

CHAPTER 2

2.0

LITERATURE REVIEW

2.1 Introduction

The objective of this chapter is to provide a review of literature relevant to: coal gasification reaction, especially as it pertains to gasification with CO_2 ; char- CO_2 reaction rates, mechanisms and kinetics; char reactivity in relation to various factors that may influence it; microstructural and microtextural changes imparted on the carbon crystallite of chars (including changes in various crystallite parameters upon devolatilisation and the effects of these changes on the gasification reactivity).

Structural models associated with char- CO_2 gasification reactions are also reviewed. The survey presented in this chapter was considered to provide the necessary background for the execution of this research work.

2.2 Coal Gasification

Coal conversion by any of the processes to produce a mixture of combustible gases is referred to as coal gasification, even though a large number of chemical reactions other than the so called gasification reactions are involved (Littlewood, 1977; van Heek and Mühlen, 1985; Kristiansen, 1996; Lee, 2007). It encompasses a series of reaction steps that convert coal containing C , H , and O , as well as impurities such as N and S , into synthesis gas and other forms of hydrocarbons. This is accomplished by introducing a gasifying agent, which can be oxygen, carbon dioxide, steam, air, and/or a mixture of two or more, or all of the above into a reactor vessel containing coal feedstock where the temperature, pressure and flow pattern are controlled (Littlewood, 1977; van Heek and Mühlen, 1985; Kristiansen, 1996; Kabe, 2004; Lee, 2007).

The proportions of the various species (CO , CO_2 , H_2 , CH_4 , H_2O , N_2 , H_2S , S_2O , etc) in the final product gas depend on the type of coal and its composition, the gasifying agent or medium, and the thermodynamics and chemistry of the gasification reactions as controlled by the process operating parameters.

Coal gasification technology can be used in the following energy systems of potential importance (Lee, 2007).

- i. Production of fuel for use in electric power generation.
- ii. Production of synthesis gas for use as chemical feedstock for liquid transport fuel and chemicals production.
- iii. Production of hydrogen for fuel cell applications.
- iv. Production of synthetic or substitute natural gas (SNG) for use as pipeline gas supplies.
- v. Generation of fuel gas for industrial purposes.

2.2.1 The Industry Context of Coal Gasification

The utilisation of coal in some of the older technologies has been marked with some undesirable environmental impacts. The major pollutants include: oxides of nitrogen and sulphur; ash and slag; particulate emissions; and green house gases such as carbon dioxide and nitrous oxide (Marban *et al.*, 1995; Spalding-Fecher *et al.*, 2000). The role of these pollutants in urban smog formation, acid rain and enhanced greenhouse effect are significant (Spalding-Fecher *et al.*, 2000). Consequently, there is strong incentive to reduce emissions and improve the efficiency of coal utilisation technologies (Hu *et al.*, 2004).

To address these challenges, new coal utilisation technologies have developed (Grainger and Gibson, 1981; Osborne *et al.*, 1996; Koornneef *et al.*, 2007). Some are variants of the Pulverised-Fuel (PF) fired coal boilers, such as Ultra Super-Critical PF units with advanced NO_x abatement techniques and flue gas desulphurisation.

Pressurised fluidized bed (PFB) combustion and gasification, and advanced variants of these technologies that are emerging are used for low rank, more reactive coals (Osborne *et al.*, 1996; Koornneef *et al.*, 2007). These low ranked coals are usually rich in inertinites and have high ash content as observed in the coals from the Highveld coalfields of South Africa. Major advances in gas turbine engineering have meant that Integrated Gasification Combined Cycle (IGCC) technologies are now a viable means of achieving high efficiency in coal based power generation with reduced emissions. The use of pulverised coal injection (PCI) in blast furnaces, which reduces the amount of high-cost coking coals required by the iron smelting processes and increases the efficiency of blast furnaces (Claudius Peters technologies, 2001), is also gaining popularity.

Most of the advanced coal utilisation technologies operate at high temperatures and pressures, thereby increasing the reaction intensity and improving the efficiency of the process. Typical thermal efficiencies of PF fired power stations are <37% whereas super-critical PF units can achieve net efficiency of 47% (Campbell *et al.*, 2000). Power generation using IGCC systems achieve a thermal efficiency of about 47% and it is believed that efficiencies of >50% are possible (Buskies, 1996; Campbell *et al.*, 2000)

An understanding of coal and coal char behaviour under conditions relevant to these new gasification technologies is required to enable optimum design of efficient coal utilisation technology, and to allow the prediction of the gasification behaviour of the coal in a given gasifier. These issues are particularly important for the vast South African coal reserves, given coal's economic importance as a major export commodity and the extent to which it is relied on domestically. In order to match these coals effectively with technology, the effects of process conditions and coal and char properties on the gasification process need to be understood.

2.2.2 History of Coal Gasification

Coal gasification is not a new technology. Littlewood (1977) reported that as far back as 1792, gas produced from the carbonisation of coking coal was used for lighting. Originally, a process similar to coking was used. However, in the 1860s, a process that converted non-coking coal via gasification was demonstrated. In the late 1880s, the chemical potential of the gasification process was demonstrated in the production of ammonia (Littlewood, 1977). This technology quickly spread through Europe, Japan and the US. The gasification of coal throughout the early to mid 1900s was used to supply piped gas ('town gas') for cooking and heating, and was produced in a fixed bed gasifier, similar in principle to early coke ovens. The subsequent use of oil as fuel and the discovery of large reserves of the relatively clean natural gas meant that the reliance on coking coals for town gas production declined.

