

CHAPTER 1

INTRODUCTION

Eskom South Africa, in collaboration with other international energy corporations, has ventured into the Pebble Bed Modular Reactor (PBMR) project to boost its electricity supply. The PBMR is a type of High-Temperature Gas Reactor (HTGR), which means that its core is gas-cooled [1, 2]. Helium gas removes the heat generated by the nuclear fission from the reactor core, in contrast to other conventional water-cooled energy reactors. The technology was extensively tested in Germany in the 1960s and 1970s and elsewhere. With the ever-increasing demand for electricity in the developing world, it is hoped that the PBMR will be the ultimate effective solution to overcoming some of the electricity supply problems currently experienced in areas far remote from the coalfields where the demand for electricity is huge. Eskom believes that it would create a market, both within South Africa and in the rest of the world, for 30 reactors per year within the next two decades. Such a project venture in nuclear energy would be a powerful strategy in the realisation of clean energy for the African Renaissance, and for the New Partnership for African Development (NePAD) as a whole [3].

The PBMR consists of a structure made of synthetic graphite blocks (the reflectors), contained within a steel pressurised vessel. Depending on their position within the structure, the blocks are of differing qualities, with the inner ones able to withstand the high temperatures (up to 950 °C) and high neutron fluxes experienced during operation. The outer blocks are loaded with boron carbide, which acts as a neutron shield, to prevent activation of the steel shell.

The fuel consists of spheres of graphite (the pebbles), 60 mm in diameter, which contains many uranium dioxide beads, evenly distributed throughout (Fig. 1.1). The uranium dioxide spheres are coated to contain the fission products. The

coatings, applied by means of chemical vapour deposition, consist of, firstly, two layers of carbon with differing porosities, then the main barrier layer of silicon carbide, then a third carbon layer.

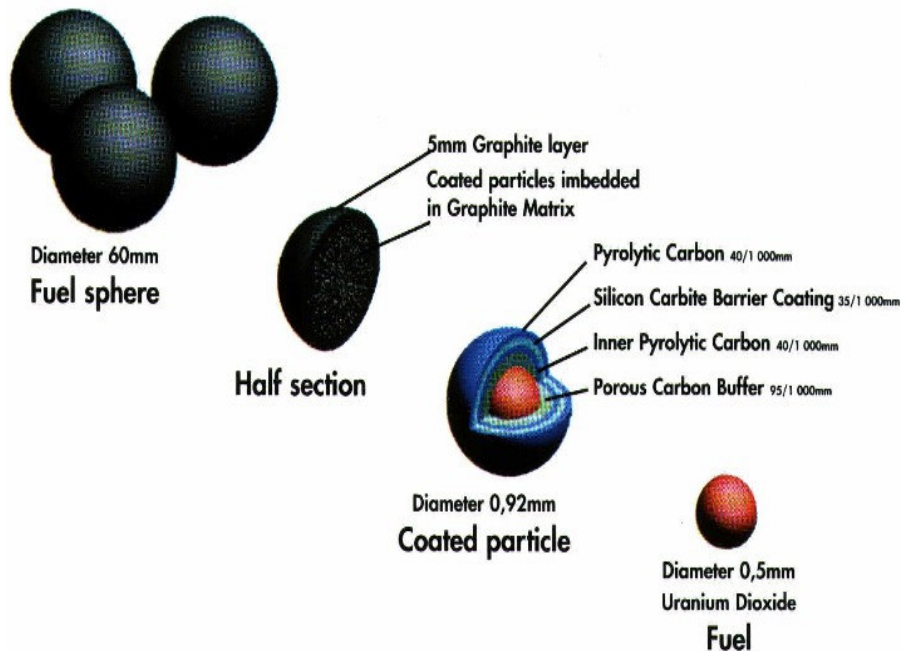


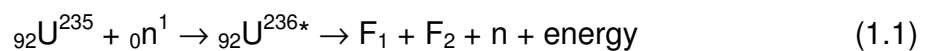
Figure 1.1: Fuel element design for PBMR [3]

The coated beads are mixed with a fine powder consisting of 75 % natural graphite and 25 % synthetic graphite, as well as a binder resin, and are then moulded into the spherical shape. After being hardened at about 1900 °C, the pebbles are ready for use. The uranium used in the start-up fuel is 4 % enriched and the equilibrium fuel has a uranium enrichment of 8 % [3].

During normal operation, 440 000 pebbles, of which 310 000 contain uranium oxide and 130 000 are pure graphite spheres that serve as additional nuclear moderators, are loaded into the top of the reactor and discharged at the bottom where their degree of “burn-up” is measured. The pebbles are then either returned to the reactor or, if fully used, retained within the reactor building to allow most of the decay of the short-lived fission products to take place. To

remove the heat generated by the nuclear reaction, helium gas at 450 °C is passed through the pressure vessel from the top. It passes between the fuel pebbles and then leaves the bottom of the reactor vessel at about 900 °C. The hot gas then passes through a conventional gas system to drive electric generators, giving a useful capacity of about 165 MWe. The helium used as a coolant for the PBMR is corrosion-resistant and has good heating properties (having a specific heat that is much greater than CO₂), it does not condense and can therefore operate at any temperature, it has a negligible neutron-adsorption cross-section and can be used in a direct cycle, driving a gas turbine with high efficiency [2]. The modular nature of the system would allow ten such reactor/generators to be built on a site, sharing services and a single control room.

The reactor is described as being inherently safe because the silicon carbide layer around the uranium oxide beads is able to contain essentially all the fission products up to a temperature of 2 000 °C [1, 2]. If the coolant helium stopped flowing, the reactor would warm up to about 1 350 °C, at which point the negative coefficient of criticality would bring the nuclear chain reaction to a close. The fission products (equation 1.1) resulting from radioactive decay would continue to heat the fuel until, at a temperature of approximately 1600 °C, the heat losses through the reactor shell would balance the heat production, and the core would begin to cool.



It is therefore impossible for the reactivity of the fission products to be lost. In addition, the thermal mass of the reactor core is such that temperature changes occur slowly, over several days, allowing problems to be solved under conditions that would not engender panic.

The graphite used for the construction of the reactor core contributes to the safety of the design due to its very high sublimation point, in an inert atmosphere,

of more than 3 000°C and its slow rate of oxidation, even at the operating temperature, in air. The graphite is required to be of high purity and physical or structural integrity. Graphite is chosen as a moderator in nuclear fission reactors because it is the most readily available material with a low thermal neutron-capture cross-section, allowing efficient use of the neutrons generated [4, 5]. The thermal neutron-capture cross-section is usually expressed in terms of an equivalent boron concentration by summing the concentrations of the individual impurities (elements, weighted by their thermal neutron-capture cross-section).

The physical structure of the graphite is of crucial importance for efficient operation and a long life. The graphite blocks must be highly isotropic to give the best dimensional stability under irradiation and to obtain uniform thermal expansion in all directions [6 - 8]. The synthetic graphite used to manufacture the fuel pebbles must be very fine, but graphite, again due to its anisotropic structure, is very difficult to mill, tending merely to flake along the planes of crystal weakness. Essentially, all of the graphites employed in fission reactors as moderators and most, but not all, of the graphites used in fusion systems are derived from blocks manufactured from petroleum or pitch cokes. Cokes employed to manufacture conventional nuclear graphites are classified as needle cokes from petroleum, pitch cokes, or Gilsonite pitch cokes from the asphalt of Santa Maria cokes. Both needle cokes and pitch cokes yield anisotropic graphite blocks, while Gilsonite pitch cokes and Santa Maria cokes yield isotropic blocks [8].

Coke made by pyrolysis of the coal extracts does not always graphitise on heating to 3 000 °C as a pre-ordering of the atoms is necessary. The coke is formed when the precursor, on heating, liquefies and forms domains of discoidal liquid crystal prior to cross-linking, with the loss of volatile material. Anisotropic needle cokes are prepared when the domains of liquid crystal grow and coalesce into a semi-coke on heat treatment. These are highly graphitisable, but difficult to convert into isotropic blocks. Cokes in which the liquid-crystal domains do not coalesce may be graphitisable, but the random orientation of the domains does

not allow isotropic blocks to be formed. Precursors that form these liquid crystals are generally materials with high aromatic carbon content.

At graphitisation temperature carbon loses most of its impurities, except for carbide elements, boron in particular, which tend to come off too slowly at high temperatures. Sulphur, if present in high proportion, comes off whilst adversely disrupting the structure, causing “puffing”. The lower the original load of impurities, the purer the final product.

1.2 Aim of the study

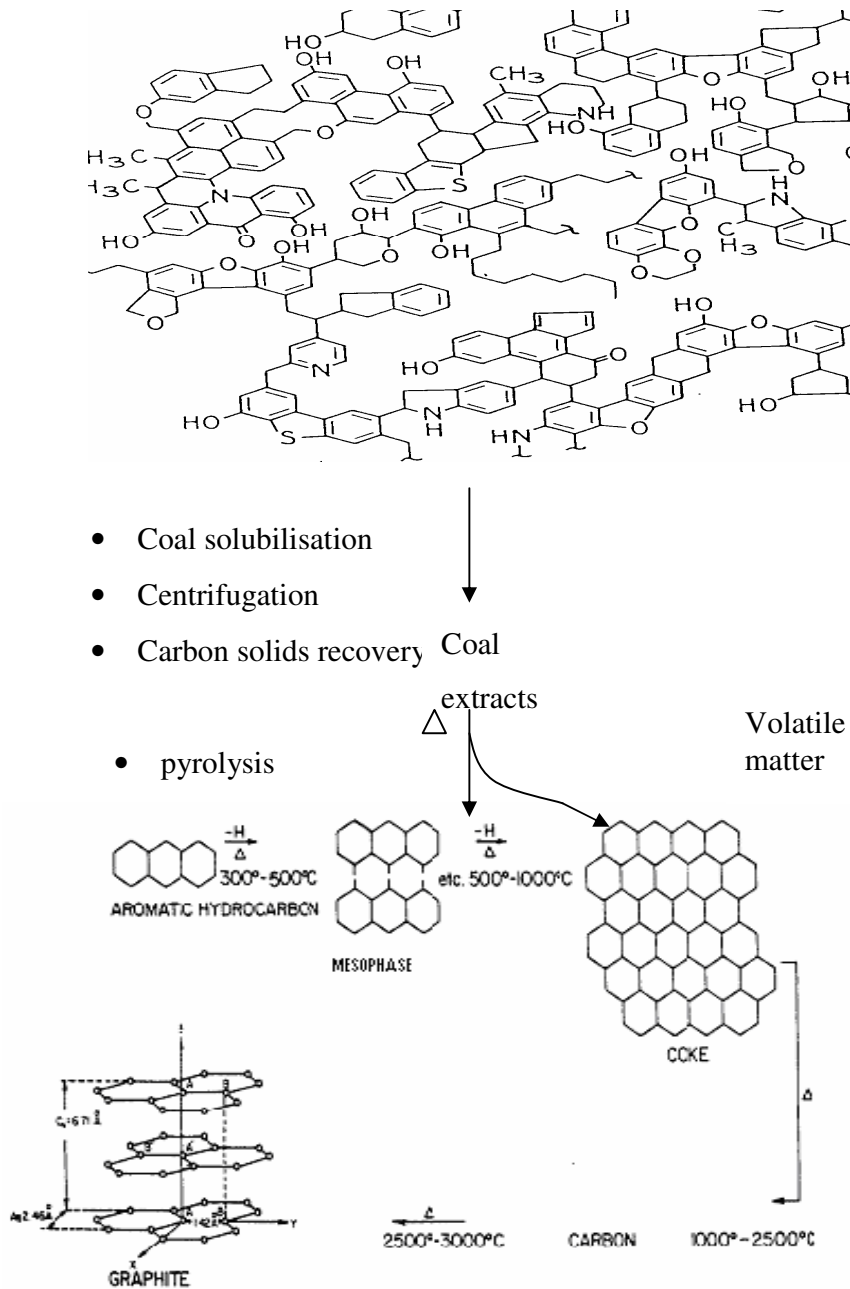
Coal is a relatively abundant mineral solid fuel worldwide and potentially adaptable for use in existing plants that have been engineered for petroleum use. When purified, coal can serve as an inexpensive substitute for, or successor to, the more expensive oil fuels in use today. The molecules present in coal have the required structures to substitute petroleum and yield cokes that graphitise well. It was therefore the aim of this study to:

- Examine the cokes prepared from coal purified by Refcoal process
- Evaluate the graphitised cokes (see Scheme 1.1).

1.3 Contents of the study

The dissertation consists of nine chapters. Chapter 1 has already given the background to the purpose of this study. Chapter 2 discusses the relevant literature on coal and its purification. Chapter 3 looks at the chemistry of the carbonisation of the coal. Chapter 4 examines the graphitisation process. Chapter 5 discusses the methods of graphite characterisation. Chapter 6 investigates the instrumentation that can be used for analysing graphitisable carbons. Chapter 7 details the experimental methods. Chapter 8 discusses the experimental results and the last two Chapters (9 and 10) the conclusions and the references respectively.

Scheme 1.1: Project outline of coal purification process, through coke formation to graphitisable carbon [9,10]



CHAPTER 2

COAL

The quality of coke and the graphite subsequently produced is determined primarily by the purity of the starting material and its biochemical formation. This chapter seeks to explain some of the previous areas studied that have a great impact on the science of coal and its purification. Previous work on coal solubilisation is discussed. The biochemical formation and the hypothesised structure of coal detailed are important to understanding the choice of the solvent-reagent suit needed to improve the purity of coal. The effects of solvents and additives on coal solubilisation are also discussed.

2.1 Coalification process

Coal is defined as a readily combustible rock containing more than 50 % by weight and more than 70 % by volume of carbonaceous material [11]. This carbonaceous material resulted from the accumulation and slow decay of plant remains under water. It involves a continuous series of alterations through the coalification process from living material > lignite > subbituminous coal > anthracite. Such succession in properties through the coalification process is called 'metamorphism', which occurred over a long period of time. The changes in the plant materials are reported to involve a *biochemical* process of diagenesis and a *geochemical* process of metamorphism [12].

The degree of coalification or 'rank' of coal increases progressively from lignite, through low-rank coal to high-rank coal, and to anthracite. This transformation of the vegetable matter into peat and then into coal of different ranks is apparently the result of decomposition due initially to bacterial action and dehydration, then to devolatilisation and densification due to chemical and geodynamic processes [11].

2.1.1 Biochemical coalification

Biochemical coalification is associated with changes within the plant residues in the sedimentary basin at low temperature and pressure to form macerals. It is described by processes defined by the availability of oxygen, viz. disintegration, mouldering, peatification and putrefaction. *Disintegration* of plant material into water and carbon dioxide occurs under normal conditions of freely available oxygen. If conditions change, some resisting plant remains are conserved into liptobiolites consisting largely of relatively stable exinite macerals [13, 14]. *Mouldering* is the process during which coal is produced in an environment of diminished oxygen supply. Bacterial and fungal activities cause the material to become enriched in carbon and oxygen, but poorer in hydrogen. The abundance of sclerotinite in South African coals suggests that mould was of importance in their formation. *Peatification* takes place by way of bacterial decomposition and weakly oxidising conditions, resulting in the formation of humic acid. In the acidic reducing environment, vitrinite and accompanying pyrite are formed, while inertinite macerals are derived from the exposure of plant remains to a lower level of acidity and stronger oxidising conditions [13, 14, 15]. Swamp fires have resulted in the formation of certain varieties of fusinite and semi-fusinite macerals, and these represent fossil charcoal. *Putrefaction* (fermentation) occurs under reducing conditions. A relatively deep water cover is also a necessary condition for this process in which anaerobic bacteria remove the oxygen of the vegetable matter, converting it into hydrogen-rich material [13, 14].

