry. Another peak for the ultraviolet (UV) excitation, the T-peak, is positioned at 1060 cm^{-1}. This peak is rarely used for the study of carbonaceous materials (Tuinstra *et al.,* 1970; Cottinet *et al.,* 1988 & Wang *et al.,* 1990). The technique was applied in this study to examine the changes induced by different treatments of samples. For example, it was expected that increasing the carbonisation temperature of the Refcoals would intensify the so-called G-peak, indicating improved molecular ordering. This was also expected when the Refcoals were modified with pitch and tetralin since these compounds were expected to control the fluidity required for better ordering.

Raman spectra were collected using a Dilor XY Raman spectroscope attached to an Olympus bh-2 microscope, a liquid-nitrogen cooled LCD detector and Labspec Version 3-01 C software. The excitation source used was 514.5 nm lines from an argon ion laser with a 2 cm^{-1} resolution. The spectrographs were calibrated using the green emission from the Hg lump. The power applied to the sample was less than 100 mW, with care being taken not to burn the sample with the laser during the measurements. Several identical spots on the sample were examined by moving the lens around the sample placed on a glass slide. The objects were observed with 50× objectives. The acquisition time was set at 120 seconds.

2.5.6 X-ray diffraction photometry

X-ray diffraction (XRD) photometry analyses provide an estimation of the ordered, the size of the aromatic lamellae, the average distance between the lamellae, and the mean bond distance of the macromolecules in carbonaceous materials. XRD can be used to give an indication of the size of the crystallites making up the ordered structure. It classifies the carbon-related peaks around 20–26° into two categories: the peak around 26° is associated with aromatic ring stacking, whereas the one around 20° is derived from the aliphatic chains. The distance between stacked lamellae is about 0.345 nm (Kabe *et al.*, 2004 & Mochida and Sakanishi, 2000). Coal heat treatment at temperatures exceeding 400°C intensifies the peak at 26°, whereas at 20° the diffraction decreases (Watanabe *et al.*, 2002).

The samples were prepared for X-ray diffraction (XRD) analysis by using a back-loading preparation method. A finely ground sample is loaded into the sample holder with or without the standard. In this case the samples were prepared without the standard, which is normally silicon. The samples were analysed using a PANalytical X'Pert Pro powder diffractometer equipped with an X'Celerator detector, variance divergence and a receiving slit with Fe-filtered Co-Kα radiation. Different phases in the material were identified using X'pert Highscore software. The resultant pattern is the amount of scattering over various scattering angles. The XRD patterns were analysed in terms of diffraction peaks, their position and their widths.

CHAPTER 3: RESULTS AND DISCUSSION

3.1 EXTRACTION

3.1.1 Monitoring the progress of extraction

The progress of extraction was monitored by taking samples of Refcoal solution in 15 minutes time intervals for the first 60 minutes, 30 minutes for the next 120 minutes and finally 1 hour until the extraction was complete. The samples were treated according to the method detailed in Section 2.2.1 and the data were interpreted with graphs and tables. The tables are placed in Appendix A1. In these plots LT extraction refers to coal extraction operated at low temperature (95°C) whereas HT extraction is the extraction carried out at high temperature (135°C).

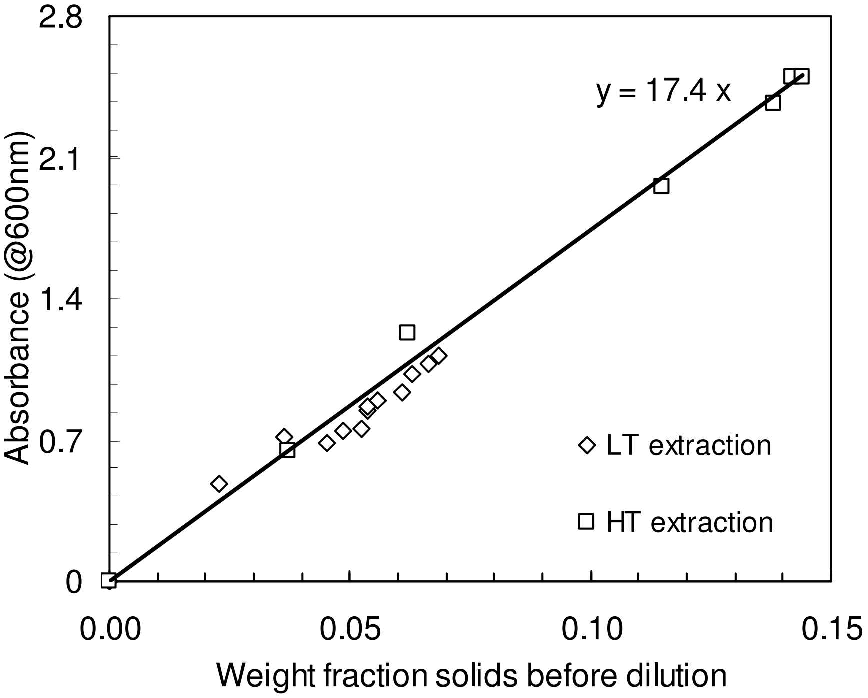


Figure 3.1 (a): Correlation between absorbance of 10x diluted extract and of coal extract concentration in DMF (Key: LT extraction: low temperature (95°C) extracted Refcoal and HT extraction: high temperature (135°C) extracted Refcoal)

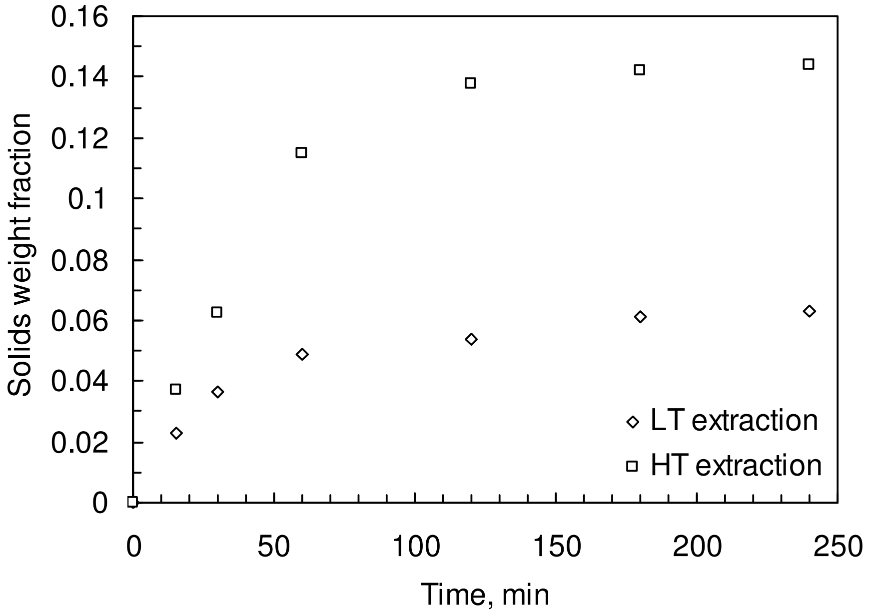


Figure 3.1 (b): Correlation between weight fraction of solid coal extracts and extraction time (Key: LT extraction: low temperature (95°C) extracted Refcoal and HT extraction: high temperature (135°C) extracted Refcoal)

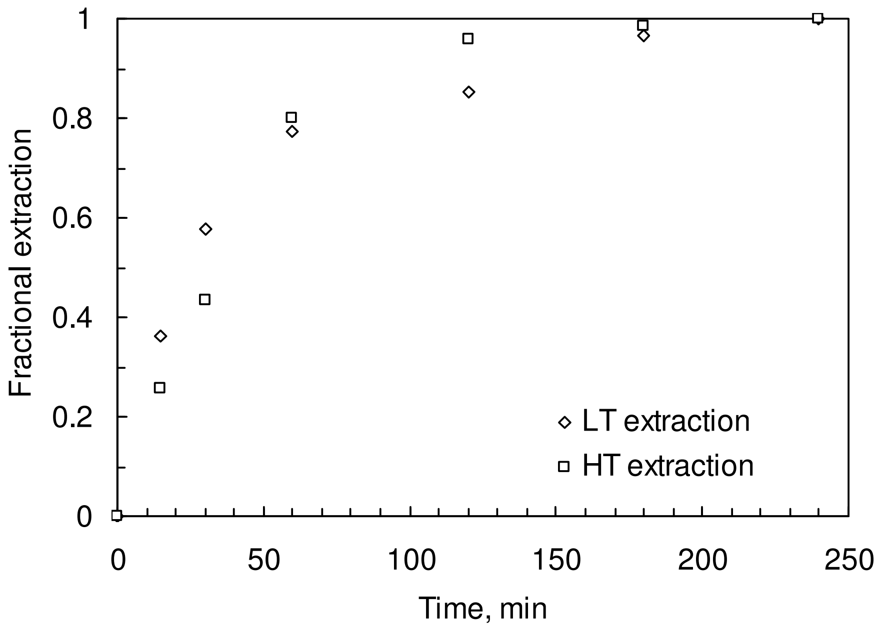


Figure 3.1 (c): Correlation between fraction coal extraction and extraction time (Key: LT extraction: low temperature (95°C) extracted Refcoal and HT extraction: high temperature (135°C) extracted Refcoal)

Figure 3.1 (a) to (c) are generated from the data captured during coal extraction in order to monitor the progress of extraction. Figure 3.1 (a) shows the correlation between absorbance of 0.1 g Refcoal in 50 ml Refcoal solution and solid fractions of coal extracts in the Refcoal solution during coal extraction process. A linear relationship exists between the concentrations of coal extracts and absorbance regardless of the extraction temperature. Thus the absorbance increases with an increase in the solid fractions of dissolved coal in the solution. Therefore absorbance can be used a measure of extend of extraction. Figure 3.1 (b) shows that the fractions of coal extracts in the extraction solution is higher in the extraction process performed at 135°C than in the 95°C coal extraction.

Morgan, (2000) reported that when coal extraction is carried out at 95°C an induction period is experienced. The induction period is an indication that the reaction mixture did not reach enough temperature for the coal to start swelling and the solvent to dissolve the soluble organics. This is normally show by clustered points at the initial stage of extraction. However this is not observed at the scale shown presently. However it is noteworthy that both processes approach the plateau absorbance at approximately the same time (i.e. 2 hours) regardless of the extraction temperature. This point is recognised by the congestion of points towards the maximum absorbance as shown in Figure 3.1 (a). Figure 3.1 (c) shows that the rate of extraction is faster in the HT extraction than in the LT coal extraction as clearly indicated by the fraction of coal extracts on the first sampling at 15 and 30 minutes. These points show about 38% extraction for HT and 36% extraction for LT at 15 minutes residence time and respectively 42 and 58% at 30 minutes. However, the rate of fractional extraction only differs in the first 30 minutes after which the rate is nearly the same.

According to Beer's law when an incident radiation passes through an absorbing species with concentration c and path length b, the absorbance of the absorbing species is directly proportional to the concentration. Beer's law is simply described as "abc" in which 'a' is the absorptivity constant, 'b' is the path length (cell width) and c is the concentration of the absorbing species in the solution. The units are normally cm^{-1} g^{-1} L for absorptivity constant 'a' and cm for a path length 'b' (Christian, 1994).

The absorptivity constant was calculated from the least square fit of the plot (Figure 3.1 (a)) of absorbance versus concentration as the gradient of this plot. Thus an average absorptivity constant of 17.4 ± 1.9 $(g/g)^{-1}$ cm^{-1} is obtained in Figure 3.1 (a) with an $R^2 = 0.9955$. The extraction of coal at 135°C produces more coal extracts as proposed by an absorbance of about two-times that of the 95°C extraction. This agrees with the proposal that absorbance can be related directly with the concentration of coal extracts in the Refcoal solution without calculating the concentration or measuring their weights in the solutions.

When the percentage of yield was calculated relative to the mass extract used (4g) and the mass of dried extract at the end of extraction in each plot from Figure 3.1 (a), the results show 8 % and 15 % yield for 95°C and 135°C respectively. This shows an improvement in the extraction yield due to an increase in extraction temperature. Another interesting observation is that the absorptive constant was not doubled as other parameters in the 135°C indicating that this value is the same regardless of the extraction temperature. The coal extracts obtained after washing each of the 200 g samples during the recovery process produced 15.3 g for 95°C and 30.5 g for 135°C extractions. It must be noted that the percentage of additives used was calculated based on these masses in the Refcoals treated with organic additives.

Summary:

- The concentration of coal extracts in the Refcoal solution is related to the absorbance of the diluted solutions, i.e. a form of Beer's law holds. The absorptive constant of 17.4 g/g^{-1} cm^{-1} is estimated for Tshikondeni coal.
- Therefore absorbance can be used confidently as a measure of the concentration of coal extracts in the coal solution.
- The time taken for coal extraction to reach the temperature-dependant equilibrium value (c.f. maximum absorbance) is independent of the extraction temperature.
- The extraction temperature affects the coal solubility with more dissolving in hot solvent.

3.2 INSTRUMENTAL ANALYSIS

3.2.1 Thermogravimetric analysis of the starting materials (Coal and Refcoal)

Thermogravimetric analysis of samples was carried out to examine the carbonisation behaviour of the starting materials and also to determine the effect of solvent on the petrographic compositions and mineral content of the coal. Thermal analysis of samples was performed under a flow of nitrogen to ensure an inert atmosphere. The amount of fixed carbon and ash were determined from the combustion products of the samples at 900°C. Proximate analysis, a measure of moisture content, volatile matters, fixed carbon, and ash provides a clear estimation of the petrographic composition of coal (England *et al.,* 1975). This was performed by heating about 10mg each sample in 70 µl alumina crucible. The crucible together with the sample was heated stepwise under a constant flow (50ml/min) of nitrogen gas and 10°C/min heating rate from 40°C to 900°C. The fixed carbon was separated from the ash by combustion of the residue at 900°C. The data for the thermal analysis of all samples is placed in Appendix A2. The volatile matter, fixed carbon and ash are reported on a dry basis (d.b).

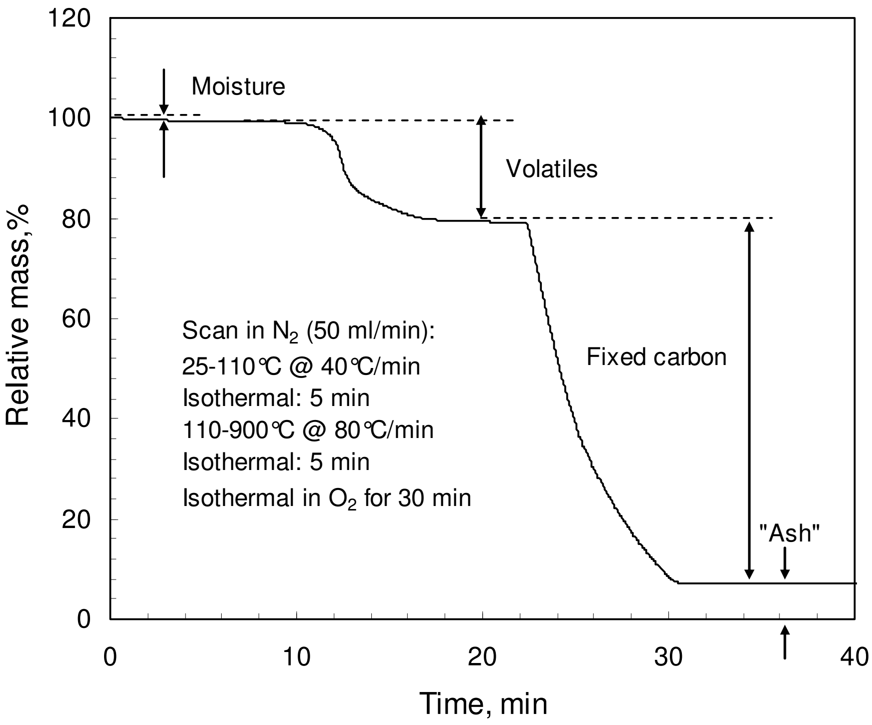


Figure 3.2 (a): Proximate analysis of bituminous Tshikondeni coal analysed from 25 to 900°C

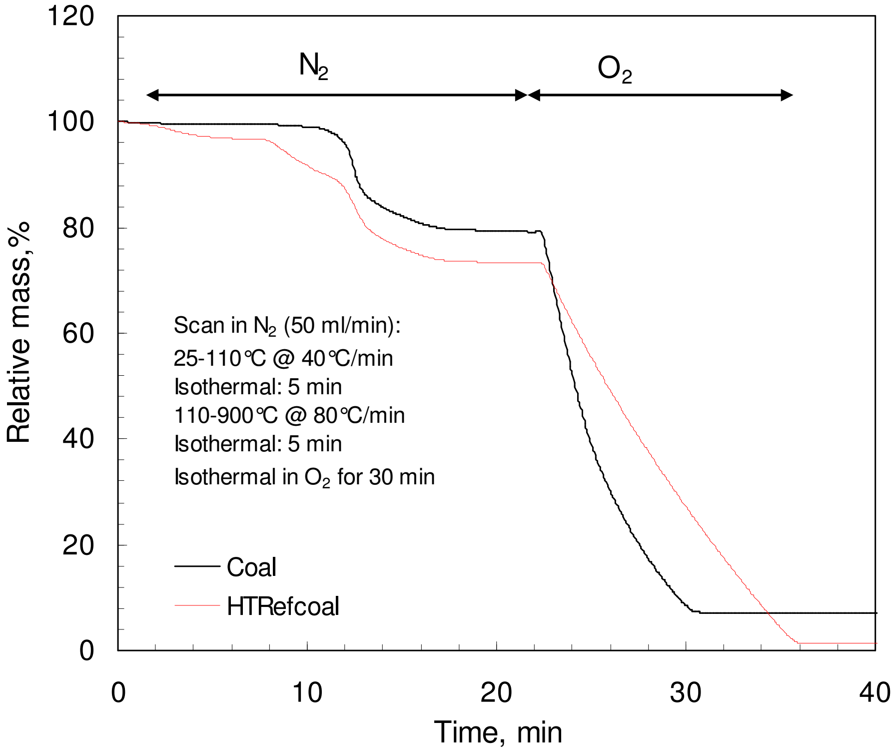


Figure 3.2 (b): Proximate analysis of coal and Refcoal analysed from 25 to 900 °C (Key: HT Refcoal: High temperature (135 °C) extracted Refcoal)