In more recent times, the large reserves of coal in South Africa, and the environmental concerns with the conventional facilities, have increased the importance of clean coal gasification and combustion processes for large scale power generation, liquid fuels and chemicals production.

2.2.3 Modern Coal Gasification

Modern coal gasification systems produce liquid fuels and various industrial chemicals and provide a cleaner, more efficient alternative to combustion-based power generation systems. Power generation from coal gasification has been of interest in recent years as the development of advanced turbine systems has made the integration of coal gasification with gas and steam turbines much more viable (Osborne *et al.*, 1996).

Considering the reactor configuration and the method of gas-solid feedstock contact, modern gasification processes can be grouped into four different types: entrained flow gasifiers; fluidised bed gasifiers; fixed bed gasifiers (Littlewood, 1977; Kristiansen, 1996; Lee, 2007); and molten salt bath reactors – such as those currently utilised by the Atgas process (van Heek and Mühlen, 1985; Kabe, 2004; Lee, 2007). It should be noted that the conditions under which these systems operate vary according to the type of coal on which they are designed to run on. The products that can be obtained from modern coal gasification are shown in Figure 2.1.

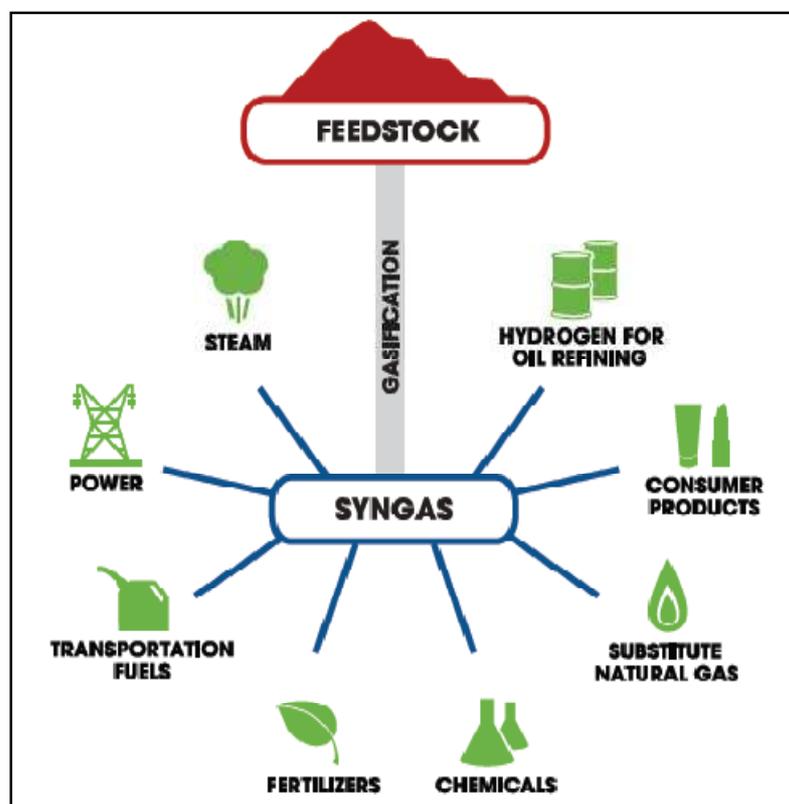


Figure 2.1: Coal gasification products (GTC, 2008)

Gasification has been used in the chemical, refining, and fertilizer industries for more than 50 years and by the electric power industry for more than 35 years. Currently, there are more than 140 gasification plants, with more than 420 gasifiers operating worldwide (GTC, 2008). In South Africa, Sasol[®] uses fixed bed dry bottom (FBDB[™]) gasification technology to produce synthesis gas which is a precursor in its liquid transport fuels and chemicals production (van de Venter, 2005). The South African power utility, ESKOM has also planned (if approved), the addition of a 350 MW UCG- IGCC ultra-high efficiency unit to its Majuba power station which could potentially be commissioned by 2012 (Eskom Annual report, 2008).

Tables 2.1 and 2.2 show various plants around the world using gasification technology for power generation, liquid fuels and chemicals production (*Note: The list of gasifiers for power generation is limited to IGCC, while that for Chemicals and liquid fuels is limited to Sasol[®] FBDB[™] gasifiers*).

Table 2.1: Gasification based power generating plants (GTC, 2008).

Plant Name	Location	Year started	Feedstock	Output (MW)
Noun	Buggenum, Netherlands	1994	Coal / Biomass	250
Wabash	Terre Haute, IN, USA	1995	Coal / Petroleum coke	260
Tampa Electric	Polk County, FL, USA	1996	Coal / Petroleum coke	250
Vrevosa	Vrevosa, Czech Republic	1996	Coal / Petroleum coke	350
Schwarze Pumpe	Lausitz, Germany	1996	Coal / Biomass	40
Pernis Refinery	Rotterdam, Netherlands	1997	Visbreaker tar	120
Elcogas	Puertollano, Spain	1998	Coal / Petroleum coke	300
ISAB Energy	Sicily, Italy	2000	Asphalt	520
Sarlux	Sardinia, Italy	2001	Visbreaker tar	545
Chawan IGCC	Jurong Island, Singapore	2001	Tar	160
api Energia	Falconara, Italy	2002	Visbreaker tar	280
Valero	Delaware City, DE, USA	2003	Petroleum coke	160
Negishi IGCC	Negishi, Japan	2003	Asphalt	342
Eni Sannazzaro	Sannazzaro, Italy	2006	Oil residue	250
Fujian Petrochemical	Quanzhou, China	2009	Oil residue	280
Eskom	Majuba, South Africa	2012 ???	Coal	350
Total				4457

Table: 2.2: Some of the Plants using FBDB™ as Sasol® (van de Venter, 2005).