2.2.2 Geochemical coalification

Geochemical coalification precedes biochemical coalification in the absence of microorganisms. The progressive development of peat occurs with increasing build-up of deposition and coverage by incoming sediments. The plant undergoes changes known as carbonification or geochemical coalification, resulting in a coal rank increase [13]. Accompanying such rank increase is a

decrease in porosity due to an increasing overburden pressure with depth. According to Stach *et al.* (14), the porosity of coal falls very rapidly in the early stages of coalification and serves as a good diagnostic indicator for peat and brown coals. Physico-structural and chemical changes take place as coalification progresses. The carbon content is reported to increase, and the oxygen and hydrogen contents decrease with the series. The reactivity of each series decreases from lignite to anthracite. While the moisture content decreases, the porosity falls. This is thought to serve as a diagenetic indicator for compressible peats and brown coal.

The difference in plant materials, the extent of their decomposition, and the subsequent action of pressure and heat during geochemical coalification determine the rank of the coal. The degree of coalification is estimated from optical properties such as the reflectivity of vitrinite, which is dependent on the chemical composition of the coal. Stach *et al.* (14) reported that Francis estimated that a period of eight million years is required for the production of bituminous coal from peat.

Physical change occurs as coalification progresses through bituminous coal to anthracite (Fig. 2.1). The top row of hexagons represents the aromatic nuclei, which slowly coalesce into larger clusters, while the lines, or aliphatic cross-links, are slowly removed during increasing coalification. The second row depicts the increasing orientation of elementary aromatic elements parallel to the bedding planes. Static pressure thus causes such physical changes as a decrease in porosity and the reorientation of the elementary aromatics, known as micelles [14]

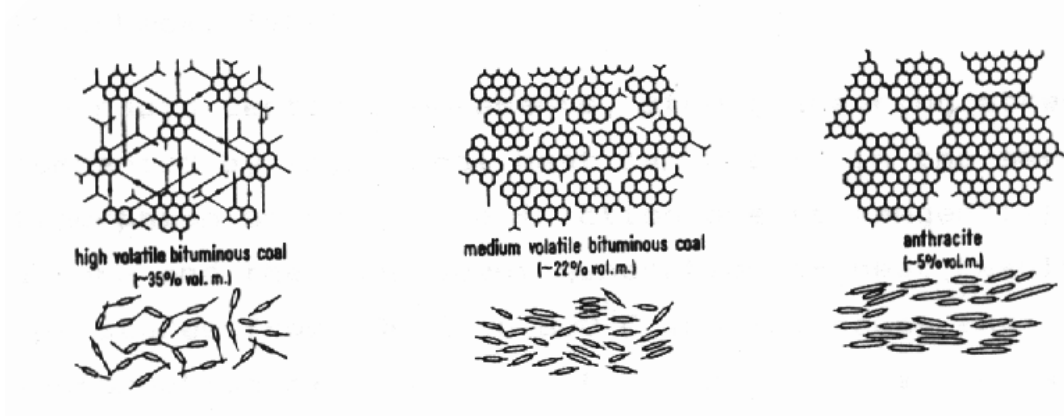


Figure 2.1: Physical changes in coalification from bituminous coal to anthracite [14]

Other physical changes are a decrease in the moisture content and an increase in the specific gravity as a result of increasing compaction with depth. Research has shown that tectonic pressure might not be the cause of the increased rank associated with regions of folds [16]. Instead, sediments and coal were buried to great depths in the foredeeps associated with ore-genesis before the onset of foldings. Consequently, the rocks were subjected to greater heating, resulting in an increase in rank. However, rapid tectonic movements occurring along the faults and over thrusts during earthquakes are reported to have occasionally caused a local rise in rank due to the concentration of frictional heat [16].

Such movements and frictional forces may result in the severe metamorphism of coal. The friction due to tangential pressure and the resultant heat generation were accompanied by a temperature rise from 300 °C to 800 °C, which may have caused the transformation of anthracite to graphite [14]. Chemical changes indicate the degree of increasing coalification in the transformation from wood to peat, lignite and bituminous coal, and to anthracite (see Table 2.1). An increase in carbon with an accompanying decrease in the hydrogen, oxygen and nitrogen contents are a reflection of metamorphism or rank increases.

Table 2.1
Coalification through time, pressure and heat
(dry ash-free values) [11]

	C	H	O	N
	%			
Wood	50.0	6.0	43.10	-
Peat	58.9	5.1	33.10	2.6
Lignite	71.0	4.4	23.10	1.2
Bituminous	81.4	5.4	10.10	1.9
Anthracite	92.9	3.1	2.40	0.9

The transformation of the vegetable matter into peat and then into coal of different ranks is reported to be the result of decomposition due to bacterial action, then dehydration, devolatilisation and densification due to chemical and geodynamic processes [11]. Factors such as heat, pressure and long periods of time determined the transformation from peat to lignite to subbituminous coal to bituminous coal, and then to anthracite. It is the porosity and moisture content of coal that decrease with pressure. In a progressive transformation of peat to anthracite, an increase in the amount of fixed carbon and a decrease in the amount of moisture, oxygen and volatile matter have been documented.

The different coalification behaviours of the individual macerals as based on the H/C and O/C ratios (Fig. 2.2) has been reported [14]. The carbon content increases rapidly with depth as the oxygen-rich substances, such as cellulose and hemi-cellulose, are decomposed microbiologically. The increase in carbon content is estimated by Stach *et al.* [14] to reach a maximum of 64 % with the fall in moisture content. Such changes in the coalification process are thought to be the result of increased compression.

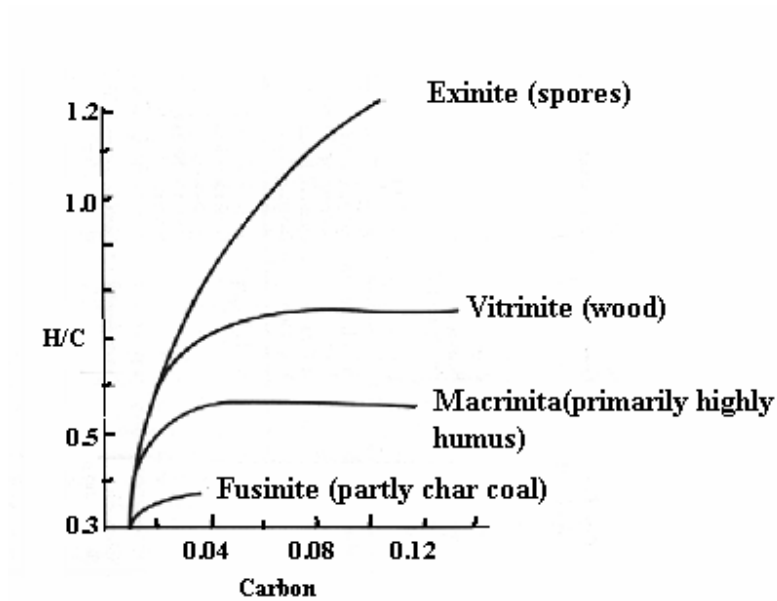


Figure 2.2: Coalification of different macerals based on H/C and O/C atomic ratio [14, 17]

2.2 Hypothetical structure of coal

Coal is thought to be a three-dimensional structure, crossed-linked, viscoelastic glassy macromolecular solid that is permeated by material of low molecular weight and the behaviour of which is similar to that of cross-linked polymeric networks [9, 11, 18, 19]. This theory attempts to describe properties such as the degree of cross-linking and the glass transition temperatures of the network nature of coal. Part of the evidence for this theory is that coal behaves as an elastic, not plastic, solid. This suggests that the cross-linkages are covalently fixed. Given *et al.* in the book edited by Marsh [20] reported a macromolecular/molecular two-phase system – the host/guest or rigid and mobile phase model. This model suggests that a substantial proportion of the organic part of coal – the mobile phase or “guest” – is composed of a phase of low molecular weight, physically trapped within an immobile phase or “ghost” of high molecular weight. The latter is extensively cross-linked.

The inorganic constituents, consisting partly of minerals such as kaolin ($\text{Al}_2\text{Si}_2\text{O}_5\cdot(\text{OH})_4$) and free silica entangled in a macromolecular structure of condensed aromatic rings, are hypothesised to form large units of 'bridges' or cross-linkages of aliphatic and/or ether groups, conferring on them a certain structural order [21, 22]. The removal of the cross-link bonds, viz. the bridges of hydrogen bonding (hydrogen bonding is reported to be a major force holding the minerals at the maceral boundaries) in the C-C and C-O bonds, provides some flexibility in a cross-linked structure. The result is differential swelling of the coal macerals as well as stresses that contribute to chemical comminution. The solvent-reagent mixture facilitates the reorganisation of aromatic units into a graphite-like structure during pyrolysis of the coal extracts [23, 24].

The mineral matter in coal has a detrimental effect on its utilisation for combustion, gasification, carbonisation, liquefaction, etc. purposes. The combustion of high-sulphur and high-ash coal leads to adverse environmental and other deleterious effects. Acid rain resulting from the emission of sulphur dioxide (SO_2) has a harmful effect on agriculture and destroys the ecological balance. The demineralisation of coal prior to its combustion and carbonisation is therefore important for environmental protection. The microscopically recognisable organic and inorganic constituents from the sedimentary rock are discrete fossilised plant fragments called 'macerals' [24].

Most of these minerals are in form of aluminosilicates, carbonates, sulphides and silica. The abundant oxygen in the macerals follows carbon and hydrogen and is found combined with other elements in coal to form various functional groups, such as carboxyl (CO_2H), carbonyl ($\text{C}=\text{O}$), and the methoxy ($-\text{OCH}_3$) and phenol (OH) groups (Fig. 2.3) [25, 26]. The mineral matter includes all inorganic non-carbonaceous material found in coal. This excludes carbon, nitrogen, sulphur and oxygen, and is estimated by an equation (equation 2.1) [11].

$$\begin{aligned} \% \text{ Mineral matter} = & \% \text{ ash} + \% \text{ pyritic S in coal} + 0.8 \text{ CO}_2 \text{ in coal} \\ & - 1.1 \times \text{SO}_3 \text{ in coal} + 0.5 \times \% \text{ Cl in coal} \end{aligned} \quad (2.1)$$

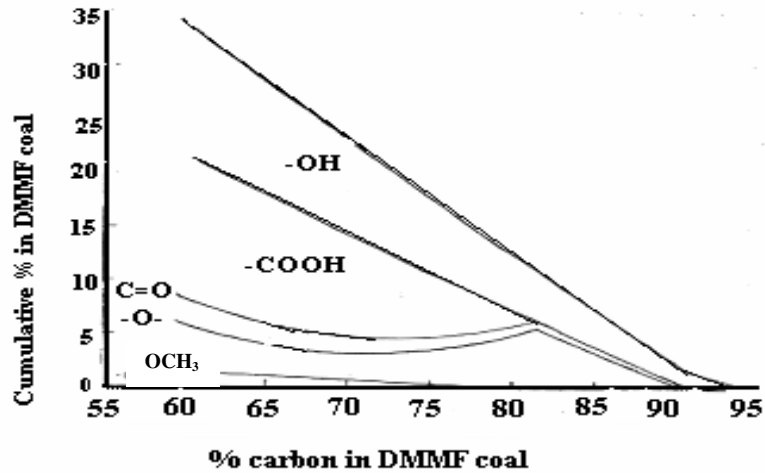


Figure 2.3: Distribution of oxygen functionality in coals [15]

The decreasing oxygen content of wood, peat, and lignite with increasing rank of coal, and expressed on a dry, mineral-matter-free basis, is shown in Table 2.2. Wood appears to be oxygen-rich, while anthracite is oxygen-poor but carbon-rich. The higher the oxygen content, the lower the carbon content.

Table 2.2

Chemical composition of wood, peat and various coals [27]

Carbonaceous materials	C	H	O N	
			%	
Wood	50	6.3	42.7	1.0
Peat	57	5.2	36.8	1.0
Lignite	65	4.0	30.0	1.0
Low-rank coal	79	5.5	14.0	1.5
Medium-rank coal	88	5.3	5.0	1.7
Anthracite	94	2.9	1.9	1.2

The surface area of coal is related to the plasticity of the coal and its agglomerating properties during heating. The release of volatile matter from the surface during heating becomes an important factor in the quality of coke.

2.3 Coal macerals

Macerals are petrographically distinct units of vitrinite, exinite and inertinite seen in thin and polished sections of coal and are analogous to minerals in ordinary rocks [12]. However, the physical and chemical properties change during geochemical coalification so that they cannot be considered as being identical with minerals [13]. Stach *et al.* [14] stated that Stopes first used the term 'maceral' for a constituent of coal isolated by maceration, from the Latin *macerare* meaning 'to soften'. The contrast between the macerals appeared when polished sections of a resin-mounted coal sample were observed under a microscope using an oil-immersion lens [13]. Though distinguishable under the microscope, their properties are different. However, the differences become smaller as the rank increases (Fig. 2.4).

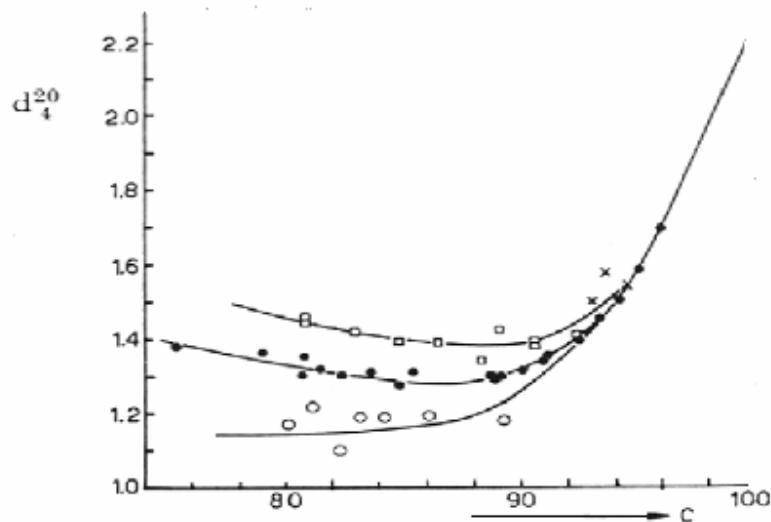


Figure 2.4: Densities of coal macerals

• Vitrites, ○ Exinites, □ Micrites, × Fusinites [16]

Vitrinite is a relatively hydrogen-rich maceral; it is composed of the humic material associated with peat formation and is formed from the coalification of lignin structures [12, 14]. It is a major petrographic constituent of coal in Britain, opaque and with a reflectance of 2.5 % – 6.0 % [27]. Vitrinite is a relatively reactive maceral and its softening point increases with the degree of oxidation, with a concomitant decrease in reactivity [28].