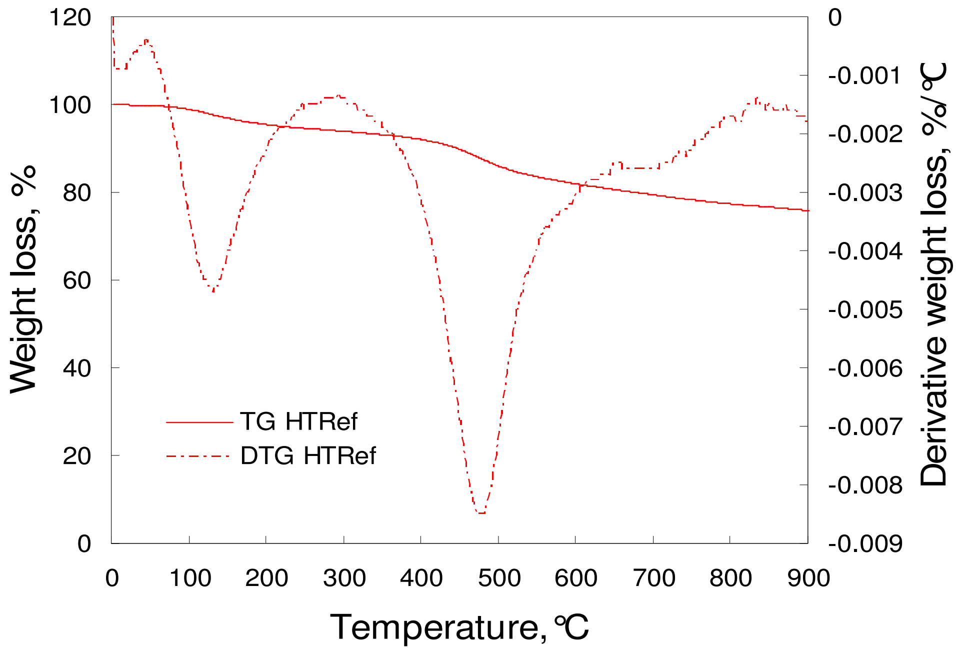


Figure 3.2 (c): Thermogravimetric curve of the neat Refcoal analysed under nitrogen gas (Key: HTRef: high temperature (135 °C) extracted Refcoal)

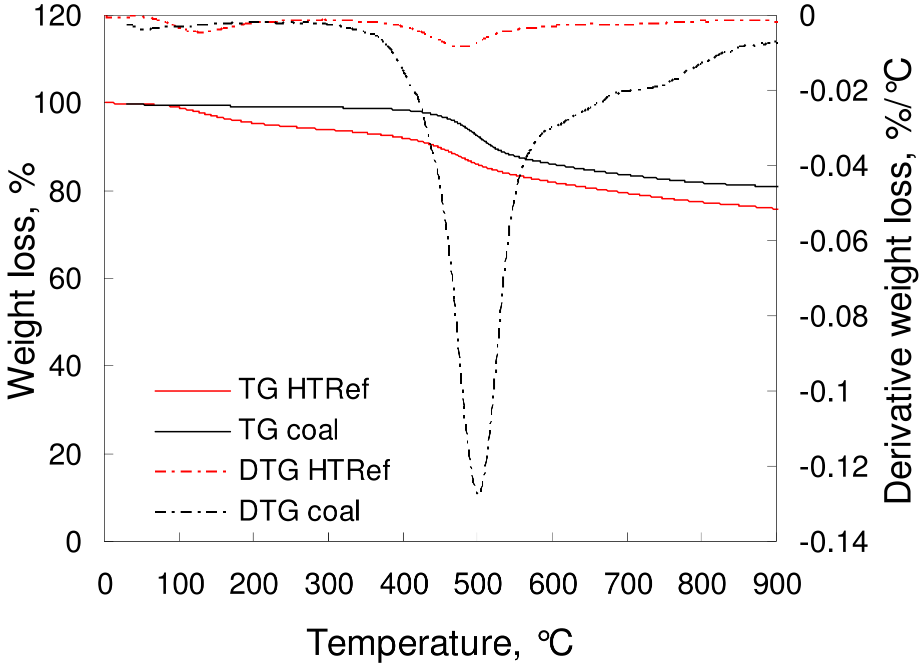


Figure 3.2 (d): Thermogravimetric curves of coal and Refcoal analysed under nitrogen gas (Key: HTRef: high temperature (135 °C) extracted Refcoal)

Figure 3.2 (a) and (b) show the proximate analysis of the parent coal and its coal extract, Refcoal produced after coal extraction with DMF through the Refcoal process. Figure 3.2 (a) shows that coal contains about 20.3% volatile matters and the remaining carbonaceous residue after carbonisation is 71.5%. About 7.3% of this coal is ash, which is mainly inorganic matter and minerals. Previous studies (Mthembi, 2003 & Kgobane, 2005) have shown that 23.3% of the same coal is volatiles, 66.4% fixed carbon and 9.4% ash. Extraction of the same coal at 135°C with DMF induced significant changes on its composition as shown in Figure 3.2 (b). The volatile matter was increased to as high as 30.5% in the HTRef. The weight loss due to DMF is shown at approximately 12 minutes. This peak is not seen in the coal sample. However, the fixed carbon is reduced to 66.6% whereas ash content is lowered to 1.6%.

When coking coal is heat treated at at elevated temperatures, it expands, undergoes a fluid stage and finally decomposes into its constituents. This process is therefore called the fusing properties of coal (Gibson *et al.*, 1971). Figure 3.2 (c) and (d) show respectively the thermal behaviour of coal and Refcoal when carbonised slowly at the rate of 10°C/min under a flow of nitrogen. Coal loses volatiles only in a single step between 300 and 500°C with some small peaks above 600°C. Refcoal loses weight in two steps of (1) moisture and retained DMF between 75 and 230°C and (2) the main isotherm for gases, oils, tar and other higher molecular weight species in the temperature interval 367 to 485°C. The later intense peak suggests that the Refcoal consists of high molecular weight aromatic species. These species are thermally stable and only start decomposing at temperatures exceeding 350°C. The temperature of initial evolution of volatiles is increased by about 65°C in the Refcoal leading to a decrease in the temperature region of evolution of volatiles.

Summary:

- Coal extraction with solvent reduces the apparent carbon yield and increases volatile matters and moisture content probably due to retained water and solvent.
- The extraction of coal with DMF lowers the mineral contents of coal as shown by reduced ash content in the Refcoal.
- Refcoal consists of mainly of aromatic compounds and it is stable at temperatures below 360°C in an inert atmosphere. Only a few low molecular weight species are lost below 300°C probably constituting mostly moisture and DMF.

3.2.2 DRIFT analysis of starting materials

DRIFT analysis was performed in this study to elucidate changes in the functional groups of the original coal due to the action of DMF. It is expected that more functional groups should be observed in the Refcoal due to the retained DMF and the increased moisture content in the Refcoal as proposed by the thermal analysis. These functional groups will mainly be those affected by moisture and aliphatic groups some of which will be the reaction products of coal and DMF during extraction.

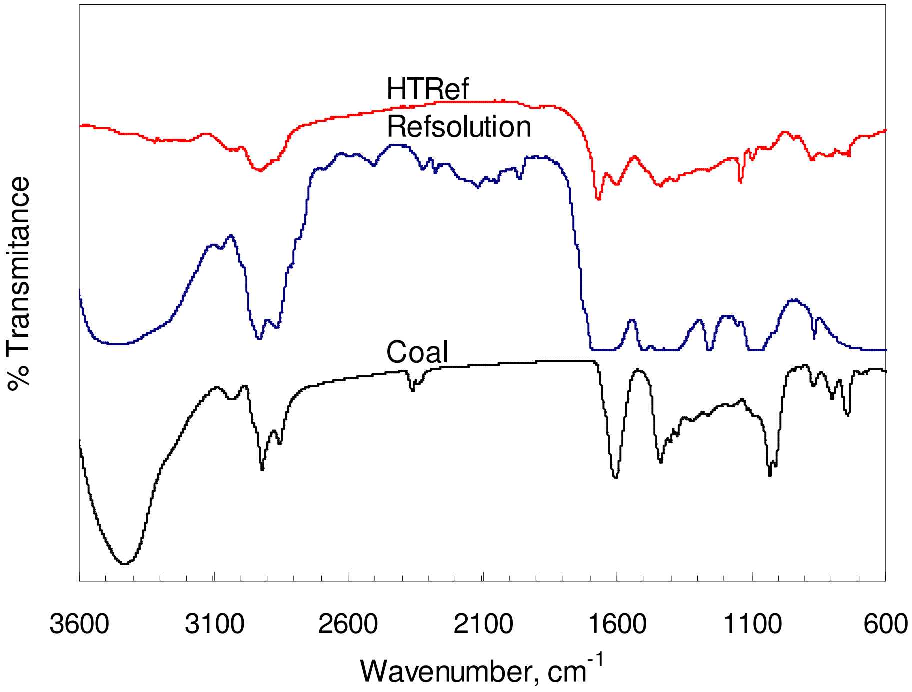


Figure 3.3: DRIFT spectra showing effects of extraction on coal functionalities (Key: HTRef: high temperature (135°C) extracted Refcoal)

Since it is expected that the most affected functional groups under the treatment conditions used in this study will be the oxygenated and aliphatic groups, attention is paid to the spectral regions related to these groups. Changes on the aromatic hydrogen stretching and bending modes will also be examined. The groups selected are the aromatic and aliphatic ν(C-H) stretching modes at 3100-3000 cm^{-1} and 3000-2800 cm^{-1} respectively; the ν(C=C) and ν(C=O) stretching modes between 1540 and 1800 cm^{-1}; the (C-O) stretching and O-H bending modes assigned for 1260-1034 cm^{-1} bands and the aromatic C-H out of plane bending modes at 900-700 cm^{-1} (Nosyrev, *et al.* 1996 and Kabe, 2004). In the same region in which phenols, ethers and ether C-O band appears, the aromatic C-H in-plane band is also found. This peak results from the deformation of the aromatic rings.

Figure 3.3 is the DRIFT spectra showing the effect of solvent on the functionalities before precipitation (Refcoal solution) and after precipitation and drying (HTRef). The O-H vibration band at 3400 cm^{-1} is less intense and broad in the Refcoal solution and significately reduced in the purified coal, HTRef. The aliphatic C-H band at 2919-2800 cm^{-1} is more intense in the Refcoal solution than in both coal and the Refcoal. This peak is less developed in the HTRef than in coal indicating that coal extraction with DMF reduces the aliphatic compositions of coal. The aromatic C=C band at 1596 cm^{-1} is more intense in coal than in the Refcoal indicating that only a certain types of aromatic compounds are extracted. The aromatic out of plane band reflecting five adjacent hydrogen atoms appearing at 735 cm^{-1} is not shown on the HTRef spectrum. The peak at 1662 cm^{-1} appearing in the Refcoal solution and HTRef spectra indicates the presence of the C=O band of the carbonyls. In addition the sharp peak at 1008 cm^{-1} on the coal spectrum is assigned to the C-O band of the phenols. This peak is not shown in the HTRef spectrum. On the other hand, an additional sharp peak appears at 1130 cm^{-1} on the HTRef spectrum. The peak starts appearing in Refcoal solution and it is intensified in the HTRef sample. This peak results from the deformation of the C-H (in plane) of the aromatic rings.

Fortunately most of the functional group induced by the solvent are not appearing in the Refcoal (HTRef) indicating the recoverability of the solvent after the washing process. For example, the peak associated with aliphatic CH_3 bends at 1375 cm^{-1} only appears in the Refcoal solution and it is not carried through to the HTRef after the Refcoal is recovered. This peak is assigned the CH_3 bending modes of DMF methyl groups attached to the nitrogen.

Summary

- Extraction of coal with DMF produces coal extracts with the structure different from that of the parent coal. The structure of the resulting extracts contains more oxygenated functional groups, mainly in the form of carbonyls (C=O) than ethers and esters (C-O-C, responsible for cross links).
- The aromatic nature of coal is reduced in the Refcoal and this is in agreement with the results shown by the thermal analysis in which the carbon yield was reduced.
- DMF is still recoverable after coal extraction and therefore it only facilitates the separation of organic from inorganic materials.

3.2.3 Microscopic analysis of the starting materials

Microscopic analysis of the coal and Refcoal was made to study the compositions, optical texture and the morphology of these materials. It is already proposed from thermogravimetric analyses that the mineral content is lower in the HTRef sample than the parent coal. Minerals are normally identified by their high reflectance (shiny) behaviour in the optical microscope and as small particles when observed at higher magnification with SEM.

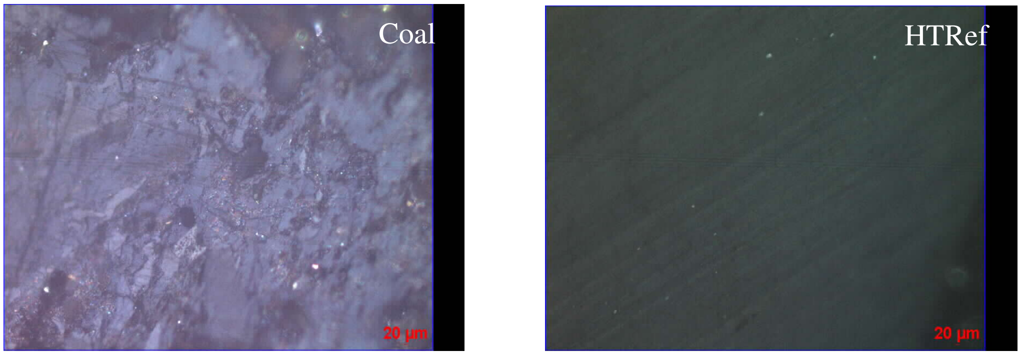


Figure 3.4: Optical micrographs of bituminous coal and Refcoal (Key: HTRef: high temperature (135°C) extracted Refcoal)

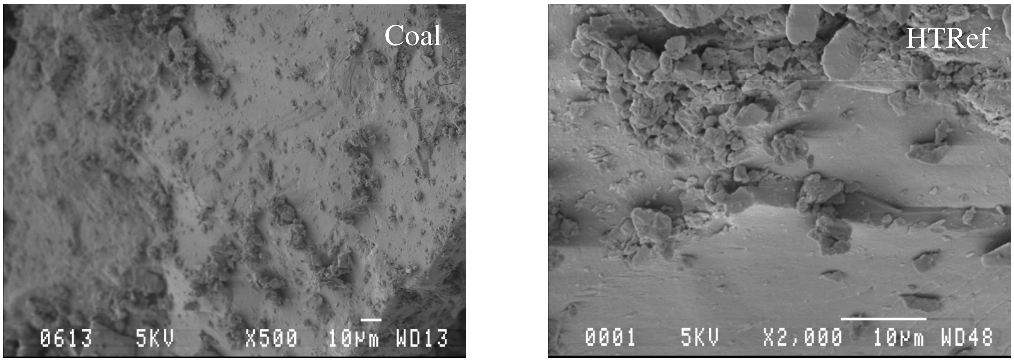


Figure 3.5: SEM micrographs of the fractured surfaces coal and Refcoal (Key: HTRef: high temperature (135°C) extracted Refcoal)

Figure 3.4 shows the optical micrographs of coal and Refcoal when examined under polarised light. The homogenous grey smooth area is the cell wall with no cell structure. The bright fine and large white particles are the minerals and inertinite dispersed in the vitrinite structure. Inertinite is carbon rich than the other macerals and therefore they appear brighter. The yellow-shiny nodules are the pyrites. These bright particles are not observed in the Refcoal sample due to the action of DMF during the extraction process. The low concentration of these bright particles, regarded herein as minerals is in agreement reduced ash content in the Refcoal as shown previously in the proximate analysis of coal and Refcoal.

Figure 3.5 shows the SEM photographs of fractured surfaces of the parent coal and Refcoal. The small irregular particles at the edge of the surface in the coal sample are the insoluble agglomerates. These particles normally appear irregular and sharp if they are eroded by the solvent. The smooth appearance of the Refcoal sample is evidence of the erosion of some particles by the solvent. When these extracts are carbonised the presence of this agglomerates may act as the nuclei of mesophase (Rodriquez-Valey *et al.*, 2002).

Summary:

- The extraction of coal with DMF lowers the concentration of the tiny particles considered as minerals under microscopic analyses.
- DMF also erodes some of the particles regarded as agglomerates and therefore leaving the surface of the Refcoal smooth.

3.2.4 XRD analysis of coal and extraction products

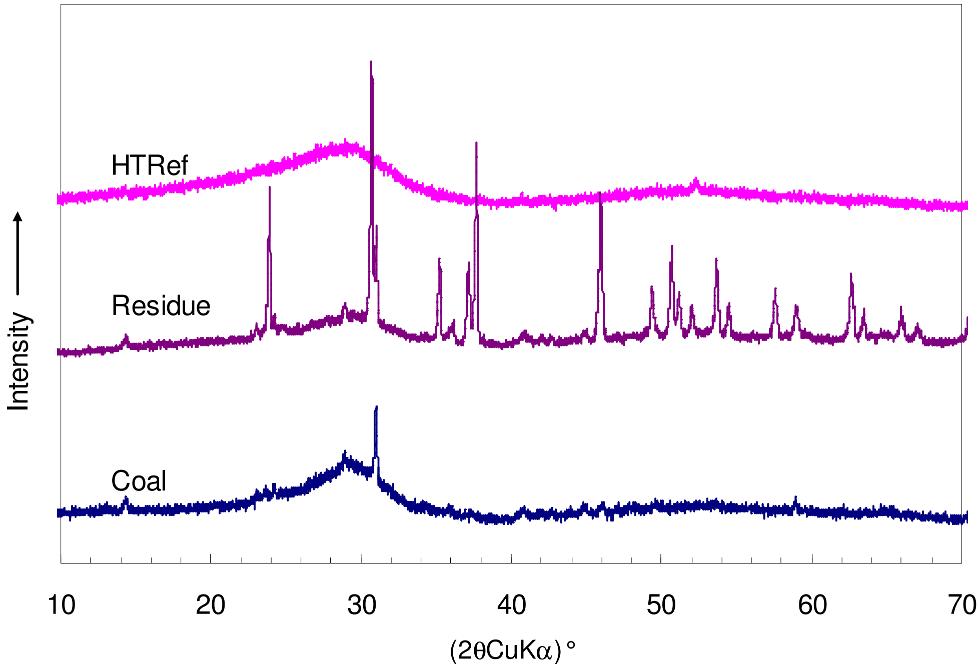


Figure 3.6: XRD patterns of a coal, residue and the extracts after the extraction process (Key: HTRef: high temperature (135°C) extracted Refcoal)

X-ray diffractometer patterns of carbon materials are normally evaluated using two Bragg lines near 2θ = 28.7° assigned to the interlayer spacing (d_{002}) of pure graphite along the c-direction and the other peak around 2θ = 43° referred to as d_{004} spacing. The broad peak in the range 20-32° is related to the aromatic ring stacking in less crystalline carbons. The presence of these peaks on an XRD pattern of carbon materials indicates the initiation of the graphitisation process. For highly graphitic or ordered materials, the d_{002} peak is more intense than the d_{004} peak.

