



2

Literature Study

2.1 Introduction

The process and mechanism whereby coal is converted to valuable chemical products through thermal degradation (devolatilization) require a thorough understanding of the characteristics and nature of coal. An in-depth look at the properties defining the coal structure and the behaviour of a particular coal provides valuable information regarding the possible pathways by which devolatilization occurs, as well as regarding the myriad of valuable chemical entities that can be produced through this process. Therefore the following topics will be addressed in the literature study:

An overview regarding the nature of coal and coal utilization is given in Section 2.2., which includes a brief discussion of available, advanced analytical techniques for investigating coal structure. A detailed discussion of devolatilization as a coal conversion process is provided in Section 2.3, where the following relevant topics are addressed:

- Mechanisms of the devolatilization process;
- Some industrial applications of devolatilization;
- Products obtainable from the devolatilization process and further processing potentials;
- Available analytical techniques for assessing the characteristics of devolatilization products.

Strategies for investigating coal devolatilization (quantitatively and kinetically) is attended to in Section 2.4, while a thorough discussion regarding the factors affecting devolatilization, both from a coal characteristic- and operating viewpoint, is provided in Section 2.5. The factors are subsequently discussed under the following headings:

- Coal properties affecting the efficiency of devolatilization;
- Operating conditions affecting the efficiency of devolatilization.

Finally the topics of coal devolatilization kinetics and -modelling are addressed in Section 2.6.

2.2 The nature of coal and coal utilization

2.2.1 Coal as an important fossil fuel

Coal is known as the product of the metamorphism of primeval vegetation, of between 200 and 300 million years ago, which underwent progressive chemical- and physical alteration through geological time (Falcon & Snyman, 1986; Horsfall, 1993; Meyers, 1982). More generally coal is therefore described to be an “organic sedimentary rock” which, in comparison to other rock types, contains more organic species than inorganic species. The mechanism whereby coalification (metamorphism) occurred had a marked effect on the coal properties and coal processing technologies present in different countries across the globe.

During the coalification process the accumulated mass of vegetation from swamps and especially great river deltas, was buried due to tectonic movements and gradually inundated by the inflow of mineral-containing water (Horsfall, 1993). In addition, the buried mass was eventually subjected to both temperature- and pressure changes through the course of time, which resulted in the formation of both different ranks of coal and different coal seams (Horsfall, 1993; University of Kentucky, 2007). The resulting properties of the different ranks (lignite, bituminous, anthracite etc.) of coal and coal seams are mainly attributed to (1) the type of accumulated vegetation, (2) the conditions under which the vegetation accumulated and (3) the conditions under which coalification occurred. Furthermore, the significant difference between climatic conditions of different sections of the world did not only contribute to the coalification process but also attributed to the marked difference between the characteristic properties of typical northern hemisphere (Laurasian) and southern hemisphere (Gondwanaland) coals today (Cadle *et al.*, 1993; Horsfall, 1993).

One of the main differences between southern- and northern hemisphere coals is evident from the composition of the different macerals contained within these coals (Cadle *et al.*, 1993; Horsfall, 1993). Northern hemisphere coals are known to contain large amounts of vitrinite, low proportions of inertinite and only appreciable amounts of liptinite, whereas some of their southern hemisphere counterparts, especially those from South Africa, are characterised by

high levels of inertinite and lower vitrinite and liptinite contents (Cadle *et al.*, 1993; Horsfall, 1993). In particular, Gondwanaland coals have been found to contain large amounts of both semifusinite and inertodetrinite maceral groups. In South African coals, these low-reflecting semifusinites (more commonly known in South African petrology as “reactive semifusinites”) can contribute up to 60% of the total inertinite content (Hagelskamp & Snyman, 1988; Snyman & Botha, 1993, Van Niekerk *et al.*, 2008). Furthermore, coals from South Africa are characterised by substantially larger amounts of mineral matter (up to 30% in some cases) (Cairncross, 2001; Kruszewska, 2003; Snyman & Botha, 1993; Van Niekerk *et al.*, 2008).

The coalification process included the steady loss of hydrogen and oxygen entities from the accumulated mass, through the evolution of moisture and methane, which eventually led to a gradual increase in the carbon content of the formed coal (Horsfall, 1993). This was accompanied by other structural changes such as the diminishment of internal pore structures and the aromatization of straight chain carbon bonds to form condensed ring structures within the coal (Horsfall, 1993).

These chemical- and structural changes contributed to the formation of a wide range of coals of different maturity (or rank). This includes coals which exhibit large amounts of evolved tarry- and gaseous products upon heat treatment or combustion (bituminous coals), to coals that emit less volatile products (lean coals) and coals that emit negligible amounts of volatile species during coal conversion (anthracites) (Horsfall, 1993).

The difference in coalification conditions between the two hemispheres also had a marked effect on seam properties. It is believed that the metamorphism process in the northern hemisphere mainly resulted from increasing pressure and some temperature elevation, as the coal seams gradually became buried at deeper levels (up to 1 km or more) which resulted in a discernible variation in seam properties with depth. In contrast, however, less mature coals are observed in the southern hemisphere due to the fact that the coal seams tend to be much shallower. The steady loss of gaseous components and the increase in coal maturity of southern hemisphere coal seams were quite often accelerated by igneous intrusions which led to the partial carbonization of the particular coal seam (Horsfall, 1993).

The vast variety of different coal properties, as dictated by the coalification process, enables coal to be used in a number of different coal processing routes, which include either being used

as a process utility in the cement- and steel making industry and for electricity generation, or for the production of petrochemical and other important chemical products. Apart from electricity generation, petrochemical production is also of utmost importance for countries like South Africa who are mainly dependent on large coal reserves. The production of valuable chemical products from coal requires that the H/C ratio be altered. This can be accomplished by mainly three different coal conversion strategies, which include (1) devolatilization or thermal degradation, (2) direct liquefaction and (3) indirect liquefaction or gasification (Dadyburjor & Liu, 2003; DTI, 1999; Horsfall, 1993; Tsai, 1986.). Although gasification is the proposed coal conversion route in South Africa, the process of devolatilization still plays an important role as the initial step of most coal conversion technologies. A wide variety of chemical species can be produced from the devolatilization of coal and is therefore the process that is the most dependent on the organic properties of the coal (Kristiansen, 1996; Solomon & Hamblen, 1985).

2.2.2 Assessing the fundamental structure of coal

A detailed description and fundamental understanding of the coal structure is one of the most important and difficult problems facing coal technologists today. This stems from the fact that in order to fully understand coal behaviour, a well-based knowledge of the chemical structure of coal should be developed (Gupta, 2007; Meyers, 1982; Levine *et al.*, 1982).

In a response to understanding the fundamental properties of coal, numerous conventional analytical techniques such as proximate-, ultimate-, petrographic-, ash fusion temperature analyses etc. have been developed (Gupta, 2007). Although these analyses provide valuable insight into elemental- and maceral composition etc. of different coals, they do however only give an overall or bulk description of coal (Gupta, 2007). The elucidation of the coal structure has however improved remarkably over the last few decades and new advanced analytical strategies such as ^{13}C NMR, Py-MS, chromatography, FTIR, solvent swelling, XRF, XRD, CCSEM, MALDI-TOF MS and HRTEM have emerged (Gupta, 2007; Kabe *et al.*, 2004; Smith *et al.*, 1994, Speight, 1994). These techniques have all been developed in an attempt to more accurately describe both the organic- and inorganic counterparts of coal.

A fundamental understanding of the thermal behaviour (devolatilization) of coal therefore requires a thorough understanding of the organic counterpart of this valuable entity. With the addition of conventional analytical techniques, advanced strategies such as ^{13}C NMR, FTIR,

HRTEM, MALDITOF-MS and XRD provide an additional perspective on the molecular constituents of coal in particular. These advanced techniques are not yet fully understood, due to their complexity and heterogeneous nature, but by combining information obtained from different techniques it is possible to obtain a comprehensive understanding of the coal structure (Lu *et al.*, 2001). It is therefore worth it to mention some details regarding these advanced analytical techniques.

Solid state ^{13}C Nuclear Magnetic Resonance spectroscopy (^{13}C NMR) provides a valuable non-destructive analytical tool for identifying different chemical-structural features of the organic matter in coals and coal chars (Gupta, 2007; Smith *et al.*, 1994; Solum *et al.*, 1989; Speight *et al.*, 1994; Suggate & Dickinson, 2004). Various ^{13}C NMR analyses are available including: cross-polarization with magic-angle-spinning (CP-MAS), dipolar dephasing (DD), single pulse excitation (SPE), MAS with block decay (BD) and chemical shielding anisotropy (CSA) measurements (Smith *et al.*, 1994; Van Niekerk, 2008). These different techniques have been applied numerously in order to investigate the chemical structure of whole coals and macerals (Alemany *et al.*, 1984; Miknis *et al.*, 1988; Pugmire *et al.*, 1982; Soderquist *et al.*, 1987; Van Niekerk *et al.*, 2008; Wilson *et al.*, 1982).

The CP-MAS technique has been widely used for establishing the relative number of aromatic and non-aromatic carbons, while DD measurements provide additional information regarding protonated and non-protonated carbon species (Smith *et al.*, 1994; Solum *et al.*, 1989, Van Niekerk, 2008). The combined CP-MAS and DD results provide the estimation of twelve structural parameters for describing the carbon skeletal structure of coal. This includes the determination of the aromaticity of the coal, the number of bridgehead carbons, the aromatic cluster size, the number of side chains, bridges and loops and the theoretical molecular weight of a cluster to only name a few (Orendt *et al.*, 1992; Smith *et al.*, 1994; Solum *et al.*, 1989). A detailed discussion of the determination and estimation of these structural parameters are provided in Smith *et al.* (1994) and Solum *et al.* (1989 & 2001).

Another useful non-destructive technique for retaining valuable information about the functional groups in coals and coal chars, is Fourier transform infrared spectroscopy (FTIR), which utilises the absorption of infrared radiation to identify both bending and stretching molecular vibrations (Smith *et al.*, 1994). The observed wave numbers can therefore be assigned to different molecular functionalities (C, H and O functionalities) as described in Smith *et al.* (1994). FTIR

has been used extensively by numerous authors such as Cloke *et al.* (1997), Gilfillan *et al.* (1999) and Solomon *et al.* (1990) in the identification of the coal molecular structure.

Apart from being a useful technique for qualitatively and quantitatively evaluating the mineral composition of coal, X-ray diffraction (XRD) has proved to also be useful for investigating the organic matrix of coal (Gupta, 2007; Lu *et al.*, 2001; Speight, 1994). Carbon materials, such as coal, have been found to contain turbostratic structures constituted by many graphite crystals (Yang *et al.*, 2006). With the application of simple mathematical equations to the obtained XRD results, important structural features such as fraction of amorphous carbon (X_A), aromaticity (f_a) as well as crystallite size and -distribution can be determined (Lu *et al.*, 2001). Aromaticity results obtained from XRD analyses have been shown to be quite consistent with aromaticity determinations from ^{13}C -NMR, which provide an additional reference to NMR data (Lu *et al.*, 2001; Orendt *et al.*, 1992; Solum *et al.*, 1989). This method has been successfully used by numerous investigators such as Lin and Guet (1990), Lu *et al.* (2001), Van Niekerk (2008) and Schoenig (1983).

Recently the occurrence of high-resolution transmission electron microscopy, also known as HRTEM, has provided a way of visually investigating the coal molecular structure. The observations made by this technique have significantly contributed to results obtained from XRD analysis. As a result of this, authors such as Sharma *et al.* (2000a) qualitatively observed a layered, graphitic microcrystal for bituminous coal, while Russel *et al.* (1999) investigated the coking transformation of Pittsburgh coal using HRTEM. In addition, quantitative image analysis of lattice-fringe extracted HRTEM micrographs has become a successful and powerful tool for the evaluation of coal structure (Sharma *et al.*, 2000b & 2000c; Aso *et al.*, 2004) and even coal chars (Sharma *et al.*, 1999; Shim *et al.*, 2000).

Molecular weight distribution is another critical parameter for understanding the fundamental structure of coal. In this particular case mass spectroscopic methods have provided a way of estimating ring distributions and identifying some individual molecular ions comprising the coal structure (Speight, 1994). Accompanying this is the use of techniques such as solvent extraction, solvent swelling behaviour, devolatilization etc. (Mathews *et al.*, 2010; Speight, 1994). Various low molecular weight benzenes, phenols, and naphthalenes, as well as C_{27} and C_{29-30} hopanes and several C_{15} sesquiterpenes could be identified with the use of both gas chromatography combined with mass spectrometry (GC-MS), as well as pyrolysis gas

chromatography combined with mass spectrometry (Py-GC-MS) (Speight, 1994). These techniques have therefore also shed some insight into the fate of heteroatom (O, N & S) functionalities present in coal (Speight, 1994). Furthermore, the molecular weight between cross links in the coal structure could also be evaluated through solvent swelling studies (Larsen *et al.*, 1985; Painter, 1990; Van Niekerk, 2008). The use of laser-desorption ionization time-of-flight mass spectrometry has also been widely used in estimating the molecular mass distributions of coals and coal derived liquids (Herod *et al.*, 2007; Van Niekerk, 2008). Estimated molecular weight values for coal do however range over several orders of magnitude mainly due to the wide variety of techniques available for establishing coal molecular weight (Mathews *et al.*, 2010). A combination of the different methods is therefore necessary for an improved understanding of the molecular weight of coal. The vast amounts of chemical and structural information have led researchers to at least one consensus: that coal is a very complex- and heterogeneous system. The use of conventional- as well as advanced analytical techniques has, however, enabled the deduction of some representations of the organic structures of coal as illustrated in Figure 2.1 (Levine *et al.*, 1982).

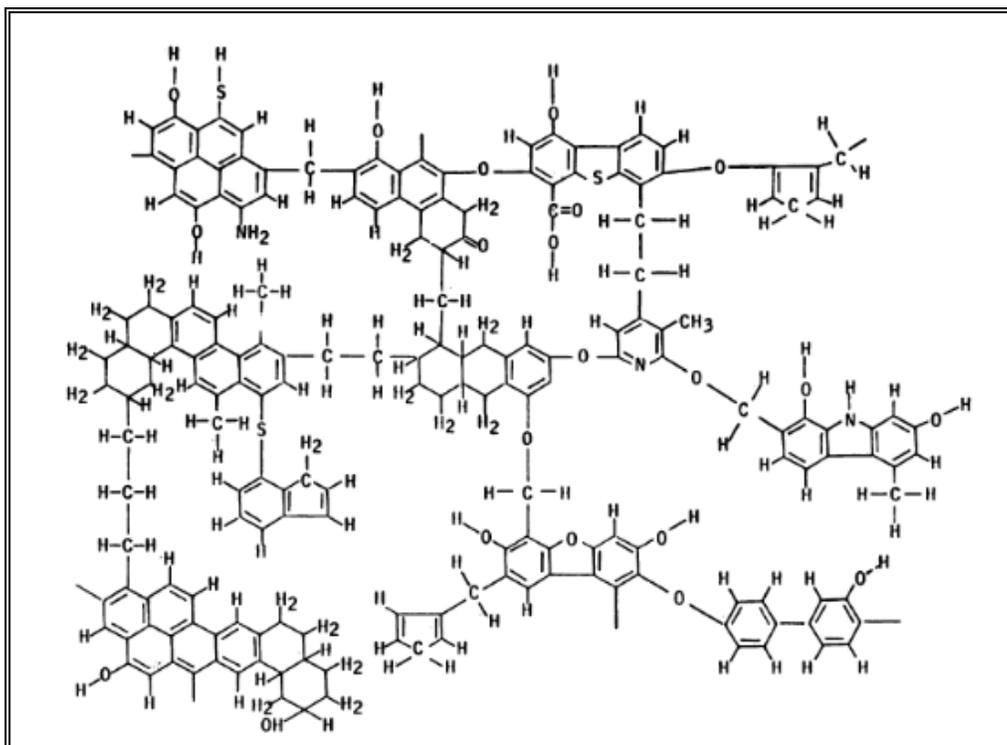


Figure 2.1 Representative structure of bituminous coal (taken from Levine *et al.*, 1982).

The addition of molecular modelling capabilities has, however, provided an additional perspective of envisaging the three-dimensional structure of coal and understanding coal behaviour, as illustrated by Van Niekerk and Mathews (2008) in Figure 2.2.