Exinite is also hydrogen-rich and originates from spores, cuticular matter, algae, resins and waxes. Carbonisation of this maceral is reported to give predominantly tar and gases. Unlike vitrinite and exinite, inertinite is found to be poor in hydrogen but rich in oxygen. During carbonisation, inertinite is thought to remain inactive, whereas vitrinite melts to varying degrees, while exinite produces tar on heat decomposition [14].

Macerals rarely occur by themselves but are usually associated with macerals of the same group or with other groups. These associations are known as microlithotypes [14]. The American Geological Institute (A.G.I.) [12] defined them as a typical association of macerals in humic coals, occurring in bands at least 50 microns wide. Macerals and microlithotypes comprise the four visible banded constituents in humic coals, called lithotypes. The lithotypes are classified according to their different physical and chemical properties and are named vitrain, clarain, durain and fusain. Vitrain is the bright, black lithotype, which breaks into roughly cubical forms and has a conchoidal fracture. In humic acid coals, vitrain is common and consists of the microlithotype group's vitrite and clarite.

Vitrite comprises vitrinite, while clarite is composed of vitrinite and exinite. The vitrinite content in each of the microlithotypes is in excess of 95 % [14]. Clarite is characterised as being semi-bright with a silky lustre and a sheetlike, irregular fracture. It contains fine bands of durain, which distinguishes it from vitrain [12].

The fine bands are less than 3 – 10 mm in thickness and can be composed of the microlithotype groups' vitrain, clarite, durite, trimacerite, as well as the microlithotype fusinite.

Durite contains at least 95 % of both exinite and inertinite, whereas fusite consists of more than 95 % fusinite. Trimacerite comprises the three maceral groups, as the name implies, namely vitrinite, exinite and inertinite, in varying proportions but always in excess of 5 % [14]. Durain forms the dull, matte lustre bands, grey to brownish-black in colour with granular fracture [12]. The bands are greater than 3 – 10 mm in thickness and usually consist of durite and trimacerite, and sometimes clarite, which is rich in exinite. Fusain has a silky lustre and a fibrous structure. It is friable and black, occurring in strands or fibres, and is soft when mineralised [12]. It is composed of microlithotype fusinite. The environment in which fusain is formed was very dry and owing to the strong resemblance between fusain and charcoal, it is also believed by van Krevelen (1951), as reported by Stach *et al.* [14], that fires could have resulted in the formation of this lithotype.

South African coals are predominantly of low rank, are inertinite-rich and possess a high mineral content [15]. Investigations into the maceral group content of the seams mined in South Africa has shown that the average distribution is as follows: vitrinite 49 %, exinite 4.4 %, inertinite 41.4 % , minerals 5.2 % and remaining is moisture [29]. The mineral distribution content of vitrinite and exinite are low compared with that of inertinite, which shows the opposite trend. In contrast, European coal shows the following maceral distribution: vitrinite 49 %, exinite 4.4 %, inertinite 14 % and minerals 3 % [15].

2.4 Reflectance of macerals

The reflectance of macerals or other particles in coal is described as the proportion of directly incident light (expressed as a percentage) that is reflected

from a plane of a polished surface under specific conditions of illumination. This property is related to the aromaticity of the organic compounds in the coal and it increases progressively for all the macerals as the rank of coal increases. Its measurement is taken by dry objectives or by the water or oil-immersion technique using oil with a refractive index of 1.518 at 23 °C and an incident light wavelength of 546 nm. The reflectance so obtained is calculated from equation (2.2) [30].

$$R = \frac{R_s \cdot A}{A_s} \quad (2.2)$$

where

R = reflectance of coal maceral

R_s = reflectance of a calibration standard

A_s = deflection of galvanometer.

The reflectance, R, is related to the optical properties of other material and the immersion medium by the following Beer's equation (2.3)

$$R = \frac{(n - n_1)^2 + n^2 k^2}{(n + n_1)^2 + n^2 k^2} \quad (2.3)$$

Where

n = refractive index of reflecting material

k = absorption index of reflecting material

n₁ = refractive index of medium in which the measurements are made

2.5 Volatile matter

According to ISO (International Organization for Standardisation) Standard 562, volatile matter is described as the loss of mass when coal is heated to 900 °C in the absence of air with gaseous combustion products allowed to escape. The correct estimation is essential in correlating many other properties of coal, viz. rank, calorific value, total carbon and hydrogen, coke yield and petrographic composition [11].

With increasing rank, the oxygen-dominated cross-linkages are thought to be replaced by a weaker hydrogen bonding. Heating of such coal breaks the hydrogen bonds to show a high degree of plasticity. With a further increase in rank, the hydrogen bonding is lost to produce a non-fusible, high-carbon-content and aromatic structure typical of anthracite. A variation in the fluidity of coals is correlated to the volatile matter released and to the strength of the hydrogen bonding in the reactive components of the coal (Fig. 2.5) [20].

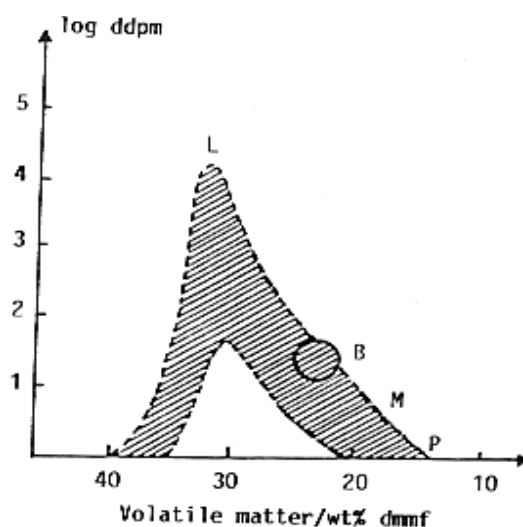


Figure 2.5: Variations in maximum fluidity (ddpm: Gieseler) with volatile matter [20]

2.6 Dissolution of coal

The conversion of coal into nuclear graphitic carbon requires relatively pure coal extracts. To provide for such purity, a suitable solvent is required in the extraction process, which separates a desired portion of coal into a solvent. The process may be achieved by physical or chemical methods [31]. The physical methods are based on the differences in the physical properties of the minerals and the carbonaceous part of coal. The chemical methods involve extraction of the

organic part in various solvents utilising various additives. It has been shown that coal extraction with organic solvents strongly affects the coking properties of the coal residue. Furthermore, dependence between the extraction yield and the coking properties of heat-treated coals has been reported [32, 33].

2.6.1 Theories on the mechanism of coal extraction

Theories on the routes for the disruption of the coal matrix have been reported. The use of reagents that attack the surface of coal has been documented. In this process, chemical transformation is thought to effectively “peel away” this surface to expose fresh surface to the reagent. The technique is believed to involve radical transformations of the coal structure, resulting in extensive carbon-carbon bond cleavage-reagent reaction times, and greater possibilities for the selective cleavage of bonds [22].

In another theory, the reagent is thought to penetrate into the coal matrix and swell the coal. This is believed to allow a greater surface area, effectively longer coal-reagent times, and greater possibilities for the selective cleavage of bonds. Swelling is thought to put a strain on the coal matrix, leading to the rupture of hydrogen bonds and the reorientation of the coal matrix, which allows reorientation of the hydrogen bonding structure to occur. It is believed that an appropriate hydrogen-bonding agent, if allowed to penetrate the swollen coal structure, would be capable of “tying up” hydrogen bonding sites in the coal. It is the combined efforts of swelling and bond breaking that appear to allow included mineral matter to “drop out” of the coal structure while weakening the coal matrix. When treated with a suitable solvent, differential swelling of coal macerals leads to stresses that contribute to chemical comminution. Research showed that maximum swelling occurs when the Hildebrand solubility parameter of the solvent matches that of the coal. Solvents such as pyridine have been found to be the most effective swelling agents. Inertinite rich-coal was found to show reduced swelling compared with vitrinite-rich coal samples of similar rank. Toluene is the

solvent most commonly used in the dissolution of coal. It has been pointed out in the literature that the solvent should have a hydrogen-donor capability in order to stabilise the free radicals generated and thereby reduce undesirable re-polymerisation reactions [24]. Systems known to increase the solubility of the coal in different solvents were observed in petroleum pitches in which a low C/H ratio favoured solubility in different solvents and reduced condensation of the hydrogen-rich aromatic molecules [34].

The removal of such materials from the structural boundaries yields a more friable, “soft” coal structure. Moreover, the leaching of fine mineral particles from the coal matrix results in a more porous structure and improves the coal’s grindability. The prior removal of some mineral matter is reported to reduce the coal’s abrasiveness. The treated coal should be more amenable to crushing and such crushing should occur along maceral boundaries due to the combined effects of external hydrogen bonding and swelling.

Large amounts of impurities of comparable particle size distribution are likely to be released. This reduces the cost of follow-up because the coal structure is most susceptible to chemical attack during the swelling process. A wide variety of chemical reagents are capable of blocking the internal hydrogen bonding of the coal. However, for a chemical coal beneficiation system to be practical, this hydrogen bonding system must be readily available, inexpensive, be of sufficiently small molecular size, and not be expected to introduce unwanted chemical elements that will lead to corrosion or pollution problems with the processed, comminuted coal. These qualifications substantially limit the number of hydrogen bonding reagents [24] that could be used.

2.6.2 Parameters affecting solvent extraction

The extraction process is influenced by many factors which interact in solution with coal to effect dissolution. Some of these factors, e.g. temperature, will not be

discussed alone but in conjunction with other factors. The parameters that affect coal solubilisation, viz. nature of a solvent, moisture and oxygen, particle size, coal properties and other sulphide additives in demetallation, are detailed in this section.

2.6.2.1 The nature of the solvent and its effect on extraction

The extraction of coal has been correlated to some physical parameters of both the solvent and the coal. It has been shown that the properties of the solvent, viz. internal pressure, surface tension, dielectric constant or dipole moment, have little correlation with coal solubilisation. A distinction between solvents that are capable of breaking the intermolecular bonds in coal and those that stabilise coal fragments has been documented. The family of solvents containing an element with an unshared electron pair, such as nitrogen or oxygen, has been found suitable for coal solubilisation [35, 36]. Coal, being hypothesised as containing micelles with a size range of 1 to 300 microns, swells on adsorption of the solvent, and forms the micellar network of smaller units from the swelled structure. According to the Dryden model of coal solubilisation, the extent of coal extraction is proportional to the swelling structure. A solvent was considered suitable if it promoted swelling of the coal structure while simultaneously stabilising the coal micelles solution. Swelling promotes loosening and the availability of an unshared pair of electrons was considered to be an important factor. Experimental findings showed that coals that were heated to 200 – 400 °C in an inert atmosphere, cooled and then extracted with the solvent, gave a higher yield than untreated coal [37]. Studies on the influence of time on extraction showed a linear relationship between time and the yield of the coal extracts. Increased temperature was found to increase the yield and the smaller particles of coal produced a higher yield of coal extracts [36].

In hydro-dissolution, dissolution of coal is thought to result from an interaction of coal with a specific chemical structure of the solvent. Different solvents with

specific chemical structures showed different types of interactions with coal. The high power of a solvent containing amines (in extraction) is thought to be attributable to its chemical structure, which shows the presence of an unshared pair of electrons on the nitrogen. A solvent with a hydroxyl group attached to an aromatic ring and a hydro-aromatic ring was found to be more effective in coal extraction. A two-ring system containing a hydroxyl group attached to an aromatic ring and a hydro-aromatic ring was even more effective [36].

It has been shown that about 65 % of mineral matter and sulphur could be removed by treatment with 20 % sodium hydroxide from Turkey lignite coal. Mukherjee and Borthakur removed about 90 % of the mineral matter from coal using aqueous sodium hydroxide solution followed by acid treatment. A polar solvent appeared to break the polar interactions and allowed the swelling of coal [31].

Increased porosity was found to occur when coal was dissolved in methanol at 25 °C. With supercritical alcohols, the coal is hydrogenated and the result is a higher conversion [38, 39]. Alcohols show greater solubility for polar organic molecules and tend to form hydrogen bonding or dipolar attractive forces, which provides an opportunity for chemical interaction (nucleophilicity of the alcohol oxygen facilitates alkylation) [40].

Sapienza *et al.* [1979] treated coal with CO₂/H₂O and removed about 15 % of the ash. The carbon dioxide penetrates the coal structure more readily and extensively, diffuses along the lines of mineral inclusions and provides a method of simultaneous cleaning and fracturing. The synergistic interaction of these two inexpensive reagents causes the selective solubilisation of alkali and alkali earth mineral matter in the coal and the swelling of the coal matrix, which then weakens the coal structure [22]. Supercritical water when used as a solvent gave an extraction yield of 40 – 50 % at 380 °C [41].

Comprehensive investigations into the solvent extraction of Polish high-volatile sub-bituminous and bituminous coals in a batch-stirred autoclave were done using hydrogenated anthracene oil as a start-up solvent. Successive recycled solvents without hydrogen or catalysts showed a steady decrease in coal conversion and extraction yield (caused by a continuous decrease in the H-donor capacity of the recycled solvent). The successive recycled solvents enriched with catalytically hydrogenated coal extracts are thought to have affected the coal conversion and extraction yield by stabilising the chemical group compound of the successive recycled solvents [42].

An extraction yield of 27.4 % was obtained from a supercritical solvent mixture of 95 % p-xylene and 5 % tetralin at a temperature of 345 – 366 °C, and a pressure of 3.5 -6.9 MPa. An improved yield of 54 % (by mass) was obtained when coal was dissolved in supercritical water, stannous chloride or molybdenum trisulphide and the catalyst impregnated at a hydrogen pressure of 2.6 – 5.4 MPa, with a system pressure of 22.3 – 34.6 MPa [43].

An attempt to match coal solubilisation with the Hilbrand solubility parameter has been strongly opposed. However, Gutmann's donor/acceptor theory was found to be acceptable [44, 45, and 46]. Acid cleaning offers an advantage over typical gravity methods in the sense that the chemical composition of the mineral matter does not influence the acid's removal. The acid attack on the mineral occurring in the partings of coal is thought to form the basis of the disintegration process for breaking coal during mining [22].

Certain solvent additives improve the extraction yield of certain coals in some solvents. These additives are typically electron-donor or electron-acceptor compounds. The addition of various salts in the extraction of coals with carbon disulphide/N-methyl-2-pyrrolidinone (CS₂-NMP) solvent mixture (1:1 by vol.) showed that lithium and tetrabutylammonium salts (0.25 mol/kg-coal) of various anions considerably increased the extraction yield from 60 to 84 %. The yields

increased in the order $F^- > Cl^- > Br^- > I^-$, indicating that the anions with a small ion radius or large electronegativity are effective in enhancing the yield. The role of anions in the enhancement of coal solubility was based on the assumption that acid-base interactions between coal acidic sites and anions are responsible for the increment in the extraction yields [47]. However, without salts, CS_2 -NMP mixed solvent gave slightly lower yields (63.7 – 69.7 wt %). The addition of a small amount (25 mg/g) of tetracyanoethylene improved the extraction yield to 85 wt %. Various additives, namely tetracyanoethylene and p-phenylenediamine improved the extraction yield. Tetracyanoquinodimethane (TCNE) was found to be effective for coals that had a large fraction of heavy extracts, increasing the extraction yields considerably. Characterisation of the fraction solubilised suggested that the enhancement of the extraction yield is attributed to suppression of the association between coal molecules [48, 49].