Figure 3.6 presents the XRD diffraction traces of coal and the products after solvent extraction (residue and Refcoal). Sharp peaks are observed in coal and residue and these peaks are not present in the Refcoal. These peaks are assigned to the minerals present in the parent coal (quartz, pyrite, calcite, etc.). The minerals remain in the residue during extraction and recovery process. Similar observations were reported elsewhere (Seehra and Pavlovic, 1993) in which the peaks were assigned to minerals such as quartz, koalinite, pyrite and calcite. The intense peak around 2θ = 32° indicates that quartz is the predominant mineral impurity in the coal. The peaks assigned to the minerals are not present in the Refcoal indicating that the Refcoal contains significantly low ash. The d_{002} peak is observed in the XRD spectrum of Refcoal but this peak is poorly developed in coal and residue. Carbonisation of this Refcoal should develop two peaks at 2θ = 29.6° and 52.9° assigned to d_{002} and d_{004} respectively as an indication of the initiation of the development of aromatic, defective graphene layers.

Summary

- The dissolution of coal in DMF facilitates the separation of minerals from coal.
- The extraction of coal with DMF reduces the mineral (ash) content of coal. The coal extracts contains molecules with the potential to form graphitizable cokes.

3.3 CARBONISATION OF SAMPLES

3.3.1 Cokes from the carbonisation of neat Refcoals

Carbonisation of unmodified Refcoal referred to herein as "neat Refcoal" was preceded by weighing 10 g of a ground sample into an aluminium can or graphite cup. The can or cup was placed in an autoclave. The system was heated at the rate of 10°C/min to the desired temperature (ranging from 400 to 1000°C) in the furnace under a constant flow of nitrogen. The remaining devolatilised carbonaceous residue, i.e. coke is removed from the can after slow cooling. The carbonisation profile of this Refcoal is given in TG trace of Figure 3.2 (c) and the procedure is detailed under experimental in Section 3.4.

3.3.1.1 DRIFT analysis of Refcoal cokes

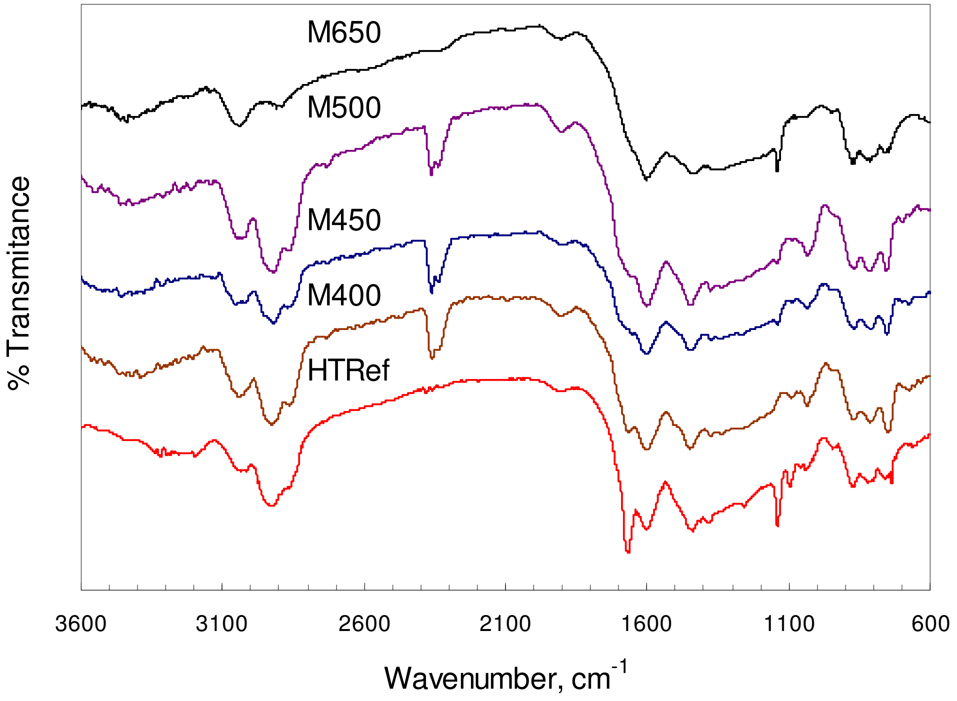


Figure 3.7: DRIFT spectra of cokes produced from the carbonisation of neat Refcoals at different temperatures (HTRef: coal extracts obtained at 135°C coal extraction, M400, M450, M500 and M650: coke from carbonisation of HTRef at 400, 450, 500 and 650°C respectively)

Figure 3.7 shows DRIFT changes in functional groups in neat Refcoal induced by different carbonization temperatures. Carbonization of Refcoal at the temperature ranging from 400 to 650°C affects mainly the oxygenated functional groups such as carbonyls and carboxylic groups as well as small aliphatic chains. The peaks at ca. 2400 cm^{-1} are not well understood but may indicate the presence of nitrile groups generated by a reaction with residual DMF. Condensation of aromatic rings is expected to occur as the carbonization temperature is increased (Keliang *et al.*, 2007).This is normally identified by the presence of the aromatic C-H band at 3030 cm^{-1} and the formation of more C=C groups assigned to the peak ca. 1500 cm^{-1}. The absorption bands at 1660 cm^{-1} and 1134 cm^{-1} correspond to C=O of the carbonyl groups and the C-H bands due to the deformation of C-H bonds of the aromatic. Their intensity decreases as the treatment temperature increases indicating de-oxygenation of the carbon precursor and aromatization. Oxygen is evolved mainly in the form of CO_2 and H_2O (Bermejo *et al.*, 2001). Thus the peaks assigned to the -OH and C=O groups are expected to decrease with carbonization temperature. The aromatic C=C and C-H bands at 1589 cm^{-1} and 3016 cm^{-1} respectively intensify as carbonization temperature increases. This provides evidence for condensation of aromatic rings. It is also noticed that for the 650°C carbonized temperature (M650) sample the nitrile band at ca. 2400 cm^{-1}, the aliphatic hydrogen band at 2907 cm^{-1} and the methylene CH2 at 1424 cm^{-1} are absent. The methylene C-H band at 1424 cm^{-1} is attributed to the naphthenic rings in the raw mesophase carbon material (Dumont *et al.,* 2005). This peak is slightly intense in the M400, M500 and M550 samples suggesting the presence of naphththenic rings in the mesophase system. The M650 spectrum defers from the other spectra and therefore it may be over 500°C in which dramatic changes in the Refcoal structure occur during pyrolysis. The phenolic O-H band at 1030 cm^{-1} is also absent. However a less significant change was observed on the phenolic and alcoholic Ar-O-H band at 3400 cm^{-1}. This peak was expected to disappear as carbonization temperature increased because phenol groups are not stable at these temperatures. It is possible that the requirement of transferable hydrogen at the early stage of carbonization is satisfied by the hydrogen contained in the carbonizing system and therefore contributing to the reduction of the aromatic out of plane band at 740 cm^{-1} in the M650 sample due to self hydrogenation. This may also be the formation of singly substituted aromatic rings assigned to this peak. The peak at 1134 cm^{-1} indicates the presence of the C-H due to the “in-plane” deformation of aromatic rings.

Summary

- Carbonisation of a neat Refcoal at temperatures below 500°C is responsible for mainly reduction of oxygen and aliphatic functional groups.
- Aromatization of the Refcoal is clearly recognised above 500°C as shown by the spectrum of the M650 sample.
- The structure of the coke obtained at 650°C is very different from those of cokes obtained temperatures up to 500°C.

3.3.1.2 Microscopic analysis of Refcoal cokes

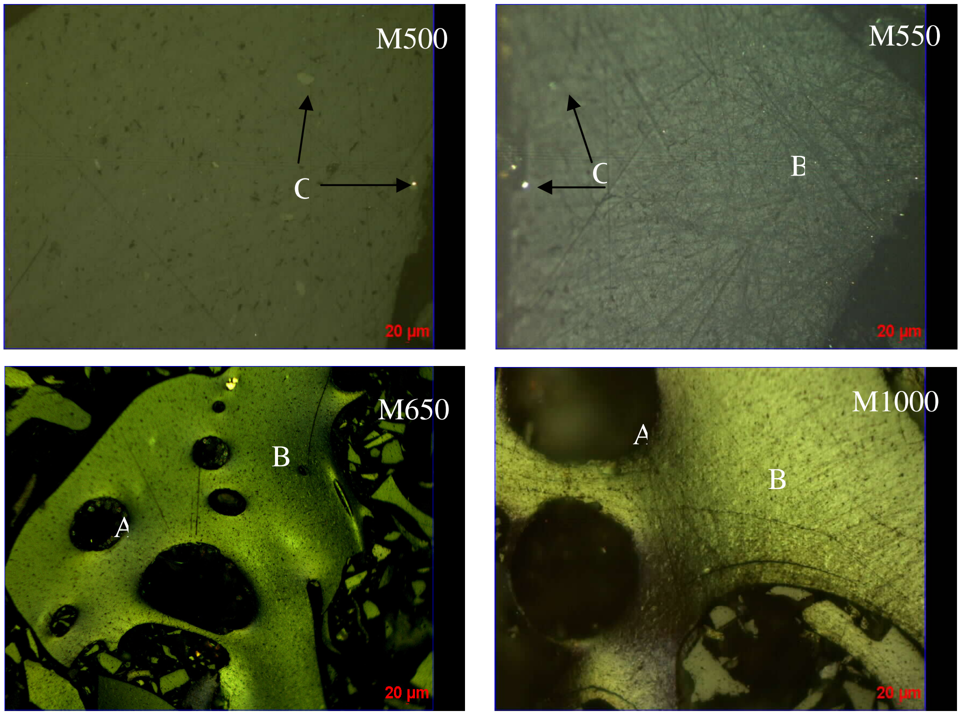


Figure 3.8: Optical micrographs of cokes from the carbonisation of Refcoal at different temperatures under a polarised light microscope (A = pore, C = mesophase sphere and B = anisotropic region) (M500, M550, M650 and M1000: coke from carbonisation of HTRef at 500, 550, 650 and 1000°C respectively)

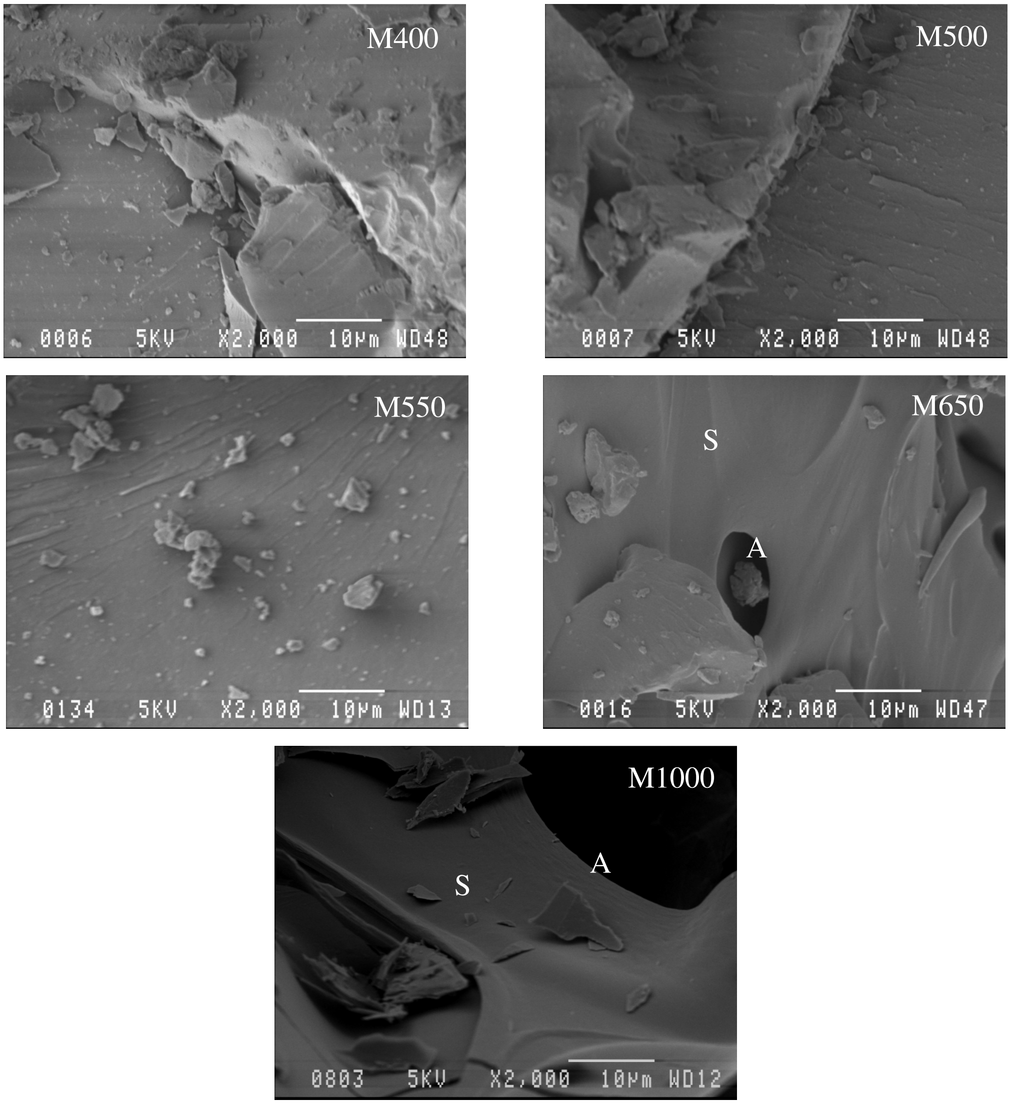


Figure 3.9: SEM micrographs of cokes from the carbonisation of Refcoal at different temperatures (M400, M500, M550, M650 and M1000: coke from carbonisation of HTRef at 400, 500, 550, 650 and 1000°C respectively) (A: pores and S: smooth area showing extend of fluidity undergone during carbonisation)

The optical textures of the samples are classified based on the size, shape and different colours appearing from a polished surface of the sample when observed under an optical microscopy with half-wave retarder plate and cross polars to create interference colours. These colours are of course not the actual colours of the carbon material, but indicate different macro-crystallinity based on graphite lattice. The interference colours may be purple-red or grey for isotropic texture, combination of pinkish purple, and blue and yellow (white) for anisotropic carbons. The interference colours alternate upon stage rotation for anisotropic carbons but blue and yellow predominate for highly anisotropic structures (Gray and Devanney, 1986 & Forrest and Marsh, 1977).

Figure 3.8 shows the effect of increasing the heat treatment temperature of a neat Refcoal (HTRef) on the optical textures of the resulting cokes. The major optical textures developed in the cokes obtained from Refcoal are fine and medium circular anisotropy. Optical microscope observation of the M500 and M550 samples show that this cokes present thick grey isotropic wall with bright tiny particles regarded as small mesophase sphere (Carreira, *et al.,* 2001). The presence of mesophase spheres could be precursor to different sizes of anisotropic coke textures on further heat treatment. Thus it is expected that with increasing heat treatment temperature, the sizes of these spheres increase and eventually coalescence into bulk mesophase that is responsible for the formation of anisotropic cokes. The M550 sample indicates the development of pores, but the isotropic area still dominating. The absence of pores at heat treatment temperatures below 550°C indicates that the evolution of oils which occur at the first critical point (Gray, 1989) is not effective. Extensive pore development is observed on the M650 samples suggesting highly fluid carbonisation system and devolatilisation. Therefore the coke produced at this heat treatment temperature contains a mixture of fine and medium circular anisotropic texture. The same observation was noticed previously in the DRIFT analysis results in which the structure of the coke obtained at 650°C was completely different from that of the cokes formed below this heat treatment temperature. The size of the anisotropic domains did not increase, as expected, when heat treatment temperature was raised to 1000°C (M1000). The only observable change was an increase in pore size. A highly porous structure indicates extensive fluidity during carbonisation.

Figures 3.9 shows SEM photomicrographs of fractured surface of cokes obtained from carbonisation of neat Refcoals (HTRef) at different temperatures. Under scanning electron microscope metallurgical cokes are categorised as smooth, lamellar, intermediate and granular surface morphologies. However this classification is subjective since various materials form components which vary is appearance (Hays *et al.,* 1983). At low treatment temperatures the current cokes show lamellar, granular and rough morphology with heterogeneous particles resembling those of the original Refcoal. These cokes show loosely packed wrinkled flakes. Samples M650 and

M1000 are examples of smooth (S) surface morphologies produced from the carbonisation of a neat Refcoal at 650°C and 1000°C respectively. This type of morphology is believed to be formed from carbon precursor that melts and passes through the mesophase stage (Rodriguez-Valero *et al.,* 2002) during carbonisation. The surface of the coke becomes smooth as carbonisation temperature increases from 400 to 1000°C. The number of tiny particles present is reduced as the heat treatment temperature increases. The particles in this case represent the mesophase spheres. The presence of well developed pores (A) is also noticed in the M650 sample. This sample shows distinctive differences from the cokes formed at lower heat treatment temperatures. The same observation was made during optical microscopy analyses. Spheres of different sizes were also observed at this temperature (see Figure A.1 in Appendix). The spheres did not coalesce indicating a poorly developed mesophase. These spheres were covered with tiny particles similar to those observed in the parent coal and Refcoal. This suggests that some of these particles may be quinoline insolubles (QIs), i.e. ash, which is known to inhibit mesophase development (Rodriguez-Valey *et al.,* 2002). When each sphere was observed on a higher magnification a very smooth morphology was observed as in the M650 sample.

Summary

- The major optical textures developed in the cokes obtained from Refcoal are of fine and medium circular anisotropy.
- The cokes obtained from carbonisation of Refcoal exhibit smooth morphology indicating that these cokes are formed through the mesophase stage.
- Refcoal contains small particles that cover the surface of the mesophase spheres. They inhibit mesogen coalescence preventing the conversion into a bulk mesophase.
- Carbonisation of Refcoal at temperatures below 550°C gives a less foamed coke and less developed coke morphology.
- The Refcoals obtained at 135°C decompose at higher temperatures and therefore do not reach sufficient viscosity for mesophase growth.