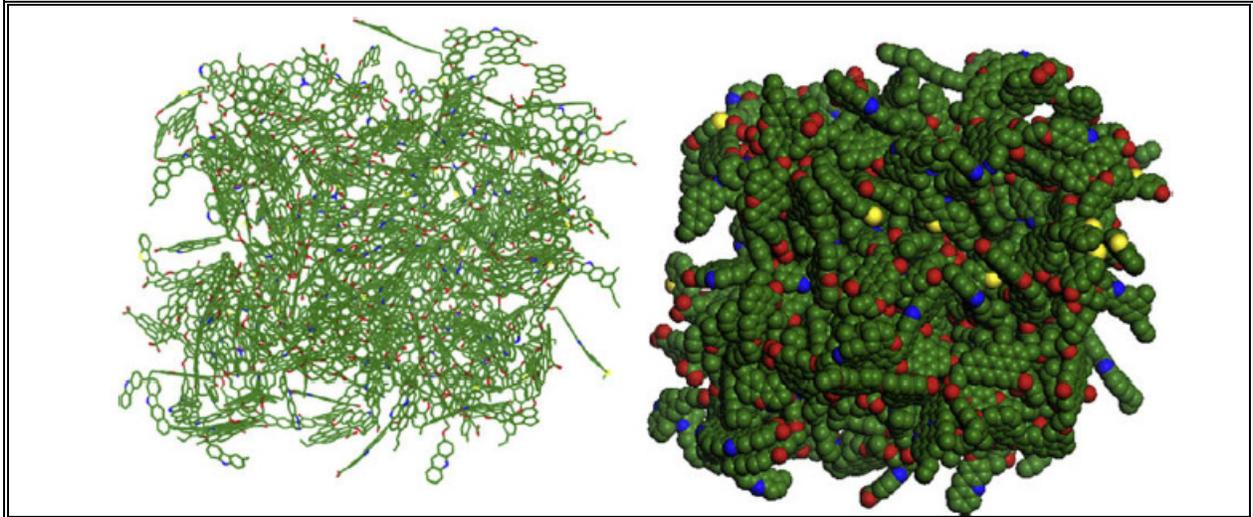


Figure 2.2 Three-dimensional molecular representation of inertinite-rich South African coal (taken from Van Niekerk, 2008; and Van Niekerk and Mathews, 2008).

2.3 Devolatilization as a coal conversion process

2.3.1 Nature and scope of coal devolatilization

Coal devolatilization, as an initial coal conversion step, forms an integral part of many coal processing technologies, where it can account for up to 70% of the weight loss of the coal used (Solomon *et al.*, 1985). As specified previously it is also the process that is most dependent on the organic features of the coal (Kristiansen, 1996). In general, the terms devolatilization, pyrolysis, thermal decomposition and carbonization are used interchangeably to refer to the process where coal is thermally decomposed or degraded to form volatile and non-volatile products. It is however custom to refer to the thermal decomposition process as coal devolatilization or coal pyrolysis, whereas carbonization more directly refers to the commercial process of char or coke production at temperatures in excess of 500°C (Speight, 1994). The details of this commercial process will be attended to in Section 2.3.3.

The heating of coal at elevated temperatures under inert conditions (pyrolysis) or under an H₂ atmosphere (hydrolysis) involves the thermal decomposition of coal to form a hydrogen-rich fraction, consisting of gases, liquor (low molecular weight liquids) and tar (high molecular weight liquids); and a carbon-rich solid residue, normally referred to as char/coke (Kristiansen, 1996; Speight, 1994).

A variety of chemical and physical changes occur when coal is heated to temperatures where devolatilization occurs. It is generally accepted that the onset temperature for devolatilization is approximately 350°C, although notable changes are observed before this temperature is reached (Speight, 1994). These changes normally involve the formation of low molecular weight species (Hessley *et al.*, 1986; Speight, 1994). As a result water, absorbed methane and CO₂ will appear as products at temperatures close to a 100°C. Occluded methane and CO₂ have, however, been reported to be driven off at temperatures as high as 200°C (Smith *et al.*, 1994). In addition, coals, such as lignites, with high proportions of carboxylic functional groups will undergo thermal decarboxylation to produce CO₂ at temperatures just in excess of a 100°C (Speight, 1994).

In the temperature range between 200°C and 370°C a wide variety of low molecular organic species are evolved, which include aliphatic- (methane and its higher homologues and olefins) and lower molecular aromatic compounds (Smith *et al.*, 1994; Speight, 1994). Products evolved in the excess of 370°C are generally characterised as polycyclic aromatics, phenols and nitrogen compounds (Speight, 1994). Oxygen functionalities are eliminated as either water or oxides of carbon, while the decomposition of nitrogen- and organic sulphur species all generally occur in the temperature range from 200°C to 500°C (Smith *et al.*, 1994). This includes the formation of H₂ which typically occurs in the range of 400°C to 500°C. The production of H₂ reaches a critical maximum at temperatures close to 700°C. Finally tar formation is estimated to begin around 300°C to 400°C, with the maximum tar yield occurring at temperatures between 500°C and 550°C, depending on the characteristic properties of the coal (Smith *et al.*, 1994). The process whereby volatile evolution occurs is, however, very complex and a consensus regarding the chemistry of devolatilization is only beginning to emerge (Smith *et al.*, 1994). In one case the thorough use of advanced analytical- and molecular modelling techniques has led researchers such as Jones *et al.* (1999) to propose possible mechanistic routes for char and gas formation. The mechanism controlling devolatilization behaviour should therefore be viewed from both a physical and a chemical perspective.

2.3.2 Proposed mechanisms for coal devolatilization

2.3.2.1 Chemical mechanism

A simplistic overview of the chemistry behind the devolatilization process is provided by Solomon *et al.* (1988), who include a description of the different kinds of reactions (not necessarily all) which can possibly occur. As an illustration, a hypothetical representation of Pittsburgh bituminous coal's organic structure at different stages of devolatilization is provided in Figure 2.3 to assist in understanding the chemistry behind this complex process.

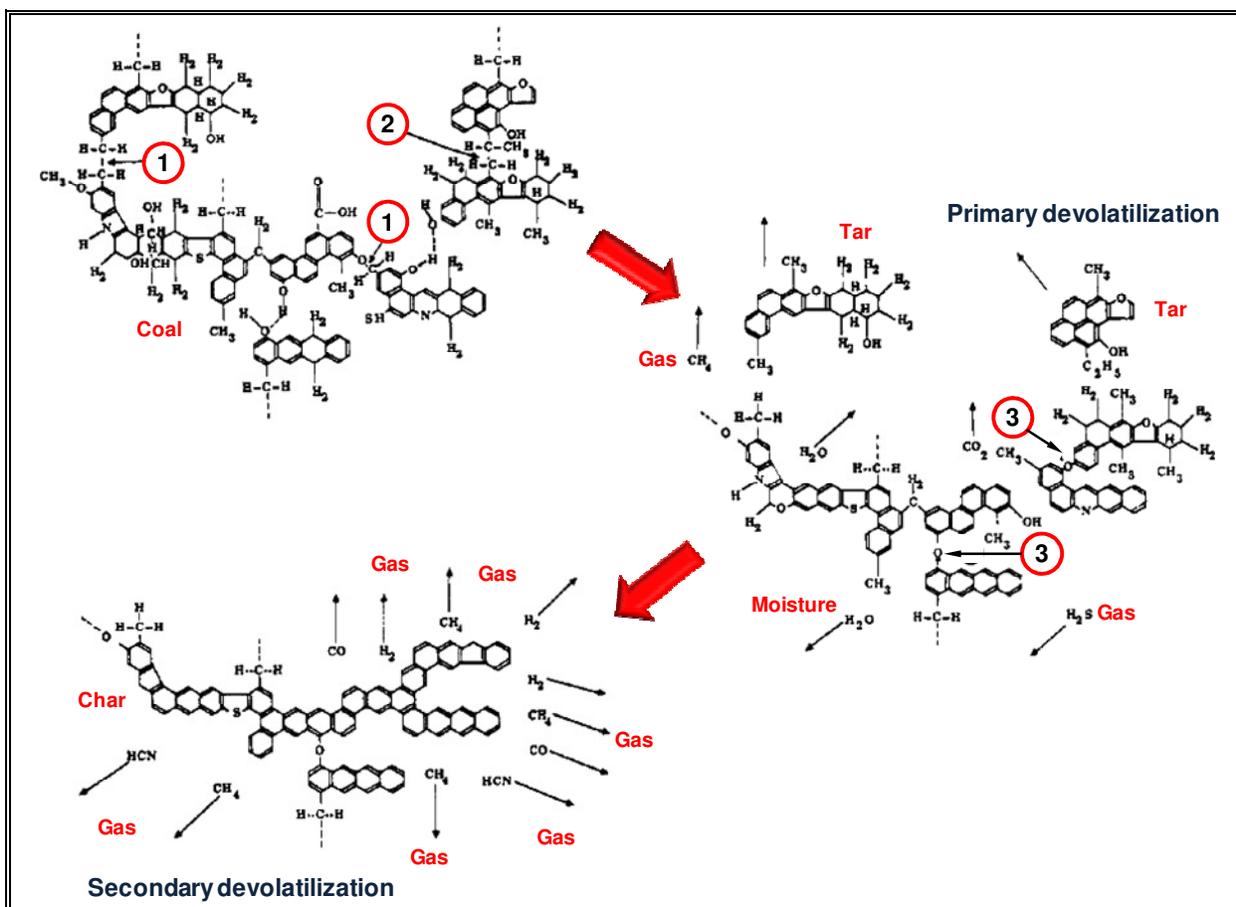


Figure 2.3 Hypothetical coal molecules during different stages of devolatilization (adapted from Solomon *et al.*, 1988).

The preliminary processes before the onset of coal devolatilization, in the temperature range between 200°C and 400°C, include hydrogen bond disruption, vaporization and transport of non-covalently bonded molecular phases and low temperature cross-linking of the coal structure. This subsequently leads to the formation of CO₂ and/or H₂O (Kristiansen, 1996; Smith

et al., 1994). A further increase in temperature leads to the primary- and secondary stages of devolatilization, which are graphically illustrated from a mechanistic viewpoint by Figure 2.4 (adapted from Göneç & Sunol, 1994). The primary stage of devolatilization is characterised by de-polymerisation- and cross-linking reactions; and coal thermoplasticity (Smith *et al.*, 1994).

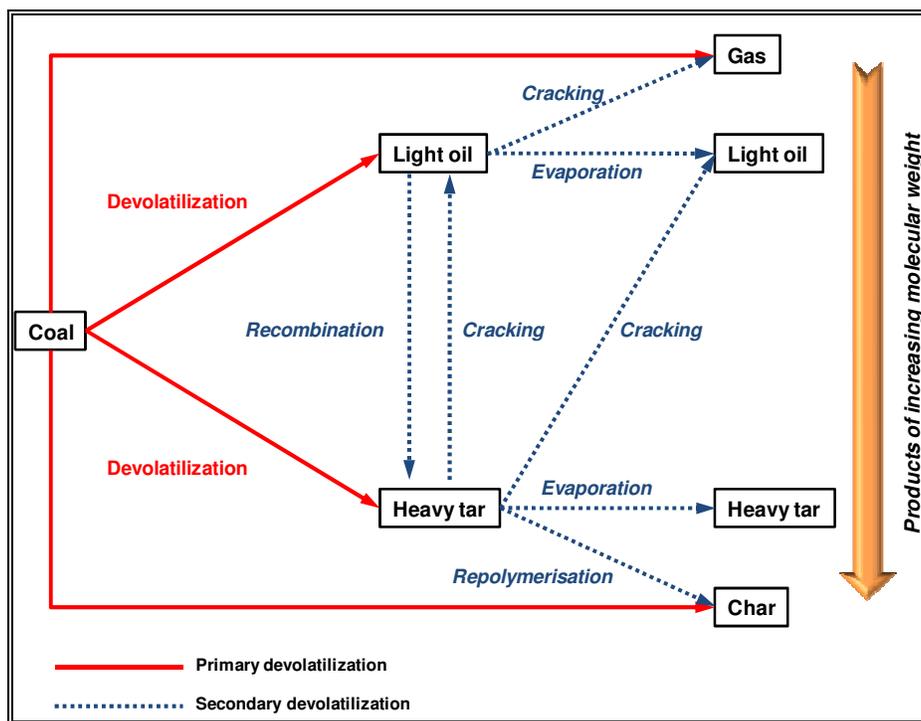


Figure 2.4 Mechanistic model of primary- and secondary devolatilization reactions.

It is during this stage that weak chemical bonds or bridges (labelled 1 and 2 respectively in Figure 2.3) are initially cleaved to form molecular fragments which increase the aromatic hydrogen content, due to the consumption of hydrogen from the hydroaromatic- or aliphatic functionalities. The subsequent cleavage of aliphatic hydrocarbon linkages can result in the formation of alkyl aromatics, alkyl radicals and aromatic ring structures (Jüntgen, 1987; Wanzl, 1988) which can be evolved as either light oils or tar if the molecules are small enough to vaporise under the specified devolatilization conditions and do not undergo secondary decomposition during molecular transport through the coal particle (Figure 2.3). In addition, the effect of metaplast formation (due to the de-polymerisation of the coal molecular structure), cross-linking and coal plastic behaviour significantly affects the tar yield, tar molecular weight distribution, fluidity and char surface area and -reactivity (Smith *et al.*, 1994). However, large molecular fragments, which do not evaporate, normally re-polymerise to form char. The additional scission of stronger aromatic carbon linkages and phenyl-carbon bonds is also

possible (Smith *et al.*, 1994). It has been shown that the cleavage of these two types of bonds are mainly due to the β -scission of radical intermediates (Stein, 1981), the hydrogenolysis of either free hydrogen atoms or cyclohexadienyl radicals or to the reverse radical disproportionation between aromatic and hydroaromatic species (McMillen *et al.*, 1987 & 1989; Smith *et al.*, 1994). The fate of oxygen functionalities is also important during devolatilization with aliphatic ether linkages counting amongst the weakest linkages to be most likely broken during this process (Smith *et al.*, 1994). With respect to the thermal reactivity of different oxygen functionalities, open ether structures are the most reactive, followed in decreasing order by aldehydes, ketones, phenols and finally furans (Brendenberg *et al.*, 1987). Oxygen is therefore removed as either water or carbon oxides during thermal degradation, most probably due to decarboxylation or dehydration reactions (Smith *et al.*, 1994). Accompanying this is the decomposition of other functional groups to produce light molecular weight gas species such as CO, CO₂, light aliphatic gases and CH₄ (Kristiansen, 1996; Smith *et al.*, 1994). The release of these gases contributes to additional cross-linking of the carbon matrix. Sulphur and nitrogen heteroatoms only play a minor role in the thermal degradation process. Organic sulphides have been shown to be reactive at temperatures lower than 750°C, whilst heterocyclic sulphur compounds only become reactive at temperatures exceeding 950°C (Calkins, 1987; Smith *et al.*, 1994). Aliphatic sulphur is normally converted to either aromatic sulphur or H₂S. In contrast however, nitrogen mainly reports to the tar or light oil fraction (pyrroles, pyridines, etc.) with some additional release of gases such as HCN, NH₃, etc. Finally, the depletion of hydrogen from the hydroaromatic- and aliphatic functionalities signals the end of primary devolatilization (Kristiansen, 1996).

Secondary reactions drastically alter product- and elemental distributions of especially the polycyclic aromatic hydrocarbons (PAHs) present in tar (Smith *et al.*, 1994). Furthermore phenols and aliphatic moieties contribute significantly to the formation of mono- and poly-aromatic units, which subsequently influence the aromaticity of the evolved tars. This is believed to occur due to Diels-Alder cyclization reactions of C₃ and C₄ olefins to produce cyclo-olefins, which are further altered by additional de-hydrogenation and decomposition (Cypres, 1987). The reactions occurring during the secondary stages of devolatilization are characterised by additional CH₄ evolution from methyl groups, the formation of HCN from ring nitrogen species, CO from ether bonds and H₂ from the condensation of ring structures (Kristiansen, 1996).

2.3.2.2 Physical mechanism

The devolatilization of coal is a dynamic process which is mainly dependent on the relative rates of bond breakage, cross-linking and transport phenomena such as mass- and heat transport (Kristiansen, 1996). Transport phenomena therefore significantly affect devolatilization behaviour, especially in large coal particles. The formation of tar in particular is generally characterised by the following progressive steps, which include mass transport limitations (Kristiansen, 1996):

- De-polymerisation of the coal matrix by cleavage of weak bridges to release small molecular fragments which make up the metaplast;
- Re-polymerisation or cross-linking of the molecular fragments to prevent further evolution of high molecular weight species. This involves the formation of char from the unreleased or condensed fragments;
- Molecular transport of the lighter tar molecules from the coal surface via combined vaporization, convection and gas phase diffusion (Gavalas, 1982; Kristiansen, 1996; Saxena, 1990);
- Volatile molecules within the coal particle are transported to the particle surface by different internal transport mechanisms, which are dependent on the plastic behaviour of the coal. Volatile transport in non-softening coals is therefore characterised by a condensed-phase diffusion process through the porous structure of the coal (Smith, 1981). In contrast, however, liquid-phase or bubble convective transport is the dominating mechanism occurring during volatile transport in softening coals (Gavalas, 1982, Smith *et al.*, 1994).