Plant name	Location	Year started	Feedstock	Output (MW)	Products
Sasol Chemical Industries	Sasolburg, S. Africa	1955	100% Sub bituminous coal	17 FBDB	Liquid chemicals
Sasol Synfuels	Secunda, S. Africa	1979	100% Sub bituminous coal	80 FBDB	Liquid fuels and chemicals
Dakota Gasification Company	Dakota, USA	1985	100% Lignite	14 FBDB	Substitute natural gas
Shanxi-Tianji Coal Chemical Company	Shanxi, China	1978	Anthracite	5 FBDB	Ammonia for fertilizer production
Swartz Pumpe	Lausitz, Germany	1996/2000	80% Waste / 10% Lignite / 10% Bituminous coal	5 FBDB	Power / Methanol
Yima	Yima, china	2000	100% Sub bituminous coal	2 FBDB	Methanol
KFX, Gillete Wyoming	Wyoming, USA	2005	100% Sub bituminous coal	2 FBDB	Coal beneficiation

2.3 The Coal Gasification Process

The conversion of coal into fuel gas generally involves three essential steps (Laurendeau, 1978; Watkinson *et al.*, 1991; Yu *et al.*, 2004):

- i. The devolatilisation of the organic matter and mineral matter leading to the formation of char;
- ii. The homogeneous reactions of the volatile species from step1 with the reactant gases; and
- iii. The heterogeneous reactions of the resultant char with the reactant gases leading to the formation of gaseous products and ash.

The first step, during which the coal is heated and rapidly loses hydrocarbons, tars and other volatiles, is referred to as pyrolysis or devolatilisation. This is by far the fastest

of the three stages and as such does not play a major role in determining the overall kinetics of the gasification system. It does, however affect the amount of char produced and the structural properties of this char (Laurendeau, 1978; Cloke and Lester, 1994). Thus, it has a strong influence on the levels of conversion achievable in the gasifier. The combustion of the released volatiles also produces much of the heat required for subsequent conversion of the char and this is the second step of the gasification process. In the third step, the resultant char undergoes heterogeneous reactions with the various gaseous species present in the gasifier. This stage produces a gas that is typically rich in CO and H_2 . The reaction of char with O_2 , if present in the gasifier also provide the much needed heat for the endothermic char- CO_2 and char- H_2O reactions that continue well after the O_2 has been consumed. The heterogeneous reactions are much slower than the pyrolysis reactions.

Under fluidised bed combustion conditions (750 - 1000 °C, 5 - 20 atm), pyrolysis is completed in less than 10 seconds, while char burnout takes approximately 1000 seconds. In the case of fixed bed gasification (750 - 1250 °C, 20 - 50 atm), pyrolysis and char burnout are in the order of 1000 and 10,000 seconds respectively (Laurendeau, 1978).

The relative slowness of the heterogeneous char-gas reaction often means that it is the rate-determining step during coal conversion (Cloke and Lester, 1994). Consequently, this step plays a major role in the planning for the design of a gasifier, and in the assessment of coal for use in a particular gasification technology. It is therefore critically important that the char reaction kinetics are understood. Thus, the role played by various properties and parameters as these relate to the parent coal and the chars form the basis of this work. The following sections look at these factors.

2.4 Chemical and Physical Structure of Coal and Char

Before the fundamentals of char gasification kinetics and the factors that affect the kinetics are discussed in detail, it is important to understand the nature of coal and char in terms of their chemical and physical structures and typical properties such as composition, pore structure, surface area, etc.

2.4.1 Chemical and Physical Structure of Coal

Coal contains practically all of the natural elements, but the organic fraction consists mainly of carbon and hydrogen, commonly referred to as macerals, with lesser quantities of oxygen, sulphur and nitrogen. The distribution of these elements within the organic matrix, impacts on the structure of the coal and influences its pyrolysis and gasification behaviour. These macerals, which are optically recognisable and distinguishable are derived from different precursors and can be significantly different chemically and physically (van Krevelen, 1981; Jones *et al.*, 1985; Falcon and Snyman, 1986; Snyman and Botha, 1993; Choi *et al.*, 1989; Taulbee *et al.*, 1989; Blanc *et al.*, 1991; Czechowski and Kidawa, 1991; dela Rosa *et al.*, 1992; Mastalerz and Marc Bustin, 1993; Cloke and Lester, 1994; Kabe *et al.*, 2004; Kruszewska, 2003; Everson *et al.*, 2008b).

Macerals are grouped into three broad classes: vitrinites, liptinites and inertinites. With increasing maturation, the structural differences between macerals become less distinct, until at high rank (anthracite), they are almost impossible to distinguish optically or chemically (van Krevelen, 1981; Falcon and Snyman, 1986). However, in the bituminous rank range, the differences among maceral groups and in some cases the differences among maceral components within a maceral group can be substantial. The carbon aromaticity of macerals determined by ^{13}C NMR, typically decreases in the order: inertinite > vitrinite > liptinite (Choi *et al.*, 1989; Palmer *et al.*, 1990). The elemental composition also varies with the H/C ratio, decreasing in the order: liptinite > vitrinite > inertinites (Blanc *et al.*, 1991; Mastalerz and Marc Bustin, 1993; Maroto-Valer *et al.*, 1994), although the values converge at higher rank (van Krevelen, 1981; Kabe *et al.*, 2004). The proton aromaticity, H_a determined from ^1H NMR indicates that maceral concentrates have H_a values that increase in the order: liptinite \leq vitrinite \ll inertinite with a low value of 0.5 and a high value of 0.76 (Vassallo *et al.*, 1991).