Previous work showed that extraction of coal with PhMe gave a conversion of approximately 30 wt %, while with water as solvent the conversion was 43 wt %. The addition of tetralin to the solvents gave higher conversions (69 wt % with PhMe and 57 wt % with water) [50].

2.6.2.2 The effect of moisture and oxygen

Moisture is an undesirable component in coal. Its existence in the solvent greatly reduces the solubility effect of the solvent on coal. In a continuous process, the solvent is recycled and the cumulative water content produced decreases the solubility effect of the solvent. In solvents immiscible with water, this effect is too great because water alone impedes the power of the solvent. Water alone is therefore not a good solvent for coal. Research conducted at West Virginia University showed that as little as 3 mole % (0.6 wt %) of water in coal cut the extraction yield by > 50 % in NMP. This makes the issue of moisture in coal very important. For this reason, the extraction process at the Institute of Applied Materials, University of Pretoria, ensures the absence of moisture in the reagents

used. The coal used is kept in nitrogen-purged plastic bags to minimise the amount of intrusion by moisture and oxygen. The little moisture that is present is driven off when the reactor containing the coal and solvent is heated to operating temperature [50].

2.6.2.3 The effect of particle size

There is a significant increase in the extraction yield with decreasing coal particle size. However, the rate of increase in the yield is too small to be accounted for, by assuming that a surface layer of constant thickness is completely extracted. In a study of the effect of coal particle size, 60 – 200 mesh size in extraction, an insignificant extraction yield was obtained. This finding is very important from the process economics point of view since with the conventional crushers, coals can be crushed down to 60 mesh size and require no grinding (this means an expensive operation would be required for this solvent extraction process) [51].

2.6.2.4 The coal properties affecting extraction

The extractability of coal decreases rapidly as the carbon composition of coal increases from 85 – 89 wt % (dry ash basis). The extractability then becomes almost negligible at 92 – 93 wt % carbon. This statement applies broadly to all temperatures and types of solvents. Of the petrological constituents, vitrain yields the most extract and fusain the least [33].

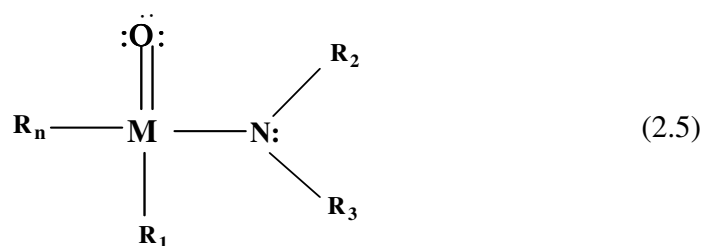
2.6.2.5 The effect of sulphide on extraction

The use of hydrogen sulphide in qualitative inorganic analysis has been well documented. Under controlled acidic media conditions, hydrogen sulphide precipitates heavy metals of group II (not related to periodic classification) (Hg^{2+} , Bi^{3+} , Cu^{2+} , As^{3+} , Sb^{3+} , Cd^{2+} and Pb^{2+}) to form insoluble metal sulphides. High acidity is believed to inhibit the dissociation of hydrogen sulphide, thereby

reducing the sulphide ion concentration. The group IV forms slightly soluble sulphides precipitates of Zn^{2+} , Mn^{2+} , Ni^{2+} and Co^{2+} . These are precipitated by the passage of hydrogen sulphide through an alkaline solution (ammonia solution). The hydroxide is reported to remove the acidic protons furnished by hydrogen sulphide to form water, thereby favouring the production of more sulphide ions, as in Scheme 2.1. This increase in sulphide ion concentration is believed to ensure that any group IV metal sulphides present are precipitated [52, 53].

2.7 Efficient coal solubilisation

The term 'supersolvent' is used to denote dipolar, aprotic solvents that are capable of dissolving a large fraction of the organic material in coal [36]. The general formula (equation 2.5), although complex, is identified with the solvents tetramethyl urea (TMU), dimethylsulphoxide (DMSO), dimethylformamide (DMF), hexamethyl phosphoramidate (HMPA), N, N-dimethyl acetamide (DMAA), and N-methyl-2-pyrrolidone (NMP) [36]. The solubilisation of coal in aprotic solvent by treatment with sodium hydroxide alone has been well documented [54, 55, 56]. Solubilisation was found to increase with an increase in reaction time, temperature, alkali concentration and decrease in particle size.



where

M = a carbon

R_2 and R_3 = hydrogen atoms or a lower alkyl group

R_1 and R_n = lower alkyl group and another group, a monocyclic group [56].

2.7.1 Extraction of coal with N-methylpyrrolidone

Coal, being a polynuclear aromatic structure, is hydrogen-deficient. The West Virginia University in the USA employs the hydrogen-rich solvent mixture of N-methylpyrrolidone (NMP) and carbon disulphide (CS_2) to obtain a carbon yield of about 87 % at 300 °C. The coal extracts produced may be suitable as precursors for the production of value-added carbon products. The dissolution of coal is reported to depend on the solvent type and on the physical and chemical properties of the solvent, and cannot be attributed to a simple diffusion-controlled process. Further, solvent extraction is dependent on time and temperature and, to a lesser extent, on the particle size of the coal, the solvent-to-coal ratio, and the oxygen and moisture content of the coal. However, a mounted coke sample in resin (produced from a heat-treated coal extract) showed isotropic texture with poor crystalline domains. NMP is a relatively expensive solvent [47, 57, 58].

2.7.2 Extraction of coal with N, N-dimethylformamide and alkali

Morgan [53] developed a coal solubilisation process referred to as the “Refcoal process”. This essentially involves mixing a polar aprotic solvent such as dimethylformamide (DMF) with coal. With the addition of a small amount of alkali to the extraction medium, solubilisation occurs. Dissolution conditions are mild – atmospheric pressure, and a temperature from room temperature to just below boiling point. The alkali moves into the solution by means of a phase-transfer catalyst and the coal appears to act in this capacity. The Refcoal process entails: 100 parts by mass of coal, 1 000 parts of the solvent and 10 parts of the base, mixed in an oil or water bath-jacketed reactor and stirred for 5 h under a nitrogen atmosphere. The progress of the extraction is monitored photometrically by taking small samples of the slurry at regular intervals. Most of the studies have been done on a flotation concentrate from Iscor’s Tshikondeni mine, with 8 % ash, when 90 – 92% of the organic material goes into the solution. The purified products are referred to as “Refcoal”, for “refined coal” [54].

CHAPTER 3

CARBONISATION

The graphitisability of the carbon is determined primarily by the quality of the carbonised starting carbon, coke. Enhancement and control of this coke quality can be achieved by the use of chemical additives. The overall effect is to bring about a certain degree of graphitisation or to promote a more graphitic structure. This chapter gives the literature background on some of the chemical processes associated with carbonisation. For a more complete understanding, some mention will also be made of non-graphitising carbons. Previous work on the effect of additives on carbonisation and the resultant coke texture is discussed.

The term 'carbonisation' is used in the literature generally to cover the pyrolysis of carbon-containing compounds at different temperatures and to different degrees of structural ordering. The definition adopted for the purpose of this work will be: *Carbonisation is the process of converting, by heating, carbon-containing compounds to carbon prior to the onset of three-dimensional ordering as detected by X-ray diffraction techniques.*

The types of carbon discussed in this text are the non-graphitising or hard carbon, and the graphitising or soft carbon. The distinction between the two carbons comes from the X-ray diffraction pattern of a hard or non-graphitising carbon, which does not develop the three-dimensional (hkl) lines of crystalline graphite upon heating as do the soft or graphitising carbons. Hard carbons can be carbonised to temperatures in excess of 2 000 °C without the development of the three-dimensional ordering, i.e. without graphitisation, whereas with soft carbons, graphitisation is a significant process at about 1 400 °C.

3.1 Mechanism of carbonisation

The mechanism by which a heated carbonaceous material decomposes and forms a char or carbon is of fundamental importance in understanding the production of carbons of all kinds. The process can be considered to occur in three broad stages. The first stage, which is termed the 'pre-carbonisation' stage, extends up to heat-treatment temperatures of the order of 400 °C and is accompanied by molecular rearrangement and initial condensation reactions. The second stage, which does not occur in hard carbons, is usually completed at about 600 °C and contains the bulk of the condensation reactions within a plastic stage; its completion is marked by the formation of a solid semi-coke. The third stage occurs after the formation of the solid semi-coke, during which volatilisation of most of the remainder of the non-carbon elements and some structural rearrangements occur. The three stages can overlap and vary according to the material concerned. However, it is in the second stage that the fundamental differences between hard and soft carbons are shown up. The existence of a plastic stage during the carbonisation of graphitising materials does not ensure a graphitising carbon [59].

3.1.1 The precarbonisation stage

The raw materials of graphite production, such as coal, coal-tar pitch and petroleum derivatives, are predominantly mixtures of aromatic, heterocyclic and multi-ring systems of various sizes. The final properties of the graphite produced are determined to a large extent by the chemical composition and reactivity of the molecular species and by the reaction intermediated. These properties usually help to follow the molecular changes occurring upon the pyrolysis of mixtures. However, it is impossible to follow the carbonisation of materials such as coal tar and petroleum pitches due to their extreme molecular complexity and due to the lack of operational techniques.

The formation of graphitic carbons from simple and polynuclear hydrocarbons has been studied in detail. The emphasis was on the nature of the resultant graphite. The studies correlated the molecular structure of the parent material with the final graphitic properties, but paid little attention to the intermediate stage. This section describes the literature dealing with possible reaction sequences proposed in the literature, particularly those that discuss graphitising carbons or those that compare and contrast the precarbonisation behaviour of graphitising and non-graphitising carbons [59].

Consideration was given to non-graphitising carbon in polyvinylidene chloride and to graphitising carbon in polyvinyl chloride. The carbonisation behaviour of polyvinylidene chloride was contrasted with that of polyvinyl chloride. Both were found to initially lose hydrogen chloride by a “zip” reaction and were thought to produce a fully conjugated polyene chain (alternate single and double bonds) by the successive release of adjacent hydrogen chloride groups along the polymer chain [58]. Subsequent reactions were found to lead to different products. Polyvinylidene chloride was found to lose more hydrogen chloride above 250 °C to give coke containing aromatic rings cross-linked by a polyene chain with little possibility of reorder and growth of the aromatic layers. Polyvinyl chloride, on the other hand, did not form aromatic regions until 400 °C, at which temperature there was a rapid evolution of hydrogen and the formation of the aromatic rings. Following the carbonisation of polyvinylidene chloride by infrared spectroscopy, it was found that the C-Cl and aliphatic C-H bonds disappeared as the carbonisation progressed, and double bonds and aromatic structures appeared [59].

The hydrogen chloride molecule released a hydrogen molecule by a “zip” reaction. This reaction was initiated by the formation of a radical, which was able to travel along the polymer, forming alternate single and double bonds. However, it was also able to eliminate hydrogen chloride from adjoining polymer chains, thus forming a cross-linkage, and also to form a cross-linkage by meeting

another radical on an adjacent chain and forming a bond. A rigid solid structure containing many cross-linkages was formed in the temperature range 150 – 190 °C, unlike the model of Winslow *et al.* [1980], which only formed cross-linkages through the loss of the second molecule of hydrogen chloride occurring at temperatures in excess of 250 – 700 °C [60]. Despite the various contradictions in the above-documented literature, the basic picture that emerges is that polyvinylidene chloride formed carbon containing aromatic rings that were cross-linked by polyene chains. These cross-linkages prevented the growth of the extensive aromatic layers that were a prerequisite for the formation of graphite. Polyvinyl chloride, on the other hand, formed aromatic rings which acted as nuclei and grew into the necessary extended aromatic layers at the expense of the surrounding aliphatic materials. The reason why polyvinyl chloride does not form cross-linkages in the initial zip reaction is not completely clear but it is thought to be due to a different type of reaction taking place. Subsequent work revealed that the loss of hydrogen chloride from polyvinylidene chloride was initiated by the formation of a radical, which then traversed the polymer chain forming either a polyene or a cross-linkage [60, 61]. The study of the effect of electron spin resonance on polyvinyl chloride and polyvinylidene chloride detected free radicals at temperatures as low as 90 °C, reaching a broad maximum at 300 – 400 °C. The temperature at which the maximum concentration was reached was 560 °C [62]. Despite their apparent similarities, polyvinyl chloride and polyvinylidene chloride form polyene chains in entirely different ways.

The precarbonisation stages of another graphitising carbon, acenaphthylene, and of a non-graphitising carbon, bifluorenyl, were followed using spectroscopic techniques (i.e. differential thermal analysis, chromatographic analysis and X-ray diffraction) [63]. Carbonisations occurred by a stepwise process, postulated by the reaction sequence shown in Fig. 3.1. At about 185 °C, the development of a disordered structure in the pyrolysis of acenaphthylene coincided with the formation of polyacenaphthylene (I) as shown by the infrared and ultra-violet

studies. The presence of decacyclene (II) was shown by its characteristic X-ray powder pattern being present, superimposed on the scattering. Ultra-violet spectra showed the development of bianaphthylidene structures (III) at temperatures below 340 °C. Examination of a plot of the average layer diameter of the molecular species present against the temperature showed two distinct steps: one at 340 °C and the other at 375 °C. Ruland [1965] postulated that the distinction was due to the formation of zethrene (IV), followed by its dimerisation to give the structure (V). The layer size increased continuously afterwards. It was then postulated to be due to the higher-order polymerisation of zethrene [63]. In the case of bifluorenyl, ultra-violet spectra showed an almost complete transition to bifluorenylidene (I) at temperatures below 400 °C. Between 400 and 500 °C there was a gradual increase in layer size, which then remained constant until 600 °C.