In addition, heat transport limitations can predominantly influence the devolatilization behaviour of particularly large coal particles. The yield of tar and the tar molecular distribution can be therefore significantly affected by time- and temperature gradients (Smith *et al.*, 1994).

2.3.3 Classification of coal carbonization/devolatilization processes

The commercial application of the devolatilization process is more commonly referred to as carbonization (Speight, 1994). Carbonization processes are well developed technologies, although in some cases devolatilization also forms the initial step for other coal conversion

processes such as gasification. Carbonization technologies can be generally classified as either low temperature- or high temperature processes. Low temperature carbonization is achieved by using temperatures in the order of 500 °C to 700 °C, whilst temperatures ranging between 900 °C and 1500 °C are generally used for the high temperature application (Speight, 1994). A brief overview regarding the different low temperature carbonization processes is provided in Table 2.1 (Lee, 1996).

Table 2.1 Summary of some known industrial processes including devolatilization (Lee, 1996).

<i>Process parameters</i>	<i>Lurgi-Ruhrigas</i>	<i>COED</i>	<i>Occidental</i>	<i>TOSCOAL</i>	<i>Clean Coke</i>	<i>Union Carbide Corp.</i>
Developer	Lurgi-Ruhrigas	FMC Corp.	Occidental	Tosco	U.S. Steel Corp.	Union Carbide Corp.
Reactor type	Mechanical mixer	Multiple fluidised bed	Entrained flow	Kiln-type retort vessel	Fluidised bed	Fluidised bed
Reaction Temperature (°C)	450-600	290-815	580	425-540	650-750	565
Reaction Pressure (bar)	1.0	1.4-1.7	1.0	1.0	6.9-10.3	69
Coal residence time	20 s	1-4 h	2 s	5 min	50 min	5-11 min
<i>Product yields (wt.%)</i>						
Char	55-45	60.7	56.7	80-90	66.4	38.4
Oil	15-25	20.1	35.0	5-10	13.9	29.0
Gas	30	15.1	6.6	5-10	14.6	16.2

Coals used for these commercial devolatilization processes are normally confined to the following criteria: (1) high volatile matter contents, (2) large amounts of producible tar, (3) medium rank and low oxygen content, (4) high hydrogen content and preferably low ash contents (Horsfall, 1993).

From a technological perspective, both fixed-bed and fluidised bed systems are used for carbonization, where the former can be heated either indirectly or directly. For fluidised bed technologies, direct contact with a heating medium is, however, required. Heat carriers can vary greatly and include: steam-oxygen mixtures (COED process), recycled gases, sand, ceramic balls (TOSCOAL), metal balls containing salt, re-circulating char particles (Lurgi-Ruhrgas), oxygen-free flue gas (Coalcon process), etc. (Lee, 1996; Speight, 1994). Down-stream processing of the obtained devolatilization products can also vary from process to process.

Furthermore, the yield and quality of the derived products (such as char, gas and tar) are mainly dependent on process parameters as well as coal characteristic properties, as is the case for all types of coal conversion technologies.

2.3.4 Valuable products obtainable from coal devolatilization

Char/coke, gas, liquor and tar form the major products obtainable from the thermal degradation of coal. The obtained liquid products are, however, unsatisfactory for immediate use as liquid fuels and some aromatic products; and therefore requires additional product upgrading before utilization (Speight, 1994). The gaseous counterpart of coal devolatilization contains an appreciable amount of valuable gas species such as H_2 , CO, CH_4 , C_2H_6 (ethane) and C_2H_4 (ethylene). In addition, this gaseous product mixture can have a calorific value of close to 18.6 MJ.m^{-3} , which makes product upgrading via methanation possible (Speight, 1994).

Light oil produced during coal devolatilization usually condenses with the formed tar, but can appear as part of the gas stream. Counter-current washing of the gas stream with a petroleum derived oil fraction or adsorption onto activated carbon are two possible process pathways of removing the light oil fraction from the gas product stream. Steam stripping can be employed to recover the light oil from the gas oil or from the activated carbon (Speight, 1994). BTX as well as alkanes, cycloalkanes, olefins and a large array of aromatic species are typical constituents of the light oil product obtained from high temperature devolatilization.

Fractional distillation of this raw oil product produces benzol, which is a crude grade of benzene. Further purification of the oils involves a sulphuric acid wash to remove the olefins followed by a neutralisation step using NaOH. The washed oils can then be distilled to produce the important BTX products as well as naphtha. Smaller amounts of indene, benzofuran and

dicyclopentadiene are however also present in the refined product and can be used as a source for industrial resins (Speight, 1994). Benzene can be converted to cumene (isopropylbenzene), once it has been extracted from the BTX fraction. The formed cumene can subsequently be used in the production of synthetic phenol and acetone through the acid-catalysed cleavage of cumene hydroperoxide (Schobert & Song, 2002).

Phenol, naphthalene, phenanthrene, pyrene, biphenyl, cresol and pyridine are some of the most valuable compounds obtainable from the tar product of devolatilization (Later *et al.*, 1981; Yoshida *et al.*, 1991; Schobert & Song, 2002; Speight, 1994). These one- to four-ring aromatic and polar compounds form important building blocks for commercially valuable products. In addition, a large proportion of the molecular entities present in tar can be readily applied in the production of coal tar fuels, refined tars, pitch and creosote (Speight, 1994). Coal tar refinement mainly consists of distillation to separate the raw product into a highly volatile fraction, a less volatile fraction consisting of creosote oil and a solid residue referred to as pitch. The refined product can be treated with aqueous caustic soda and sulphuric acid to respectively remove the tar acids (phenol and its derivatives; and cresylic acids) and tar bases (N-containing compounds such as quinoline). The extractions produce neutral naphthalene oil that can be further processed by either fractional distillation or crystallization techniques (Speight, 1994).

Phenol is currently one of the top twenty organic chemicals and can be used in the synthesis of various compounds which include phenolic resins (Bakelite, Novolacs), adipic acid, alkylphenols, caprolactam, catechol as well as monomers such as bisphenol A and 2,6-xyleneol for use in the production of aromatic polymers and engineering plastics (Schobert & Song, 2002; Weissermel & Arpe, 1997). Caprolactam is used in the manufacture of Nylon-6, while catechol is a useful industrial chemical for photographic materials (Schobert & Song, 2002).

Naphthalene can be used commercially for the production of chemicals, speciality chemicals and solvents (Song & Schobert, 1995). One example is the production of 2,6-dialkyl substituted naphthalene (2,6-DAN) through shape-selective alkylation over a molecular sieve catalyst. The latter is needed as monomer feedstock in the production of advanced polyester materials such as polyethylene naphthalate (PEN), polybutylene terephthalate (PBN) and liquid crystalline polymers (LCPs) (Schobert & Song, 2002). The production of commercial decalins (*cis*-decalin and *trans*-decalin) is also possible through the hydrogenation of naphthalene (Song & Moffat, 1994). Due to their thermal stability, possible applications of these two compounds include high-

temperature heat-transfer fluids and advanced thermally stable jet fuels (Schobert & Song, 2002). 2,6 Xylenol, which is also an important constituent of coal derived liquids, can be used as a starting material in the synthesis of polyphenylene oxide. This synthesised product can subsequently be applied as a thermoplastic with high heat- and chemical resistive properties as well as excellent electrical properties (Song & Schobert, 1993; Schobert & Song, 2002). The use of phenanthrene and its derivatives, as obtained from coal derived liquids, is still limited, although the same cannot be said for anthracene and its derivatives, which have found wide industrial application (Song & Schobert, 1993). The production of *sym*-octahydroanthracene (*sym*-OHAn), from the ring aromatisation of *sym*-octahydrophenanthrene (*sym*-OHP) has proved to be a valuable compound which can be used in various commercial applications. Synthetic anthracene for making dyestuffs, anthraquinone which can be used as a pulping agent and pyromellitic dianhydride, a monomer used in the production of polyamides can all be manufactured from *sym*-OHAn (Song & Schobert, 1993).

The solid residues obtained from coal devolatilization are however also important for further processing. Low-temperature char has the advantage of being used both domestically and commercially (as in gasification) due to its smokeless combustion and relatively high reactivity (Speight, 1994). Furthermore, the coke/char product can be either used in the metallurgical industry as a reductant or can be further processed to manufacture activated carbon and molecular sieving carbons (MSCs). Activated carbons can be applied in water purification, food processing, gold recovery, etc., while MSCs have found industrial application in gas separation via pressure-swing adsorption (Song & Schobert, 1995). In addition, coal tar pitches have also been shown to be useful in the manufacturing of carbon fibres and other carbon derived products such as mesocarbon microbeads (Song & Schobert, 1993).

2.4 Current strategies available for assessing coal devolatilization behaviour

A number of strategies are currently available for assessing devolatilization kinetics and/or product formation. Thermogravimetric (TG) systems are commonly used to evaluate the rate or kinetic behaviour of the devolatilization of coal. The use of TG systems for assessing small particle rate as well as large particle rate behaviour has been attended to in literature (Alonso *et al.*, 1999; Beukman, 2009; Mani *et al.*, 2009; Mianowski & Radko, 1995; Van der Merwe, 2010; Sun *et al.*, 1997; Zhang *et al.*, 2007). Estimation of coal devolatilization kinetics has also seen

the use of apparatus such as fixed-bed reactors (Adesanya & Pham, 1995), entrained flow reactors (Lee *et al.*, 1991) and drop tube furnaces (Ulloa *et al.*, 2004; Yip *et al.*, 2009).

The determination of product (tar, gas and char) quantity is another important parameter for understanding coal devolatilization behaviour. Apart from normal operational variables such as coal characteristic properties, temperature, pressure, gaseous atmosphere, heating rate etc., the production of pyrolytic products from coal devolatilization experiments are also sensitive to the design and configuration of the specific experimental setup used (Kandiyoti *et al.*, 2006). The flow of carrier gas, location of the reaction zone, reactor shape and particle size are only some of the variables that dictate the quality and yield of a particular tar, gas and char formation. A number of reactor configurations have been proposed in the past for assessing the devolatilization behaviour of solid fuels (Howard, 1963; Kandiyoti *et al.*, 2006). These techniques included some primitive laboratory assay methods for estimating coking properties as well as the “short path vacuum still” method used for applying a uniform heating rate to the sample and to suppress the occurrence of possible secondary reactions (Kandiyoti *et al.*, 2006). In a response to solving design constraints such as particle stacking, uniform heating to solid particles, condensation and and/or cracking of transmitted coal-derived tars over a distance, investigators proposed and designed several types of bench scale reactors. These experimental systems include: fixed- and fluidised bed reactors, entrained flow (drop tubes) reactors and versatile wire-mesh (heated grids) instruments (Kandiyoti *et al.*, 2006). The first basic design of wire-mesh reactors in literature was constructed by Loison and Chauvin (1964). The use of wire-mesh reactors has found profound use in the work of numerous authors such as Anthony *et al.* (1974), Arendt and Van Heek (1981), Howard *et al.* (1975 and 1976), Kandiyoti *et al.* (2006), Suuberg *et al.* (1985) to only name a few. Basically the apparatus consists of loading milligram quantities of fuel between two layers of folded mesh, which are heated through the aid of a current flowing through two electrodes connected to the mesh. This apparatus allows experiments to be carried out at wide ranges of heating rates (1-20000 °C/s), temperatures of up to 2000 °C and pressures of close to 160 bar. A discussion of design improvements and further details regarding wire-mesh reactors can be found in Kandiyoti *et al.* (2006).

In fixed-bed reactors, coal particles are stacked to the desired bed depth (normally of sample masses ranging between 0.5 to 10 g of coal) and heat is normally introduced inwards from the reactor walls. The use of an inert carrier gas through the fixed bed also helps to reduce the residence times of evolved products during experimentation (Kandiyoti *et al.*, 2006). Apart from

inherent problems associated with secondary reactions between packed particles and volatiles, the “hot-rod” type fixed-bed reactor has proven useful. In addition, fixed-bed reactors are easy to construct and to operate in comparison to wire-mesh reactors. Furthermore fixed bed reactors can only attain heating rates of very low to up to about 20°C/s, with temperatures up to 1000°C and pressures of 150 bar depending on the construction material (Fermoso *et al.*, 2010; Gönenç *et al.*, 1990; Kandiyoti *et al.*, 2006; López *et al.*, 2010). Different investigations have seen the design and development of non-isothermal and isothermal heating fixed-bed reactors. Fixed-bed reactors of quartz tube heated by external heating resistances were used in the investigations of Dufour *et al.* (2007), López *et al.* (2010) (non-isothermal) and Luo *et al.* (2010) (isothermal). Municipal waste was devolatilized isothermally by allowing the quartz tube reactor to reach the desired temperature before introducing the sample in a feed box into the warm reaction zone (Luo *et al.*, 2010). Fixed-bed reactors equipped with coal feeders or hoppers and constructed of more rigid material such as stainless steel are also well known (Fermoso *et al.*, 2010).

Fluidized or entrained flow (drop tube) reactors are normally used to conduct flash devolatilization of solid fuels. A sample of coal or biomass is injected within the already heated bed of inert solids, where the fluidized gas sweeps the evolved products away from the main reaction zone (Kandiyoti *et al.*, 2006). Gas velocities of about five times that of the minimum fluidization velocity are preferably used, while reactor temperatures can reach up to 2200°C (Kimber & Gray, 1967). Drop tube reactors are widely used for simulating typical pulverized fuel firing conditions (Fletcher, 1989). Disadvantages of this type of apparatus include the uncertain fate of evolved tars due to secondary reactions with free or forced falling particles as well as the distortion of tar and char yields due to solid particle carry-over to the quench zone (Kandiyoti *et al.*, 2006). Char morphology, tar and gas production studies with the aid of fluidized bed or drop tube configurations have been extensively used by a large number of investigators (Alonso *et al.*, 1999; Hayashi *et al.*, 2000; Matsuoka *et al.*, 2003; Miura *et al.*, 1992; Song *et al.*, 2001; Yeasmin *et al.*, 1999).

2.5 Factors affecting the efficiency of devolatilization

Wide variability in terms of volatile yield, tar quality and propensity, swelling and char reactivity exists amongst most coals. The devolatilization behaviour of coal is therefore not only dependent on the chemical and physical nature of the coal, but also on the conditions under which devolatilization is carried out (Solomon & Hamblen, 1985). The efficiency of devolatilization, with respect to product yield, product quality and devolatilization rate, can therefore be influenced by (1) coal properties such as mineral content and composition, rank, maceral content, etc., and (2) experimental conditions such as temperature, pressure, heating rate, gas composition etc. The following text provides an overview of factors affecting the efficiency of devolatilization. Although discussed separately, it should be noted that these factors are also interchangeably dependent on each other.

2.5.1 Coal characteristic properties affecting the efficiency of devolatilization

2.5.1.1 Rank dependent phenomena

Coal rank is an important parameter, not only dictating coal properties but also the quality and quantity of volatile products during devolatilization (Smith *et al.*, 1994; Speight, 1994). A number of coal properties are dependent on coal rank and include: (1) elemental composition, (2) functional-group composition, (3) molecular weight of ring clusters, (4) plasticity, (5) bridging material, (6) porosity, (7) hydrogen bonding, (8) catalytic species and (9) chemically unbound species such as methane and other hydrocarbons (Solomon & Hamblen, 1985).

Effect on volatile yield and quality:

The total yield of volatile products is strongly affected by both the elemental- and functional group composition. From a characterisation perspective it is well known that the total amount of volatile matter contained in coal decreases with increasing rank (Borrego *et al.*, 2000). Gas yield has been shown to increase with a decrease in coal rank, whilst the yield of tar has been found to increase up to a certain coal maturity level and decrease thereafter (Fletcher *et al.*, 1990 & 1992; Pugmire *et al.*, 1991; Smith & Smoot, 1990; Solum *et al.*, 1989; Smith *et al.*, 1994). It has been established from quantitative FTIR that the distribution of elemental moieties and functional groups differs considerably between different ranks of coal (Solomon & Hamblen,

1985). Lower-rank coals produce higher amounts of oxygen-containing gases (H₂O, CO₂ and CO) during devolatilization due to larger amounts of hydroxyl-, carboxyl- and ether functionalities in their molecular structure. This, however, is not the case for higher rank coals which produce larger amounts of tar and hydrocarbon gases due to their higher aliphatic- or hydro-aromatic hydrogen content (Borrego *et al.*, 2000; Solomon & Hamblen, 1985). In addition, low rank coals exhibit an earlier onset of tar and gas formation with a greater extent of cross-linking in comparison to higher rank coals (Pugmire *et al.*, 1991; Van Heek & Hodek, 1994). Furthermore, the onset temperature of gas evolution increases with increasing rank, indicating that weaker bonds have been eliminated during the coalification process (Van Heek & Hodek, 1994).