This shows a significant difference in the distribution of hydrogen within the maceral groups. From the elemental composition, and proton and carbon aromaticities, the aliphatic atomic hydrogen to carbon ratio can be determined. There are some ambiguities about these values, with values below 2.0 discounted by Love *et al.* (1993) as unreasonable. However, these values for some coals are probably high as a

result of the addition of the highly aliphatic liptinite maceral group which may be significant for Northern Hemisphere coals. Furthermore, values > 2.0 would indicate either a higher amount of CH_2 groups or a combination of CH_3 and CH groups. This would essentially lower the amount of hydroaromatics present. While atomic H/C values > 2.0 are possible for coals, vitrinites have been reported to have lower values for most of the rank range due to their hydroaromatic nature (dela Rosa *et al.*, 1992; Hanna *et al.*, 1992). Hence, maceral composition impacts on coal structure and behaviour. Hanna *et al.* (1992) also reported that macerals from Australian coals may be very different from macerals from similar ranks of coal from the Northern or Southern Hemisphere, and this further substantiates the complexity of coal structural investigations.

The age or maturation of coal also influences the chemical structure and is best represented by the parameter called rank of coal. The rank of coal is directly related to the carbon content, with a highly graphitic material representing the ultimate product of the coalification process. The oxygen content decreases with increasing rank, while the hydrogen content remains relatively constant until about 89% elemental carbon content, above which a sharp decrease occurs (van Krevelen, 1981; Falcon and Snyman, 1986; Kabe *et al.*, 2004). Hatcher (1988) reported that the fraction of carbon that is both aromatic and protonated for vitrinites has considerable scatter and as the rank increases, there is a rapid decrease. With increasing maturation, aromaticity increases, the size of aromatic carbon per cluster also increases slowly up to anthracite at which point a rapid increase occurs (Maroto-Valer *et al.*, 1994). Disordered or non-crystalline carbon (usually referred to as the fraction of amorphous carbon) also decreases with increasing rank and decreasing atomic hydrogen content (Franklin, 1951; Hirsch, 1954; Lu *et al.*, 2001; Maity and Mukherjee, 2006).

While the absolute quantities of the atoms C , H , O , N , and S contained in the organic component of coal impacts on the physical structure, their spatial arrangement and orientation in the molecule also has an influence. This is observed in the density of the molecules and is referred to as 'helium density' or 'skeletal density' due to the fact that helium which is the smallest inert molecule and as such fits best to penetrate the pore system of coals is used. Gan *et al.* (1972), however, noted that helium will not penetrate closed porosity, thus giving a lower value than the 'true density'. The

corrected helium density for macerals is rank dependent increasing in the order: liptinite < vitrinite < inertinite (Falcon and Snyman, 1986). With increasing rank (% C), Gan *et al.* (1972) reported helium density values of approximately $1.4 \text{ g}\cdot\text{cm}^{-3}$, decreasing to a minimum of approximately $1.25 \text{ g}\cdot\text{cm}^{-3}$ at 80% C and then, increasing sharply at around 90% C for US coals of various rank – from anthracite to lignite. This agreed well with the investigations of Senneca *et al.* (1998) who investigated, among other parameters, the helium density of petroleum coke and two different coals, one of which was from South Africa. The elemental carbon content of the three carbon materials was 77.3, 68.0 and 89.05 % C and their determined helium densities were 1.5, 1.4 and $1.6 \text{ g}\cdot\text{cm}^{-3}$ respectively. Strugala (1994) calculated the real densities of hard coals from the proximate, ultimate and mineral analyses using empirical formulae.

There have been substantial efforts to elucidate the molecular structure of coal. This task is made difficult due to large variety of coals, the heterogeneity of a single coal and the complexity of individual constituents. Despite these hindrances, there were a number of early successful modelling efforts (Given, 1960; Shinn, 1984; Carlson, 1992). Given (1960) proposed a hypothetical structure for a bituminous coal vitrinite with 82% carbon as one possible arrangement of the atoms present in the coal molecule in line with the facts available at that time.

Major advances in the area of molecular modelling as applied to coal structure have evolved over the years. These advances helped in the investigations of Jones *et al.* (1999); Mathews *et al.* (2001); and more recently Narkiewicz and Mathews (2008); and Van Niekerk (2008). The molecular representations of two South African, Permian-aged vitrinite-rich Waterberg and inertinite-rich Highveld coals were elucidated by Van Niekerk (2008). He reported an elemental composition of $C_{1000}H_{846}O_{69}N_{16}S_2$ and $C_{1000}H_{673}O_{78}N_{20}S_4$ for the vitrinite-rich Waterberg and inertinite-rich Highveld coal respectively. The molecular models of these coals are shown in Figures 2.4 and 2.5 in line and van der Waals radii rendering (Van Niekerk, 2008). It should be noted that hydrogen is not shown, while the other atoms: carbon, oxygen, nitrogen and sulphur present in the models are coloured as: green red, blue and yellow respectively.