3.3.1.3 Raman spectroscopic analysis of Refcoal cokes

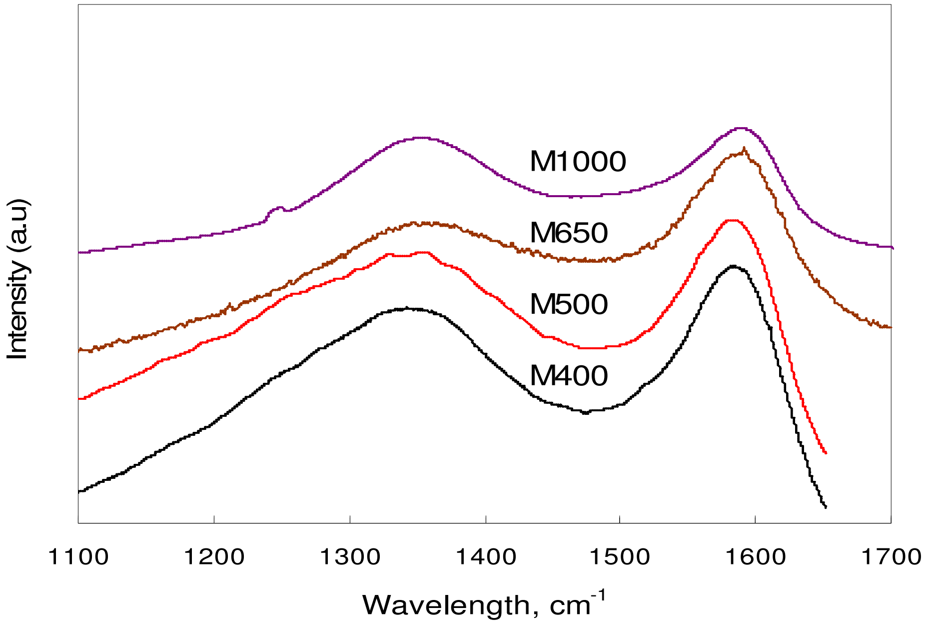


Figure 3.10: Raman spectra of cokes produced from the carbonisation of Refcoal at different temperatures (M400, M500, M650 and M1000: coke from carbonisation of HTRef at 400, 500, 650 and 1000°C respectively)

Figures 3.10 shows Raman spectra of cokes prepared from neat Refcoal after it was carbonised to different temperatures. Raman analysis of carbon materials is concerned with the behaviour of the characteristic D-peak (sp^3) and G-peak (sp^2) positioned at 1359 and 1590 cm^{-1} respectively. The D-peak is associated with defects such as disordered graphene layers within the carbon microstructure. These peaks help to estimate the degree of graphite-like crystalline order present in the carbon materials (Tuinstra *et al.,* 1970).

Carbonisation of neat Refcoal in the temperature region 400 to 1000°C shows the D-peak and G-peak well positioned at 1359 and 1590 cm^{-1} as shown in Figure 3.10. For highly disordered carbons such as coal D-peak dominates the G-peak whereas graphite shows a sharp G-peak positioned at 1580 cm^{-1} (Ferrari & Robertson, 2000). The relative intensity of the G-peak and the D-peak here shows the G-peak dominating the D-peak except for the M1000 coke. This is in agreement with the results reported elsewhere (Rogovoi and Amerik, 1993) in which the ratio d/g increased with an increase in carbonisation temperature. However increasing the temperature from 400 to 1000°C does not seem to increase relative intensity of the G-peak but only reduces the broadness of the D-peak. This is clearly visible on the M650 coke sample that shows the D-peak highly dominating the G-peak. The relative intensities calculations show a minor variation in the ratio I_D/I_G with increase in carbonisation temperature up to 650°C (see Table 3.3). This indicates minor changes with respect to ordering of the liquid crystals with increasing temperature. XRD analysis is expected to show the d_{002} starting to be well positioned $\sim 2\theta = 29$ and intensifying with increasing treatment temperature.

Summary

- Raman spectra of cokes shows the D-peak and G-peak positioned at 1359 and 1590 cm^{-1} respectively.
- The cokes produced from high temperature extracted Refcoal exhibit features similar to those obtained from disordered carbon materials.
- Carbonisation of Refcoals at temperatures up to 1000°C show little change on the relative intensities of the Raman peaks.

3.3.1.4 XRD analysis of Refcoal cokes

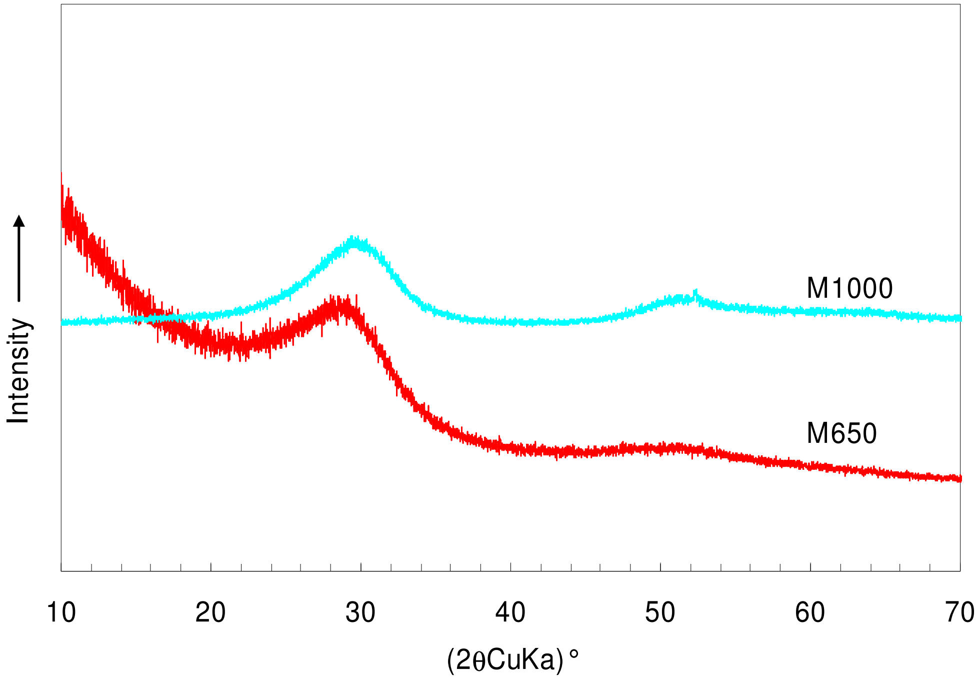


Figure 3.11: XRD patterns of cokes produced from the carbonisation of Refcoal at different temperatures (M650 and M1000: coke from carbonisation of HTRef at 650 and 1000°C respectively)

Figure 3.11 shows the XRD patterns of cokes prepared from Refcoal after carbonised to 650°C (M650) and 1000°C (M1000). The d_{002} peak is better developed in the M1000 than in the M650 sample. This indicates slightly improved stacking of aromatic rings in the M1000 coke than in the M650 coke. The d_{004} peak is more intense in the M1000 coke than in the M650 sample. This peak is the second reflection of the d_{002} also indicating the parallel stacking of crystalline molecules.

Summary

- Increasing the carbonisation temperature of Refcoals slightly improves the degree of ordering in Refcoal cokes.
- Increasing the carbonisation temperature also increases the intensity of both the d_{002} and d_{004} peaks with that of the former dominating.

3.3.2 Cokes from Refcoals treated with additives

3.3.2.1 Thermal analysis of Refcoal cokes

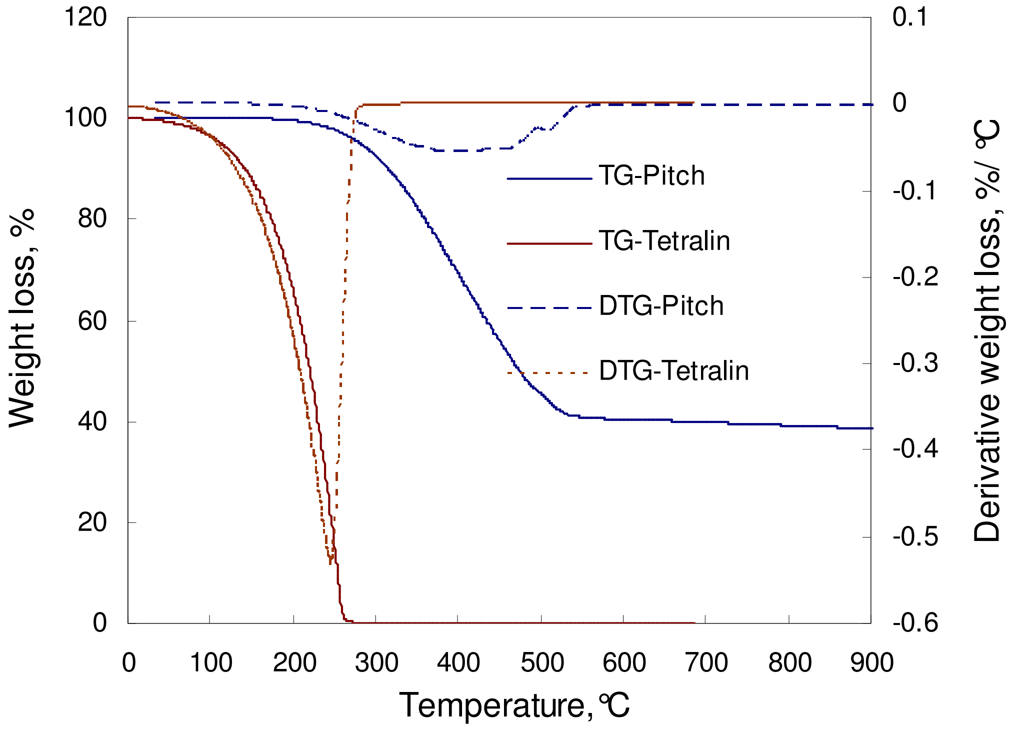


Figure 3.12 (a): TG and DTG curves of the additives used: pitch and tetralin

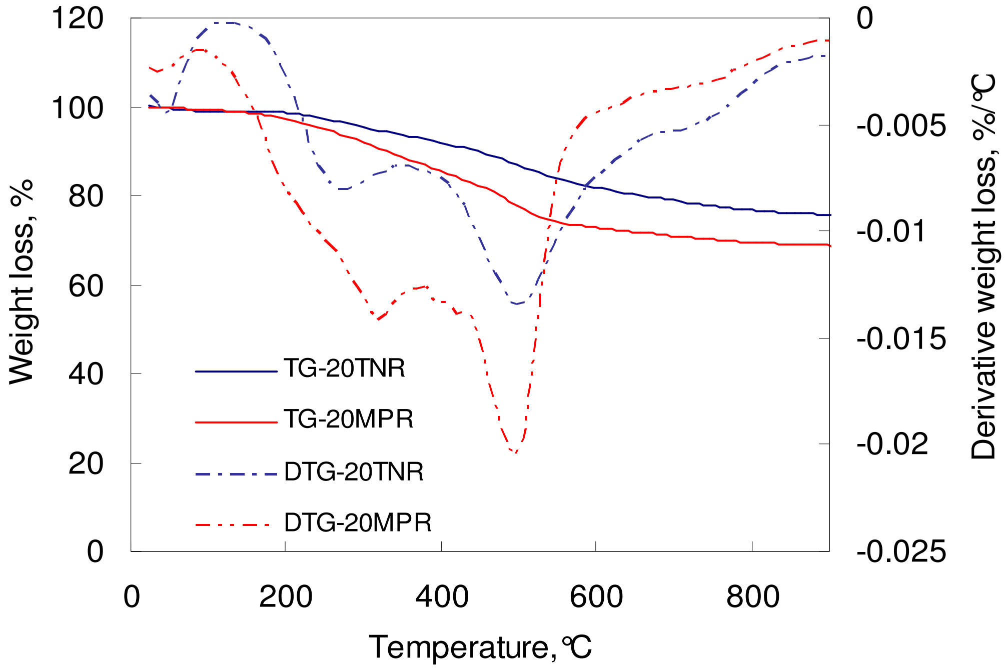


Figure 3.12 (b) TG and DTG curves showing the carbonisation profile of Refcoals treated with additives (Key: 20TNR: Refcoal mixed with 20% tetralin and 20MPR: Refcoal mixed with 20% Mittal pitch)

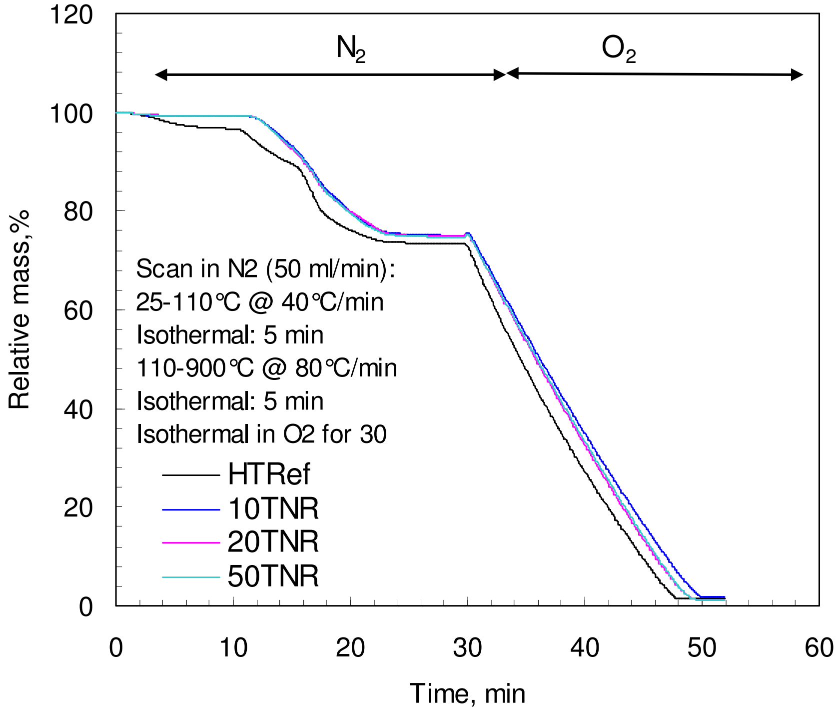


Figure 3.12 (c): Proximate analysis curves showing the carbonisation profile of Refcoals treated with tetralin (Key: HTRef: Coal extracts obtained from 135°C coal extraction; 10TNR: Refcoal mixed with 10% tetralin, 20TNR: Refcoal mixed with 20% tetralin and 50TNR: Refcoal mixed with 50% tetralin)

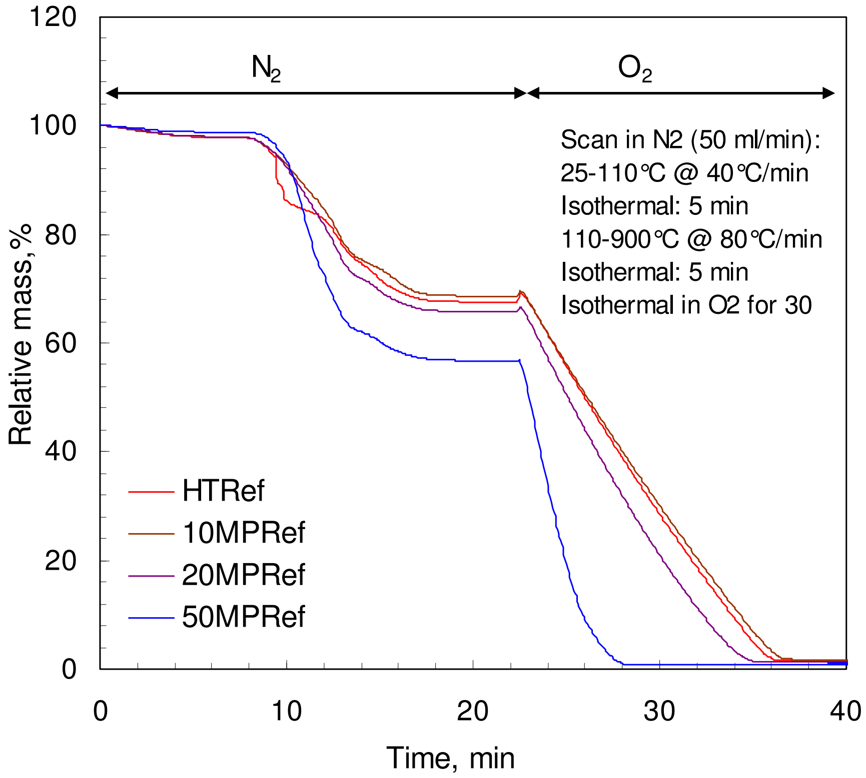


Figure 3.12 (d): Proximate analysis curves showing the carbonisation profile of Refcoals treated with pitch (Key: HTRef: Coal extracts obtained from 135°C coal extraction; 10MPR: Refcoal with 10% Mittal pitch, 20MPR: Refcoal mixed with 20% Mittal pitch and 50MPR: Refcoal mixed with 50% Mittal pitch)

Figure 3.12 (a) shows the thermal behaviour of the tetralin and pitch used as modifying agents for Refcoal carbonisation. Tetralin shows a single step weight loss between 100 and 248°C and leaves no carbonaceous residue above 250°C. This simply means that the tetralin has evaporated. On the other hand, the pitch shows two-step weight loss with a very broad peak at 184 and 420°C and the second sharp shoulder positioned at 510°C in the DTG trace. Thus the temperature of final weight loss in the tetralin is about 40°C below the initial temperature of weight loss for the Refcoal whereas the temperature interval of weight loss for the pitch overlaps that of Refcoal. To facilitate reactions with each other, it is desirable for the mixture components to be retained in a homogeneous condensed fluid phase. This means that tetralin is too volatile to act as a hydrogenation agent at ambient pressure whereas the pitch might be a suitable alternative.

In Figure 3.12 (b) both tetralin and pitch treated Refcoals show two steps-weight loss. Tetralin modified Refcoal samples show earlier weight loss as expected. In fact, this peak is found to coincide with the temperature interval for the loss of moisture and low molecular weight species in the thermal analysis of neat Refcoal. This indicates that most tetralin is lost simultaneously with moisture and low molecular weight species even when co-carbonised with Refcoal. On the other hand, the co-pyrolysis of Refcoal with pitch indicates that the interaction between this additive and Refcoal give a variety of low molecular weight species with a few evolving at the moisture region and others at higher temperatures than tetralin. Increasing the pitch content from 10 to 50 % slightly shifts the temperature of initial weight loss to higher temperatures. Although the curves show that the initial temperature of weight loss for both tetralin and pitch treated Refcoal is nearly at the same position, it is their final weight losses that determine their ability to interact with Refcoal. Figure 3.12 (b) shows that the maximum weight loss for tetralin treated Refcoal is around 650°C whereas that of Refcoals treated with Mittal pitch is positioned around 580°C.