Although high rank, low-volatile bituminous coals are generally more cross-linked they yield significantly more tar than lignites. Cross-linking reactions during the devolatilization of low rank coals have shown that the chemical modification of carboxyl groups by methylation not only increased the tar yield of these coals but also produced tars with similar molecular weight distributions as obtained by bituminous coals (Desphande *et al.*, 1988). Furthermore, field ionization mass spectrometry (FIMS) conducted on the tars produced during vacuum devolatilization at slow heating rates have also provided valuable insight into the rank dependence of the molecular weight of tars (St. John *et al.*, 1978; Solomon & Hamblen, 1985). From these studies it was established that the molecular weight of the tars decreased with decreasing rank, which could most probably be attributed to lower ring-cluster sizes within lower rank coals, transport limitations, cross-linking or the combined effect of these three factors (Solomon & Hamblen, 1985). An investigation concerning the structure of tars derived from the devolatilization of pure vitrinites from sub-bituminous and bituminous coals have led to the conclusion that the predominant phenolic structure of tars could be described by the presence of condensed ring systems within the coals (Iglesias *et al.*, 2001). The tar derived from the lowest rank coal was characterised by the presence of shorter alkyl chain aromatics, which could most probably be attributed to a decrease in the degree of branching of the aliphatic moieties with increasing rank (Iglesias *et al.*, 2001). Furthermore a reduction in the amount of *n*-alkanes and -alkenes in coal tars with increasing rank was observed by Chaffee *et al.* (1983).

Coal plasticity also has a predominant effect on the devolatilization behaviour of a particular coal. Plastic properties of coals have been found to be more pronounced at higher heating rates, which in turn can drastically affect the swelling behaviour of a specific coal (Solomon &

Hamblen, 1985; Smith *et al.*, 1994). Melting and softening of coal particles can have a substantial influence on the radiative heat transfer as well as the fluid mechanical properties. It is during this stage that the coal porous structure is substantially altered, and volatiles such as light gas and tar vapour is trapped in the form of bubbles that cause coal particles to swell (Simons, 1983; Smith *et al.*, 1994). The subsequent swelling of coal is believed to have a strong influence on the molecular weight distribution of the devolatilization products (Solomon & Hamblen, 1985; Solomon & King, 1984).

The type of bridges linking aromatic clusters within the coal molecular structure is another factor attributing especially to the very low temperature evolution of tars from lower rank coals such as lignites (Suuberg & Scelza, 1982). Devolatilization studies conducted on oxymethylene-bridged polymers have shown that tar evolution starts at a much lower temperature compared to the devolatilization of ethylene-bridged polymers. This indicates that oxymethylene bridges, possibly contained within lignites, undergo bond scission at lower temperatures compared to ethylene bridges. Although this tends to agree with the low temperature initiation of devolatilization in lignites, the bulk of lignite tar is however still released at higher temperatures, which is consistent with the decomposition of ethylene bridges (Solomon & Hamblen, 1985).

Sulphur and nitrogen heteroatoms generally do not contribute significantly to the devolatilization process (Smith *et al.*, 1994) but some rank dependence is envisaged for nitrogen functionalities (Cai *et al.*, 1998b). X-ray photoelectron spectroscopy studies (XPS) performed by Burchell *et al.* (1987), to investigate the nitrogen functionalities of different ranked UK coals have confirmed the predominance of pyrrolic nitrogen functionalities over pyridinic species. Within this investigation it was established that the amount of pyridinic functionalities increase with increasing rank (Wojtowicz *et al.*, 1995). Therefore it is believed that coal tars should contain higher proportions of pyridinic nitrogen, mainly due to the extent of the distribution of nitrogen species within different rank coals (Cai *et al.*, 1998b).

Fundamental research conducted on tars produced from different coal types, under rapid devolatilization and varying pressure conditions, has led to the formulation of an empirical equation for describing tar yield (Ko *et al.*, 1987). In this equation Ko *et al.* (1987) account for rank dependent properties such as aromaticity, elemental C and O content and the amount of hydroxyl functional groups present in the coal. Similar empirical equations for estimating tar

yield by including elemental H and S content was also proposed by Neavel *et al.* (1981) and Saxby (1980).

Effect on devolatilization rate and kinetics:

Rank dependent phenomena, as described above, significantly affect the amount and quality of the volatile matter as well as the physical properties and reactivity of the formed chars. It appears, however, from a rate perspective, that coal maturity does not significantly affect the primary kinetic rate constants of devolatilization, although some inconsistency exists in literature (Solomon & Hamblen, 1985). Devolatilization studies conducted by Anthony *et al.* (1975), and Badzioch and Hawksley (1970) have, however, shown that variations in devolatilization rate between different types or ranks of coal were less than a factor three, while Solomon and Hamblen (1983) suggested that rank variations could account for up to a factor five in rate. According to Kobayashi *et al.* (1977), no devolatilization rate difference exists between lignite and bituminous coal. The inconsistency in literature suggests that the substantial variations in the apparent rate of devolatilization could possibly be attributed to variations in reactor conditions and setups as well as transport limitations (Solomon & Hamblen, 1985).

2.5.1.2 Maceral content

Maceral composition is another coal characteristic factor playing a major role in coal conversion technologies such as devolatilization.

Effect on volatile yield and quality:

The presence of different macerals in a particular coal can have a significant effect on the product yield and -quality of the produced volatile matter (Speight, 1994). During devolatilization in the temperature range from 400 °C to 500 °C, the highly reactive constituents of coal (liptinite and vitrinite) soften and act as binder material for the less reactive inertinite macerals (Speight, 1994). For a given temperature and gaseous environment it has been observed from investigations by Strugnell and Patrick (1996) that the amount of total volatiles and tar decreases in the order: liptinite, vitrinite and inertinite. This has also been confirmed by numerous authors such as Borrego *et al.* (2000), Cai *et al.* (1998a & b), Joseph *et al.* (1991), Li *et al.* (1993a & b), Tsai and Scaroni (1987); White *et al.* (1989) and Zhao *et al.* (2011). The

difference in extent of volatile propagation of different macerals has led investigators such as Borrego *et al.* (2000) and Duxbury (1997) to derive empirical equations (allowing for maceral content and rank) to predict the proximate volatiles as well as total volatile matter evolution in coals.

Apart from producing larger amounts of volatile products, it has also been established, with the aid of size exclusion chromatography (SEC), that molecular weight distributions of tars derived from liptinite concentrates appear to be significantly greater than that of vitrinite and inertinite tars (Li *et al.*, 1993a & b). This is consistent with what was observed by Macrae (1943) for the relative yields of condensable products obtained from reactive maceral (liptinite and vitrinite) concentrates. The results obtained from the investigation performed by Macrae (1943) are reflected in Table 2.2. From the results it was also evident that oxygen functionalities play a prominent role in the devolatilization process for lower rank coals (Macrae, 1943; Speight, 1994).

Table 2.2 Relative yields of condensable products (Macrae, 1943).

Product classes	Relative yields (wt.%)	
	Liptinite	Vitrinite
Light oils	2.8	1.0
Heavy oils	29.8	2.3
<i>Heavy- oil composition</i>		
Acids	0.3	2.0
Phenols	3.8	21.6
Bases	1.6	6.4
Neutral oils	90.5	70.0

Furthermore, the work of Li *et al.* (1993a & b) has confirmed the thermally sensitive nature of the liptinite tar fractions as well as the characteristic predominance of aliphatic or hydro-aromatic functionalities within the tars. Ultra violet (UV) fluorescence spectroscopy has additionally indicated that the aromatic cluster size distributions of the vitrinite and liptinite tars were similar, although it is suggested that the tars derived from the vitrinite concentrates are more aromatic and/or polar in nature due to higher UV fluorescence intensities (Li *et al.*, 1993a).

An investigation into the devolatilization behaviour of two maceral (vitrinite and inertinite) concentrates of a Chinese coal has revealed the substantial difference in gaseous products formed during devolatilization (Zhao *et al.*, 2011). The evolution of H₂ from both concentrates started roughly at 400°C and consisted of a two step evolution process. According to Zhao *et al.* (2011), the evolution of H₂ within the 400°C to 550°C temperature range could be described by the degradation of the coal matrix. The second stage occurring at temperatures exceeding 600°C was attributed to the condensation of aromatic or hydro-aromatic structures or the possible decomposition of heterocyclic compounds within the concentrates (Arenillas *et al.*, 1999 & 2003; Zhao *et al.* 2011). From the profiles of H₂ and C₁-C₄ hydrocarbon evolution it was further evident that the inertinite-rich concentrate displayed the lowest intensity of these products, but a higher peak temperature compared to the vitrinite concentrate. Accordingly Zhao *et al.* (2011) attributed this behaviour to the lower hydrogen content, lower aliphatic content and more stable structure of inertinite macerals, which were also observed by Sun *et al.* (2003). The formation of larger amounts of lighter hydrocarbons for vitrinite concentrates, in comparison to inertinite concentrates, also confirmed the more aliphatic and less thermally stable nature of the vitrinite macerals (Sun *et al.*, 2003). The evolution of CO₂ was mainly attributed to the decomposition of carboxyl groups, whilst the presence of sulphur-containing gases such as H₂S, COS, SO₂ and CS₂ could be related to the decomposition of pyritic, aliphatic and aromatic sulphur, thiols, disulfides and unstable aromatic sulphur forms (Zhao *et al.*, 2011).

Effect on devolatilization rate and kinetics:

The effect of maceral composition on the devolatilization rate has been extensively studied with the aid of TG and/or DTG (differential thermogravimetric) methods (Joseph *et al.*, 1991; Sun *et al.*, 2003; Zhao *et al.*, 2011). From these investigations it has been concluded that the weight loss rate of the macerals increases in the order: inertinite, vitrinite and liptinite. The lower devolatilization rate of the inertinite macerals has been subsequently attributed to its higher thermal stability due to the presence of large multinuclear aromatic clusters (Joseph *et al.*, 1991; Zhao *et al.*, 2011). Of particular interest, however, was the presence of two weight loss maxima observed for vitrinite devolatilization (Joseph *et al.*, 1991) which were described by the scission of weaker bonds at low temperatures and stronger bonds at higher temperatures. Meuzelaar *et al.* (1989) attributed the low temperature bond scission to a thermally extractable mobile phase in coal.

2.5.1.2 Presence of catalytic species and minerals

Coal is also known to contain abundant inorganic species apart from its organic components. The relationship between inorganic species (either inherent or loaded) and the devolatilization behaviour of coal has been reviewed to some extent by numerous authors (Ahmad *et al.*, 2009; Franklin *et al.*, 1982; Liu *et al.*, 2004; Öztaş & Yurum, 2000; Samaras *et al.*, 1996; Ye *et al.*, 1998) and it has been concluded that the effect influences both product yield and quality, as well as devolatilization rate.

Effect on volatile yield and quality:

Certain additives such as ZnCl₂, AlCl₃, NaOH, Fe₂O₃, Al₂O₃, CaO, CaCO₃, K₂CO₃ etc. have been noted to have a marked effect on the evolution of tarry and gaseous species evolved during devolatilization (Ahmad *et al.*, 2009; Franklin *et al.*, 1982; Liu *et al.*, 2004; Speight, 1994). The presence of inherent inorganic elements has also been found to influence the devolatilization of coals (Schaffer, 1980). Specifically, the presence of clay groups within the coal structure has been found to affect overall devolatilization and to catalyze the transfer of H₂ to the coal (Howard, 1963). In addition Al₂O₃ forms a valuable active catalyst for de-alkyl and dehydrogenation reactions at higher temperatures (Liu *et al.*, 2004).

Devolatilization studies conducted on raw and demineralised Pakistani coals have shown that tar and liquid yields decreased while gas evolution increased with the removal of the inherent minerals (Ahmad *et al.*, 2009). Ahmad *et al.* (2009) attributed these observations to the high hydrogen transfer capabilities associated with inorganic elements. According to Solomon *et al.* (1988), high hydrogen transfer increases product release, whilst minimizing re-solidification and is responsible for the formation of tars and oils. McMillen *et al.* (1989) have, however, ascribed the increase of char production in the absence of inorganic elements to the ineffective capping, disproportioning and stabilization of free radicals generated during devolatilization. Furthermore, the presence of some inorganic species may also alter some coal properties such as softening and swelling behaviour (Bexley *et al.*, 1986).

The addition of mineral additives to demineralised coal samples has also caused a decrease in both total volatile and tar yield (Franklin *et al.*, 1982). From the work of Franklin *et al.* (1982) it was found that the addition of the mineral montmorillonite ((Na,Ca)_{0.33}(Al,Mg)₂(Si₄O₁₀)(OH)₂) led

to a reduction in total volatile yield due to the subsequent re-polymerisation of tars to char. The decrease in volatile yield as a result of the addition of kaolinite to the coals was, however, attributed to the reduction of C₄-C₈ hydrocarbons, rather than to the tar yield. Addition of CaO and CaCO₃ led to a decrease in the yield of volatile hydrocarbon products as well as an increase in CO production due to the cracking of acidic and non-acidic oxygen functional groups within the coal (Franklin *et al.*, 1982). It is also believed that the use of K₂CO₃ as a catalyst results in the formation of K-oxygen surface groups and clusters due to interactions with –COOH and –OH functionalities within the coal molecular structure. The formation of these surface functional groups have been considered as active sites on the coal-carbon matrix surface (Liu *et al.*, 2004; Mims & Pabst, 1983; Öztaş & Yurum, 2000). An investigation into the effect of iron oxide mixtures on devolatilization has shown a decrease in tar- and gaseous alkane yields in the primary devolatilization zone between 300 °C and 600 °C. Cypres and Soudan-Moinet (1980) have attributed this to the release of H₂ during aromatization and condensation of the coal structure, which subsequently lowers the extent of cracking of alkyl side-chains. Above a temperature of 600 °C an increased production of methane was, however, favoured.

Effect on devolatilization rate and kinetics:

From a rate perspective not much has been reported on the relationship between inorganic matter and the kinetics of coal devolatilization (Liu *et al.*, 2004). A quantitative relationship between catalyst loading and devolatilization kinetics was, however, established to some extent, by Liu *et al.* (2004). According to Liu *et al.* (2004) the addition of Al₂O₃, CaO and K₂CO₃ to the demineralised coal sample greatly affected the devolatilization weight loss curve, indicating a substantial influence of mineral addition to devolatilization rate. A maximum of 11% weight loss was achieved for the Al₂O₃ loaded coal followed by smaller extents of weight loss for the other two minerals. By defining a catalytic effectiveness parameter Liu *et al.* (2004) determined that Al₂O₃ is mainly active in the high temperature range while K₂CO₃ has an optimum catalytic temperature. With the aid of non-isothermal modelling techniques it was found that the activation energy decreased for all three cases of mineral addition to the demineralised coal sample, therefore establishing the catalytic possibility of Al₂O₃, CaO and K₂CO₃ (Liu *et al.*, 2004). From the study conducted by Cypres and Soudan-Moinet (1980) an increase in maximum devolatilization rate was also observed with an increase in Fe₂O₃ and Fe₃O₄ addition to coal.

2.5.2 Operational conditions affecting the efficiency of devolatilization

The course of thermal degradation of coal depends not only on characteristic coal properties, but also on operational conditions which include (1) temperature, (2) heating rate, (3) pressure, (4) gaseous environment, (5) particle size and (6) reactor type (Alonso *et al.*, 1999; Kristiansen, 1996; Ladner, 1988; Solomon & Hamblen, 1985).

2.5.2.1 Temperature

Effect on volatile yield and quality:

Temperature is considered to be the most important parameter controlling the devolatilization behaviour of coal (Hu *et al.*, 2004). From numerous studies it has been established that the amount of volatiles produced increases with increasing temperature although substantial differences in product spectrum do occur (Hu *et al.*, 2004; Kandiyoti *et al.*, 2006; Kristiansen, 2006; Ladner, 1988). Investigators have commonly divided the devolatilization process into a number of distinctive temperature regions (Kandiyoti *et al.*, 2006; Ladner, 1988; Speight, 1994). The individual yields of tar, liquor, char and gas have been found to behave differently from the general trend as observed for total volatile yield. It has been established that tar and liquor yields increase monotonously to a maximum value between 525°C and 575°C, whereafter these yields decrease and the formation of gaseous species are favoured more (Ladner, 1988; Speight, 1994).