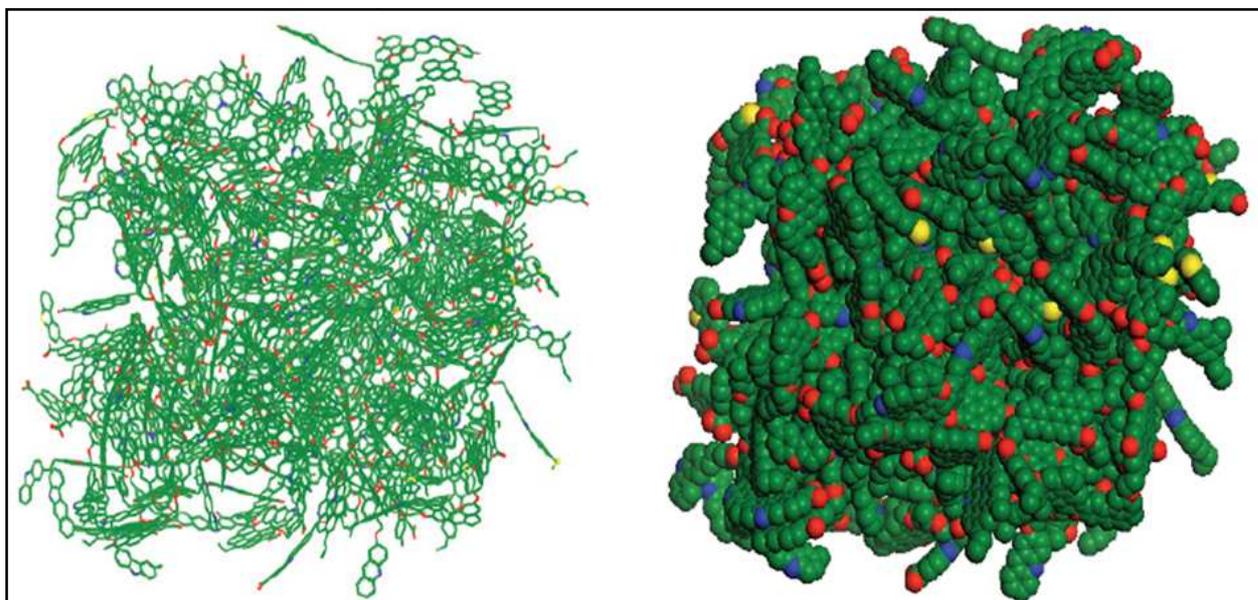


Figure 2.2: Molecular model for the inertinite-rich Highveld coal
(Van Niekerk, 2008).

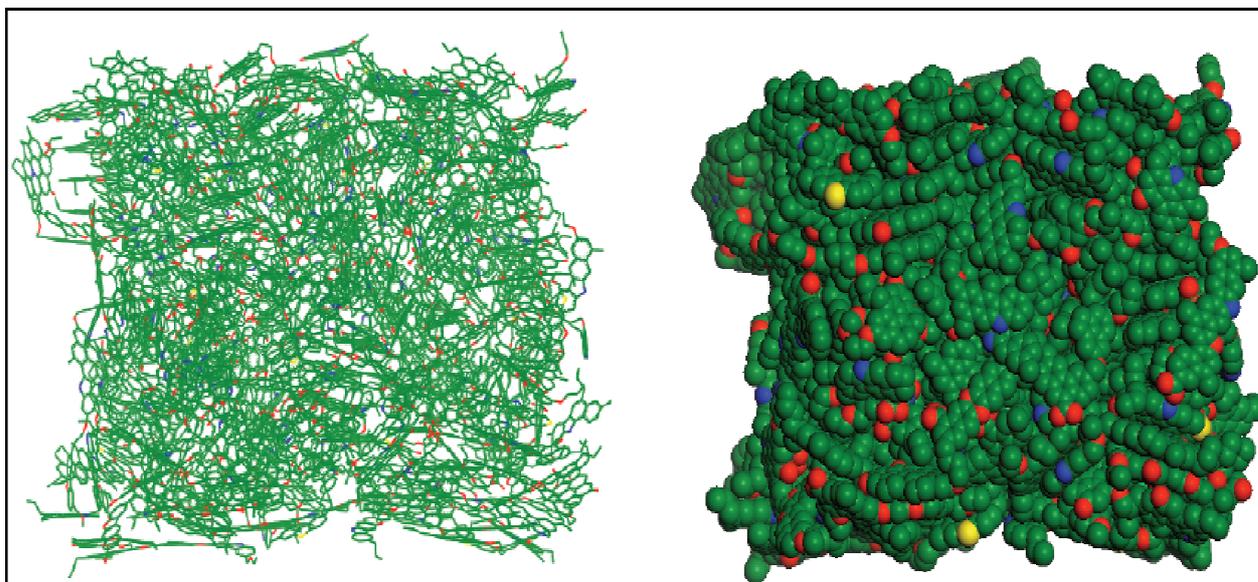


Figure 2.3: Molecular model for the vitrinite-rich Waterberg coal
(Van Niekerk, 2008)

2.4.2 Chemical and Physical Structure of Coal Char

The exact nature of chars derived from coal is difficult to describe in general terms, as almost all the variables that describe the physical properties of chars are dependent on the conditions under which the char was made, the parent coal rank, maceral composition and particle size. Unfortunately, the study of the chemical structure of char has not been as common as the study of its physical structure. Generally speaking, coal chars are porous solids consisting primarily of carbon and mineral matter, incorporating small amounts of nitrogen, sulphur, hydrogen and oxygen into this framework (Laurendeau, 1978).