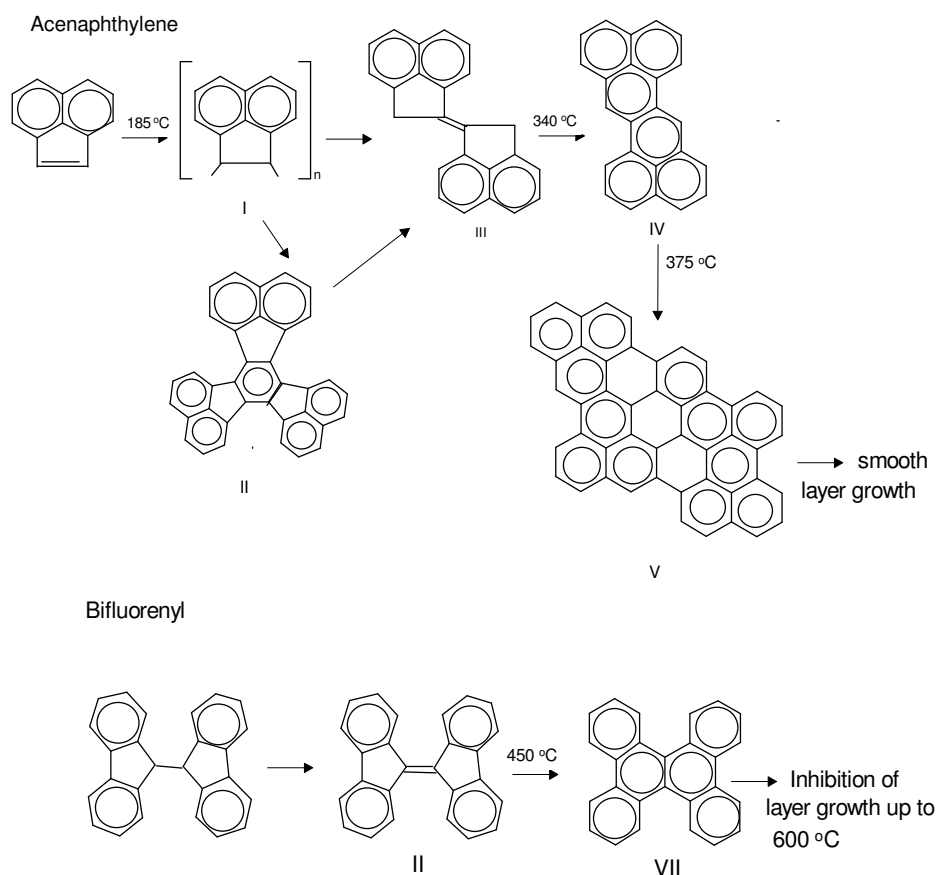


Figure 3.1: Initial stages of carbonisation [63]

The structural changes in the region of 400 – 500 °C indicated the formation of a planar molecule and this was postulated to be tetrabenzonaphthalene. In contrast to zethrene, this molecule cannot build up aromatic layers without vacancies and this explains the fact that there is no growth in layer size after its formation. Research findings showed that the mechanism of carbonisation of organic compounds by electron spin resonance techniques is accompanied by the formation of large concentrations of free radicals (up to 3×10^{20} unpaired electron per gram), making it possible to follow the carbonisation process by electron spin resonance [62, 64, 65]. However, this proved difficult due to the fact that only one unresolved line was observed for practically all chars and the identification of the radical giving rise to the electron spin resonance signal was not possible. A well-resolved hyperfine structure was obtained by carbonising in the inert liquid. This overcame the difficulty. However, later it was shown that metaquinquephenyl does not behave as an inert liquid. Carbonising in metaquinquephenyl was found to give rise to a great number of phenylated and/or polyphenylated compounds. By comparing the observed spectra with the computed spectra for certain free radicals, some of the radical intermediates in the carbonisation of aromatic species were identified. The perinaphthyl radical in the carbonisation of acenaphthylene was thought to be an intermediate in the formation of zethrene.

Carbonisation of aromatic hydrocarbons is initiated by thermal C-C or C-H bond cleavage to yield reactive free radicals. These radicals can then undergo hydrogen abstraction, molecular rearrangements and growth to give condensed aromatic entities. The final stage of the carbonisation was thought to be the growth of these entities by dehydrogenation and side-chain elimination. A further study on the pyrolysis of acenaphthylene up to a temperature of 500 °C showed that decacyclene was the main product in the non-volatile residue [66]. This is inconsistent with the work of Ruland, which showed that decacyclene was an insignificant side-reaction product.

Warburton [67] reported that it was found that naphthalene undergoes self-condensation on heating to give, first, 1,1'-binaphthyl and, finally, the five aromatic ring system, perylene. Examination of the tars produced from the pyrolysis by mass spectrometry of the methylnaphthalenes at 475 °C showed the presence of dimers and other condensation products. Subsequent to that, it was reported that the coke formed from the pyrolysis of tetrabenzola [a, c, h, j] phenazine consisted primarily of the dimer, trimer and tetramer [67].

The mass spectrometry study of the liquid-phase pyrolysis on 20 aromatic compounds confirmed that the gas that evolved from thermally stable compounds (e.g. naphthalene, pyrene, chrysene) was primarily hydrogen, comparable to the methane and higher hydrocarbons from thermally reactive compounds (e.g. acenaphthylene, methylnaphthalene). Twice to 20 times as many molecular ions were detected in the mass spectra of these thermally reactive species compared with the residues from the pyrolysis of binary mixtures of these compounds, which did not show products having molecular weights higher than those of the pure compound [68, 69].

Examination of the spectra of the intramolecular and intermolecular vibrational frequencies for a series of polynuclear aromatic hydrocarbons heat-treated by neutron inelastic scattering revealed that the structural ordering of the resultant carbon depended upon both the skeletal structure and the molecular dynamics of both the original hydrocarbon and the reaction intermediates [70, 71]. The results suggested that graphitising carbons had temperature intervals for a major and stable species with a definite skeletal structure. The structure so formed persisted and finally fused together to form graphitic layers (e.g. acenaphthylene, bifluorenyl, etc.). Conversely, compounds which had large-amplitude skeletal or intramolecular vibrations, or which formed strained non-planar intermediates, did not form graphitising carbons (e.g. p. terphenyl) [71].

Evans and Marsh [72] provided some insight into the reaction sequence that takes place in the first and second stages of carbonisation. A high-resolution mass spectrometer was used to identify the products formed in the pyrolysis of acenaphthylene, anthracene, 9,9'-bifluorylidene, chrysene, phenanthrene, pyrene and mixtures of these. The condensation reactions to mass numbers in excess of 700 were followed [72].

Evans and Marsh found that the reactions taking place upon pyrolysis were predominantly dehydrogenative dimerisations, trimerisations, etc., which produced large flat sheets of condensed aromatic molecules. Little evidence of co-condensation of components was found when mixtures of two components were heated together; condensations appeared to be between identical molecules. Further interesting evidence from this study was that, in an attempt to reverse the carbonisation process by hydrogenating the solid cokes using atomic hydrogen, no new species were found. This suggested that the molecules going to make up the coke were simply condensation products of the type identified in the first and second stages of the carbonisation [72].

3.1.2 The mesophase stage

The phase-transition state similar to nematic liquid crystal, which is formed when coal of a particular rank is heated to a temperature of 400 - 500 °C, is called the 'mesophase'. Associated with this process is swelling from gases trapped within the plasticised macerals of the heated coal particle, coalescence of spherical bodies and consumption of the isotropic parent liquor. The softening and expansion of the coal particle is enhanced by the expansion of the trapped gas generated within the particle (Fig. 3. 2) [14, 73]. The result is the formation of an anisotropic mosaic coke structure. This intermediate stage was recognised by Brooks and Tailor as spherical bodies in the plastic carbonaceous material [74, 75]. The fluidity of the plasticised mass is thought to facilitate the suitable mobility of the aromatic molecules in the system. The aromatic molecules rearrange

themselves to create an intermediate anisotropic nematic liquid-crystal phase [76, 77, 78, 79].

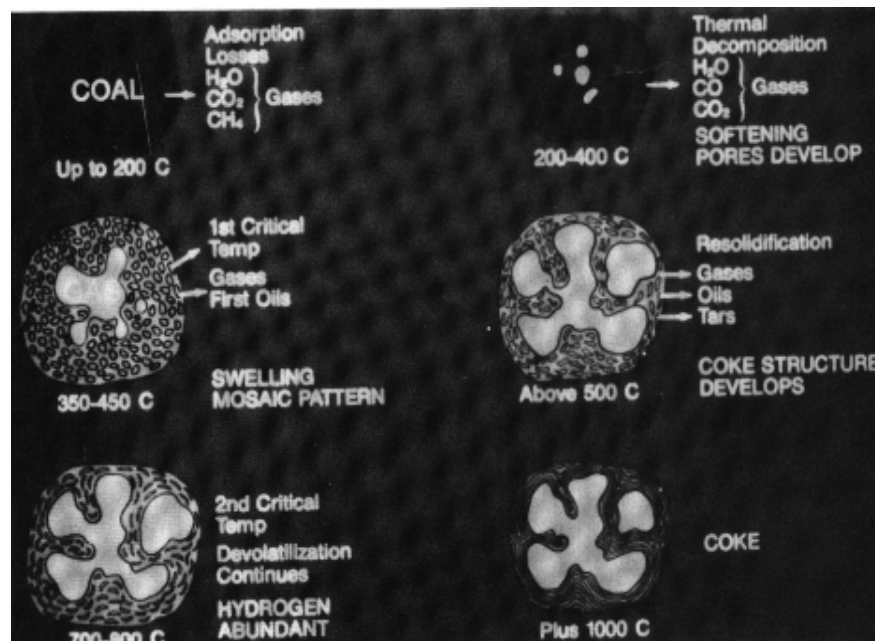


Figure 3.2: The transformation process during coking of a single particle of coal [14, 76]

Coalescence of the spherical bodies into a mesophase during pyrolysis of the coal has been extensively studied [80]. At a temperature of 475 °C, fine points of light were detected in the sample at the limit of the optical resolution. With a further increase in temperature to 480 °C (on Wongowilli seam vitrinite), these points grew until they resolved as spheres in the isotropic liquid vitrinite. When the number of spheres occupied about half the volume, they started to perturb each other's growth and their shape became progressively less uniform due to their coalescence. So long as the isotropic matrix persisted, there was continuous initiation of spheres and these existed in all sizes in the matrix. The final disappearance of the isotropic phase coincided with the solidification of the material to give semi-coke at 490 °C. Conclusively, the stages in the transition from the isotropic plastic vitrinite to the anisotropic semi-coke occurred over the

narrow temperature range of 10 – 15 °C [80]. Pyrolysis in pitches took place over a narrow temperature range of 480 – 500 °C [81].

The behaviour of these spheres under singly and doubly polarised light suggested that the spheres must have had the structure with equatorial stacking of layers perpendicular to the surface (Fig. 3.3). Despite the optical evidence to confirm this structure (using the electron diffraction technique), it was thought to be inherently improbable and an alternate structure was proposed in which the layers were flat and stacked on top of each other, and were parallel to the optical observations. The structure was thought to have inherent stresses due to shrinkage [80, 82, 83].

Initiation of spheres occurred in a variety of pitches, bitumens and single compounds, such as polyvinyl chloride and naphthacene, all of which produced graphitising carbons. However, compounds such as dibenzanthrone appeared to form the mesophase directly from the crystalline material without spheres being formed. Dibenzanthrone has been classed as a graphitising compound [59]. However, on the basis of X-ray diffraction it was classified as a non-graphitising carbon [59]. If the pitch-like material was stirred before cooling, a more complex structure arose in which the mesophase and isotropic phase became intimately mixed (as shown under a polarised light microscope). However, each retained its own identity. The mesophase, as well as the pitch, each behaved as a liquid. These observations led Brooks and Taylor to conclude that the spheres had the properties of nematic liquid crystals [82].

Carbonised pitch ($C_{100}H_{53}O$) showed a slightly different analysis of the spheres formed within it ($C_{100}H_{49}O_{1.4}$). More extensive condensation was observed in the molecules making up the spheres than in the original pitch. The carbonised pitch contained 27 % of spheres and the molecular species making up these spheres were found to have a molecular weight (as measured by a vapour-pressure osmometer) of about 1 626 compared with 415 in the pitch. The two important

factors controlling the rate of growth of the spheres were found to be temperature and time. The shape of these spheres was easily distorted by the presence of fine solid particles impeding symmetrical growth during coalescence. The edges were sharp and fluid at a particular temperature. The ultra-thin section showed the characteristic electron diffraction pattern, typical of parallel lamellae (Fig. 3.3). The position of the arc of the lamellae corresponded to an interlamellar spacing of $3.47 \text{ \AA} \pm 0.01$ [82]. The lower the temperatures of carbonisation, the fewer and larger were the spheres formed. Higher temperatures and prolonged heating led to a complete conversion into the mesophase. The higher the temperature, the shorter was the time required for complete conversion [82].

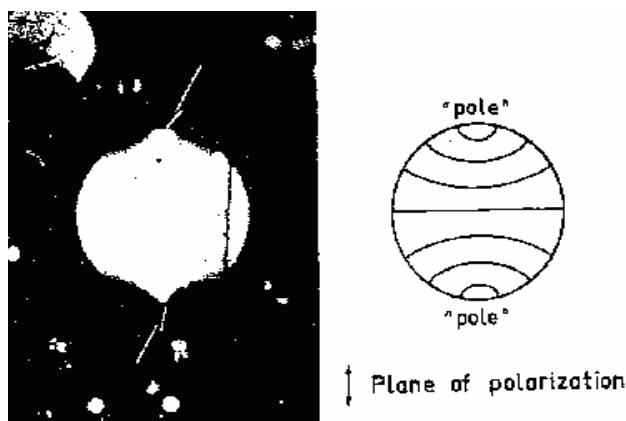


Figure 3.3: Development of a mesophase sphere in the transformation to a coke [80, 82, 83]

Proton nuclear magnetic resonance spectroscopy (NMR) in polynuclear aromatic hydrocarbons containing oxygen and nitrogen showed that 90 % of the protons observed were attached to aromatic rings, and that the spheres formed were soluble in pyridine and toluene. The components of the carbonaceous material from which spheres were formed consisted partly of two or more smaller rings joined in a non-planar fashion, presumably by diaryl-type linkages or methylene bridges or dihydroaromatic structures. The calculated potential ionisation energy of the reactive hydrocarbons from para position in the ultra-violet visible spectra

was less than 7.1 eV (p-band at about 387 m/u). Ultra-violet analysis of partly carbonised coke in benzene-pyridine showed absorption of about 4.2 eV. The results suggested that carbonisation forms more reactive hydrocarbons and that these decomposed, via a radical mechanism involving the loss of hydrogen, to form larger, more complex planar entities, and ordered lamellae of the mesophase [82].

Mesophase spheres are initially formed in the region adjacent to insoluble particles, also formed during carbonisation. Instead of the particles being incorporated into the spheres, they are rather aggregated around the surface of the sphere causing it to have irregular margins. The use of finely divided graphite on the toluene-soluble fraction of the carbonaceous material was found to induce nucleation successfully on carbonisation. Pronounced orientation of the mesophase spheres on the graphite surface was observed. Growth of the mesophase spheres was reported to be dependent on the rate of carbonisation. The lower the rate of carbonisation, the fewer and larger was the spheres formed. It was shown that at temperatures of 400 °C and above, for an increased time of carbonisation, the number of spheres remained constant. Prolonged heating at high temperatures above 400 °C was reported to result in the complete conversion of carbonaceous material to the mesophase. Stirring and the presence of fine particles are also factors proved to accelerate slightly the formation of mesophase spheres [82].