Figure 3.12 (c) and 3.12 (d) show the proximate analysis curves of the Refcoal (HTRef) modified with tetralin and pitch respectively. These curves show that co-carbonisation of Refcoal with these additives changes the carbonisation profile. The evolution of volatiles was decreased from 29.9 % in the neat Refcoal to about 24 % in the Refcoal sample modified with 10 % tetralin (10TNR). The lower devolatilisation degree of the tetralin treated Refcoal favours the formation of coke with more carbon. However, increasing the tetralin content to 20 % and 50 % slightly increases the fixed carbon but the increment was not proportional to the amount of tetralin used. The carbon content was increased to about 74 % in the 10TNR sample, showing that some tetralin components are retained in the carbonising system and therefore contributing to the residual carbon. However the increased carbonaceous residue in this case contradicts the expectation from the observation in the TG curve suggesting the absence of residue above 300°C for neat tetralin.

When the Refcoal was modified with 10 % pitch the amount of residual carbon was lowered to about 66 % with the evolution of volatile matters slightly increasing. Increasing the proportion of pitch to 20 % and 50% increased the volatile matter to 32 % and 42 % respectively. The fixed carbon was further lowered respectively to 64 %

in the 20MPR and 56 % in the 50MPR after carbonising to 900°C. There was no conclusive relationship between the ash content and an increase in the proportion of pitch used. The reduction in carbon yield suggests that the pitch react with Refcoal to form low molecular weight species, which are easily evolved at lower temperatures. The unchanged carbonising behaviour of the tetralin modified Refcoal suggests a poor interaction between tetralin and the Refcoal or some components of tetralin reacting with the Refcoal to form stable compounds which are retained in the sample and therefore contributing to the increased carbonaceous residue (fixed carbon).

Summary

- Tetralin slightly reduces the evolution of volatile matters from the Refcoal sample during carbonisation.
- Only a small amount of tetralin actually reacts with Refcoal to form stable compounds that increase the effective carbon yield. The rest is lost with moisture and low molecular weight species.
- On the other hand a well-defined trend between the amount of pitch in the carbonising system and the fixed carbon was established. However, in this case the fixed carbon decreased with an increase in Mittal pitch content in the blend.
- The pitch clearly interacts with Refcoal as it reduces the carbon yield.

3.3.2.2 DRIFT analysis of Refcoal cokes

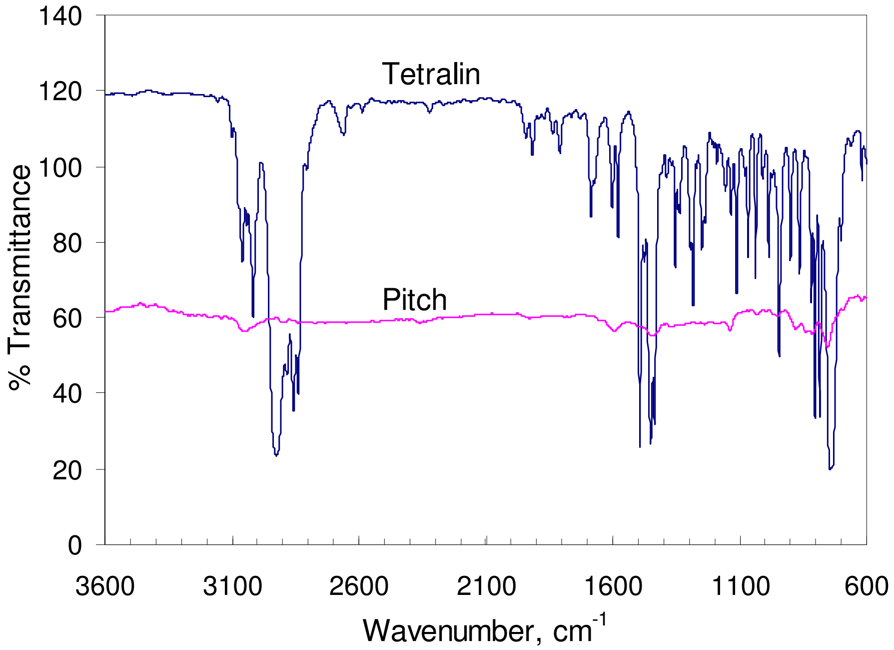


Figure 3.13 (a): DRIFT spectra showing the functional groups involved in the additives

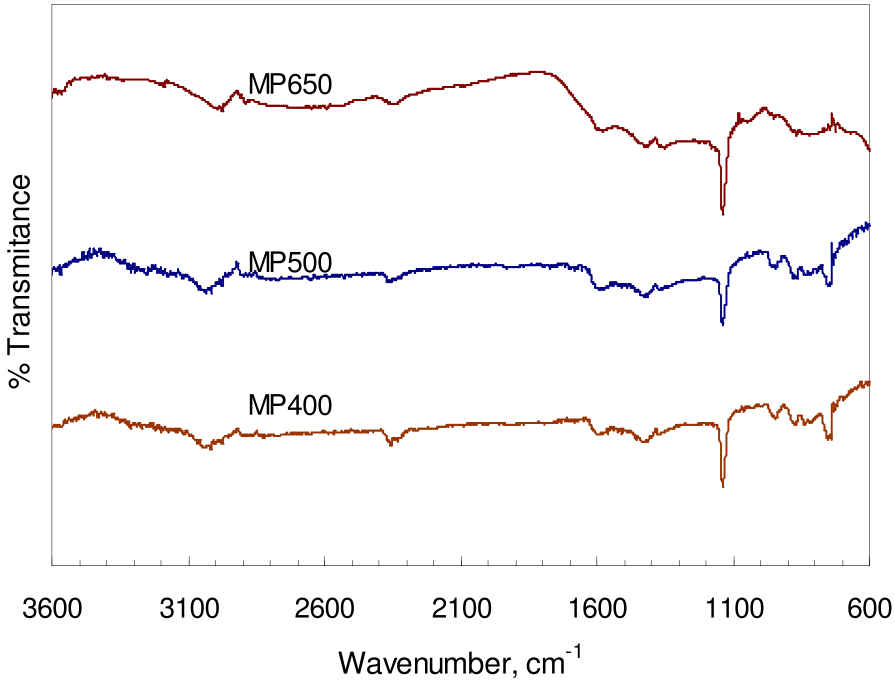


Figure 3.13 (b): DRIFT spectra of cokes produced from Mittal pitch carbonised at different temperatures (MP400, MP500, and M650: coke from carbonisation of Mittal pitch at 400, 500, and 650°C respectively)

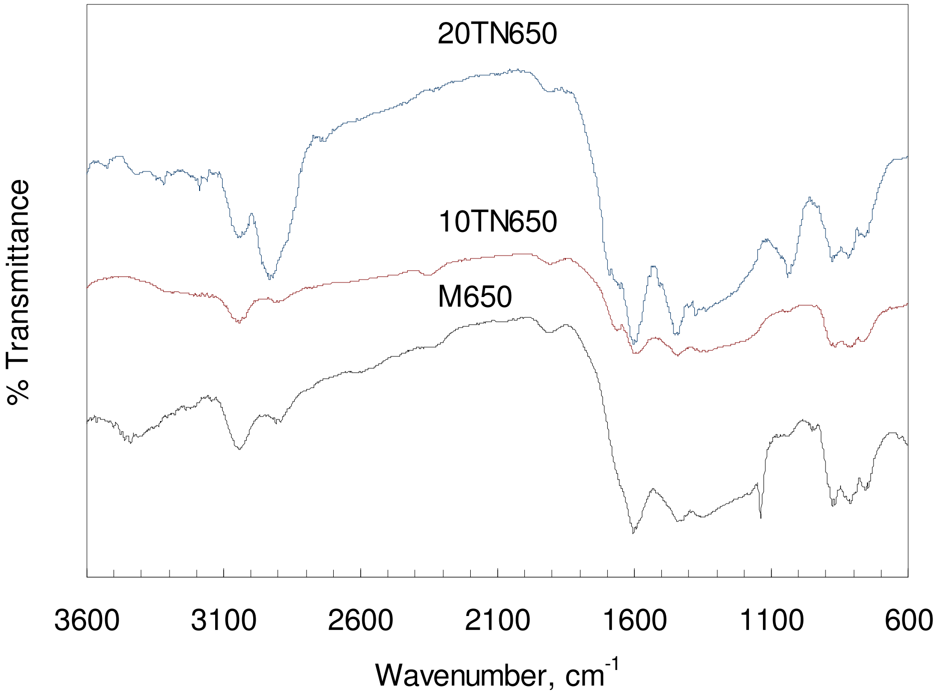


Figure 3.13 (c): DRIFT spectra of cokes produced from carbonisation of Refcoals with different TN content (Key: M650: HTRef carbonised at 650°C, 10TN650: coke from HTRef with 10% tetralin after carbonised to 650°C and 20TN650: coke from HTRef with 20% tetralin after carbonisation to 650°C)

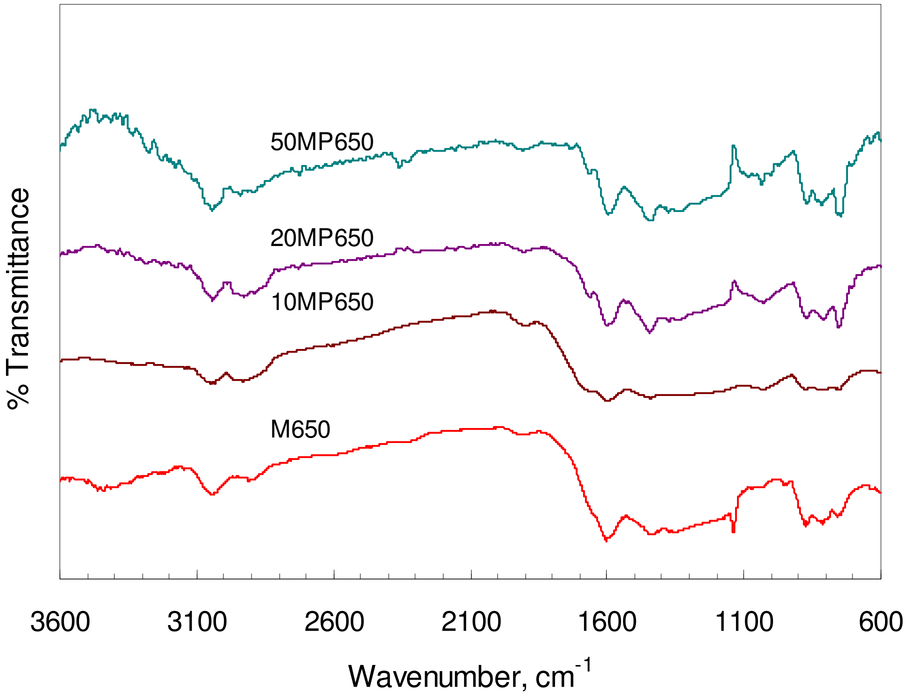


Figure 3.13 (d): DRIFT spectra of cokes produced from Refcoals with different Mittal pitch (MP) content after carbonised to 650°C (Key: M650: HTRef carbonisation at 650°C, 10MP650: coke from HTRef with 10% pitch after carbonisation to 650°C, 20MP650: coke from HTRef with 20% tetralin after carbonisation to 650°C and 50MP650: coke from HTRef with 50% tetralin after carbonisation to 650°C)

Figure 3.13 (a) is the DRIFT spectra of the modifying agents, tetralin and pitch. Tetralin shows strong absorption bands at 3021, 1490, and 726 cm^{-1} assigned to the C-H aromatic stretching, CH_2 band and the aromatic C-H with three to four adjacent hydrogen (less substituted) respectively. On the other the hand, Mittal pitch shows additional peaks at 1585 and 1133 cm^{-1} that are assigned to condensed aromatic C=C band and the C-H of the in plane deformation of the aromatic rings in addition to the aromatic C-H band, CH_2 band and the aromatic out of plane band at 3039, 1429 and 745 cm^{-1} respectively. It is the aromatic hydrogen at 726 cm^{-1} and 745 cm^{-1} and their aromatic nature that make these compounds good modifying agents and hydrogen donor additives. Tetralin shows additional bands showing different environments of hydrogen in the region 720-860 cm^{-1}.

Figure 3.13 (b) is the DRIFT spectra monitoring the changes in functional groups when a neat MP is carbonized at different temperatures. A very sharp peak at 1130 cm^{-1} is highly intense in the sample carbonized at 400°C (MP400) and its intensity is lower in the pitch carbonized at 500°C (MP500) sample. This peak is assigned to the formation of deformation of the aromatic C-H bonds in the planar. The peak shows the present of less substituted benzene rings. The aromatic C-H band at 3020 cm^{-1} was expected to increase with temperature but there was no conclusive observation in this case. The formation of aromatic rings is only confirmed by the present of aromatic C-H band at 1130 cm^{-1}.

The DRIFT spectra for the co-carbonization of the Refcoal with hydrogen donor additives tetralin and pitch are shown in Figures 3.13 (c) and (d) respectively. The use of these additives is expected to reduce the formation of cross-links by stabilizing the free radicals formed during thermal decomposition of Refcoal as shown in Figure 5 (I) of Chapter 2. The stabilization reactions are expected to be more pronounced in the pitch modified systems than those modified with tetralin as suggested by the thermal analysis of the Refcoal modified with these additives. Although phenols are not desired in the carbonization system, their presence may signify the ability of these additives to transfer hydrogen to the radicals formed from the cleavage of C-O-C bonds. On the other hand, the phenols are unstable at the carbonization temperatures employed in this study.

The aromatic C=C band positioned at 1558 cm^{-1} in Figure 3.13 (c) (M650) is more intense in the coke produced from the co-carbonization of 20% tetralin with Refcoal. This suggests the condensation of more aromatic rings in the system, thus complementing the increased carbonaceous residue as suggested by the proximate analysis of the addition of tetralin. In addition the methylenic C-H in plane bending band at 1424 cm^{-1} is more intense in the 20TN650 sample indicating the formation of aromatic rings. Contrarily, the aliphatic C-H band at 2819 cm^{-1} is very broad and more intense in 20TN650 than in the coke formed from carbonization of a neat Refcoal and 10TN650. This may suggest that some aromatic rings with aliphatic chains substitutions are formed. Raman spectroscopy should show the formation of more sp^3 vibrational modes as the amount of tetralin increases indicating the formation of aliphatic disordered carbons. In the 20TN650 sample an additional intense peak assigned to C-O stretching band of the alcohols is appearing at 1022 cm^{-1}. Phenols, if presence in the carbonizing system, retard mesophase growth and it is expected that a poorly developed mesophase will be observed in microscopic analysis of the tetralin treated Refcoals.

When the Refcoal is co-carbonized with 20% pitch, the resulting coke shows a reduction of both the aliphatic peak at 2932 cm^{-1} and the carbonyl C-O band at 1130 cm^{-1}. The aromatic out of plane peak at 740 cm^{-1} is slightly intensified with increasing concentration of pitch in the carbonizing system. This indicates the formation of highly substituted aromatic compounds. The peak at 740 cm^{-1} increases with increase in pitch content from 20% to 50%. The presence of this shows the formation of aromatic rings and therefore contradicting the results from proximate analysis.

Summary

- Tetralin increases mainly the concentration of aliphatic compounds in the carbonizing system.

- Co-pyrolysis of Refcoal with the pitch reduces both the oxygenated groups and aliphatic compounds in the carbonizing system. It also forms highly substituted benzene rings.
- Condensation of aromatic rings is evident in the Refcoal treated with tetralin than the pitch.