The amounts of nitrogen, sulphur, hydrogen and oxygen in the char (relative to the carbon) are often less than their amount in the parent coal, due to their removal during devolatilisation. With increasing devolatilisation temperature and residence time, char aromaticity increases with a corresponding loss of aliphatic groups (Pugmire *et al.*, 1991; Lu *et al.*, 2001, 2002a and 2002b; Kawakami *et al.*, 2006) and decreasing fraction of disordered or amorphous carbon (Schoening, 1982 and 1983; Senneca *et al.*, 1998; Russell *et al.*, 1999; Lu *et al.*, 2001; Kawakami *et al.*, 2006; Maity and Mukherjee, 2006). Fletcher (1993) reported that rapid heating of Pittsburgh # 8 coal showed little evidence of char cluster size growth, and suggested that cross-linking is occurring at the same time as aliphatics are lost. The atomic H/C and O/C ratios decreases (Fletcher, 1993), and the proton aromaticity increases (Chen *et al.*, 1992), as the coals transit to chars.

Laurendeau (1978) also noted that as a result of the heat treatment during pyrolysis, the carbon in the char is usually more ordered than that in the parent coal giving rise to increased crystallinity and decreased fraction of amorphous carbon (Davis *et al.*, 1995). Ordering of the carbon crystallite structure reduces the occurrence of carbon edge sites and unpaired surface electrons often associated with the reactivity of the char (Kashiwaya and Ishii, 1991; Davis *et al.*, 1995; Russell *et al.*, 1999; Shim and Hurt, 2000; Takagi *et al.*, 2004). The extent of structural ordering with respect to the different annealing temperatures is represented in the schematic of Figure 2.4.

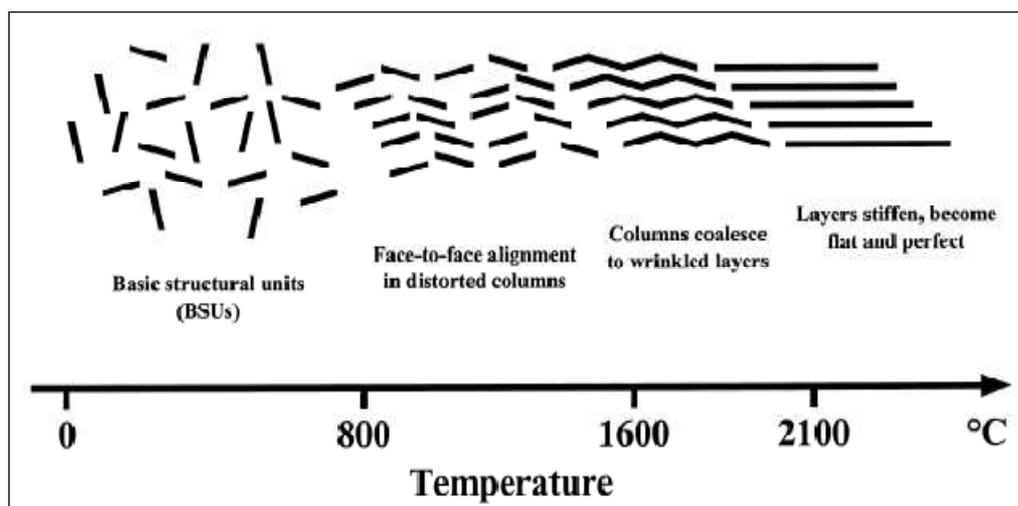


Figure 2.4: A schematic representation of the structural changes that occurs upon heating of coal (Russell *et al.*, 1999).

Heat treatment of chars, in particular its effect on char reactivity, is discussed in detail later in this review. However, fully devolatilised chars of various coal ranks have been reported to be similar in their chemical structure (Fletcher, 1993; Chen *et al.*, 1992). The physical structural evolution of chars is related to thermoplasticity and hence to char morphology (Cloke and Lester, 1994). Thermoplasticity influences particle size and fragmentation which is very important for the hydrodynamics and heat and mass transfer in fluidised bed and entrained flow gasifiers (van Heek and Mühlen, 1987). The controlling feature of char morphology appears to be the extent of fluidity that the particle can achieve. However, thermoplasticity is a transient property, and appears to be more transient for certain macerals and for certain conditions. Upon heating, thermal swelling generally occurs in vitrinites and liptinites (Cloke and Lester, 1994; du Cann, 2008). The swelling can be substantial. Vitrinites swell to a greater extent than the other macerals (Tsai and Scaroni, 1987). Fletcher (1993) also noted that swelling can occur with little or no mass loss, prior to and during tar release.

Generally, inertinites do not readily swell; although micrinites usually associated with liptinites have been reported to vesiculate with liptinite during combustion. Micrinites have also been known to yield more volatile matter than other inertinite macerals, probably due to their connection to the liptinite fragments (Cloke and Lester, 1994).

Char porosity depends to a large extent on the nature of porosity, maceral content and rank of the precursor coals. The devolatilisation process, through the softening of the particle and the release of volatiles, affects this pore structure dramatically (Tsai and Scaroni, 1987; Cloke and Lester, 1994). The high temperatures present during pyrolysis have been found to reduce the microporous nature of these pores, as the plastic nature of the intermediate phase causes the closing of the fine structures. The volatile matter released also impact on the porosity of the char, as the release of volatile material through the softened particle can form larger pores and voids. However, it is difficult to present a general description of the nature of the pore structure of chars since the temperature, pressure and heating rate of pyrolysis all seem to affect it in some way (Ng *et al.*, 1988). Depending on these pyrolysis conditions, the pores of a char range in size from nanometres to millimetres across. They can be interconnecting with eventual paths to the external surface of the char, or they can be the so-called 'blind' pores, which are not connected to the surface but which are often exposed after reaction as carbon is removed (Laurendeau, 1978).