The fate of devolatilization products with an increase in temperature is summarised in Table 2.3. With the aid of Py-MS spectrometry (Holden & Rob, 1960; Herod *et al.*, 1983; Herod & Smith, 1985) it was established that even at temperatures below 100°C, hydrocarbons, including aromatic hydrocarbons such as benzene and toluene, are evolved from the coal structure. Furthermore, volatiles produced in the temperature range below 350°C are characterised by the presence of complex structures including not only hydrocarbons up to the C₁₉H₁₆ homologue range, but also a myriad of species containing both O, S and N hetero-functionalities (Ladner, 1988).

Table 2.3 Temperature regions in coal devolatilization (Adapted from Ladner, 1988).

Temperature range (°C)	Reactions	Products	Application
< 350	Mainly evaporation	Water and volatile organics	Fundamental studies
400 – 750	Primary degradation	Gas, tar and liquor	Smokeless fuels and chemicals
750 – 900	Secondary reactions	Gas, tar liquor and additional H ₂	Smokeless fuels and chemicals
900 – 1100			Metallurgical coke and chemicals
> 1650	Cracking	Acetylene and carbon black	Uneconomic

The primary degradation range, however, consists of the production of additional hydrocarbons, especially CH₄, while light oils formed are generally composed of a complex mixture of straight chain- and cyclo paraffins as well as olefins with some aromatics. Devolatilization at temperatures above 900°C favours the formation of a concentrated char/coke product as well as the subsequent increase in gaseous species such as H₂, whilst a decrease in light oils and tars can be observed (Ladner, 1988). The significant difference in product quality and quantity of the high- and low temperature devolatilization range is reflected in both Tables 2.4 and 2.5 (Kabe *et al.*, 2004; Ladner, 1988).

Table 2.4 Product yields for low- and high temperature devolatilization.

Product (wt.%, d.b.)	Temperature range	
	400 °C to 750 °C	900 °C to 1100 °C
Gas	7.6	17.2
Liquor	13.0	2.5
Light oils	1.4	0.8
Tar	8.0	4.5
Coke/Char	70.0	75.0

Table 2.5 Compositional difference between products (Adapted from Ladner (1988)).

Low temperature devolatilization (400°C to 750°C)					
Gas	wt.%	Light oil	wt.%	Tar	wt.%
H ₂	10	Paraffins	46	BTX	1.5
Hydrocarbons	65	Olefins	16	Phenol	1.5
CO	5	Cyclo-paraffins	8	Cresols	4.5
CO ₂	9	Cyclo-olefins	9	Xylenols	7.0
Other	11	Aromatics	16	Other phenols	16.0
		Other	5	Tar bases	2.0
				Naphtha	3.5
				Other aromatics	38.0
				Pitch	26.0
High temperature devolatilization (900°C to 1100°C)					
Gas	wt.%	Light oil	wt.%	Tar	wt.%
H ₂	50	BTX	89	BTX	0.6
Hydrocarbons	34	Alicyclics	5	Phenols & cresols	1.6
CO	8	Aliphatics	6	Xylenols	0.5
CO ₂	3			Other phenols	1.0
Other	5			Naphthalene	8.9
				Anthracene	1.0
				Other aromatics	24.6
				Tar bases	1.8
				Pitch	60.0

From the above table it is clear that a significant shift in product distribution occurs for high temperature devolatilization where the formation of lower molecular weight species such as gases and light oils are favoured, mainly due to secondary gas-phase degradation reactions (Kandiyoti *et al.*, 2006; Ladner, 1988; Nelson *et al.*, 1988). Accompanying this is the progressively larger aromatic nature of coal tars and the presence of increased amounts of unsubstituted polycyclic aromatic hydrocarbons at high temperatures (Nelson *et al.*, 1988; Smith *et al.*, 1994). Sequential elution solvent chromatography (s.e.s.c.) performed on liquids obtained from the rapid devolatilization of Pittsburgh No.8 coal, at temperatures between 500°C and

725°C, has shown a monotonous increase in poly-phenolic, carbonyl, nitrogen heterocyclics and highly poly-functional molecules with an increase in temperature (Khan, 1989).

The final devolatilization temperature has also been found to progressively alter the micropore surface areas of the formed chars. Studies conducted by Çakal *et al.* (2007) on Turkish lignites have shown the increase of micropore surface area with increasing temperature, and the subsequent decrease thereof again at higher temperatures. This observation was attributed to the initial opening of previously closed pores, the creation of new pores and the enlargement of existing ones followed by the decrease in surface area at higher temperatures due to the melting of some minerals and the subsequent filling of the pores with this molten material (Çakal *et al.*, 2007; Beukman, 2009).

Effect on devolatilization rate and kinetics:

Coal particle temperature is of significant importance in establishing the kinetics of devolatilization. Devolatilization studies performed on powdered coal samples in a drop tube furnace at constant pressure have shown that the rate of devolatilization increases with increasing final temperature (Yeasmin *et al.*, 1999). This was also the general trend observed by numerous authors as summarised in the review by Solomon and Hamblen (1985). Some inconsistency in the results (between similar rank coals) obtained by different authors could, however, be ascribed to inaccurate estimations of the particle temperature (Kristiansen, 1996; Solomon & Hamblen, 1985). This discrepancy suggested that the major factors influencing the apparent rate of devolatilization, from a temperature perspective, are: (1) the external rate of heat transfer as well as (2) the internal rate of heat transfer within the coal particle (Solomon & Hamblen, 1985).

Furthermore, the majority of product formation rates of the different gaseous- and tarry components increase with increasing temperature up to a maximum yield value whereafter the rate decreases with any further temperature increase (Khan, 1989; Nelson *et al.*, 1988). From a kinetic perspective it has been established that the mean activation energy obtained from isothermal devolatilization experiments increases with an increase in temperature. The kinetic parameters obtained for the higher temperature range therefore indicates that reactions with high activation energies are favoured in this region, whilst the opposite is true for the lower temperature range (Lázaro *et al.*, 1998).

2.5.2.2 Heating rate and holding time

Effect on volatile yield and quality:

The rapid heating of coal samples leads to the subsequent shifting of the different stages of thermal degradation to a higher temperature range and shorter time interval (Howard, 1981; Kandiyoti *et al.*, 2006). It has been shown that at a heating rate of 1000 °C/s, maximum tar release shifted to between 600 °C and 700 °C as compared to a maximum tar release observed between 550 °C and 600 °C for a heating rate of ~1 °C/s. In addition, an increase in heating rate has also been shown to boost volatile yields with up to 6-8 wt.% depending on the type and origin of coal sample used (Gibbins & Kandiyoti, 1989; Gibbins-Matham & Kandiyoti, 1988; Kandiyoti *et al.*, 2006). The effect of heating rate is justifiable irrespective of the apparatus used, due to the fact that similar trends were observed by Peters and Bertling (1965) using a fluidised bed reactor and Anthony *et al.* (1976), who investigated the devolatilization behaviour in a crucible, wire-mesh and electrical strip furnace.

The increase in volatile yield with increasing heating rate is directly relatable to a subsequent increase in tar formation (Kandiyoti *et al.*, 2006; Ladner, 1988). This could be either ascribed to the rapid build-up of internal pressure forcing out tar precursors (Gray, 1988) or to the overlapping of hydrogen release and covalent bond scission to facilitate the partial inhibition of re-polymerisation reactions (Kandiyoti *et al.*, 2006). Gibbins and Kandiyoti (1989) therefore suggested that, at high heating rates secondary reactions are minimized, while greater mass transfer resistances are possible for lower heating rates. In addition, the increase in tar yield with rapid heating rate comes with a loss in tar quality as explained by the atomic H/C ratio (Khan, 1989). A comparison between tars obtained from entrained flow and fixed-bed reactors have shown that for slow heating rate apparatus such as fixed bed reactors the atomic H/C ratio was generally higher than those from entrained flow analyses. This was also evident from the larger molecular weight distributions obtained from FIMS analyses on tars obtained from entrained flow reactors (Khan, 1989). S.e.s.c analyses performed on the two different tar types also illustrated the presence of more poly-phenolic carbonyl moieties in the tars obtained from entrained flow reactors.

The effect of holding time is also important for devolatilization reactions to run to completion. Gibbins and Kandiyoti (1989) have shown that an increase in holding time leads to an increase

in volatile yield, although this increase could occur in a matter of seconds for fine coal samples. The effect of holding time on larger coal particles is, however, dictated by heat- and mass transfer effects.

Effect on devolatilization rate and kinetics:

Non-isothermal devolatilization experiments conducted by Lázaro *et al.* (1998) at low heating rates (5°C/min, 15°C/min and 30°C/min) have shown the independence of heating rate of kinetic parameters such as mean activation energy. For high heating rates non-isothermal work could, however, suffer from many experimental errors due to mass- and heat transfer effects (Lázaro *et al.*, 1998).

2.5.2.3 Pressure and devolatilization atmosphere

Effect on volatile yield and quality:

Gaseous atmosphere and pressure are two additional factors affecting devolatilization behaviour. The effect of pressure has been widely attended to by numerous authors including Arendt and Van Heek (1981), Howard, (1981), Ko *et al.* (1987), Sathe *et al.* (2002), Seebauer *et al.* (1997), etc. The general consensus was that at reduced pressures (below atmospheric) both volatile and tar yields increase, whilst the opposite is true for external pressures exceeding atmospheric operating conditions and that these observations suggest a strong dependence on mass transfer (Sathe *et al.*, 2002). According to Kandiyoti *et al.* (2006), depending on the sample, a reduction in pressure to near vacuum could account for up to 5 wt.% increase in tar yield. In addition Ko *et al.* (1987) have shown that a pressure increase from 0.1 bar to 90 bar could induce a decrease of up to 13.2 wt.% in tar yield. This was also the general observation made by Howard (1981). Kandiyoti *et al.* (2006) have ascribed this behaviour to a decrease in re-condensation reactions of tar precursors for lower devolatilization pressures, while the reduction in tar yield at higher external pressures could be described by an increase in diffusional resistance of volatiles towards the external particle surfaces. Accompanying this is the substantial change in the quality of the tars produced. Sathe *et al.* (2002) have shown with the aid of UV fluorescence and -absorbance studies that the yield of larger aromatic rings increased with increasing pressure up to about 20 bar, whereafter it decreased slightly up to 61 bar. Furthermore, according to Solomon *et al.* (1990), pressure exerts the greatest effect on

those gaseous products that are related to cross-linking reactions during coal devolatilization. Seebauer *et al.* (1997) have shown that both CO₂ and methane yields increase with increasing pressure, while the opposite is true for hydrogen and higher order hydrocarbon gases such as ethane and ethene.

Gaseous atmosphere can also significantly affect both the yield of devolatilization products as well as the quality. Devolatilization studies conducted at 750 °C under different atmospheres (N₂, H₂, CH₄, CO₂ and CO₂ reforming methane process conditions (CRMP)) have shown that CO₂ and CRMP conditions promote tar formation, with CRMP conditions enhancing tar yields with up to 3.2 and 2.6 times as much as that obtained under N₂ and H₂ atmospheres respectively (Wang *et al.*, 2010). GC-MS (gas chromatography-mass spectrometry) analyses conducted on the tars obtained from the different atmospheres have shown that phenols constitute the major portion of the tar volatile fractions.

In addition, it was evident from ¹H NMR and ¹³C NMR analyses that the tar obtained from the CRMP atmosphere was rich in aliphatic protons mainly bounded to the α and β positions of the aromatic ring with an accompanying low fraction of aromatic carbons in comparison to the other tars (Wang *et al.*, 2010). Similar observations are made when comparing tars obtained from coal gasification to tars obtained from coking activities. The amount of poly-aromatic hydrocarbons are distinctively higher in the tars obtained from the coking process, which can be mainly attributed to secondary reactions destructively altering the nature of the produced aromatic moieties (Song *et al.*, 2005)

Effect on devolatilization rate and kinetics:

Devolatilization experiments performed at elevated pressure on Illinois No.6 bituminous coal have shown that devolatilization kinetics are pressure dependent (Lee *et al.*, 1991). It was evident from this study that the derived apparent first order rate constants decreased with an increase in pressure. In addition, at a specific external pressure, the devolatilization rate decreased with increasing extent of devolatilization (Lee *et al.*, 1991). Kinetic modelling performed with the assumption of competitive reactions during devolatilization has led Sun *et al.* (1997) to observe a decrease in activation energy for an accompanying increase in external pressure.

2.5.2.4 Particle size limitations

Effect on volatile yield and quality:

Particle size has an effect analogous to that of pressure (Kristiansen, 1996). The propagation of volatile species as a function of particle size has been addressed by authors such as Anthony *et al.* (1976), Howard (1981), Kandiyoti *et al.*, (2006), Kk *et al.* (1998), Seebauer *et al.* (1997), etc. Coal devolatilization and hydrogasification studies performed by Anthony *et al.* (1976) have revealed the fact that total volatile yield decreases slightly with an increase in particle size (ranging from 0.07 mm to 1 mm particles) which corresponds to the findings of Kandiyoti *et al.* (2006). This was also confirmed by kinetic modelling work done by Devanathan and Saxena (1987).

In contrast, however, Seebauer *et al.* (1997) observed no significant difference between the total volatile yields of particles ranging in 0.1 mm to 2 mm in size. Consequently the amount of tar is heavily dependent on particle size and a decrease in tar yield with a subsequent increase in char yield has been identified in the studies conducted by Park *et al.* (1989). Furthermore, it has been established that larger particles offer more resistance to volatile transport and promotes the formation of lighter gaseous products with an accompanying decrease in tar quality due to secondary reactions (Howard, 1981).

The fact of the matter is that no single phenomenon describes the devolatilization behaviour of large particles and in general it is believed that the evolution of volatile products are controlled by (i) heat transfer to and within the particle, (ii) chemical reactions and (iii) mass transfer of volatile products within the particle and from the external surface (Beukman, 2009; Solomon & Hamblen, 1985). Additional research by Agarwal *et al.* (1984) and, Stubington and Sumaryono (1984) have however proven that the devolatilization mechanism is dominated by heat transfer and chemical kinetics. According to Smith *et al.* (1994) and Bliet *et al.* (1985), the role of mass transfer does however form an integral part in understanding the devolatilization behaviour of large coal particles.

Effectively no or little information is available regarding the composition of tars obtained from the devolatilization of large coal particles (greater than 5 mm in size).

Effect on devolatilization rate and kinetics:

The work of Devanathan and Saxena (1987) has shown that particle size has a significant influence on devolatilization time. A decrease in devolatilization rate is observed for an increase in particle size, due to the transient nature of both heat and mass transfer resistances during large particle devolatilization. From a kinetic parameter perspective, Kök *et al.* (1998) have observed an increase in activation energy with an increase in particle size from -10+14 up to 48 mesh, whereafter the activation energy decreases for mesh sizes up to 400 mesh. Activation energy values obtained by Kök *et al.* (1998) are in agreement with those reported by Ozbas (2008). According to Ozbas (2008), the calculated activation energies take the sum of effective activation energies for the various types of chemical reactions as well as the physical changes simultaneously occurring during pyrolysis into account.

2.6 Modelling coal devolatilization behaviour

2.6.1 Modelling strategies

2.6.1.1 Overview of kinetic models

Numerous models have been proposed in an attempt to fully understand devolatilization rates and kinetics. A large variation does, however, exist in reported rate constants and activation energies. Solomon *et al.* (1993) has attributed this to a possible inaccurate estimation of particle temperatures, which is of utmost importance for especially large coal particles. Coal devolatilization models can be divided into either general weight-loss models or structural models. Typical weight-loss models include models employing a (1) single rate (Badzioch & Hawksley, 1970; Kristiansen, 1996; Serio *et al.*, 1987), (2) two rates (Gürüz *et al.*, 2004; Lu, 1991), (3) multiple rates (Gürüz *et al.*, 2004; Sommariva *et al.*, 2010) and (4) distributed rates (Braun & Burnham, 1987; Cai & Liu, 2008; Navarro *et al.*, 2008; Solomon *et al.* 1988). Although very descriptive, these models do not account for variations in tar yield and gaseous evolutions with reaction conditions (Solomon *et al.* 1988). In a response to this, recent advances in the understanding of the coal structure has led to the development of some structural/network models of which the FG-DVC (Functional Group-Depolymerization Vaporization Cross linking) (Solomon *et al.*, 1993), the FLASHCHAIN (Niksa & Kerstein, 1991) and the percolation lattice

theory (Grant *et al.*, 1989) are the most commonly known. More comprehensive chemical models have also been formulated for describing char and tar formation (Solomon *et al.*, 1993). A brief overview of the different models is provided in the following text:

Single rate reaction model:

The most commonly used model for describing devolatilization is the single rate first-order model, where the devolatilization process is assumed to follow one single reaction under isothermal conditions of which the first order rate constant can be determined with the aid of the Arrhenius equation (Beukman, 2009; Kristiansen, 1996). The single rate model has been successfully applied by several researchers to predict overall mass loss during coal devolatilization (Kök *et al.*, 1998; Strezov *et al.*, 2004). Although simplistic in nature it has been shown that kinetic parameters such as the pre-exponential constant (k_0) and apparent activation energy (E_a) determined for one heating rate is generally not appropriate for use with other heating rates (Donskoi & McElwain, 1999; Solomon *et al.*, 1992). For non-isothermal conditions the single rate expression can be expressed as a function of varying heating rate.

n^{th} order reaction model:

Donskoi and McElwain (1999) expanded the single rate model to an n^{th} order approximation model which accounts for the reaction order (n). In this model the rate constant is defined in a similar manner as was done for the single rate model. For modelling purposes, a large range of heating rates can be used to express both k_0 and E_a as simple functions of heating rate. The application of this model does have the advantage of cutting down numerical solving time compared to a model accounting for a distribution of activation energies (Donskoi & McElwain, 1999). A similar approach was followed by Gürüz *et al.* (2004) to model non-isothermal coal devolatilization.