3.3.2.3 Microscopic analysis of Refcoal cokes

3.3.2.3.1 *Optical microscope*

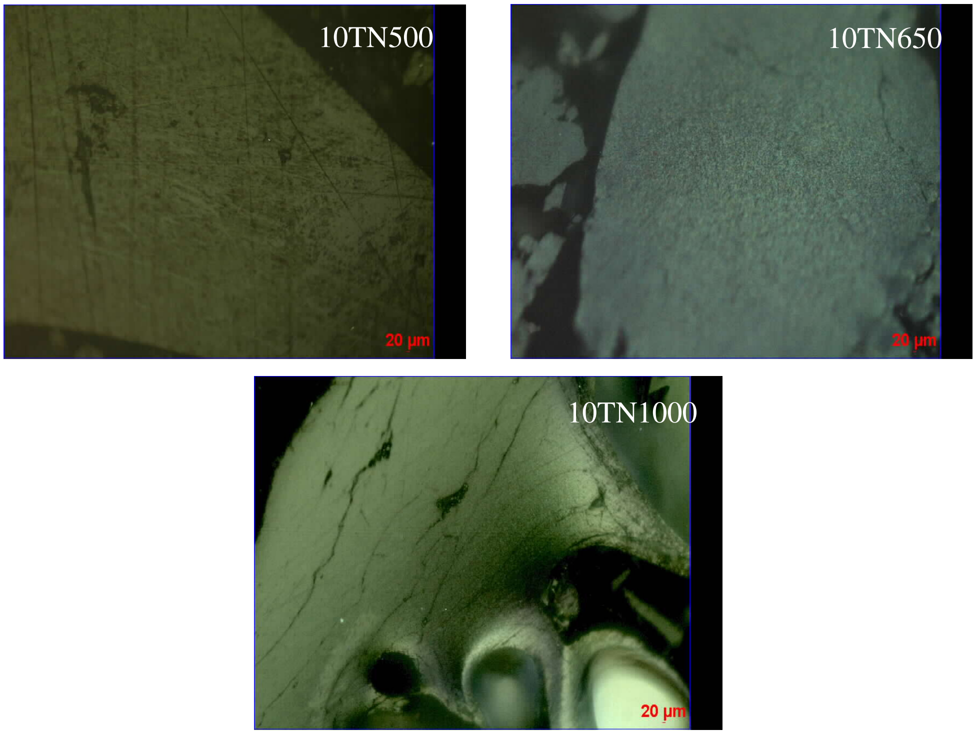


Figure 3.14 (a): Cokes produced from Refcoals with 10% TN after carbonised at different temperature (10TN500: coke from HTRef with 10% tetralin after carbonised to 500°C, 10TN650: coke from HTRef with 10% tetralin after carbonised to 650°C and 10TN1000: coke from HTRef with 10% tetralin after carbonised to 1000°C)

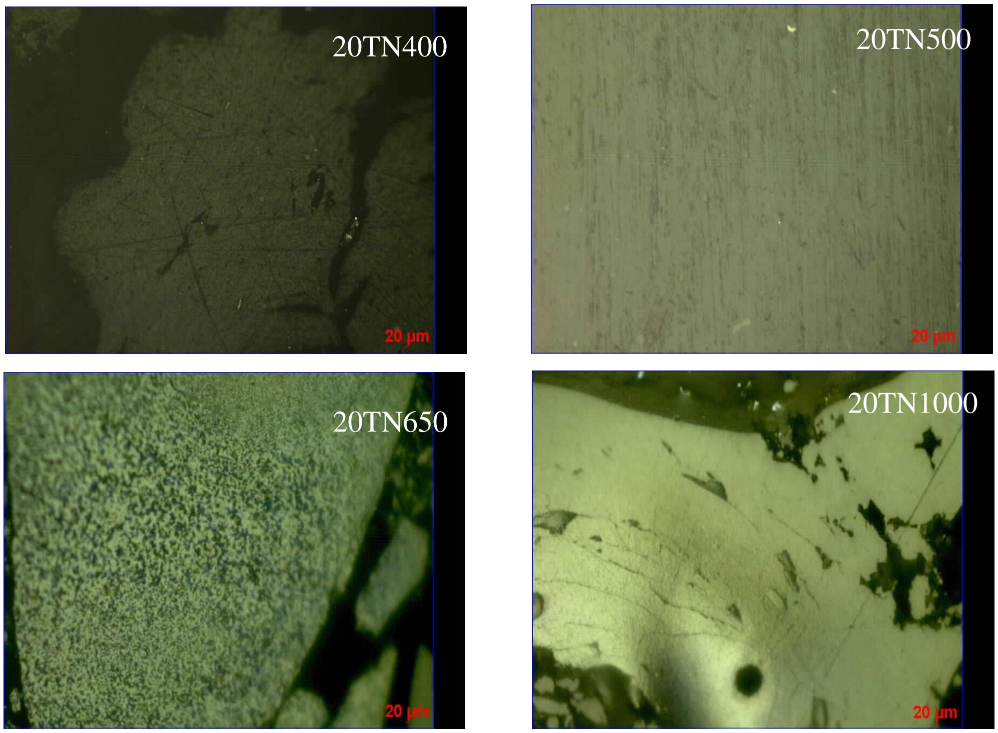
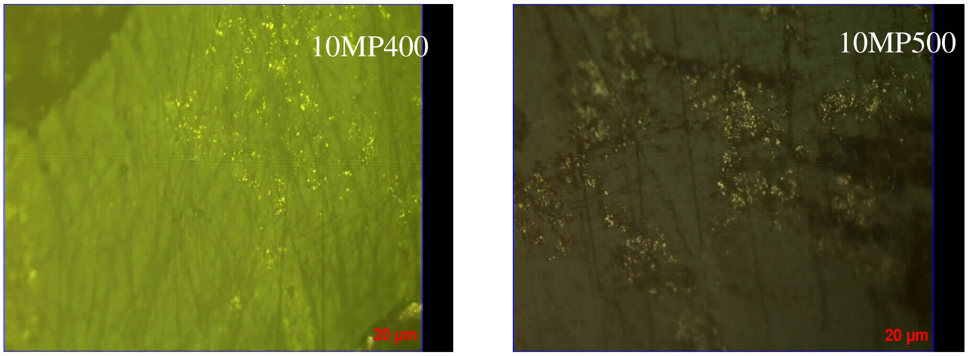


Figure 3.14 (b): Cokes produced from Refcoals with 20% TN (Key: 20TN500: coke from HTRef mixed with 20% tetralin after carbonised to 500°C, 20TN650: coke from HTRef mixed with 20% tetralin after carbonised to 650°C and 20TN1000: coke from HTRef mixed with 20% tetralin after carbonised to 1000°C)



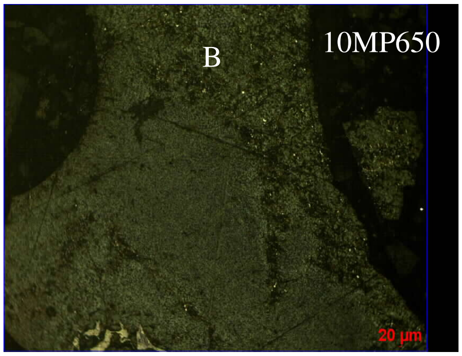


Figure 3.14 (c): Cokes produced from Refcoals treated with 10% MP (Key: 10MP400: coke from HTRef mixed with 10% pitch after carbonised to 400°C, 10MP500: coke from HTRef mixed with 10% pitch after carbonised to 500°C, 10MP650: coke from HTRef mixed with 10% pitch after carbonised to 650°C) (B= anisotropic region)

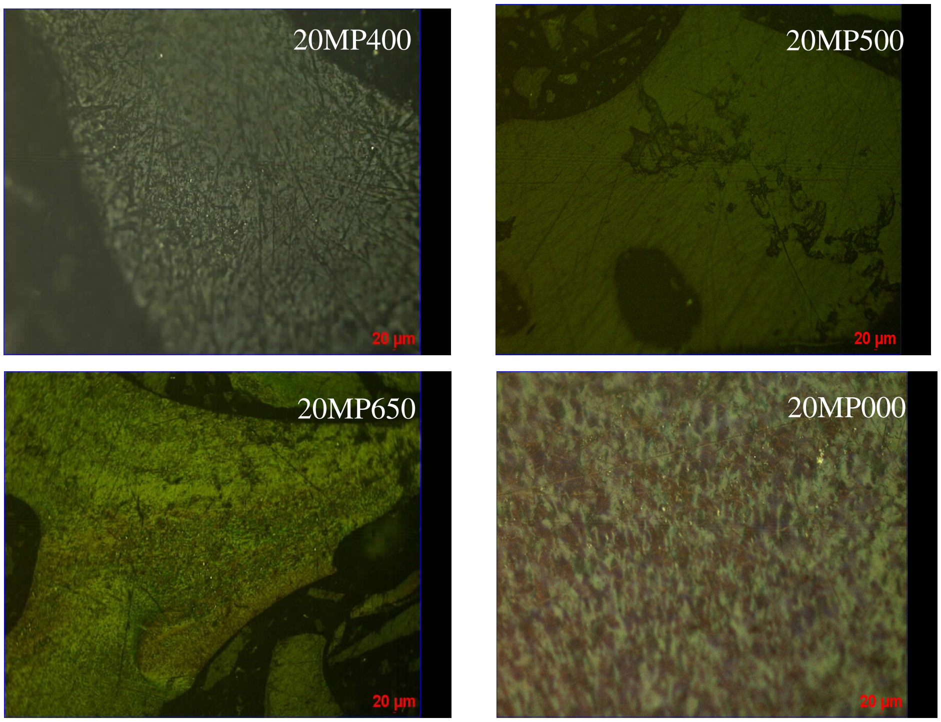


Figure 3.14 (d): Cokes produced from Refcoals treated with 20% MP (Key: 20MP400: coke from HTRef mixed after with 20% pitch carbonised to 400°C, 20MP500: coke from HTRef mixed with 20% pitch after carbonised to 500°C,

20MP650: coke from HTRef mixed with 20% pitch after carbonised to 650°C and 20MP000: coke from HTRef mixed with 20% pitch after carbonised to 1000°C)

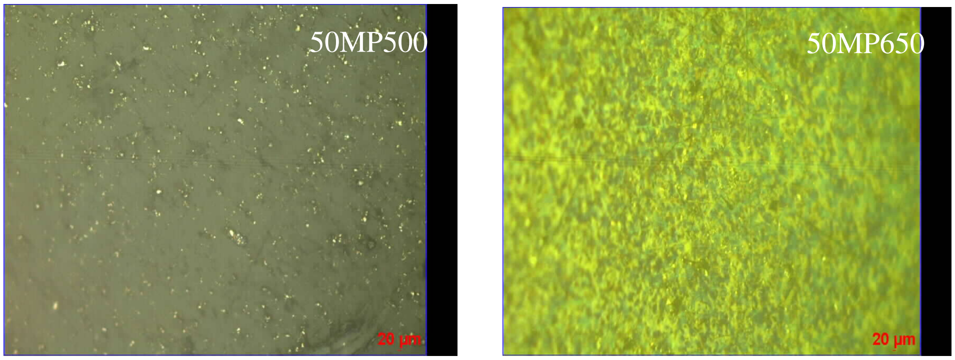


Figure 3.14 (e): Cokes produced from Refcoals with 50% MP carbonised at different temperatures (Key: 50MP500 and 50MP650: coke from HTRef mixed with 50% pitch after carbonised to 500 and 650°C respectively)

Figure 3.14 (a) to (e) show the optical micrographs of cokes prepared from the Refcoals mixed with different portions of the additives, tetralin and Mittal pitch when viewed under a polarised light microscope. The changes observed upon the addition of these hydrogen donor additives are expected to be more pronounced in the Refcoals mixed with pitch than tetralin. This is due to the fact that the evolution of oils and gases was mainly experienced in the pitch modified Refcoals than those modified with tetralin. On the other hand the formation of phenols upon tetralin addition could results in mesophase growth being inhibited. The major optical textures obtained from co-carbonisation of 10% tetralin with Refcoal shows cokes with a very fine circular anisotropy only after carbonising the blends to 650 and 1000°C. The optical texture sizes of these cokes are smaller than those of the cokes obtained from neat Refcoals. Unlike the neat Refcoal carbonisation case, the coke obtained at 500°C (10TN500) shows no evidence of mesophase spheres. The isotropic texture dominates. The development of pores in 10TN650 and 10TN000 cokes is analogous to those in HM650 and HM000. This indicates that 10% tetralin addition has little effect on the optical texture. This is in agreement with the results shown by thermogravimetric analysis: Only the 10 % tetralin addition affected the Refcoal carbonisation profile. This makes it less effective during decomposition of Refcoal and also in the fluid stage mesophase in which ordering of planar molecular is occurs.

Surprisingly, on increasing the concentration of tetralin to 20% the optical textures size increases to a mixture of coarse circular and fine lenticular anisotropy after carbonisation to 650°C. This is indicated by the dominance of yellow and blue colours in the 20TN650 samples. No pore development is observed in the 20 % tetralin modified Refcoal cokes. However the coke obtained after heat treating the same blend to 1000°C (20TN000) shows large pores and cracks similar to those observed in the M1000 coke sample. The coke obtained in this case shows reduced anisotropic textures sizes as compared to those in the 20TN650 and 20MP000.

The cokes obtained upon co-carbonisation of Refcoal with 10 % Mittal pitch (Figure 3.14 (c)) shows optical textures with very small mesophase spheres and pores. There is no evidence that these spheres increase in size as the temperature is increased. However, the formation of coalesced mesophase spheres is confirmed by the appearance of fine circular anisotropic texture at 650°C (10MP650 sample). Nevertheless, the isotropic area is still dominant as identified by the grey domains. When the pitch content was increased to 20 % (in the Figure 3.14 (d)) cokes with coarse circular and fine lenticular anisotropic textures are obtained after carbonisation of the blends at 650°C. Increasing the heat treatment temperature to 1000°C did not increase the anisotropic domains sizes. The coke did not show any cracks or development of pores as in the 20 % tetralin treated Refcoal. The addition of 50 % pitch produced coke with coarse lenticular anisotropy after carbonisation of this sample to 650°C. However the coke obtained at 500°C heat treatment (50MP500) shows highly reduced size of optical textures. This shows that the pitch provides sufficient mobility for the carbonising system to evolve gasses without causing cracks and large pores.

Summary

- Co-carbonisation of Refcoal with tetralin and Mittal pitch produces significant changes in the optical textures mainly after when the additive content exceeds 20% and carbonisation temperature is 650°C or higher.
- Tetralin shows anisotropic coke textures even at 10% level whereas the cokes obtained from pitch treated samples at the same composition exhibit only disjointed mesophase spheres.
- Although the pitch changes the carbonisation profile of the Refcoal, its effect of the formation of anisotropic coke textures is less pronounced than the

changes caused by tetralin. However in both additives considerable changes are obtained from treatment of Refcaols with 20 % additive upon heat treating to 650°C.

- A change in carbonisation profile of Refcoal does not guarantee the formation of anisotropic cokes.
- The cokes obtained from tetralin treated Refcoals are highly porous and contain cracks upon carbonisation to 1000°C.

3.3.2.3.2 Scanning electron microscope of cokes

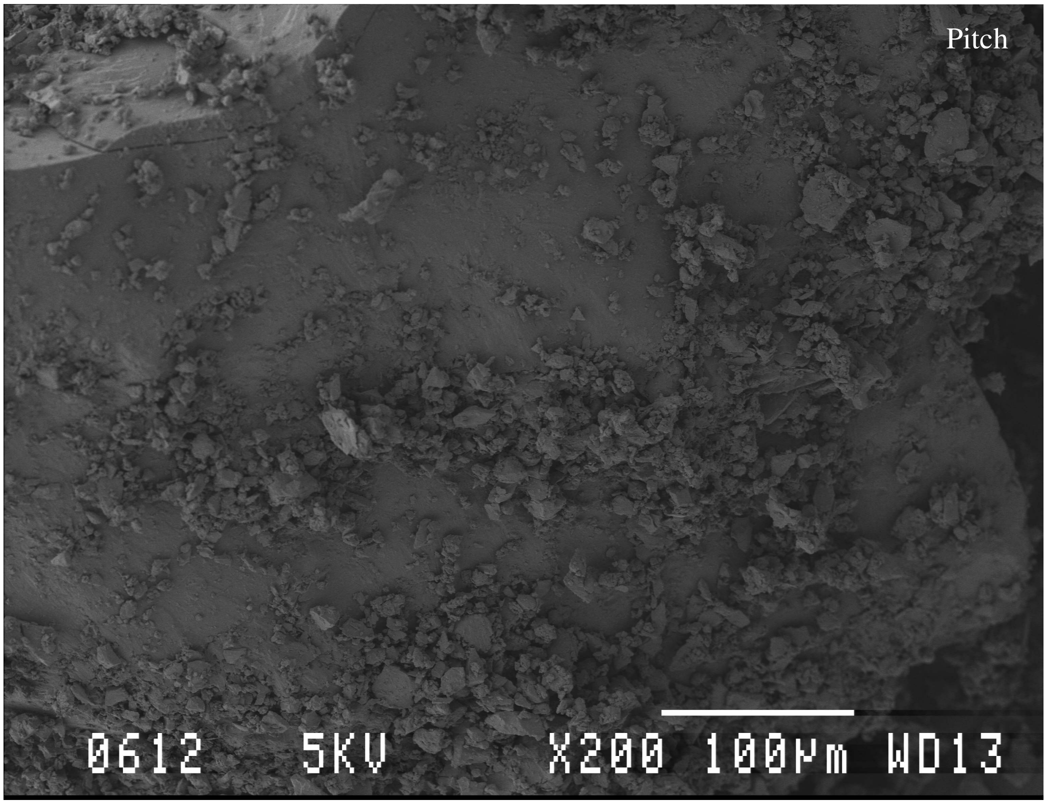


Figure 3.15 (a): SEM photograph of the as received Mittal pitch

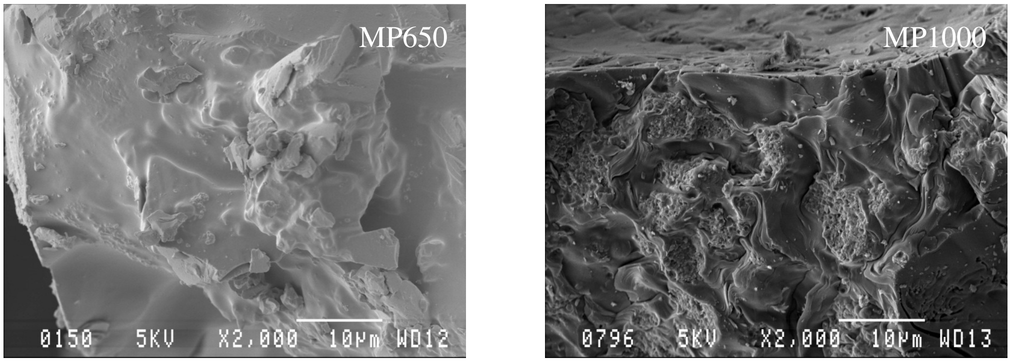


Figure 3.15 (b): SEM photograph of cokes from the pitch carbonised at different temperatures (Key: MP650 and MP000: Mittal pitch carbonised at 650 and 1000°C respectively)

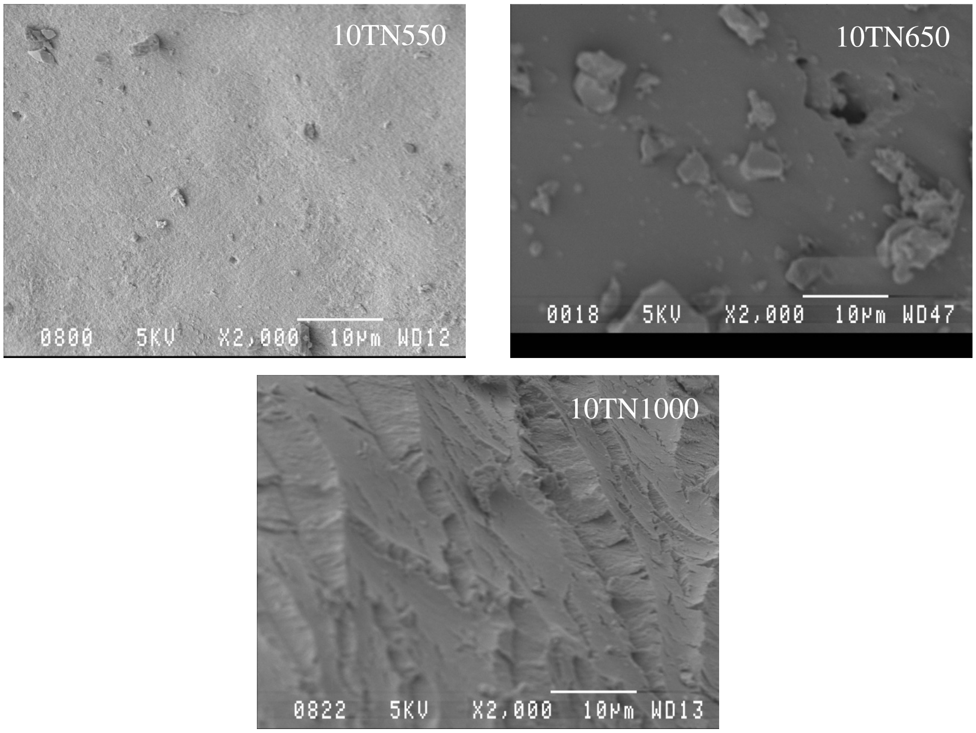


Figure 3.15 (c): SEM photograph of cokes produced from Refcoals treated with 10% tetralin (Key: 10TN550, 10TN650 and 10TN1000: coke from HTRef mixed with 10% tetralin after carbonised to 550, 650 and 1000°C respectively)