The shapes of the pores in chars also vary. Models depicting the pore structure of chars often simplify the case and use uniformly cylindrical pores. In reality, pores can be cylindrical, spherical, or 'bottlenecked' (pores that are large but have a restricted opening or slits), or combinations of these. The size of pores is rarely uniform. Often long cylindrical pores taper or expand, and the diameter of spherical pores is rarely the same throughout a sample (Laurendeau, (1978).

Chars generally have higher CO_2 and BET surface areas than the parent coal (Ng *et al.*, 1988) with values greater than $400 \text{ m}^2 \cdot \text{g}^{-1}$ reported for bituminous chars by Tsai and Scaroni (1987). Surface area is clearly dependent on physical structure, with potentially large differences in surface areas among chars of the same coal. Skeletal density of chars are significantly higher than those of the parent coals (Nsakala *et al.*, 1978), with reported values in excess of $2.0 \text{ g} \cdot \text{cm}^{-3}$ (Ng *et al.*, 1988), close to the theoretical density of graphite- $2.26 \text{ g} \cdot \text{cm}^{-3}$. These high values are indicative of the efficient packing of the carbon sheets, similar to that existing in graphite (Hirsch, 1954).

Not much effort has been put into the molecular modelling of char structure. Jones *et al.* (1999) modelled the char structural evolution of Pittsburgh #8 coal during the pyrolysis process in a wire-mesh reactor. They were able to render the geometry optimised structural conformations of the coal, its char and the intermediate volatiles by energy minimisation as shown in Figure 2.5. They also reported an average molecular formula of $C_{563}H_{401}O_{46}N_9S_5$ for the parent coal. Average molecular formulae of $C_{469}H_{193}O_{26}N_6S_2$ and $C_{418}H_{125}O_5N_5S_2$ were reported for the chars with holding times of 0.3 second and 1.0 second respectively (Jones *et al.*, 1999).

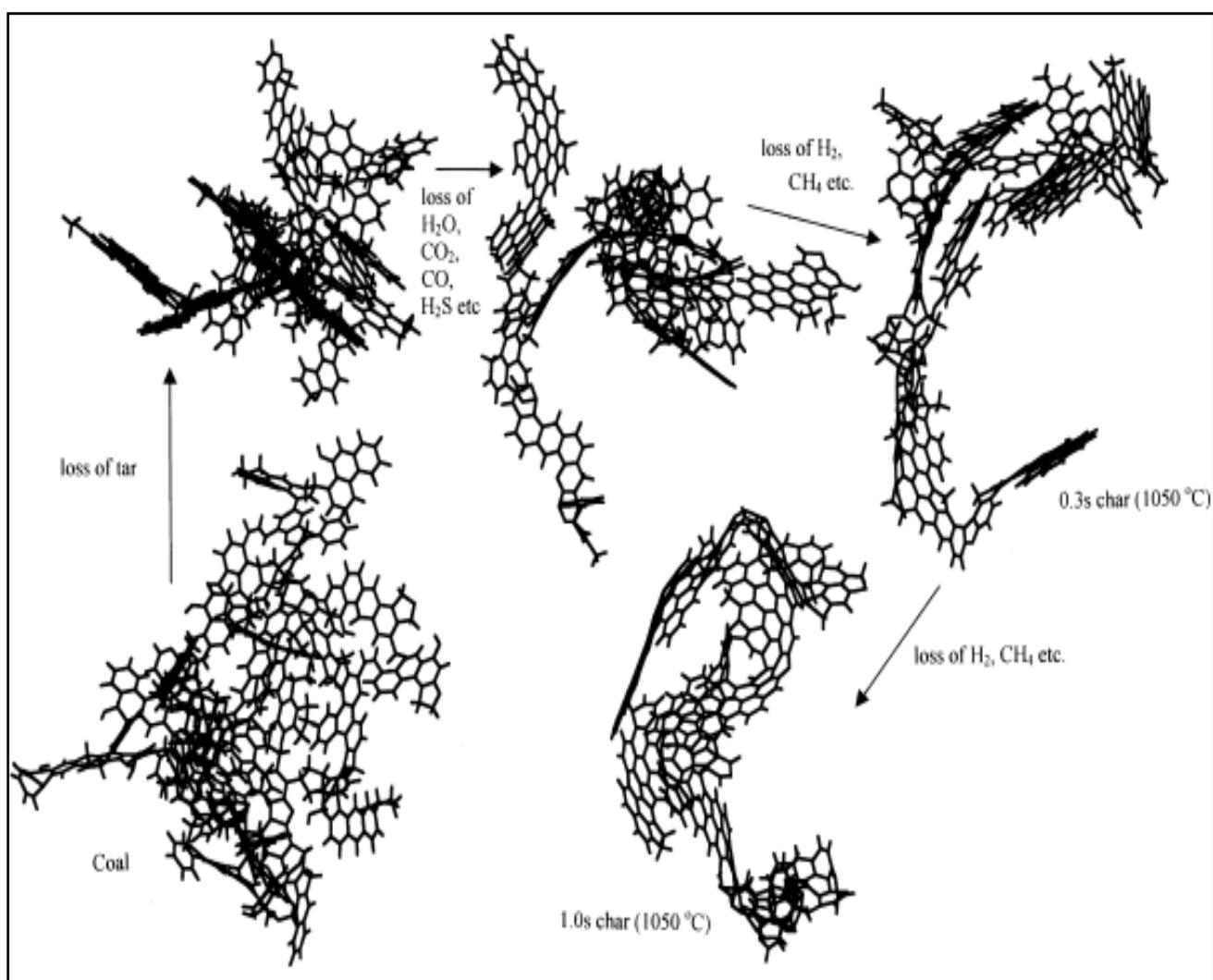


Figure 2.5: Geometry optimised structural conformations of average coal and char molecules and intermediates, in the coal to char pyrolysis reaction (Jones *et al.*, 1999)