Multiple reaction rate models:

A number of kinetic models have been proposed previously in an attempt to describe the complex nature of devolatilization. In some circumstances first order and n^{th} -order reaction rate models are appropriate for describing the devolatilization process with a limited range of validity (Sommariva *et al.*, 2010). The use of multi-step kinetic mechanisms has introduced the

possibility of describing competitive reactions occurring during thermal breakdown of coal (Sommariva *et al.*, 2010). One such model was proposed by Chermin and Van Krevelen (1957), who suggested that coal devolatilization consists of a three step first-order reaction mechanism as illustrated below:

Coal → Metaplast → Semi-coke/char + primary volatiles → Coke/char + secondary volatiles

Numerous other studies have, however, assumed that the devolatilization mechanism consists of a system of parallel first-order reactions (Gürüz *et al.* 2004; Solomon *et al.*, 1992; Suuberg *et al.*, 1978). An overview of some of the descriptive equations of three different mechanistic models for isothermal kinetics can be found in Gürüz *et al.* (2004). All three models assume first-order reactions. For the first model the rate constant is assumed to be a function of conversion. More recently Sommariva *et al.* (2010) have proposed a predictive multi-step kinetic model based on the elemental properties of three reference coals. The devolatilization of any coal can therefore be predicted by considering the coal to be a linear combination of the three reference coals and their mechanisms of devolatilization. This model has been successfully applied to thermogravimetric-, Curie point- and drop tube experimental results (Sommariva *et al.*, 2010).

Distributed activation energy model (DAEM):

A more complicated model as proposed by Pitt (1962) assumes that the devolatilization process involves an infinite series of independent parallel first-order reactions, each containing its own respective activation energy and common constant pre-exponential factor (Beukman, 2009; Kristiansen, 1996). The devolatilization process can therefore be explained by a distribution of activation energies about some mean activation energy value ($E_{a,0}$). The function within the model $f(E_a)$ accounts for a distribution of activation energies and is assumed to be of Gaussian form. Although a very powerful model for estimating devolatilization behaviour, it requires an extensive numerical discretization procedure for solving the required parameters. Calculations become even more complicated if external transport phenomena, such as temperature distribution, play a role (Donskoi & McElwain, 2000). Recent progress has been made in the field of simplifying the numerical estimation of the DAEM (Braun & Burnham, 1987; Cai & Liu, 2008; Donskoi & McElwain, 1999; Donskoi & McElwain, 2000). Donskoi and McElwain (2000) have proposed a novel method which consists of a modified Gauss-Hermite quadrature to

optimize modelling with the aid of the DAEM. Others have proposed approximate analytical expressions for describing and simplifying the temperature integral within the DAEM (Braun & Burnham, 1987; Cai & Liu, 2008; Miura & Maki, 1998). The DAEM (either isothermal or non-isothermal) was successfully applied by numerous authors including Arenillas *et al.* (2001), Braun and Burnham (1987), Cai and Liu (2008), Donskoi and McElwain (1999, 2000), Heidenreich *et al.* (1999) and Mani *et al.* (2009).

In most studies the application of the DAEM normally only pertains to coal particles in the small particle range (< 1mm). The accuracy of the application of the DAEM to larger particles might be questionable due to external and internal transport effects playing a role. The evaluation of the devolatilization of larger coal particles was first performed in 1993 by Adesanya and Pham (1993) on coal particles ranging from 8 mm to 18 mm in size. This investigation subsequently led to a modified DAEM, allowing for large coal particles (Adesanya & Pham, 1993). This model has also been successfully applied by Heidenreich *et al.* (1999).

Other advanced modelling techniques:

The availability of advanced characterisation techniques has led to the development of more comprehensive chemical models. The model proposed by Gavalas *et al.* (1981a, 1981b) and Gavalas (1982) is one example of a structural devolatilization model. The model is based on a collection of 14 functional groups, which includes aromatic rings, aliphatic chains, and bridges as well as oxygen functionalities (Gavalas *et al.*, 1981a & b; Gavalas, 1982; Smith *et al.*, 1994). Although the model could conveniently describe devolatilization kinetics it consists of lengthy rate expressions and several kinetic parameters are assigned arbitrarily and differ from the best-estimated values (de Souza-Santos, 2005). A better understanding of the molecular structure has led Niksa and Kerstein (1987) to propose another class of structural models formally known as the DISKIN and DISCHAIN models. These models address the influence of coal molecular structure on volatile evolution rate by assuming that aromatic groups are linked by bridges and peripheral groups are attached to aromatic groups (de Souza-Santos, 2005; Niksa & Kerstein, 1987). A full description of the mechanism of the DISKIN or DISCHAIN process is provided in de Souza-Santos (2005) and Niksa and Kerstein (1987). In addition, both these models include a distributed activation energy approach for describing the decomposition of bridges and aromatic units. DISKIN and DISARAY models present the advantage of solving a system of first-order differential equations and provides the amounts of gas, tar and char produced against

time (de Souza-Santos, 2005). The DISKIN and DISARAY models were subsequently followed by the formulation of two new models: FLASHTWO (Niksa, 1988) and FLASHCHAIN (Niksa & Kerstein, 1991).

The formulation of a general model for devolatilization has led investigators such as Serio *et al.* (1987), Solomon and Hamblen (1985), Solomon *et al.* (1986), Solomon and Squire (1985); and Squire *et al.* (1986) to propose two separate structural models known as the FG (functional group) and DVC (depolymerisation-vaporization-cross-linking) models. The FG-model allows for gas species evolution and can provide information on the composition of the gas at each state of devolatilization, whilst the DVC model statistically accounts for the formation of tar (Solomon *et al.*, 1988). Solomon *et al.* (1988) later combined these two subroutines of modelling to form the FG-DVC model which gives a general description of the whole devolatilization process. Other structural models include the CPD (chemical percolation devolatilization model) as proposed by Grant *et al.* (1989), which accounts for lattice statistics important for characterising the devolatilization process. The application of this model provides an analytical way of describing the size distribution of discrete coal clusters consisting of molecular sites (Grant *et al.*, 1989). Details regarding this modelling strategy are provided in Grant *et al.* (1989).

2.6.1.2 Accounting for transport limitations

Mathematical modelling of coal particles in the large particle regime is receiving increasing attention due to its application in commercial coal conversion units (Heidenreich *et al.*, 1999). Larger coal particles do however display vastly different devolatilization characteristics than pulverised coal particles and therefore need a more rigorous treatment of comprehensive models (Johnsson, 1994). One general aspect which was shown to be important is the effect of intra-particle tar deposition reactions on the ultimate weight loss and tar yield from large coal particles (Bliek *et al.*, 1985). The understanding of large particle devolatilization therefore necessitates the use of transport phenomena such as intra-particle heat- and mass transfer. The influence of temperature- and product diffusion gradients on the devolatilization behaviour of large coal particles have generally been attended to by authors such as Agarwal (1986), Agarwal *et al.* (1984), Agarwal and Pedler (1986), Bliek *et al.* (1985), Heidenreich *et al.* (1999); Sadukhan *et al.* (2011), Wildegger-Gaissmaier & Agarwal (1990) and Zhang *et al.* (2012).

2.7 Summary of findings in the literature

The evaluation of characteristic properties and operating conditions plays an important role in understanding coal behaviour during a particular coal conversion process. A fundamental understanding of the significance of devolatilization, as the first step of all coal conversion processes, therefore requires the assessment of the influence of governing factors not only on rate considerations but also on the quantity and quality of products evolved. Numerous studies have been conducted to assess the quality and quantity of devolatilization products particularly pertaining to small particle sizes as well as coals originating from the northern hemisphere. Due to the significant difference in coal morphology of southern hemisphere coals, this study will therefore attempt to describe the devolatilization behaviour of South African coal particles confined to typical large/lump particle size ranges. This will consist of evaluating both devolatilization rate as well as product composition and; -yield obtained at different operating conditions.

Bibliography

Adensanya, B.A. & Pham, H.M. 1995. Mathematical modelling of devolatilization of large coal particles in a convective environment. *Fuel*, 74(6): 896-902.

Agarwal, P.K., Genetti, W.E. & Lee, Y.Y. 1984. Devolatilization of large coal particles in fluidized beds. *Fuel*, 63: 1748-1752.

Agarwal, P.K. & Pedlar, I. 1986. Drying, devolatilization and volatile combustion for single coal particles: a pseudo steady state approach. *Fuel*, 65: 640-643.

Agarwal, P.K. 1986. A single particle model for the evolution and combustion of coal volatiles. *Fuel*, 65: 803-810.

Ahmad, T., Awan, I.A., Nisar, J. & Ahmad, I. 2009. Influence of inherent minerals and pyrolysis temperature on the yield of pyrolysates of some Pakistani coals. *Energy Conversion and Management*, 50: 1163-1171.

Alonso, M.J.G., Borrego, A.G., Alvarez, D. & Menéndez, R. 1999. Pyrolysis behaviour of pulverised coals at different temperatures. *Fuel*, 78: 1501-1513.

Anthony, D.B., Howard, J.B., Meissner, H.P. & Hottel, H.C. 1974. Apparatus for determining high pressure coal-hydrogen reaction kinetics under rapid heating conditions. *Review of Scientific Instruments*, 45: 992.

Anthony, D.B., Howard, J.B., Hottel, H.C. & Meissner, H.P. 1975. Rapid devolatilization of pulverised coal. (*In The Combustion Institute. Papers read at the 15th International Symposium of Combustion held in Pittsburgh. Pittsburgh, P.A. p. 1303.*)

Anthony, D.B., Howard, J.B., Hottel, H.C. & Meissner, H.P. 1976. Rapid devolatilization and hydro-gasification of bituminous coal. *Fuel*, 55:121-128.

Arendt, P. & Van Heek, K.-H. 1981. Comparative investigations of coal pyrolysis under inert gas and H₂ at low and high heating rates and pressures up to 10 MPa. *Fuel*, 60(9): 779-787.

Arenillas, A., Rubiera, F. & Pis, J.J. 1999. Simultaneous thermogravimetric-mass spectroscopic study on the pyrolysis behaviour of different rank coals. *Journal of Analytical and Applied Pyrolysis*, 50: 31-46.

Arenillas, A., Rubiera, F., Pevida, C. & Pis, J.J. 2001. A comparison of different methods of predicting coal devolatilization kinetics. *Journal of Analytical and Applied Pyrolysis*, 58-59: 685-701.

Arenillas, A., Rubiera, F., Pis, J.J., Cuesta, M.J., Iglesias, M.J., Jiménez, A. & Suárez-Ruiz, I. 2003. Thermal behaviour during the pyrolysis of low rank perhydrous coals. *Journal of Analytical and Applied Pyrolysis*, 68-69: 371-385.

Aleman, L.B., Grant, D.M., Pugmire, R.J. & Stock, L.M. 1984. Solid state magnetic resonance spectra of Illinois No. 6 coal and some reductive alkylation products. *Fuel*, 63: 513-521.

Aso, H., Matsuoka, K., Sharma, A. & Tomita, A. 2004. Evaluation of size of graphene sheet in anthracite by a temperature-programmed oxidation method. *Energy & Fuels*, 18(5): 1309-1314.

Badzioch, S. & Hawksley, P.G.W. 1970. Kinetics of thermal decomposition of pulverised coal particles. *Industrial and Engineering Chemistry Process Design and Development*, 9: 521.

Beukman, M.T. 2009. Coal pyrolysis modelling and the influence of pyrolysis conditions on char reactivity for large particles. Potchefstroom: University of North-West. RSA. (Dissertation-M.Eng). 103p.

Bexley, K., Green, P.D. & Mark Thomas, K. 1986. Interaction of mineral and inorganic compounds with coal. The effect on caking and swelling properties. *Fuel*, 65(1): 47-53.

Bliek, A., Van Poelje, W.M., Van Swaaij, W.P.M. & Van Beckhum, F.P.H. 1985. Effects of intraparticle heat and mass transfer during devolatilization of a single coal particle. *Journal of the American Institute of Chemical Engineers*, 31(10): 1666-1681.

Borrego, A.G., Marbán, G., Alonso, M.J.G., Álvarez, D. & Menéndez, R. 2000. Maceral effects in the determination of proximate volatiles in coals. *Energy & Fuels*, 14: 117-126.

Braun, R.L. & Burnham, A.K. 1987. Analysis of chemical reaction kinetics using a distribution of activation energies and simpler models. *Energy & Fuels*, 1(2): 153-161.

Brendenberg, J.B., Huuska, M. & Vuori, A. 1987. Latest advances in thermal and catalytic reactions of the ether bond in coal and related model compounds. (*In* Volborth, A., ed. *Coal Science and Chemistry*. Amsterdam: Elsevier. p. 1-30.)

Burchill, P. 1987. Some observations on the variation of nitrogen content and functionality with coal rank. (*In* Moulijn, J.A., ed. *Papers read at the 1987 International Conference on Coal Science held in Maastricht, Netherlands*. Amsterdam: Elsevier. p.5.)

Cadle, A.B., Cairncross, B., Christie, A.D.M. & Roberts, D.L. 1993. The Karoo basin of South Africa: type basin for the coal-bearing deposits of Southern Africa. *International Journal of Coal Geology*, 23: 117–157.

Cai, H.-Y., Megaritis, A., Messenböck, R., Dix, M., Dugwell, D.R. & Kandiyoti, R. 1998a. Pyrolysis of coal maceral concentrates under pf-combustion conditions (I): changes in volatile release and char combustibility as a function of rank. *Fuel*, 77(12): 1273-1282.

Cai, H.-Y., Megaritis, A., Messenböck, R., Vasanthakumar, L., Dugwell, D.R. & Kandiyoti, R. 1998b. Pyrolysis of coal maceral concentrates under pf-combustion conditions (II): changes in heteroatom partitioning as a function of rank. *Fuel*, 77(12): 1283-1289.

Cai, J. & Liu, R. 2008. New distributed activation energy model: numerical solution and application to pyrolysis kinetics of some types of biomass. *Bioresource Technology*, 99: 2795-2799.

Cairncross, B. 2001. An overview of the Permian (Karoo) coal deposits of Southern Africa. *African Earth Sciences*, 33: 529–562.

Çakal, G.O., Yücel, H. & Gürüz, A.G. 2007. Physical and chemical properties of selected Turkish lignites and their pyrolysis and gasification rates determined by thermogravimetric analysis. *Journal of Analytical and Applied Pyrolysis*, 80:262-268.

Calkins, W.H. 1987. Investigation of organic sulphur-containing structures in coal by flash pyrolysis experiments. *Energy & Fuels*, 1: 59-64.

Chaffee, A.L., Perry, G.J. & Johns, R.B. 1983. Pyrolysis-gas chromatography of Australian coals. 2. Bituminous coals. *Fuel*, 62: 311-316.

Chermin, H.A.G. & Van Krevelen, D.W. 1957. Chemical structure and properties of coal XVII – A mathematical model of coal pyrolysis. *Fuel*, 36:85-104.

Chapter 2: Literature Study

Cloke, M., Gilfillan, A. & Lester, E. 1997. The characterization of coals and density separated coal fractions using FTIR and manual and automated petrographic analysis. *Fuel*, 76: 1289-1296.

Cypres, R. & Soudan-Moinet, C. 1980. Pyrolysis of coal and iron oxides mixtures. 1. Influence of iron oxides on the pyrolysis of coal. *Fuel*, 59: 48-54.

Cypres, R. 1987. Aromatic hydrocarbon formation during coal pyrolysis. *Fuel Processing Technology*, 15: 1-15.

Dadyburjor, D.B. & Liu, Z. 2003. Coal liquefaction. (*In Kirk-Othmer Encyclopaedia of Chemical Technology*, 6:832-869.)