In a study of the relationship between the development of the mesophase spheres and residence time, within the temperature range of 400 – 450 °C for various pitches, it was shown that the first hour at a specific temperature corresponded to the nucleation region [84]. From one to 40 h was the growth region and longer times produced little change. The activation energy for the growth process was estimated to be 35 – 45 kcal per mole (146.44 - 88.28 kJ mol⁻¹); this is equated with the rearrangement of C–C bonds and with the vaporisation of the low-molecular-weight material. In further studies in which

anthracene was heated under pressure of 2.5 kilobars (250 MNm^{-2}) and at temperatures of about $550 \text{ }^\circ\text{C}$ the mesophase spheres were formed. The effect of pressure prevented the coalescence of the spheres by enhancing the viscosity of both the isotropic liquid matrix and the liquid crystal structure [85].

3.2 Structure of solid carbon

Solid carbon may be formed either from a liquid crystal phase, by deposition from the vapour or gaseous phase, by charring of a non-fusing solid or by charring of a fusing solid. Further heating of the resultant solid causes the volatilisation of the remaining non-carbon elements and some ordering of the carbon atoms. This section describes the determination of the structure. First, the turbostratic model will be described, followed by the reasons why this was considered inadequate and finally the proposed modified structure is given.

3.2.1 The turbostratic model

The scattering pattern of a carbon black in Fourier integral analysis revealed radical distribution of the carbon atoms around each other. This suggested the presence of graphite-like layers. The layers were arranged in parallel and equidistant from each other but randomly in translation parallel to the layer and randomly with respect to rotation about the normal to the layer. The term “turbostratic” (i.e. not ordered layers) for this type of structure was then suggested [86]. The size of the two-dimensional layer (L_a) was related to the breadth of the two-dimensional reflection at half-maximum intensity (β) by equation (3.2.1):

$$L_a = \frac{1.84 \lambda}{\beta \cos \theta} \quad (3.2.1)$$

The value of the constant was later found (by a more rigorous technique) to be 1.77. From small-angle scattering of X-rays by carbon blacks, it was concluded that carbon blacks consisted of clusters of a few hundred angstroms in size, within which the parallel layers were arranged as shown in Fig. 3.4. Heat treatment increased the size of the parallel layer groups, without markedly increasing the three-dimensional ordering, until a temperature was reached at which the carbon black changed discontinuously to a more crystalline graphite structure. The thinking was that graphitisation occurred when layers were given sufficient thermal energy to rotate into the graphite configuration.

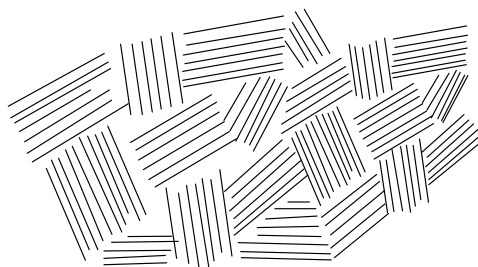


Figure. 3.4: Schematic representation of carbon black cluster [86]

An X-ray diffraction study on carbon from polyvinylidene chloride carbonised to 1 000 °C showed that not all carbons were in the form of graphite-layers: only about two-thirds of carbon was in the form of graphite-like layers, the rest of the carbon atoms were in a disorganised state. The graphite-like layers, although perfect, were very small (15– 20 Å). About 65 % of the carbon was calculated to be highly perfect and planar graphite-like layers of diameter 16 ± 1 Å and 35 % of the carbon was in a highly disordered form. Moreover, about 55 % of the graphite-like layers were grouped in pairs of parallel layers with an interplanar spacing of 3.7 Å and 45 % of the layers showed no mutual orientation [76]. The structure determined was specific and believed to be not necessarily representative of all carbons. An extended study, to include other carbons, revealed that for carbons containing, on average, fewer than five orientated layers, the interplanar spacing changed very markedly. For two orientated layers,

the d value was 3.7 Å, for two to three layers the d-value was 3.6 Å and for four to five layers, the d value was 3.44 – 3.445 Å. For more than five orientated layers, the change was small. The conclusion reached was that all carbons that show undeformed (hk) bands have an interplanar spacing of greater than 3.44 Å [87].

The X-ray diffraction study was extended to include carbons that graphitise on heating to sufficiently high temperature. This showed a gradual change to the ordered structure of graphite. Although some non-graphitic carbons showed a continuous and homogeneous evolution (to temperatures between 1 700 and 3 000 °C from a non-graphitic to a graphitic structure), other non-graphitic carbons that were termed “non-graphitising carbons” showed no trace of homogeneous development of a graphite structure, even after heating to 3 000 °C. The contribution from non-organised carbon was neglected in graphitic carbons because in all cases, where measurable graphitisation occurred, the layer diameter was in excess of 80 Å and the proportion of non-organised carbon was negligible in carbons where the layer diameter was greater than 25 Å [87].

It was found that if a series of graphitic carbons were arranged in order of increasing degree of graphitisation, i.e. increasing development of (hkl) lines, then the other parameters would be in the same sequence. These parameters included the diameter of the graphitic layers, the average number of layers arranged three-dimensionally and the interlayer spacing (d). The decrease in interlayer spacing that accompanies graphitisation had been previously reported [88]. Further research showed that for non-graphitic graphitising carbons, i.e. those capable of forming graphite at high temperatures but in which the graphite structure had not yet developed, the interlayer spacing was virtually constant and equal to 3.44 Å, whereas in a single-crystal graphite the d-spacing was 3.354 Å.

However, it was believed that the d-spacing of a graphitic carbon changed continuously from 3.44 Å to 3.354 Å. The widths of (002) and (004) reflections in

graphitic carbons were found to be different; this meant that the d-spacing was not rigorously constant but a mean value. In this case it was concluded that graphitic carbons contained a mixture of orientated and disorientated layers which were intimately mixed, forming a single phase, otherwise the (001) bands would have been resolved into doublets [87].

The graphite model showed a random distribution of orientated and disorientated layers. The term 'p' was used as a measure of the degree of graphitisation and was defined as the probability that a random disorientation had occurred between any two given neighbouring layers. However, the d-spacing was 3.354 Å at each orientation, and 3.44 Å at each disorientation. There was a random distribution of orientated and disorientated layers, and a linear relationship between them could be explained if there were layers separated by a distance of less than the 3.44 Å for a disorientated layer but greater than 3.354 Å for an orientated layer. The spacing, a, is 3.354 Å and corresponds to the spacing between orientated layers, b is the normal disorientation spacing of 3.44 Å, c is an intermediate value caused by having a group of orientated layers on one side of it and d is another intermediate value caused by having groups of orientated layers on either side of it [87].

$$d = 3.44 - 0.086(1 - p^2) \quad (3.2.2)$$

Using a simplified version of this model ($c = d = 3.399\text{Å}$), a relationship (equation 3.2.2) showed an agreement with the experimental results over the whole range of graphitic carbons. The non-graphitic carbon, even after heating to 3 000 °C, was found to have no layer diameter of more than about 70 Å and the number of layers per parallel group was no more than 12. Graphitising carbons with a layer diameter of about 70 Å, produced by heating to only 1 720 °C, had about 30 parallel layers. This difference in the number of layers per stack was considered to be a method of distinguishing between the graphitising and non-graphitising carbons even at temperatures as low 1 000 °C, where graphitising carbons had

approximately four layers per stack whereas non-graphitising carbons had 2 to 2.5. Density measurements on the graphitising and non-graphitising carbons showed a sharp divergence, graphitising carbons having a density of $1.99 - 2.25 \text{ g cm}^{-3}$. This meant that the non-graphitising carbons must have a more open type of structure compared with the graphitising carbons (Fig. 3.5) [86].

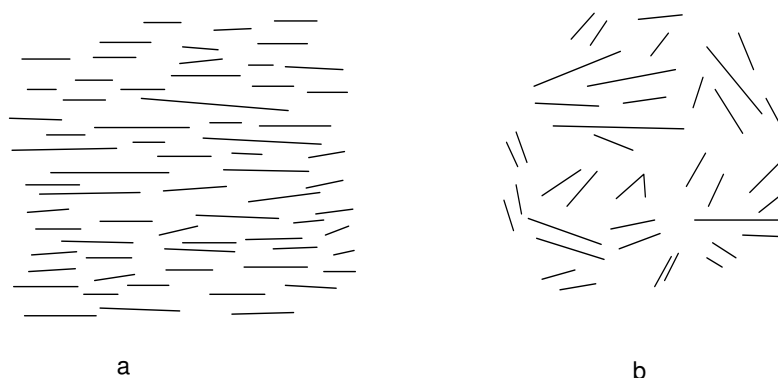


Figure 3.5: The proposed models for the structure of (a) graphitising carbon and (b) non-graphitising carbon [86]

Graphitising carbon shows the orientation of all the groups of parallel layer planes within a few degrees of each other, whereas the groups of parallel layers planes in non-graphitising carbon are orientated randomly and heavily cross-linked into a rigid structure. Further study on the turbostratic model initially proposed by Franklin resulted in a relationship (equation 3.2.3) [89]:

$$d = 3.44 - 0.86(1 - p) - 0.064p(1 - p) \quad (3.2.3)$$

The equation gives a better agreement for carbons with a low degree of graphitisation. It accommodates reduced spacing for the disorientations that were next to an orientated group with increasing graphitisation. However, allowance would have to be made for a reduced spacing for those disorientations that were next but one to an orientated group, a factor Franklin ignored.

3.2.2 Determination of crystallite sizes

The approximations made in deriving the equation relating L_a to the breadth of a (hk) reflection are such that the values obtained become progressively less reliable as the size of the layer plane decreases [76]. Attempts to develop a new technique for determining the layer plane size for carbon with very small layer planes has been done [90]. X-ray diffraction scattering pattern for randomly orientated, perfect aromatic molecules was calculated from the radical distribution function for various classes of molecules and the molecules in each class being approximately to the same size, ranging from 5.8 – 30 Å [90].

A description of a technique whereby a linear combination of these theoretical curves fits the observed curve by the method of least squares refinement has been documented [67]. The layer plane size distribution and the proportion of disorganised carbon were determined. Using this technique and the Hirsch method for calculating the distribution of numbers of stacks containing 2, 3, 4... orientated layers, a picture of the structure of four British coals and their carbonisation products was formulated and reported [65]. Up to 500 °C, the main process is one of the volatilisation of the disordered material. Between 500 °C and 600 °C, growth was started by the coalescence of neighbouring layers because of a wider distribution of molecular sizes. The stacking in this region, however, deteriorated due to the realignment of the molecules necessary for coalescence. The layer growth was found to be approximately linear up to 1 000 °C, although the layers produced were imperfect, probably bent coalescence junctions. Above 700 °C, the stacking improved by gradual realignment. The rate of growth was found to be greater for anthracites than for lower-rank coals, probably as a result of layers already being in reasonably good alignment and because of their greater initial size [67].

The method has been the subject of much criticism. An attempt to use Diamond's method for determining the distribution of layer sizes gave a negative weight

fraction for the 5.8 Å size group in certain anthracite samples [91]. The corrections for Compton (incoherent) scattering and the scattering caused by the presence of non-carbon elements (ignored by Diamond) were found to be most important and could not be neglected. The method was applied to a number of liquid hydrocarbon specimens (which represents a reasonable test). The results showed that amongst the four non-aromatic compounds examined, only one, cyclohexane, was found to be predominantly amorphous (i.e. non-planar), while of the 17 aromatic structures examined, only two were found to have appreciable amorphous (i.e. non-aromatic) content [92]. The method was concluded to be inaccurate and, with these inaccuracies, shown to be inconsistent. The main criticism of Diamond's method was that each single layer scattered independently and no allowances were made for layer-layer orientation. Further research on Diamond's work concluded the case of parallel layer groups containing several layers, and a rigorous correction for Compton scattering was made. This method led to the theoretical diffraction patterns, which gave a better approximation to the structure of carbon containing small layer planes. Various models for calculating L_a for turbostratic carbons showed that the Warren-Bodenstein approach was the most satisfactory. It was concluded that L_a calculated from a (10) reflection could give a higher result, by a factor of 1.09, than from a (11) reflection [93].

3.2.3 Tetrahedral carbon atoms in non-graphitic carbons

The turbostratic model of carbon is based on the fact that the atoms give rise to the (hk) and (002) reflections observed in the X-ray diffraction pattern, where all are arranged in perfect graphite-like layers. However, the hardness, density and non-graphitability of some carbons did not appear to be entirely compatible with a structure containing only graphite-like layers. This basic assumption of perfect graphite-like layers was challenged, as was whether tetrahedrally bonded carbon atoms could explain the anomalies [94]. The X-ray diffraction curves for the 26-atom molecule arranged in a graphite-like layer, a cubic diamond-like lattice and

a hexagonal diamond lattice were then calculated. All the structures gave rise to reflections in the same region as the (hk) reflections of graphite. It was then concluded that although there was no proof of the existence of the tetrahedrally bonded carbons in non-graphitic carbons, a claim that the evidence showed that they were non-existent was not valid, and it was felt that some of the anomalies in certain carbons might be explained by postulating a model in which tetrahedrally bonded carbon atoms were present [94, 95].

3.2.4 The influence of oxygen on carbonisation

Carbonisation of an aromatic hydrocarbon in the presence of oxygen was found to lead to the formation of a quinone intermediate. Further studies showed that heat treatment of an aromatic quinone at 3 000 °C led to a carbon with higher interplanar spacing than the 3 000 °C corresponding hydrocarbon. This effect was thought to be due to the fact that carbonisation of the quinone resulted in the degradation of the aromatic ring system through the elimination of carbon dioxide. This degradation led in general to non-planar free radicals, which polymerised to give a cross-linked disordered carbon, although it was found that in certain cases a rearrangement to give planar aromatic structures was possible [63]. Fitzer *et al.* [66] extensively examined various additives that influence the carbonisation process. Of the various materials, oxygen has been most widely studied. Severe oxidation is believed to reduce drastically the graphitisation of pitch. Oxidation has also been found to inhibit mesophase development [53, 61, 96]. X-ray diffraction analysis of oxygen-containing aromatics showed that oxygen substitution could result in both well and poorly ordered graphite [63]. Mild oxidation has been shown to reduce dehydrogenative polymerisation without necessarily leading to a less graphitic final structure [96]. Lewis and Singer used electron spin resonance to study the air oxidation of aromatic hydrocarbons. Aryloxy radicals were identified as intermediates. The formation of quinines that lost carbon monoxide (CO) on pyrolysis to give non-planar radicals led to a dramatic decrease in the final graphitisability of the starting material (Fig. 3.6).

The results of the electron spin resonance study suggested that oxygen had inhibited the formation of graphitisable carbon [14, 20, 61].

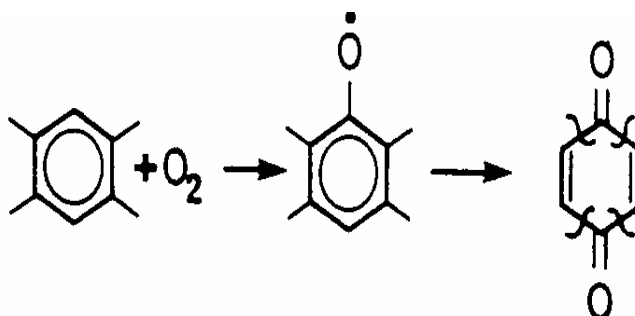


Figure 3.6: Reaction of oxygen with aromatic hydrocarbons during carbonisation [14, 20,57]

The bond cleavage in the absence of oxygen is believed to lead to molecular rearrangement, thermal polymerisation and aromatic condensation to form graphitic carbons. Although these processes are believed to occur in parallel during carbonisation, they can be considered separately from the mechanistic viewpoint [20,59]. Extensive work has been reported in the literature on the effect of oxygen on the growth of the mesophase spheres. Exposure of coals and pitches to oxygen showed that, in the presence of oxygen content of greater than 7 %, mesophase spheres were formed in the liquid phase. With oxygen content of 5 %, small isolated spheres were formed and more extensive growth of spheres only occurred in those coals that had oxygen content of less than 5 % [97]. The results suggested that there is a minimum amount of oxygen that inhibits the formation of the mesophase spheres.