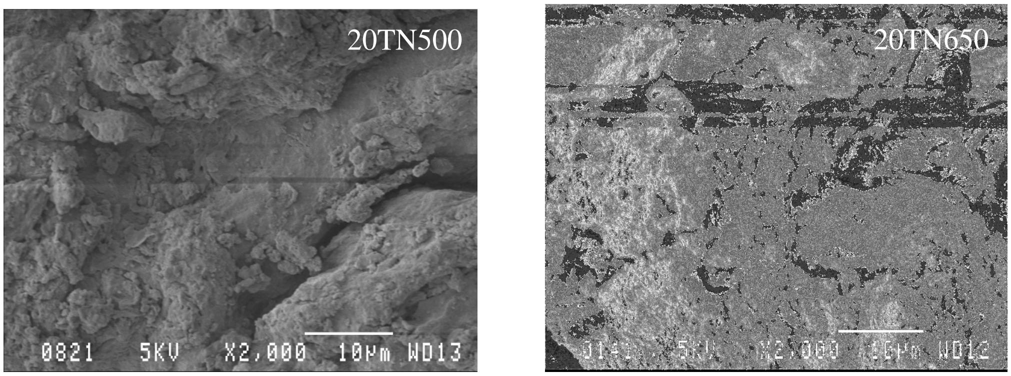


Figure 3.15 (d): SEM photographs of cokes produced from Refcoals modified with: 20% tetralin (top) and 50% tetralin (bottom) (Key: 20TN500: coke from HTRef mixed with 20% tetralin after carbonised to 500°C, 20TN650: coke from HTRef mixed with 20% tetralin after carbonised to 650°C)

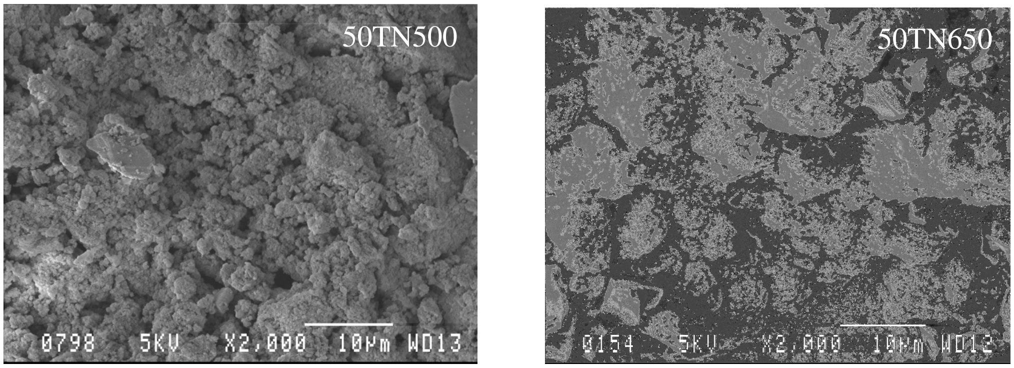


Figure 3.15 (e): SEM photographs of cokes produced from Refcoals modified with: 50% tetralin (Key: 50TN500: coke from HTRef mixed with 50% tetralin after carbonised to 500°C, 50TN500: coke from HTRef mixed with 50% tetralin after carbonised to 650°C)

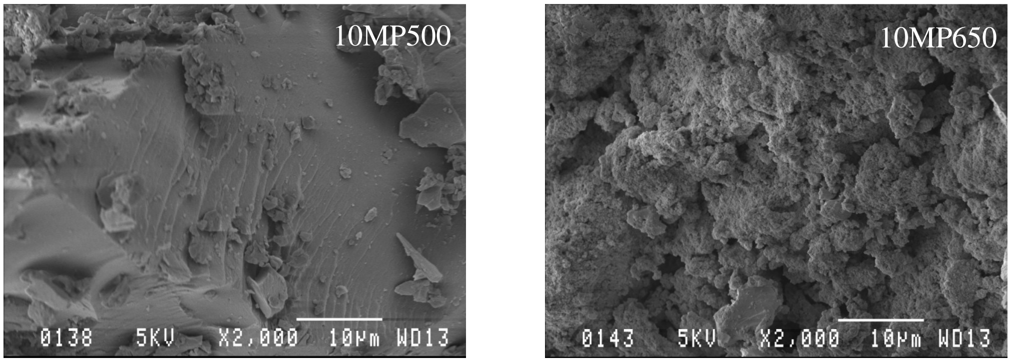


Figure 3.15 (f): SEM photographs of cokes produced from Refcoals modified with 10% Mittal Pitch (Key: 10MP500 and 10MP650: coke from HTRef mixed with 10% pitch after carbonised to 500 and 650°C respectively)

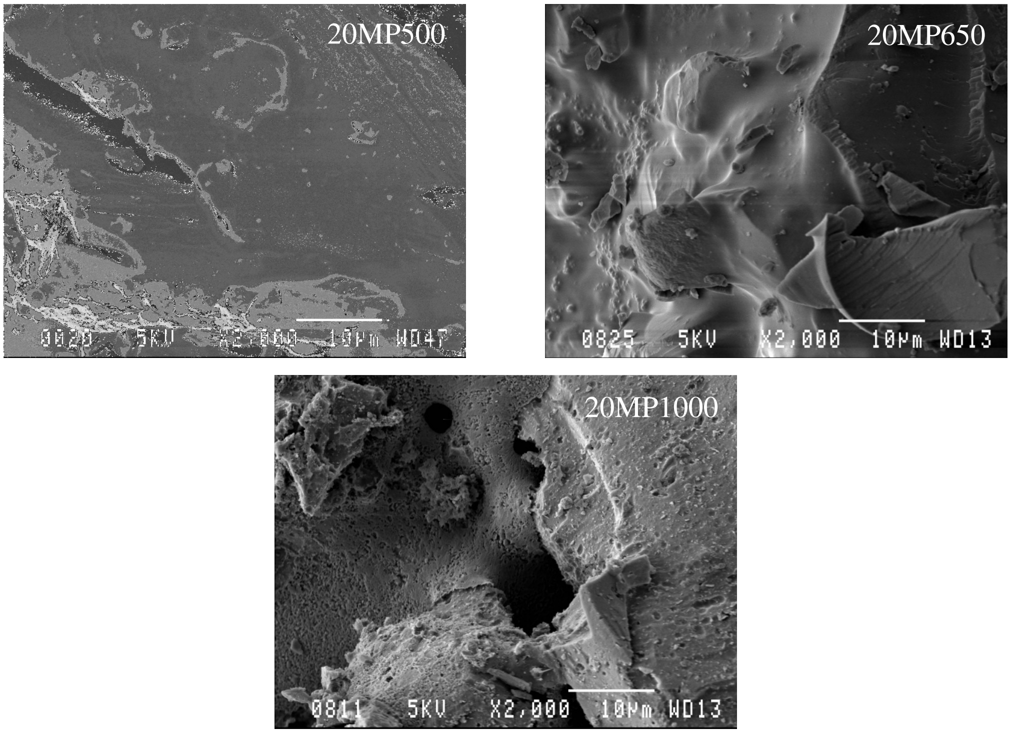


Figure 3.15 (g): SEM photographs of cokes produced from Refcoals modified with 20% Mittal pitch (Key: 20MP500: coke from HTRef mixed with 20% pitch after carbonised to 500°C, 20MP650: coke from HTRef mixed with 20% pitch after carbonised to 650°C, 20MP1000: coke from HTRef mixed with 20% pitch after carbonised to 1000°C)

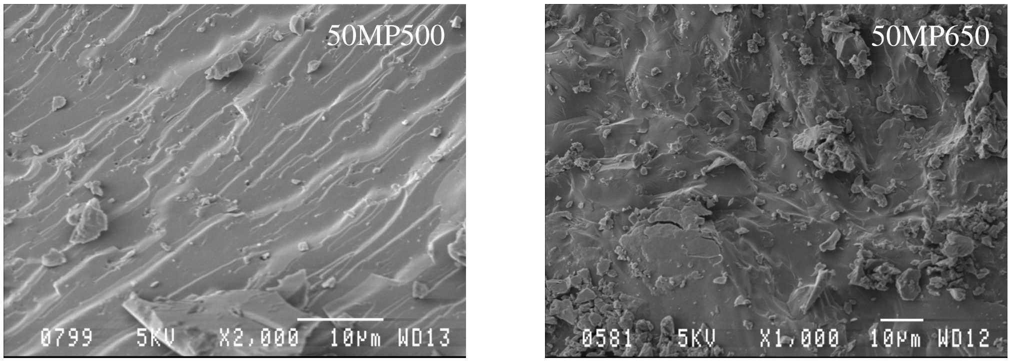


Figure 3.15 (h): SEM photographs of cokes produced from Refcoals modified with 50% Mittal pitch (Key: 50TN500: coke from HTRef mixed with 50% pitch after carbonised to 500°C and 50TN650: coke from HTRef mixed with 50% pitch after carbonised to 650°C)

An SEM photograph of the fractured surface of the parent pitch is shown in Figure 3.15 (a). The pitch shows a slightly smooth surface containing agglomerates similar to those observed in the coal and Refcoal. These particles are more pronounced in this case than in the coal and Refcoal. The smooth surface suggests that this pitch is passing through the mesophase (Kolar-Legin *et al.,* 1999). The pitch is formed from the distillation of coal tar.

Figure 3.15 (b) shows the SEM micrographs of pitch after carbonisation to 650 and 1000°C. These cokes exhibit smooth morphologies showing that the cokes from the Mittal pitch are formed through the fluid stage. The fluidity exhibited by this pitch is required to control the carbonisation of Refcoal during carbonisation for the development of anisotropic cokes.

Figure 3.15 (c) to (h) show the SEM photographs of cokes produced from the co-pyrolysis of Refcoal with different proportions of additives, tetralin and Mittal pitch. In this case it is observed that increasing the amount of tetralin additive increases the content of agglomerates similar to those identified in parent material. This is clearly observed on the 50TN650 coke, which shows round globular like particles covered with fine agglomerated particles. Carbonisation of the Refcoal with 10% tetralin to 1000°C (i.e. 10TN1000) produces a coke exhibiting extensive parallel cracks without any devolatilisation pores. The same behaviour was observed in the optical micrograph of cokes after carbonisation of HTRef to 1000°C with 10 (10TN1000) and 20% (20TN1000) tetralin as shown in Figure 3.14 (a) and (b). However, co-carbonisation of the Refcoal with as little as 10% pitch (10MP500) shows a mixture of smooth and lamellar morphology even at 500°C carbonisation temperature. Increasing the heat treatment temperature from 500 to 650°C increases the smoothness of the coke surfaces. The textures formed from the co-carbonisation of Refcoal with pitch resemble those observed on a single carbonisation of the parent pitch in Figure 3.15 (a). This indicates that the coke forms via a fluid stage mesophase during carbonisation (Iglesias *et al.*, 2001). This confirms optical textures observed in the optical microscopic analysis, in which small mesophase spheres were observed upon the addition of 10% pitch. It is not understood as what causes the 20MP1000 sample to shows the morphology that differs from the other pitch treated Refcoal cokes. When the proportion of pitch was increased to 50%, the surface of the coke exhibits smooth textured morphology resembling that of the steps with the resembling that of the cokes obtained from singly carbonised pitch.

Summary

- Co-carbonisation of Refcoal with tetralin produces cokes with smooth surfaces with few agglomerates only when 10% tetralin is used.
- Increasing the concentration of tetralin to 20 and 50% shows a morphology featuring large dispersed agglomerates considered to be the mesophase domains. The concentration of these particles increases with increasing TN concentration.
- Carbonisation of a neat MP produces cokes with a mixture of smooth and granular morphology.
- Carbonisation of Refcoal with Mittal pitch produces cokes that pass through the fluid stage mesophase during carbonisation. The cokes exhibit smooth morphologies similar to those obtained from the delayed.
- Unlike in the other techniques in which changes where mainly observed mostly on the the samples obtained at 650°C, SEM shows smooth morphology from as low as 500°C.

3.3.2.4 Raman spectroscopy of Refcoal cokes

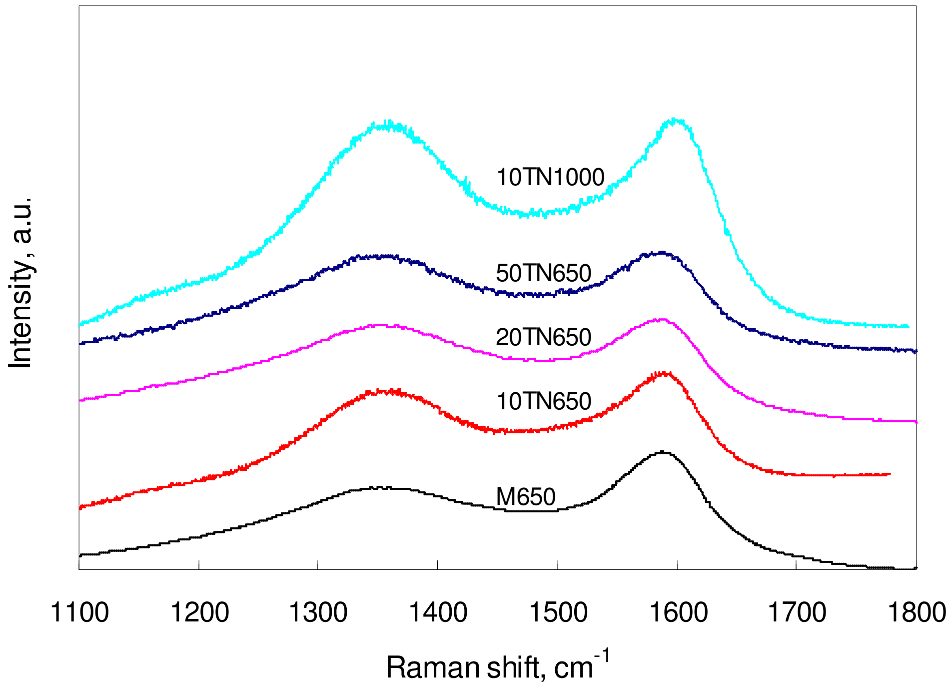


Figure 3.16 (a): Raman spectra of cokes produced from Refcoal with different tetralin content (Key: M650: HTRef carbonisaed at 650°C, 10TN650: coke from HTRef mixed with 10% tetralin after carbonised to 650°C, 20TN650: coke from HTRef mixed with 20% tetralin after carbonised to 650°C and 50TN650: coke from HTRef mixed with 50% tetralin after carbonised to 650°C and 10TN1000: coke from HTRef mixed with 10% tetralin after carbonised to 1000°C)

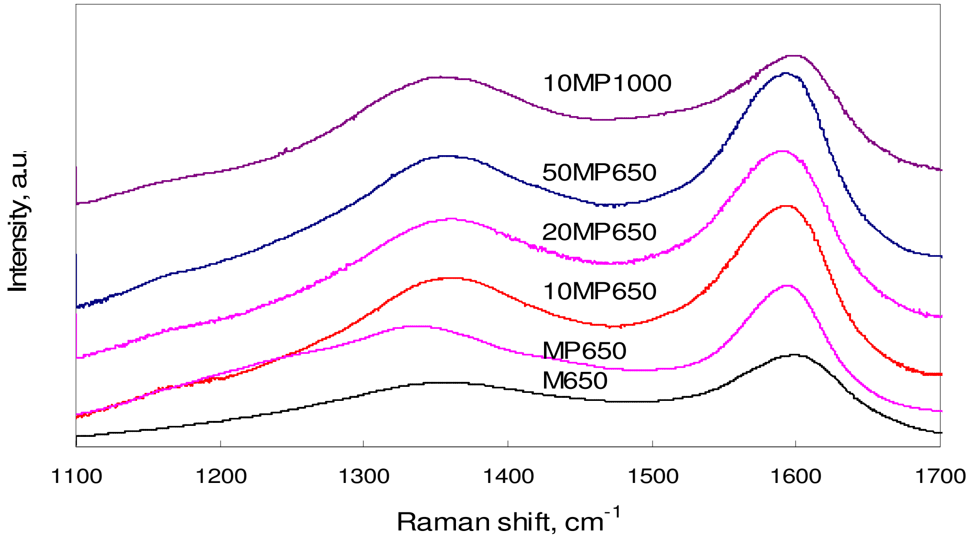


Figure 3.16 (b): Raman spectra of cokes produced from Refcoal with different pitch content (Key: M650: HTRef carbonised at 650°C, MP650: Mittal pitch carbonised at 650°C, 10MP650: coke from HTRef mixed with 10% pitch after carbonised to 650°C, 20MP650: coke from HTRef mixed with 20% pitch after carbonised to 650°C and 10MP1000: coke from HTRef mixed with 10% pitch after carbonised to 1000°C)

Table 3.3 Summary of the behaviour of Raman first order spectra of cokes produced in this study

Sample	**D-peak**		**G-peak**		**Ratio**
	Intensity	Position	Intensity	Position	I_D/I_G
M400	1464	1342	1592	1581	0.92
M500	1534	1356	1634	1582	0.94
M650	630	1348	860	1592	0.73?
M1000	487	1353	518	1589	0.94
10TN650	463	1316	554	1592	0.84
20TN650	500	1352	527	1589	0.94
50TN650	473	1340	495	1587	0.96
10TN1000	1393	1356	1399	1597	0.99
10MP650	645	1361	1136	1593	0.57
20MP650	644	1361	1104	1590	0.58
50MP650	670	1358	1231	1592	0.54
10MP1000	607	1353	754	1597	0.81

Figure 3.16 (a) is the Raman spectra showing the effect of tetralin on the molecular ordering of Refcoal cokes. These spectra show that the presence of tetralin in the carbonising system induces some disordering behaviour in the resulting coke after carbonising the tetralin/Refcoal mixture to 650°C. When the composition of tetralin was increased from 10% to 50% the D-peak was broadened and its intensity was also increasing. The relative intensity ratios (I_D/I_G) increased with an increase in the amount of tetralin used. This shows the formation of disordering behaviour in the resulting cokes.