DTI (Department of Trade and Industry). 1999. Coal liquefaction. <http://www.dti.gov.uk/files/file18326.pdf> Date of access: 25 September 2010.

De Souza-Santos, M.L. 2005. Solid fuels, combustion and gasification: Modelling, simulation and equipment operation. New York: Marcel Dekker. 462p.

Desphande, G.V., Solomon, P.R. & Serio, M.A. 1988. Crosslinking reactions in coal pyrolysis, *Preprint, American Chemical Society, Division of Fuel Chemistry*, 33(2): 310-321.

Devanathan, N. & Saxena, S.C. 1987. Transport model for devolatilization of large non-plastic coal particles: The effect of secondary reactions. *Industrial & Engineering Chemistry Research*, 26: 539-548.

Donskoi, E. & McElwain, D.L.S. 1999. Approximate modelling of coal pyrolysis. *Fuel*, 78: 825-835.

Donskoi, E. & McElwain, D.L.S. 2000. Optimization of coal pyrolysis modelling. *Combustion and Flame*, 122: 359-367.

Dufour, A., Girods, P., Masson, E., Normand, S., Rogaume, Y. & Zoulalian, A. 2007. Comparison of two methods of measuring wood pyrolysis tar. *Journal of Chromatography A*, 1164: 240-247.

Duxbury, J. 1997. Prediction of coal pyrolysis yields by maceral separation. *Journal of Analytical and Applied Pyrolysis*, 40-41: 233-242.

Falcon, R.M.S. & Snyman, C.P. 1986. An introduction to coal petrography: Atlas of petrographic constituents in the bituminous coals of Southern Africa. Johannesburg: The Geological Society of South Africa. 106 p.

Fermoso, J., Gil, M.V., Borrego, A.G., Pevida, C., Pis, J.J. & Rubiera, F. 2010. Effect of the pressure and temperature of devolatilization on the morphology and steam gasification reactivity of coal chars. *Energy & Fuels*, 24: 5586-5595.

Fletcher, T.H. 1989. Time-resolved particle temperature and mass loss measurements of a bituminous coal during devolatilization. *Combustion & Flame*, 78(2): 223-236.

Fletcher, T.H., Solum, M.S., Grant, D.M., Critchfield, S. & Pugmire, R.J. 1990. Solid state ^{13}C and ^1H NMR studies of the evolution of the chemical structure of coal char and tar during devolatilization. *Symposium (International) on Combustion*, 23(1): 1231-1237

Fletcher, T.H., Solum, M.S., Grant, D.M. & Pugmire, R.J. 1992. Chemical structure of char in the transition from devolatilization to combustion. *Energy & Fuels*, 6: 643-650.

Franklin, H.D., Peters, W.A. & Howard, J.B. 1982. Mineral matter effects on the rapid pyrolysis and hydrolysis of a bituminous coal. 1. Effects on yields of char, tar and light gaseous volatiles. *Fuel*, 61: 155-160.

Gavalas, G.R., Cheong, P. H-K. & Jain, R. 1981a. Model of coal pyrolysis. 1: Qualitative development. *Industrial & Engineering Chemistry Fundamentals*, 20: 113-122.

Gavalas, G.R., Cheong, P. H-K. & Jain, R. 1981b. Model of coal pyrolysis. 2: Qualitative formulation and results. *Industrial & Engineering Chemistry Fundamentals*, 20: 122-132.

Chapter 2: Literature Study

Gavalas, G.R. 1982. Coal Science and Technology 4: Coal Pyrolysis. Amsterdam: Elsevier. 168 p.

Gibbins, J.R. & Kandiyoti, R. 1989. The effect of variations in time-temperature history on product distribution from coal pyrolysis. *Fuel*, 68: 895-903.

Gibbins-Matham, J.R. & Kandiyoti, R. 1988. Coal pyrolysis yields from fast and slow heating in a wire-mesh apparatus with a gas sweep. *Energy & Fuels*, 2(4): 505-511.

Gilfillan, A., Lester, E., Cloke, M. & Snape, C. 1999. The structure and reactivity of density separated coal fractions. *Fuel*, 78(14): 1639-1644.

Gönenç, Z.S., Gibbins, J.R., Katheklakis, I.E. & Kandiyoti, R. 1990. Comparison of coal pyrolysis product distributions from three captive sample techniques. *Fuel*, 69: 383-390.

Gönenç, Z.S. & Sunol, A.K. 1994. Pyrolysis of coal in O. Kural ed *Coal resources, properties, utilization, pollution*. Istanbul: Istanbul Technical University. p. 337-351.

Grant, D.M., Pugmire, R.J., Fletcher, T.H. & Kerstein, A.R. 1989. Chemical model of coal devolatilization using percolation lattice statistics. *Energy & Fuels*, 3: 175-186.

Gray, V.R. 1988. The role of explosive injection in the pyrolysis of coal. *Fuel*, 67(9): 1298-1304.

Gupta, R. 2007. Advanced Coal Characterisation: A Review. *Energy & Fuels*, 21: 451-460.

Gürüz, G.A., Üçtepe, Ü. & Durusoy, T. 2004. Mathematical modelling of thermal decomposition of coal. *Journal of Analytical and Applied Pyrolysis*, 71: 537-551.

Hagelskamp, H.H.B. & Snyman, C.P. 1988. On the origin of low-reflecting inertinites in coals from the Highveld coalfield, South Africa. *Fuel*, 67: 307-313.

Hayashi, J.-I., Takahashi, H., Iwatsuki, M., Essaki, K., Tsutsumi, A. & Chiba, T. 2000. Rapid conversion of tar and char from pyrolysis of a brown coal by reactions with steam in a drop-tube reactor. *Fuel*, 79: 439-447.

Heidenreich, C.A., Yan, H.M. & Zhang, D.K. 1999. Mathematical modelling of pyrolysis of large coal particles – estimation of kinetic parameters for methane evolution. *Fuel*, 78: 557-566.

Herod, A.A., Hodges, N.J., Pritchard, E. & Smith, C.A. 1983. Mass spectrometric study of the HCl and other volatiles from coals during mild heat-treatment. *Fuel*, 62: 1331.

Herod, A.A. & Smith, C.A. 1985. Release of oxygen and sulphur compounds from coal. *Fuel*, 64: 281-283.

Herod, A.A., Lazaro, M.-J., Domin, M., Islas, C.A. & Kandiyoti, R. 2007. Molecular mass distributions and structural characterisation of coal derived liquids. *Fuel*, 79: 323-337.

Hessley, R.K., Reasoner, J.W. & Riley, J.T. 1986. Coal Science: An introduction to chemistry technology and utilization. New York: Wiley. 269 p.

Holden, H.W. & Rob, J.C. 1960. A study of coal by mass spectrometry. *Fuel*, 39: 39-46.

Horsfall, D.W. 1993. Coal Preparation and Usage. Parklands: Coal Publications (Pty) Ltd. 64p.

Howard, H.C. 1963. Chemistry of coal utilization. Supplementary Volume (H.H. Lowry, ed.). New York: Wiley. p. 340.

Howard, J.B., Anthony, D.B., Hottel, H.C. & Meissner, H.P. 1975. Rapid devolatilization of pulverised coal. *Symposium (International) on Combustion*, 15(1): 1303-1317.

Howard, J.B., Anthony, D.B., Hottel, H.C. & Meissner, H.P. 1976. Rapid devolatilization and hydrogasification of bituminous coal. *Fuel*, 55: 121-128.

Howard, H.C. 1981. Fundamentals of coal pyrolysis and hydro pyrolysis. (In M.A. Elliott, ed. The chemistry of coal utilization. Second supplementary volume. New York: Wiley. 2374p).

Hu, H., Zhou, Q., Zhu, S., Meyer, B., Krzack, S. & Chen, G. 2004. Product distribution and sulphur behaviour in coal pyrolysis. *Fuel Processing Technology*, 85: 849-861.

Iglesias, M.J., Cuesta, M.J. & Suárez-Ruiz, I. 2001. Structure of tars derived from low-temperature pyrolysis of pure vitrinites: influence of rank and composition of vitrinites. *Journal of Analytical and Applied Pyrolysis*, 58-59: 255-284.

Johnsson, J.E. 1994. Formation and reduction of nitrogen-oxides in fluidised bed combustion. *Fuel*, 73(9): 1398-1415.

Jones, J.M., Pourkashanian, M., Rena, C.D. & Williams, A. 1999. Modelling the relationship of coal structure to char porosity. *Fuel*, 78: 1737-1744.

Joseph, J.T., Fisher, R.B., Masin, C.A., Dyrkacz, G.R., Bloomquist, C.A. & Winans, R.E. 1991. Coal maceral chemistry. 1. Liquefaction behaviour. *Energy & Fuels*, 5: 724-729.

Jüntgen, H. 1987. Coal characterisation in relation to coal combustion. *Erdöl und Kohle-Erdgas-Petrochemie*, 40: 153-165.

Kabe, T, Ishihara, A., Qian, E.W., Sutrisna, I.P. & Kabe, Y. 2004. Coal and coal related compounds: Structures, reactivity and catalytic reactions. Tokyo: Kodansha Ltd. and Amsterdam: Elsevier. 350 p.

Kandiyoti, R., Herod, A.A. & Bartle, K.D. 2006. Solid fuels and heavy hydrocarbon liquids: Thermal characterisation and analysis. Oxford: Elsevier Ltd. p. 36-89.

Khan, M.R. 1989. A literature survey and an experimental study of coal devolatilization at mild and severe conditions: influences of heating rate, temperature, and reactor type on products yield and composition. *Fuel*, 68: 1522-1530.

Kimber, G.M. & Gray, M.D. 1967. Rapid devolatilization of small coal particles. *Combustion & Flame*, 11: 360-362.

Kristiansen, A. 1996. Understanding coal gasification. London : IEA Coal Research. 70 p.

Kruszewska, K.J. 2003. Fluorescing macerals in South African coals. *International Journal of Coal Geology*, 54: 79–94.

Ko, G.H., Peters, W.A. & Howard, J.B. 1987. Correlation of tar yields from rapid pyrolysis with coal type and pressure. *Fuel*, 66: 1118-1122.

Kobayashi, H., Howard, J.B. & Sarofim, A.F. 1977. Coal devolatilization at high temperatures. *Symposium (International) on Combustion*, 16(1): 411-425.

Kök, M.V., Özbas, E., Karacan, O. & Hicyilmaz, C. 1998. Effect of particle size on coal pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 45: 103-110.

Ladner, W.R. 1988. The products of coal pyrolysis: properties, conversion and reactivity. *Fuel Processing Technology*, 20: 207-222.

Larsen, J.W., Green, T.K. & Kovac, J. 1985. The nature of the macromolecular network structure of bituminous coals. *Journal of Organic Chemistry*, 50: 4729-4735.

Later, D.W., Lee, M.L., Bartle, K.D., Kong, R.C. & Vassilaros, D.L. 1981. Chemical class separation and characterisation of organic compounds in synthetic fuels. *Analytical Chemistry*, 53:1612-1620.

Lázaro, M.-J., Moliner, R. & Suelves, I. 1998. Non-isothermal versus isothermal technique to evaluate kinetic parameters of coal pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 47: 111-125.

Lee, C.W., Jenkins, R.G. & Schobert, H.H. 1991. Mechanism and kinetics of rapid, elevated pressure pyrolysis of Illinois No. 6 bituminous coal. *Energy & Fuels*, 5: 547-555.

Chapter 2: Literature Study

Lee, S. 1996. *Alternative Fuels*. Washington: Taylor & Francis. p. 165-174.

Levine, D.G., Schlosberg, R.H. & Silbernagel, B.G. 1982. Understanding the chemistry and physics of coal structure (A Review). *Proc. Natl. Acad. Sci. USA*, 79:3365-3370.

Li, C-Z., Bartle, K.D. & Kandiyoti, R. 1993a. Characterisation of tars from variable heating rate pyrolysis of maceral concentrates. *Fuel*, 72: 3-11.

Li, C-Z., Bartle, K.D. & Kandiyoti, R. 1993b. Vacuum pyrolysis of maceral concentrates in a wire-mesh reactor. *Fuel*, 72(11): 1459-1468.

Lin, Q & Guet, J.M. 1990. Characterisation of coals and macerals by X-ray diffraction. *Fuel*, 69: 821-825.

Liu, Q., Hu, H., Zhou, Q., Zhu, S. & Chen, G. 2004. Effect of inorganic matter on reactivity and kinetics of coal pyrolysis. *Fuel*, 83: 713-718.

Loison, R. & Chauvin, R. 1964. *Chim. Ind. Paris.*, 91: 269. Translation by University of Sheffield (DJB/WBD), May 1964, National Coal Board, Coal Research Establishment Library (Sept 194).

López, D., Acelas, N. & Mondragón, F. 2010. Average structural analysis of tar obtained from pyrolysis of wood. *Bioresource Technology*, 101: 2458-2465

Lu, G.Q. 1991. Preparation and characterization of an effective sorbent for SO₃ and NO_x removal using coal washery reject. Australia: University of Queensland. (Thesis – Ph.D.) 230p.

Lu, L., Sahajwalla, V., Kong, C. & Harris, D. 2001. Quantitative X-ray diffraction analysis and its application to various coals. *Carbon*, 39:1821-1833.

Luo, S., Xiao, B., Hu, Z. & Liu, S. 2010. Effect of particle size on pyrolysis of single-component municipal solid waste in fixed bed reactor. *International Journal of Hydrogen Energy*, 35: 93-97.

Macrae, J.C. 1943. The thermal deposition of spore exinites from bituminous coal. *Fuel*, 22:117.

Mani, T., Murugan, P. & Mahinpey, N. 2009. Determination of distributed activation energy model kinetic parameters using simulated annealing optimization method for non-isothermal pyrolysis of lignin. *Industrial & Engineering Chemistry Research*, 48: 1464-1467.

Mathews, J.P., Fernandez-Also, V., Jones, A.D. & Schobert, H.H. 2010. Determining the molecular weight distribution of Pocahontas No. 3 low volatile bituminous coal utilizing HRTEM and laser desorption ionization mass spectra data. *Fuel*, 89: 1461-1469.

Matsuoka, K., Ma, Z.-X., Akiho, H., Zhang, Z.-G., Tomita, A., Fletcher, T., Wójtowicz, M.A. & Niksa, S. 2003. High-pressure coal pyrolysis in a drop tube furnace. *Energy & Fuels*, 17: 984-990.

McMillen, D.F., Malhotra, R., Chang, S.-J. & Hum, G.P. 1987. Hydrogen-transfer-promoted bond scission initiated by coal fragments. *Energy & Fuels*, 1: 193-198.

McMillen, D.F., Malhotra, R. & Nigenda, S.E. 1989. The case for induced bond scission during coal pyrolysis, *Fuel*, 68(3): 380-386.

Meuzelaar, H.L.C., Yun, Y., Simmleit, N. & Schulten, H.-R. 1989. The mobile phase in coal viewed from a mass spectrometric perspective. *Preprint, American Chemical Society, Division of Fuel Chemistry*, 34(3): 693-701.

Meyers, R.A. 1982. Coal structure. New York: Academic Press. 340 p.

Mianowski, A. & Radko, T. 1995. Thermokinetic analyses of coal pyrolysis process. *Journal of Thermal Analysis*, 43: 247-259.

Miknis, F.P., Turner, T.F., Ennen, L.W. & Netzel, D.A. 1988. NMR characterisation of coal pyrolysis products. *Fuel*, 67:1568-1577.

Chapter 2: Literature Study

Mims, C.A. & Pabst, J.K. 1983. Role of surface salt complexes in alkali-catalysed carbon gasification. *Fuel*, 62(2): 176-179.

Miura, K., Mae, K., Sakurada, K. & Hashimoto, K. 1992. Flash pyrolysis of coal-following thermal pre-treatment at low temperature. *Energy & Fuels*, 6: 16-21.

Miura, K. & Maki, T. 1998. A simple method for estimating $f(E)$ and $k_0(E)$ in the distributed activation energy model. *Energy & Fuels*, 12: 864-869.

Navarro, M.V., Aranda, A., Garcia, T., Murillo, R. & Mastral, A.M. 2008. Application of the distributed activation energy model to blends devolatilization. *Chemical Engineering Journal*, 142: 87-94.

Neavel, R.C., Smith, S.E., Hippo, E.J. & Miller, R.N. 1981. (*In Proceedings of the 8th International Symposium on Coal Science held in Düsseldorf in September. Düsseldorf, Germany. p. 1-9.*)

Nelson, P.F., Smith, I.W., Tyler, R.J. & Mackie, J.C. 1988. Pyrolysis of coal at high temperatures. *Energy and Fuels*, 2(4): 391-400.

Niksa, S. 1988. Rapid coal devolatilization as an equilibrium flash distillation. *AIChE J*, 34: 790-802.