The exposure of coal to oxygen and heat (~170 °C) was presumed to result in various types of microcracks or darker microfissure structures, an increase in the reflectance of vitrinite with temperature of oxidation and the development of oxidation rims (bright edges) around the grain. Such highly oxidised coals are reported to be difficult to burn effectively in thermal power stations.

Photomicrographs (Fig. 3.7) showed the typical oxidation rims formed by the heating of crushed samples (< 3 mm) at 250 °C. In addition to oxidation, microfissures are reported to be associated with the quick release, in substantial quantities, of gas in the final stage of carbonisation. Occasionally, vitrinite is surrounded by darker edges (or rims) due to the formation of humic acid (soluble in KOH). Oxidation rims are favoured by coal oxidised at temperatures above 200 °C [14].

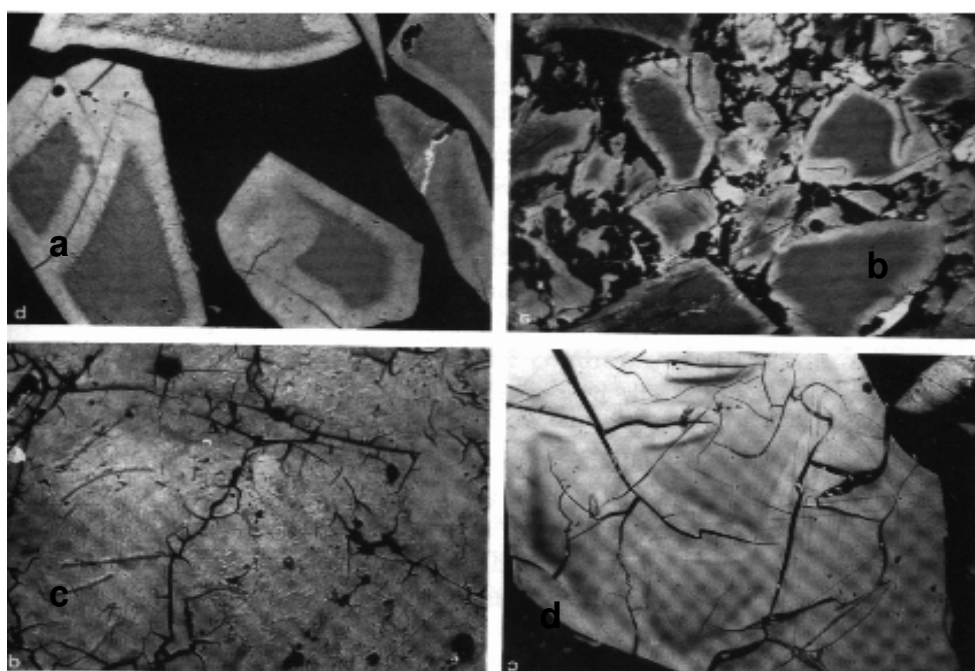


Figure 3.7: Photomicrographs of the polished surface of oxidised coal carbonised at 300 °C (oil immersion) [14]

- (a) Oxidation rims of coal heated at 300 °C
- (b) Oxidation rims of bituminous coal after heating at 250 °C for 120 min
- (c) Oxidation rims of coal heated at 300 °C after 300 min
- (d) Strongly weathered coking coal with fine pores, desiccation cracks, dark oxidation rims and black holes.

3.2.5 The influence of additives on carbonisation

The thermal reactions of carbonisation can be altered considerably through the use of certain additives. These are chemical substances that influence the thermoplastic properties of coal. Their effect on coal structure takes place via active centres of the coal macromolecules (functional groups, labile hydrogen) and influences the condensation reactions at pre-coking temperatures with the evolution of free radicals at increasing carbonisation temperatures. This effect depends on the nature of the additive used, the amount added and also the structure of the parent coal [95].

3.2.6 The influence of sulphur on carbonisation

Little is known about the effect of sulphide on the carbonisation of coal. However, elemental sulphur has been used extensively as an additive. Sulphur could increase the yield of carbon obtained from acenaphthylene. High sulphur dosage in the starting carbonaceous material is non-graphitising. The reverse was found to be true for lower levels of sulphur [67, 98, and 99]. Sulphur-containing radicals were proposed as intermediates in some reactions. When it was incorporated (as sulphur heterocyclic compounds) into strained ring systems, it was possible to eliminate sulphur readily in the early stages of carbonisation [100, 101]. The reaction of sulphur with aromatic hydrocarbons has been reported to give sulphur-containing polymers, which were stable at high temperatures [102].

Elemental sulphur has also been used extensively as a dehydrogenating reagent in the synthesis of polycyclic aromatic hydrocarbons and their derivatives [103]. At temperatures above 200 °C, sulphur extracts hydrogen from aromatic compounds [17]. Further reaction of sulphur with aromatic compounds gave Ar–S–Ar-type compounds [104, 105]. Subsequently, molecular condensation of aromatics with or without the incorporation of sulphur significantly increased their softening points and carbon yields. Shevkoplyas showed that on carbonisation,

thioether C-S bonds are broken to release active fragments that could participate in radical polymerisation, addition and substitution reactions [106].

3.2.7 The carbon solid and its influence on carbonisation

The structure of carbon black (Fig. 3.8) has larger layers. Ergun made a careful analysis of the radical distribution functions of a carbon black [107]. The analysis indicated the presence of extensive but faulty stacking, rather than short stacks of small layers. However, the most easily appreciable evidence for the existence of extensive but defective layers in a graphitisable carbon black comes from the electron micrographs, which showed visible orientation of the atomic layers. The graphitic layers visible in a carbon layer were significantly larger than those that a conventional X-ray diffraction analysis would have shown. The lower values of X-ray diffraction analysis were considered to be attributable to layer plane bending due to non-basal edge dislocations [107].

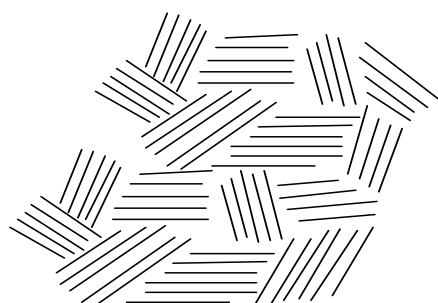


Figure 3.8: The line diagram of carbon black [107]

Carbon black is widely used in polymers as a filler of free space made by the grains of conductive materials in the rubber industry (90 % of world carbon black consumption), and as a black pigment. It is known to provide an enhanced ultra-violet stability to the polymers. Its performance property is explained by its chemical structure and physical properties. Its end-use depends on its particle

size distribution, the morphology of the particles and aggregates, its specific surface area, its elementary grain microtexture, its surface chemical bonds, etc [108]. The most common constituents of carbon black are a polyaromatic structure containing hydroxyl, carboxyl and quinone groups, which are prone to absorb ultra-violet light, and smaller particles (1-30 nm) with an ordered microstructure and a smooth surface [109].

There are many reports about the formation of carbonaceous mesophase spheres and the influence of inert solids [110 - 116]. Mesophase nucleation is initiated homogeneously because the chemical composition of the precursor pitch and the dynamic motion in the fluid are related to the nucleation of the mesophase spheres [110, 111]. Brooks and Tailor [72, 78] found that primary quinoline-insoluble and carbon blacks in coal tar pitch, gathered on the surface of the mesophase spheres, tend to produce a larger number of smaller spheres by limiting growth and coalescence [117, 118, 119]. Further work showed that there was no significant effect on the nucleation or the rate of mesophase formation. However, Kuo *et al.* noticed the difference in the size and structure of primary quinoline insoluble and carbon black [120] The primary quinoline is distinct from carbon black because it has a broader particle size distribution and a different shape, whereas carbon black forms chain aggregates that are well defined by transmission electron microscopy. There was no indication of carbon black behaving as nucleation centres for the mesophase formation [121].

It has been reported that the presence of carbon black in carbonisation systems delays the appearance of liquid crystals and causes to some degree the supersaturation of mesogens so that they do not precipitate [120]. Gentziz *et al.* studied the effect of carbon additives on the mesophase induction period of Athabasca bitumen [121]. Without carbon additives, the mesophase occurred after 61 to 67 min at reaction temperatures of 450 °C to 440 °C respectively. With carbon additives (ca. 5 wt %), the mesophase formation time was shortened to almost 45 – 50 min. However, the coke was reported to have a surface area of

1.65 m²/g, with enhanced bitumen fluidity and a large-textured mesophase [121]. Such supersaturation is thought to lead to a large number of smaller sized spheres. The interaction between carbon black and the mesophase is believed to take place in the early stage of carbonisation.

The surface functionality of carbon black is thought to advance its chemical interaction with the pitch [122]. Carbon black enhances mesophase pitch formation by increasing the number of spheres through restricting their coalescence [123]. Korai *et al.* showed that carbon black enhances the nucleation and inhibits the growth and coalescence of the mesophase spheres [124, 125 and 126]. Kanno *et al.* showed that a 5 % carbon black addition is sufficient to suppress the swelling of mesophase pitch by initiating pyrolysis at lower temperatures, thus avoiding the intense evolution that leads to severe swelling and to an increase in the size of the optical units [127].

Pyrolysis of coal-tar pitch showed that adding 10 % of various polymers increases the kinetics of conversion and affects the morphology of the mesophase. The result is an accelerated growth of the mesophase and an increase in the proportion of areas of isotropic appearance in the optical texture [128]. In a similar study in which quinoline-insoluble material (inert material) was added to coal-tar pitch, it was found that the inert material tended to concentrate on the surface of the mesophase spheres. This was reported to inhibit the growth and coalescence of the spheres, leading to the deterioration of the coke's optical texture [74, 116 and 129]. It was established by Jakab and Blazso that carbon black has an influence on chain cleavage and on the H-transfer reaction in polypropylene [117]. It participated in the termination of the chain reactions, resulting in a reduced yield of the oligomers from vinyl polymer. Its involvement in the H-transfer reaction was confirmed by increased yield of the hydrogenated product [130].

The interaction of carbon black with pitch is temperature-dependent ($< 425\text{ }^{\circ}\text{C}$). However, hydrogenation, polymerisation and an increase in carbon yield did not affect the pitch fluidity. Consequently, the porosity of the coke was observed at an initial stage, with the formation of a smaller mosaic texture [131]. When 10 % of carbon black was dispersed in pitch, chain-like aggregates that possessed a 3D-expandable cage structure were formed. The structure hindered the growth and stacking of mesophase molecules, thus reducing the size of the optical units to provide a fine-grained mosaic texture [122].

3.3 Chemistry of carbonisation

Carbonisation is considered to be a process in which a small aromatic structure is polymerised to an aromatic polymer, which ultimately achieves the three-dimensional order of graphite. Aromatics are the key building blocks for carbon, so that non-aromatic structures are first aromatised before undergoing the carbonisation process. For example, the aliphatic polymer polyvinyl chloride thermally converts to a pitch containing polycyclic aromatic structures, prior to the formation of carbon [131, 132]. The overall process of carbonisation is exceedingly complex. However, the individual processes that represent some of the major reactions involved in the pyrolysis of aromatic hydrocarbons can be considered: C-H, C-C bond cleavage to form reactive free radicals, molecular rearrangement, thermal polymerisation, aromatic condensation and elimination of side-chains.

Although all these processes can occur in parallel during carbonisation, they can be considered separately from a mechanistic viewpoint. The initial thermal reaction in the carbonisation of an aromatic hydrocarbon is only poorly understood, but it is believed to involve the formation of free radicals. There are two types of radicals that can be formed by bond cleavage in the aromatic molecule. The first is a σ -radical produced by breaking an aromatic molecule. This reaction is a high-energy process since the bond dissociation energy is of

the order of 100 kcal/mole [133]. The σ -radical intermediate is very unstable and the free electron is localised. For example, the naphthyl radical has been detected by electron spin resonance only when frozen in a solid matrix at 77 kcal/mole. The second type of radical is an aromatic π -radical, which is considerably more stable. Much less energy (77 kcal/mole) is needed to break the methyl C-H bond in toluene. The unpaired electron is resonance-stabilised and simple π -radicals, such as the benzyl radicals, can be detected by electron spin resonance at room temperature [133, 134].

Stein *et al.* used principles of thermochemical analysis to predict the initial reaction pathways in the pyrolysis of polynuclear aromatic hydrocarbons [135, 136]. The π -radical (I) could be generated by a small amount of the unstable anthryl σ -radical. Theoretical studies such as these, coupled with recent experimental breakthroughs in observing unstable radicals, could greatly clarify the initial reactions of carbonisation [136].

Once formed, the reacting intermediate can undergo direct polymerisation as in the formation of naphthalene polymer from naphthalene. These initial polymerisation reactions involve the loss of hydrogen, which can often be accomplished through internal hydrogen transfer. Hydrogen transfer in pyrolysis is important because major condensable volatile materials (identified during the pyrolysis of several polynuclear aromatic hydrocarbons) are produced. These products all consist of hydrogenated derivatives of the original compound, with hydrogen added at the most reactive position in the molecule [136].

An important step in the early stages of carbonisation is the thermal rearrangement. It is this reaction that often makes it difficult to relate the starting structure to the subsequent course of graphitisation. Research on the polymerisation of acenaphthylene and bifluorene showed that an unstable five-membered ring is transformed to a stable six-membered ring system without the loss of carbon atoms. It is believed that either the starting molecule or a

rearranged entity serves as the building block in carbonisation. One of the factors that make carbonisation so complex is believed to be numerous polymerisation sites in an aromatic molecule [137, 138]. In a simple dimerisation of anthracene, 11 reaction products are possible and, as the reaction proceeds, the number of isomeric structures increases rapidly.

The site in the aromatic ring at which polymerisation predominantly occurs can be predicted. Various reactivity parameters are used, including free valences, unpaired spin densities, localisation energies, and thermochemical kinetic analysis [52, 61, 63]. Steric effects are, however, important in the polymerisation process and can override reactivity factors. The polymerisation process of aromatic hydrocarbons occurs in two stages, viz. the condensed or non-condensed polymers. In naphthalene, the loss of two hydrogen atoms between two reacting molecules leads to polymers in which the units are linked by single bonds. An additional loss of two hydrogen atoms produces a fully condensed polymer (Fig. 3.9). Although the non-condensed and condensed polymers have virtually the same molecular weights, they vary considerably in structure and properties. The non-condensed polymers are non-planar and their reactivities and ionisation potentials change very slowly with increasing polymerisation. The condensed polymers are fully planar and show marked changes in reactivity and ionisation potential with increasing size. The relative role of these two processes is thought to be critical in carbonisation [139].