The Raman spectra of the cokes produce from co-carbonisation of Refcoal with Mittal pitch shown in Figure 3.16 (b). Similar to the tetralin modified Refcoal cokes the D-peak becomes broad as the amount of pitch is varied from 10 to 50%. The increasing broadness of the D-peak with increasing pitch content is in agreement with the increasing aliphatic (C-H) band as shown by the IR analysis (Figure 3.13). However, in this case the intensity of the G-peak did not vary significantly with pitch content, but was decreased relative to the M650 coke sample and the cokes obtained from Refcoal treated with tetralin. It was expected that D-peak will decrease and the G-peak will sharpen when carbonising at 1000°C. However, this was not observed with 10MP1000 coke. Relative intensity ratios (I_D/I_G) of the all the samples are calculated and tabulated in Table 3.3 These values are very high for Refcoal coke without and with 10 % tetralin prepared at 1000°C. However, there is a significant improvement when Mittal pitch is added at 10%. Beyond this level, not much further change occurs.

Summary

- Incorporating tetralin leads to cokes with a disordered structure.
- Co-carbonisation of Refcoal with pitch increases the D-peak and even more the G-peak.
- The relative intensities of the Raman shifts (D/G) are larger for the tetralin treated Refcoal cokes than the cokes from Refcoals treated with pitch.
- The relative intensities of the Raman shifts (D/G) approaches zero as the pitch concentration in the carbonising system increases, whereas the values increase with increasing tetralin content.

3.3.2.4 X-ray diffraction photometry of Refcoal cokes

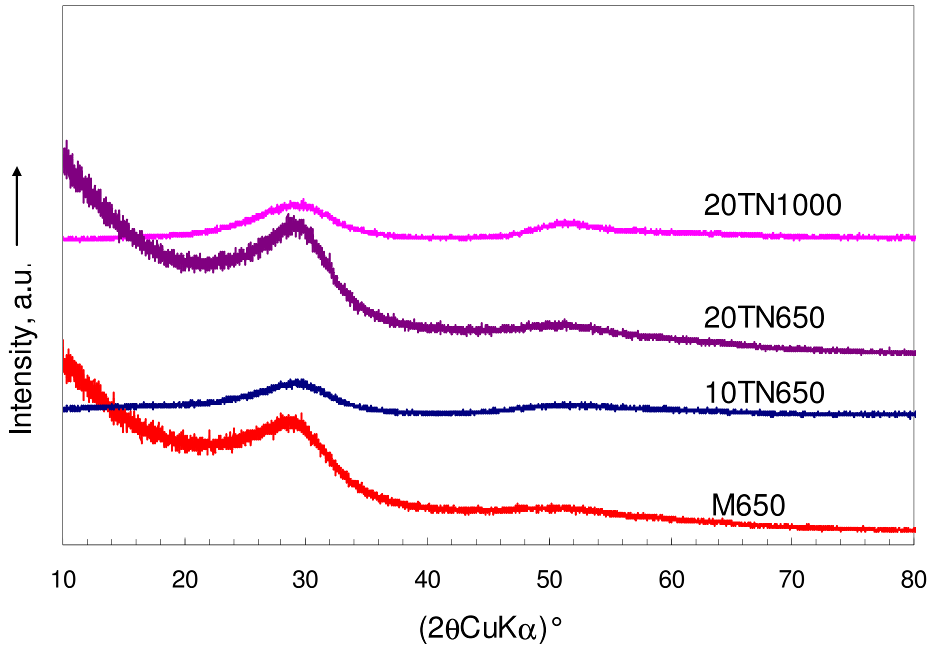


Figure 3.17 (a): XRD pattern of cokes showing the effect of tetralin on Refcoal carbonisation (Key: M650: HTRef carbonised at 650°C, 10TN650: coke from HTRef mixed with 10% tetralin after carbonised to 650°C, 20TN650: coke from HTRef mixed with 20% tetralin after carbonised to 650°C and 20TN1000: coke from HTRef mixed with 20% pitch after carbonised to 1000°C)

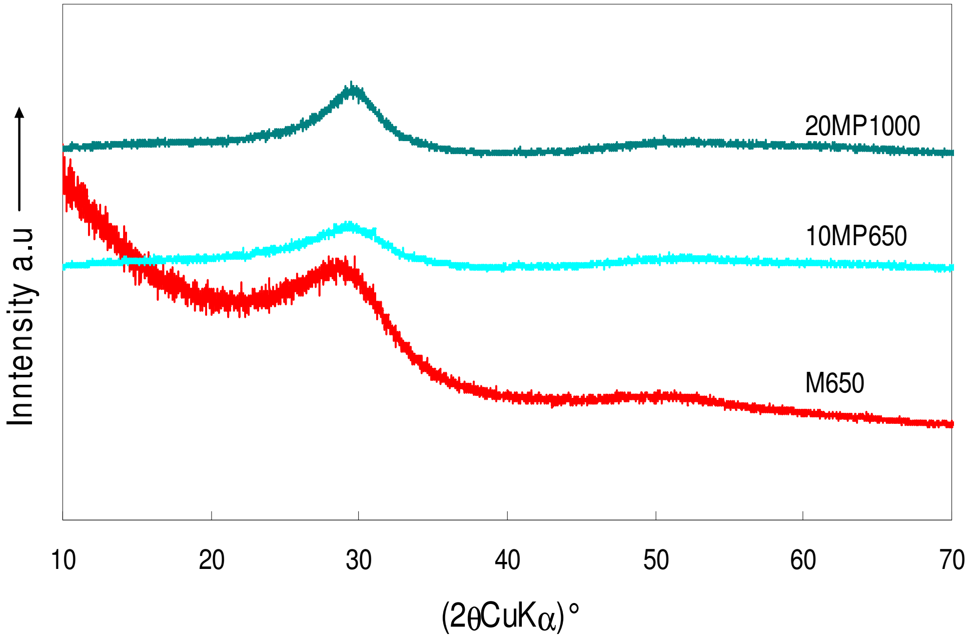


Figure 3.17 (b): XRD pattern of showing the effect of pitch on Refcoal carbonisation (Key: M650: HTRef carbonised at 650°C, 10MP650: coke from HTRef mixed with 10% pitch after carbonised to 650°C and 20MP1000: coke from HTRef mixed with 20% pitch after carbonised to 1000°C)

Figure 3.17 (a) and (b) show the XRD patterns of the cokes prepared from the carbonisation of tetralin and Mittal pitch modified Refcoals respectively. Co-carbonisation of Refcoal with 20% tetralin slightly intensifies the d_{002} peak after carbonisation at 650°C. However in the Refcoals modified with pitch (Figure 3.7(a)), the d_{002} peak was more intense than that of the 20TN1000 coke. This shows that the pitch brings along some structural ordering in the coke. The d_{004} is poorly developed in the Mittal pitch modified Refcoal cokes than in the tetralin modified Refcoal cokes.

Summary

- Treatment of Refcoals with the pitch induces better stacking of lamellae in the cokes.
- Tetralin contains molecules that inhibit mesophase liquid crystals from stacking parallel to each other as in graphite.

CHAPTER 4: CONCLUSION

Refcoal is a carbon precursor obtained by the "Refcoal process" (Morgan, 2000). This involves an alkali-mediated extraction of coal using an aprotic solvent, e.g. DMF. Precursors obtained by coal extraction below 95°C, carbonise to form anisotropic graphitizable cokes. Kgobane (2005) suggested increasing the extraction temperature to 135°C in order to improve extraction yield. However this study found that the resulting Refcoal product showed a reduced tendency to form anisotropic cokes. Ludere (2006) studied the effect of organic hydrogen donor additives, e.g. diabietic acid, on the coking properties of Refcoal. The main aim of this study was to investigate Refcoals obtained at 135°C. In particular the target was to improve its coking properties. To this end the effect of addition the organic additives tetralin and Mittal pitch were investigated.

The progress of the Refcoal extraction process was monitored by following the solid content in the solvent (DMF) with time. The resulting Refcoal was modified by adding tetralin and Mittal pitch. The effect of additive content and coking temperature on coke structure was determined. Note that the effect of coking time was not considered in this investigation.

It was found that diluted Refcoal solutions follow Beer's law at a wavelength of 600 nm. This makes it possible to measure the extract solids content indirectly using the absorption of a diluted solution using a mass-based absorption coefficient of 17.4 ± 1.9 g/(g.cm) at 25°C for extracts obtained at 135°C.

The extraction rate was determined at 95°C and 135°C using absorbance as a direct measure of the concentration of coal extracts. It was found that the equilibrium solids content was reached in similar extraction times of approximately 2 hours. However, solubility of coal in DMF increased with temperature: The measured solids contents at 95°C and 135°C were 8% and 15% respectively.

Surprisingly the solid Refcoals had higher volatile matter and moisture contents, and showed lower carbon yields than the parent coal. It is speculated that this is due to residual DMF trapped in the Refcoal structure. However, the ash content was lower, i.e. 1.6 % for the Refcoal compared to 9.4% for the coal used here.

Refcoal is composed primarily of stable aromatic compounds that start to decompose at ca. 350°C. The DMF extracts appear to contain enhanced levels of oxygen-containing functional groups. DRIFT data indicates the loss of these groups on carbonization; especially as the heat treatment temperature is increased. Carbonisation at 500°C and above shows an increase in the coke aromaticity. DRIFT indicates that above this temperature C-H bands of the aromatic rings are formed. Optical and SEM microscopy indicated the presence of particles that appear to inhibit mesophase development and little evidence for degassing upto this heat treatment temperature. The resulting coke microstructure is a mixture of ordered and disordered domains. The XRD and Raman results, for Refcoal carbonised at temperatures up to 1000°C, provided little evidence for the development of graphite-like ordering. However, some degree of improved ordering behaviour was observed at a coking temperature of 650°C. However, the improvement was minor and did not warrant further investigation.

Addition (up to 50% of the total) of the organic additives, tetralin and pitch, changed the carbonisation behaviour. Tetralin was found to inhibit the evolution of volatile matter whereas the pitch was found to facilitate such evolution. Tetralin is highly volatile and leaves virtually no residue in a TG scan. TG data for blends clearly indicated that tetralin reacts with Refcoal because mass loss is delayed and the carbon yield is increased. Hydrogen donor additives stabilize aromatic radicals formed during pyrolysis. This ultimately facilitates reorganization and reassembly of aromatic components in planar configurations, i.e. graphene layers. Tetralin was previously used as a hydrogen donor solvent. Owing to this precedent it was hypothesized that it might also be a suitable hydrogen donor additive. Instead, tetralin addition increased disorder in the Refcoal cokes! The reason for this behaviour is not presently understood. However, the addition as little as 10% tetralin gives cokes with anisotropic domains after carbonisation.

In contrast, addition of Mittal pitch decreased the amount of fixed carbon. The decrease was roughly proportional to the pitch content of the blend. Co-carbonizing Refcoal and pitch also showed a reduction in oxygen-containing functional groups and a decrease in the aliphatic nature of the cokes. Raman and XRD data support the hypothesis that aromatic ring condensation occurs during coking. The resulting cokes showed reduced anisotropy compared to neat Refcoal and Refcoal co-carbonised with tetralin.

The main findings on the investigation about the effects of the tetralin and pitch on the Refcoal cokes are:

- Refcoal which was co-carbonized with Mittal pitch pass through mesophase fluid stage. The smooth appearance of Refcoal coke obtained from Refcoals mixed with Mittal pitch is an indication that these cokes passed through the fluid mesophase stage.
- However, despite significant gas evolution, the cokes do not show the preferred orientations and growth of the mesophase domains. This means that the change in the carbonisation profile of Refcoal does not guarantee the formation of anisotropic cokes. The carbonisation profile is changed but its effects on the optical texture of the resulting cokes are less pronounced.
- The addition of 20 % additive (tetralin or pitch) produced cokes with optical textures exhibiting medium circular mosaic and fine lencticular anisotropy.
- Cokes obtained from the co-carbonisation of Refcoal with tetralin contains small agglomerated particles. The concentration of agglomerates increased with tetralin content. These agglomerates appear to be small mesophase spheres that are not joined (Rodriguez-Valero *et al.*, 2002), i.e. were prevented from coalescencing.
- Improved ordering and planar arrangement of molecules is obtained with pitch modified Refcoals cokes. This is confirmed by a better stacking of lamellae in the cokes as indicated by the low ratio of D/G peaks in the Raman spectroscopy and also the d_{002} in XRD being closer to that of graphite. Angell and Lewis (1978) obtained d/g ratios of 0.65 to 0.67 from the carbonisation of petroleum pitch and coal tar pitch. This is comparable to the values obtained in this study for the Refcoals treated with the Mittal coal tar pitch.

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APPENDIX

Table A.1: Progress of coal extraction with DMF

	Low-temperature Extraction			High-temperature Extraction		
Extraction time	Absorbances	Mass extracts	Solids weight fractions	Absorbances	Mass extracts	Solids weight fractions
Minutes		g	g/g		G	g/g
0	0	0	0	0	0	0
15	0.481	0.0913	0.2282	0.640449	0.1487	0.37175
30	0.717	0.1452	0.0363	1.1231872	0.249	0.06225
45	0.686	0.1805	0.04512	-	-	-
60	0.742	0.1951	0.048775	1.956481	0.4605	0.11515
75	0.76	0.2098	0.05245	-	-	-
90	0.849	0.2145	0.05362	-	-	-
120	0.871	0.2148	0.0537	2.366574	0.5521	0.1380
150	0.895	0.2237	0.05592	-	-	-
180	0.934	0.2438	0.06095	2.5	0.5679	0.14197
240	1.027	0.2519	0.062975	2.496226	0.576	0.144
300	1.08	0.2655	0.066375			
360	1.12	0.2737	0.068425			

Table A.2: Proximate analysis of neat and treated Refcoals

Sample	Parameters (Content %)			
	Moisture	Volatile matter (d.b)	Fixed carbon (d.b)	Ash (d.b)
HTRefcoal	2.1	30.5	66.6	1.6
10TNRef	0.7	24.3	73.5	1.7
20TNRef	0.6	24.3	74.0	1.1
50TNRef	0.6	24.6	73.7	1.2
10MPRef	2.1	29.9	67.7	1.8
20MPRef	2.1	32.6	65.3	1.3
50MPRef	1.2	42.4	56.3	0.8

Table A.3: Major infrared absorption bands of coal (Tsai, 1982 and Cagniag *et al.,* 1994)

Vibration	Frequency / cm^{-1}
O-H and NH alcohol and phenol	3500-3650
C-H aliphatic, aromatic	2850, 3050
$-CH_2-$, $-CH_3$ (bend)	1465, 1375
C=O stretching	1650–1780
Aromatic C=C vibration (oxygen enhanced)	1475, 1680
Condensed aromatic C=C	1575
Aliphatic CH_2	1460
$-CH_3$ (bend)	1370
C-O and C-O-C , ether	1250
C-O, in phenolics, quinines, etc,	1175
Aromatic out of plane C-H	760

Table A.4: Nomenclature used to describe optical textures in the polished surface of cokes (Gray, 1986)

Optical texture	Parent coal vitrinite class (V-class)	Domain size	Interference colours
Isotropic	6,7	0.0	Purple
Incipient anisotropy	8	0.5	Purplish hue
Circular anisotropic			
Fine	9	0.5–1.0	Pinkish purple
Medium	10	1.0–1.5	Pinkish purple, blue and yellow
Coarse	11	1.5–2.0	Blue and yellow
Lenticular anisotropy			
Fine	12	1.0–3.0	Pinkish purple
Medium	13	3.0–8.0	Pinkish purple, blue and yellow
Coarse	14	8.0–12.0	Blue and yellow
Ribbon anisotropy			
Fine	15	2.0–12.0	Pinkish purple
Medium	16	12.0-25.0	Pinkish purple, blue and yellow
Coarse	17, 18	25.0+	Blue and yellow

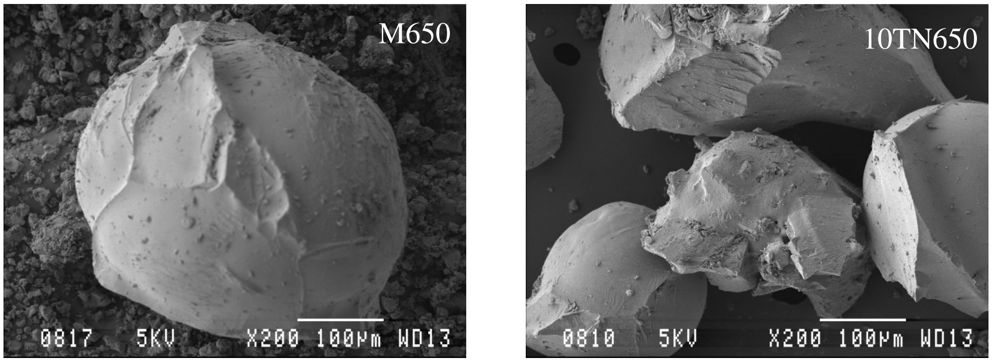

Figure A.1: SEM photomicrographs of mesophase spheres

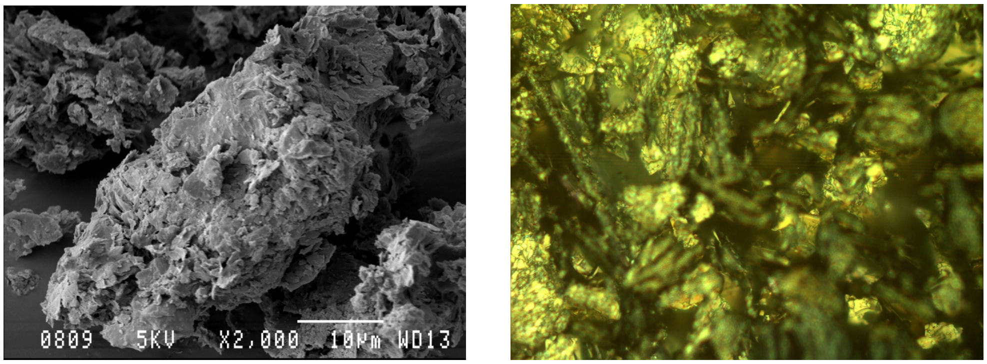

Figure A.2: SEM and optical photomicrographs of synthetic graphite