Niksa, S. & Kerstein, A.R. 1987. On the role of macromolecular configuration in rapid coal devolatilization. *Fuel*, 66: 1389-1399.

Niksa, S. & Kerstein, A.R. 1991. FLASHCHAIN theory for rapid coal devolatilization kinetics. 1. Formulation. *Energy & Fuels*, 5: 647-665.

Orendt, A.M., Solum, M.S., Sethi, N.K., Pugmire, R.J. & Grant, D. M. 1992. *Advances in Coal Spectroscopy*. New York: Plenum Press.

Ozbas, K.E. 2008. Effect of particle size on pyrolysis characteristics of Elbistan lignite. *Journal of Thermal Analysis and Calorimetry*, 93(2): 641-649.

Öztaş, N.A. & Yürüm, Y. 2000. Pyrolysis of Turkish Zonguldak bituminous coal. Part 1. Effect of mineral matter. *Fuel*, 79: 1221-1227.

Painter, C.P. 1990. Coal solubility and swelling. 2. Effect of Hydrogen bonding on calculations of molecular weight from swelling measurements. *Energy & Fuels*, 4: 384-393.

Park, W.-H., Park, K.-W., Baik, N.-J. & Park, D. 1989. Low temperature pyrolysis of high volatile coals in a fluidised bed. (*In Proceedings of the Sixth Korea-USA joint workshop on coal utilization technology, Korea Institute of Energy and Resources, Energy and Environmental Research Division, Seoul, Korea, 17-18 October 1989. p.IV59-IV72.*)

Peters, W. & Bertling, H. 1965. Kinetics of the rapid degasification of coals. *Fuel*, 44:317-331.

Pitt, G.J. 1962. The kinetics of the evolution of volatile products from coal. *Fuel*, 41:267-274.

Pugmire, R.J., Zilm, K.W., Woolfenden, W.R., Grant, D.M., Dyrkacz, G.R., Bloomquist, C.A.A. & Horwitz, E.P. 1982. Carbon-13 NMR spectra of macerals separated from individual coals. *Organic Geochemistry*, 4: 79-84.

Pugmire, R.J., Solum, M.S., Grant, D.M., Critchfield, S. & Fletcher, T.H. 1991. Structural evolution of matched tar-char pairs in rapid pyrolysis experiments. *Fuel*, 70: 414-423.

Russell, N.V., Gibbins, J.R. & Williamson, J. 1999. Structural ordering in high temperature carbon materials and the effect on reactivity. *Fuel*, 78: 803-807.

Sadhukhan, A.K., Gupta, P. & Saha, R.K. 2011. Modelling and experimental investigations on the pyrolysis of large coal particles. *Energy & Fuels*, 25: 5573-5583.

Samaras, P., Diamadopoulos, E. & Sakellariopoulos, G.P. 1996. The effect of mineral matter and pyrolysis conditions on the gasification of Greek lignite by carbon dioxide. *Fuel*, 75: 1108-1114.

Sathe, C., Hayashi, J.-I. & Li, C.-Z. 2002. Release of volatiles from the pyrolysis of Victorian lignite at elevated pressures. *Fuel*, 81: 1171-1178.

Saxby, J.D. 1980. Atomic H/C ratios and the generation of oils from coals and kerogens. *Fuel*, 59: 305-307.

Saxena, S.C. 1990. Devolatilization and combustion characteristics of coal particles. *Progress in Energy and Combustion Science*, 16: 55-94.

Schaffer, N.H.S. 1980. Pyrolysis of brown coals. 3. Effect of cation content on the gaseous products containing oxygen from Yallourn coal. *Fuel*, 59: 295-301.

Schobert, H.H. & Song, C. 1995. Non-fuel uses of coals and synthesis of chemicals and materials. *Fuel*, 75(6): 724-736.

Schobert, H.H. & Song, C. 2002. Chemicals and materials from coal in the 21st century. *Fuel*, 81: 15-32.

Schoenig, F.R.L. 1983. X-ray structure of some South African coals before and after heat treatment at 500 and 1000 °C. *Fuel*, 62: 1315-1320.

Seebauer, V., Petek, J. & Staudinger, G. 1997. Effects of particle size, heating rate and pressure on measurement of pyrolysis kinetics by thermogravimetric analyses. *Fuel*, 76(13): 1277-1282.

Serio, M.A., Hamblen, D.G., Markham, J.R. & Solomon, P.R. 1987. Kinetics of volatile evolution in coal pyrolysis: experiment and theory. *Energy & Fuels*, 1: 138-152.

Sharma, A., Kyotani, T. & Tomita, A. 2000a. Direct observation of layered structure of coals by a transmission electron microscope. *Energy & Fuels*, 14(2): 515-516

Sharma, A., Kyotani, T. & Tomita, A. 2000b. Comparison of structural parameters of PF carbon from XRD and HRTEM techniques. *Carbon*, 38(14): 1977-1984.

Sharma, A., Kyotani, T. & Tomita, A. 2000c. Direct observation of raw coals in lattice fringe mode using high-resolution transmission electron microscopy. *Energy & Fuels*, 14(6): 1219-1225.

Sharma, A., Kyotani, T. & Tomita, A. 1999. A new quantitative approach for microstructural analysis of coal char using HRTEM images. *Fuel*, 78: 103-1212.

Shim, H-S., Hurt, R.H. & Yang, N.Y.C. 2000. A methodology for analysis of 002 lattice fringe images and its application to combustion-derived carbons. *Carbon*, 38: 29-45.

Simons, G.A. 1983. The role of pore structure in coal pyrolysis and gasification. *Progress in Energy and Combustion Sciences*, 9(4): 269.

Smith, J.M. 1981. *Chemical Engineering Kinetics*. New York: McGraw-Hill. 676 p.

Smith, K.L. & Smoot, L.D. 1990. Characteristics of commonly-used U.S. coals-towards a set of standard research coals. *Progression in Energy and Combustion Science*, 16: 1-53.

Smith, K.L., Smoot, L.D., Fletcher, T.H. & Pugmire, R.J. 1994. The structure and reaction processes of coal. New York: Plenum Press. 473p.

Snyman, C.P. & Botha, W.J. 1993. Coal in South Africa. *Journal of African Earth Sciences*, 16: 171-180.

Soderquist, A., Burton, D.L., Pugmire, R.J., Beeler, A.J., Grant, D.M., Durand, B. & Hulk, A.Y. 1987. Structural variations and evidence of segmental motion in the aliphatic region in coals observed with dipolar dephasing NMR. *Energy & Fuels*, 1: 50-55.

Solomon, P.R. & Hamblen, D.G. 1983. Finding order in coal pyrolysis kinetics. *Progression in Energy and Combustion Science*, 9(4): 323-361.

Solomon, P.R. & Hamblen, D.G. 1985. Chapter 5: Pyrolysis. (*In* Schlosberg, R.H., ed *Chemistry of coal conversion*. New York : Plenum press. p. 121-251).

Solomon, P.R., Serio, M.A., Carangelo, R.M. & Markham, J.R. 1986. Very rapid coal pyrolysis. *Fuel*, 65: 182-194.

Solomon, P.R. & King, H.H. 1984. Pyrolysis of model polymers: Theory and experiment. *Fuel*, 63: 1302.

Solomon, P.R. & Squire, K.R. 1985. Experiments and modelling of coal depolymerisation. *Preprint-American Chemical Society, Division of Fuel Chemistry*, 30(4): 346-356.

Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A. & Deshpande, G.V. 1988. General model of coal devolatilization. *Energy & Fuels*, 2(4): 405-422.

Solomon, P.R., Serio, M.A., Deshpande, G.V. & Kroo, E. 1990. Cross-linking reactions during coal conversion. *Energy & Fuels*, 4: 42-54.

Solomon, P.R., Serio, M.A., & Suuberg, E.M. 1992. Coal pyrolysis: experiments, kinetic rates and mechanisms. *Progress in Energy and Combustion Science*, 18(2): 133-220.

Solomon, P.R., Fletcher, T.H. & Pugmire, R.J. 1993. Progress in coal pyrolysis. *Fuel*, 72:587-597.

Solum, M.S., Pugmire, R.J. & Grant, D.M. 1989. ¹³C Solid-State NMR of Argonne Premium Coals. *Energy & Fuels*, 3:187-193.

Solum, M.S., Sarofim, A.F., Pugmire, R.J., Fletcher, T.H. & Zhang, H. 2001. ¹³C NMR Analysis of Soot Produced from Model Compounds and Coal. *Energy & Fuels*, 15:961-971.

Sommariva, S., Maffei, T., Migliavacca, G., Faravelli, T. & Ranzi, E. 2010. A predictive multi-step kinetic model of coal devolatilization. *Fuel*, 89: 318-328.

Song, C. & Schobert, H.H. 1993. Opportunities for developing speciality chemicals and advanced materials from coal. *Fuel Processing Technology*, 34(2): 157-196.

Song, C. & Moffatt, K. 1994. Zeolite-catalysed ring-shift isomerisation of *sym*-octahydrophenanthrene and conformational isomerisation of *sym*-decahydronaphthalene. *Microporous Materials*, 2: 459-466.

Song, B.-H., Jang, Y.-W., Kim, S.-D. & Kang, S.-K. 2001. Gas yields from coal devolatilization in a bench-scale fluidized bed reactor. *Korean Journal of Chemical Engineering*, 18(5): 770-774.

Song, C., Schobert, H.H. & Andresen, J.M. 2005. Premium carbon products and organic chemicals from coal. London: IEA Coal Research Publications- CCC. 88 p.

Speight, J.G. 1994. The chemistry and technology of coal. 2nd Ed. New York: Marcel Dekker. 642p.

Squire, K.R., Solomon, P.R., Carangelo, R.M. & Ditaranto, M.B. 1986. Tar evolution from coal and model polymers. 2: The effects of aromatic ring sizes and donatable hydrogens. *Fuel*, 65: 833-843.

Stein, S.E. 1981. A fundamental chemical kinetics approach to coal conversion. (In Blaustein, B.D, Blockrath, B.C and Friedman, S., eds. New approaches in Coal Chemistry. Washington, D.C.: ACS Symposium Series, 169, p. 97-129.)

St.John, G.A., Burtill, S.E. & Anbar, M. 1978. Field Ionization and field desorption mass spectroscopy applied to coal research. (In Larsen, J., ed. Organic chemistry of coal. ACS Symposium Series, 71, p.223.)

Strezov, V., Lucas, J.A. & Strezov, L. 2004. Experimental and modelling of the thermal regions of activity during pyrolysis of bituminous coals. *Journal of Analytical and Applied Pyrolysis*, 71:375-392.

Strugnell, B. & Patrick, J.W. 1996. Rapid hydrolysis studies on coal and maceral concentrates. *Fuel*, 75: 300-306.

Stubington, J.F. & Sumaryono. 1984. Release of volatiles from large coal particles in a hot fluidized bed. *Fuel*, 63(7): 1013-1019.

Suggate, R.P. & Dickinson, W.W. 2004. Carbon NMR of coals: the effects of coal type and rank. *International Journal of Coal Geology*, 57:1-22.

Chapter 2: Literature Study

Sun, C.L., Xiong, Y.Q., Liu, Q.X. & Zhang, M.Y. 1997. Thermogravimetric study of the pyrolysis of two Chinese coals under pressure. *Fuel*, 76(7): 639-644.

Sun, Q., Li, W., Chen, H. & Li, B. 2003. The variation of structural characteristics of macerals during pyrolysis. *Fuel*, 82: 669-676.

Suuberg, E.M., Peters, W.A. & Howard, J.B. 1978. Product composition and kinetics of lignite pyrolysis. *Industrial and Engineering Chemistry Process Design and Development*, 17(1): 37-46.

Suuberg, E.M. & Scelza, S.T. 1982. Gas evolution during low-temperature pyrolysis of a North Dakota lignite. *Fuel*, 61: 198.

Suuberg, E.M., Unger, P.E. & Lilly, W.D. 1985. Experimental study on mass transfer from pyrolysing coal particles. *Fuel*, 64: 956-962.

Tsai, S.C. 1982. Coal science and technology 2: Fundamentals of coal beneficiation and utilization. Amsterdam: Elsevier Scientific Publishing Company. 375p.

Tsai, C.Y. & Scaroni, A.W. 1987. Pyrolysis and combustion of bituminous coal fractions in an entrained-flow reactor. *Energy & Fuels*, 1:263-269.

Ulloa, C., Gordon, A.L. & García, X. 2004. Distribution of activation energy model applied to the rapid pyrolysis of coal blends. *Journal of Analytical and Applied Pyrolysis*, 71: 465-483.

University of Kentucky. 2010. Classification and rank of coal. <http://www.uky.edu/KGS/coal/coalkinds.htm>. Date of access: 28 September 2010.

Van der Merwe, G.L. 2010. The influence of particle size and devolatilization conditions on the CO₂ gasification of Highveld coal. Potchefstroom: University of North-West. RSA. (Dissertation-M.Eng). 131p.

Van Heek, K.H. & Hodek, W. 1994. Structure and pyrolysis behaviour of different coals and relevant model substances. *Fuel*, 73(6): 886-896.

Van Niekerk, D. 2008. Structural elucidation, molecular representation and solvent interactions of vitrinite-rich and inertinite-rich South African coals. Pennsylvania: Pennsylvania State University. USA. (Thesis-PhD). 195p.

Van Niekerk, D. & Mathews, J.P. 2008. Molecular representations of Permian-aged vitrinite-rich and inertinite-rich South African coals. *Fuel*, 89: 73-82.

Van Niekerk, D., Pugmire, R.J., Solum, M.S., Painter, P.C. & Mathews, J.P. 2008. Structural characterisation of vitrinite-rich and inertinite-rich Permian-aged South African bituminous coals. *International Journal of Coal Geology*, 76: 290-300.

Wang, P., Jin, L., Liu, J., Zhu, S. & Hu, H. 2010. Analysis of coal tar derived from pyrolysis at different atmospheres. *Fuel*, (In press)

Wanzl, W. 1988. Chemical reactions in thermal decomposition of coal. *Fuel Processing Technology*, 20: 317-336.

Weissermel, K. & Arpe, H.-J. 2003. Industrial organic chemistry. 4th Ed. Weinheim: Wiley-VCH. 495 p.

White, A., Davies, M.R. & Jones, S.D. 1989. Reactivity and characterisation of coal maceral concentrates, *Fuel*, 68: 511-519.

Wildegger-Gaissmaier, A.E. & Agarwal, P.K. 1990. Drying and devolatilization of large coal particles under combustion conditions. *Fuel*, 69: 44-52.

Wilson, M.A., Collin, P.J., Pugmire, R.J. & Grant, D.M. 1982. Relaxation of ¹³C and ¹⁵N nuclei by solvent-refined coal. *Fuel*, 61: 959-967.

Wojtowicz, M.A., Pels, J.R. & Moulijn, J.A. 1995. The fate of nitrogen functionalities in coal during pyrolysis and combustion. *Fuel*, 74(4): 507-516.

Chapter 2: Literature Study

Yang, J., Cheng, S., Wang, X., Zhang, Z., Liu, X. & Tang, G. 2006. Quantitative analysis of microstructure of carbon materials by HRTEM. *Transactions of Nonferrous Metals Society of China*, 16: 796-803.

Ye, D.P., Agnew, J.B. & Zhang, D.K. 1998. Gasification of a South Australian low-rank coal with carbon dioxide and steam: kinetics and reactivity studies. *Fuel*, 77: 1209-1219.

Yeasmin, H., Mathews, J.F. & Ouyang, S. 1999. Rapid devolatilization of Yallourn brown coal at high pressures and temperatures. *Fuel*, 78:11-24.

Yip, K., Wu, H. & Zhang, D.-K. 2009. Mathematical modelling of Collie coal pyrolysis considering the effect of steam produced in situ from coal inherent moisture and pyrolytic water. *Proceedings of the Combustion Institute*, 32: 2675-2683.

Yoshida, T., Chantal, P.D., Sawatzky, H. 1991. A simple method for analysis of nitrogen and phenolic compounds in synthetic crude naphtha. *Energy & Fuels*, 5(2): 299-303.

Zhao, Y., Hu, H., Jin, L., He, X. & Wu, B. 2011. Pyrolysis behaviour of vitrinite and inertinite from Chinese Pingshuo coal by TG-MS and in a fixed bed reactor. *Fuel Processing Technology*, 92: 780-786.

Zhang, C., Jiang, X., Wei, L. & Wang, H. 2007. Research on pyrolysis characteristics and kinetics of super fine and conventional pulverized coal. *Energy Conversion & Management*, 48: 797-802.

Zhang, K., You, C. & Li, Y. 2012. Experimental and numerical investigation on the pyrolysis of single course lignite particles. *Korean Journal of Chemical Engineering*, 29(4): 540-548.