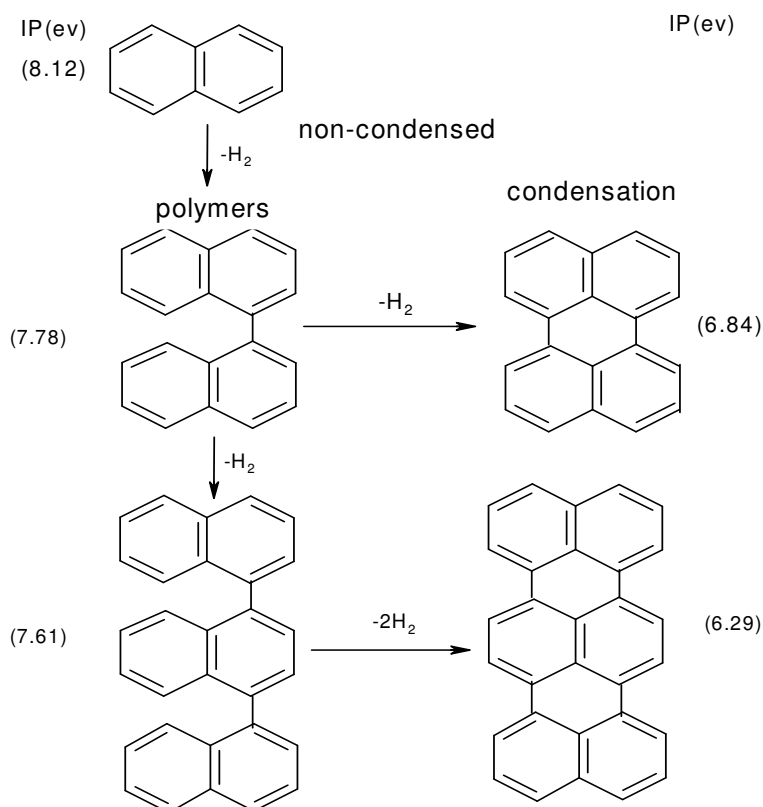


Figure 3.9: Polymerisation-condensation process in carbonisation [139]

Thermal polymerisation pathways were determined for a number of aromatic hydrocarbons. In the pyrolysis of anthracene, a number of initial non-condensed products were identified [133, 140]. However, only certain of these structures, which have the right steric conformation to undergo an additional dehydrogenation reaction to give a fully condensed molecule containing the most reactive 9-position in the anthracene ring, do achieve this result (Fig. 3.10).

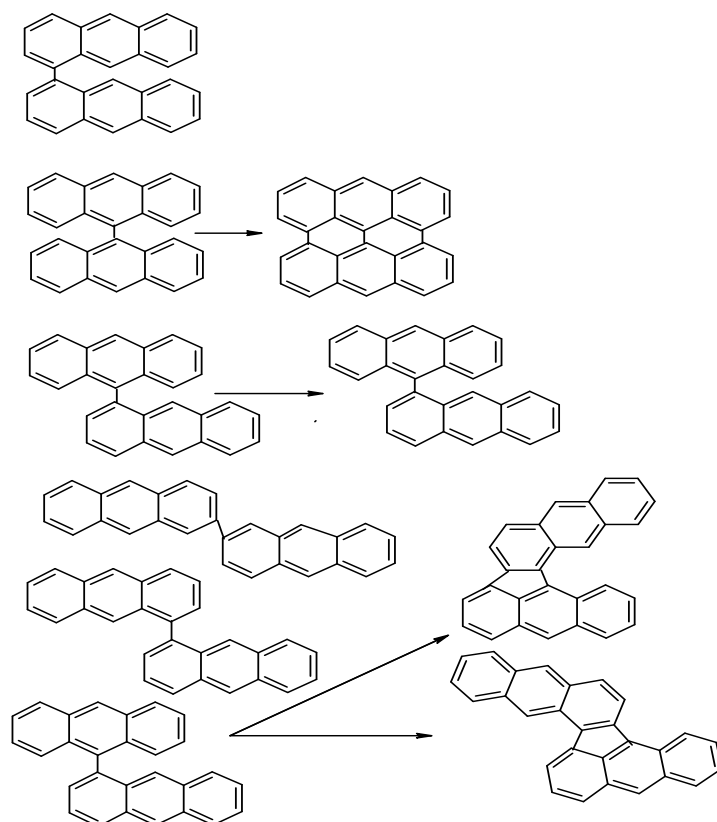


Figure 3.10: Reaction products from the pyrolysis of anthracene [133]

Research data from the pyrolysis of naphthalene showed that polymerisation at the most reactive 1-position leads to naphthalene polymers which can form fully condensed polymers composed of only six-member rings, while polymerisation utilising the less reactive 2-position can inhibit condensation (Fig. 3.11).

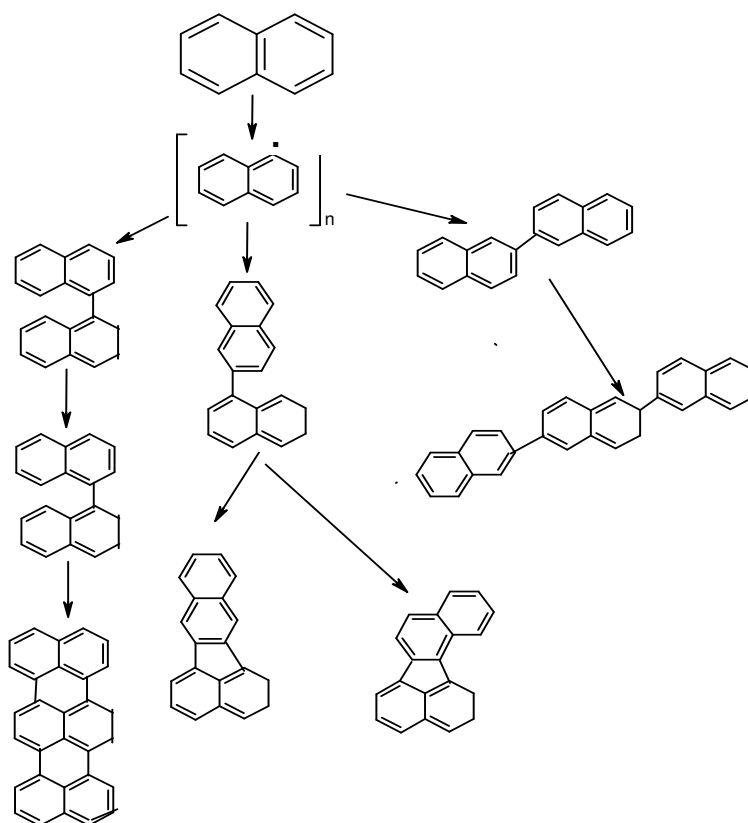


Figure 3.11: Reaction products from the pyrolysis of naphthalene [133, 141]

Lewis and Singer [142] used the reaction scheme in Fig. 3.12 to show how alternate radicals are involved in the polymerisation-condensation process in carbonisation. In naphthalene, a non-condensation polymer (111) is formed by rapid polymerisation. This polymer contains three non-condensed naphthalene units and a total of 30 carbon atoms. The loss of a single hydrogen atom from the polymer leads to a free radical (1V), which contains 30 carbon atoms with a single sp^3 tetrahedral carbon. The total aromatic π -system contains 29 carbon atoms and the unpaired electron is stabilised by resonance delocalisation. The loss of an additional hydrogen atom would create a fully condensed molecule, but would not result in a substantial increase in resonance stabilisation. A further complication of the carbonisation process is that the eventual polymerisation to carbon occurs in two dimensions [142].

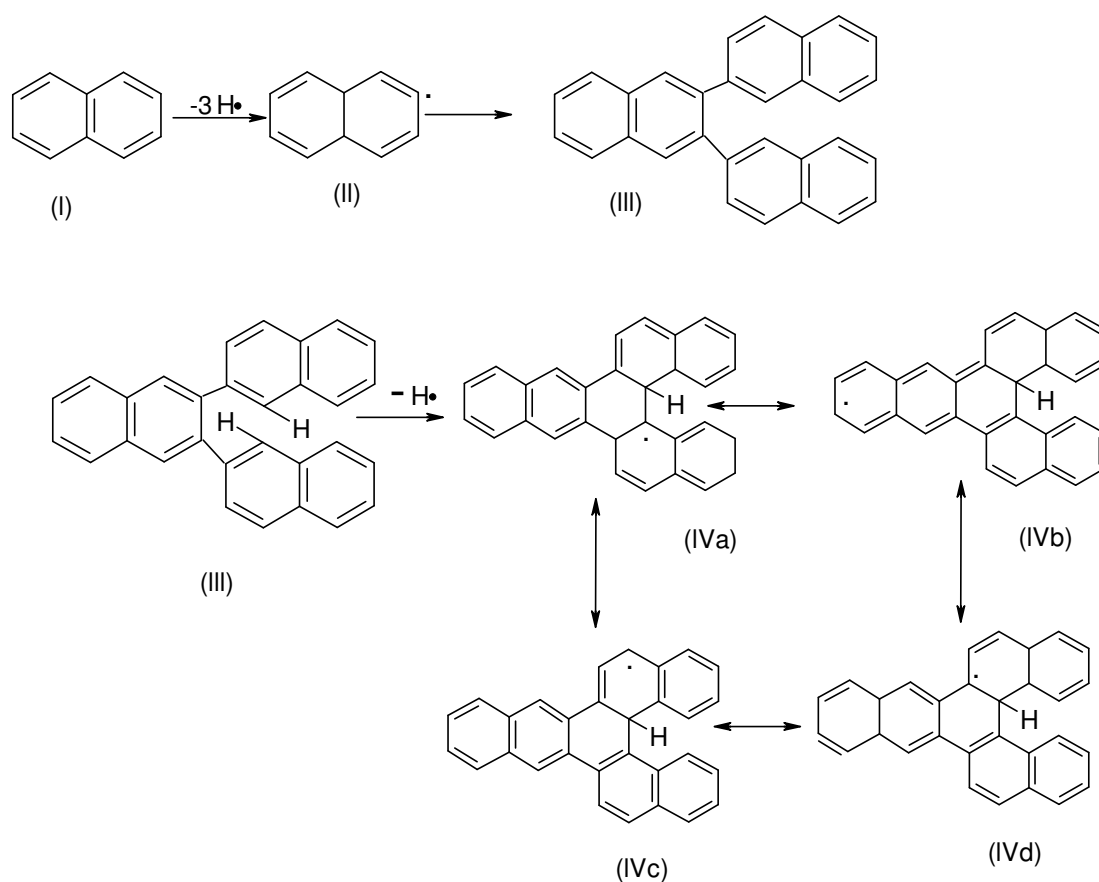


Figure 3.12: Formation of stable odd-alternate free radical structures during carbonisation [142]

The key to this process is how well the aromatic building blocks polymerise to develop a perfect graphitic network. Fig. 3.13 shows how the molecule zethrene, identified from the pyrolysis of zenaphthylene [63, 143] has the perfect shape and reactivity to polymerise in two dimensions to a planar graphite-like structure without vacancies.

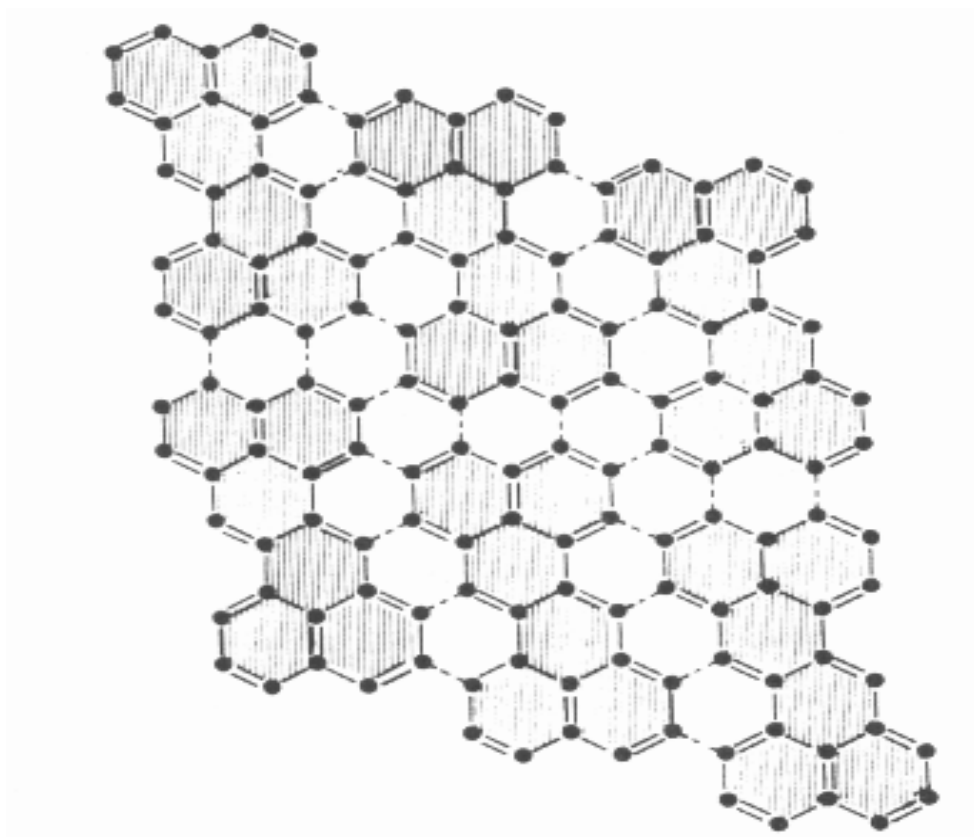


Figure 3.13: Two-dimensional polymerisation scheme for zethrene [63]

In contrast, poorly graphitising compounds such as tetrabenzonaphthalene, which has a non-planar structure, cannot polymerise without creating vacancies.

It can be concluded that carbonisation involves a stepwise molecular rearrangement in which intermediates formed through radical formation condense into solid coke on further heat treatment. The intermediates formed are radicals generated by homolytic cleavage of bonds and condense into solid graphitising or non-graphitising carbon. The intermediate stage formed during carbonisation is called 'mesophase'. This is a liquid phase, which is rich in aromatic radical produced around 400-500 °C as coal of particular rank soften

and swells from trapped gas and produce an anisotropic mosaic coke texture. This liquid phase is formed from spheres, which grow and coalesce into isotropic phase that solidifies to give a solid coke. Further heat-treatment of the coke produce graphite whose quality is measured by the d-spacing of orientated layers and calculated to be 3.354 Å. The mesophase is inhibited by the presence of oxygen. The aromatic compounds are oxidised by the oxygen into quinines intermediates that loose carbon dioxide to form non-planar radicals with subsequent decrease in the degree of graphitisation. Carbon additives inhibit formation of the mesophase by suppressing release of volatiles during carbonisation. Reaction of sulphur with aromatics compounds occurs during carbonisation and form sulphur containing polymer, which through sulphur radicals form S-Ar-type polymers. Molecular condensation of aromatics with sulphur is known to increase the softening points and carbon yields of the cokes.