2.4.3 The Crystallite Structure of the Carbon Basic Structural Unit (BSU)

The crystallite structure of carbonaceous material refers to the microtextural and microstructural characterisation of the carbon contained in them. Various investigators have described char microstructure using analytic techniques such as HRTEM and XRD. Such techniques are able to characterise the structure of the carbonaceous materials at atomic level (Franklin, 1951; Hirsch, 1954; Ergun, 1968; van Krevelen, 1981; Rouzaud, 1990; Kashiwaya and Ishii 1991; Davis *et al.*, 1995; Marsh, 1989; Lu *et al.*, 2001; Sharma *et al.*, 2002; Feng *et al.*, 2003; Takagi *et al.*, 2004, Trejo *et al.*, 2007).

They concluded that the crystallite of coal and char consists of polyaromatic basic structural units (BSU) of about 1 nm, formed by polyaromatic layers (4 to 10 rings) isolated or stacked by 2 or 3. The BSUs are ordered in stacked planes of the aromatic layers often referred to as lamellae (Essenhigh, R. H. 1981; van Krevelen, 1981; Marsh, 1989; Kashiwaya and Ishii, 1991; Kabe *et al.*, 2004), or molecular orientation domains (MOD) or local molecular orientation (LMO) (Rouzaud *et al.*, 1988; Feng *et al.*, 2003). A schematic representation of a crystallite of graphite is as given in Figure 2.6. Inside the MODs the polyaromatic basic structural units (BSUs) are either misorientated or locally orientated in parallel (Rouzaud, 1990).

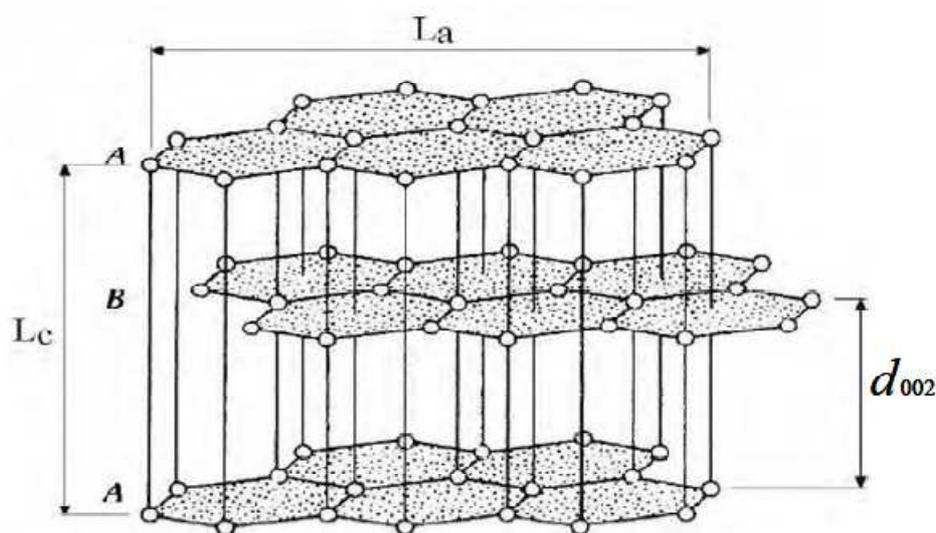


Figure 2.6: Schematic representation of a crystallite of graphite (Essenhigh, 1981)

The X-ray diffraction (XRD) pattern of a carbonaceous material such as coal and coal chars shows diffuse peaks at (002) , (10) and (11) bands that correspond to (002) , (100) and (110) reflections of graphite and strong low-angle or background scattering (Franklin, 1951; Hirsch, 1954; Short and Walker, 1963; Schoening, 1982 and 1983; Davis *et al.*, 1995; Kashiwaya and Ishii, 1991; Lu *et al.*, 2001, 2002a and 2002b; Takagi *et al.*, 2004; Kawakami *et al.*, 2006; Bouhadda, 2007; Wu *et al.*, 2008). The diffuse peaks of the (002) , (10) and (11) reflections indicate the presence of small graphite-like domains (Franklin, 1951; Hirsch, 1954; Short and Walker, 1963; Lu *et al.*, 2001). It is also widely reported that the non-crystalline carbon or amorphous carbon, forms the background intensity of the X-ray diffraction pattern (Franklin, 1951; Hirsch, 1954; Short and Walker, 1963; Schoening, 1982 and 1983; Davis *et al.*, 1995; Kashiwaya and Ishii, 1991; Lu *et al.*, 2001, 2002a and 2002b; Takagi *et al.*, 2004; Kawakami *et al.*, 2006; Bouhadda, 2007; Wu *et al.*, 2008).

The crystallite is usually layered in the form ABABAB. The (002) reflection indicates the stacking of the aromatic layers and both the (10) and (11) reflections correspond to the two-dimensional lattices of the aromatic layers. The crystallographic parameters that can be determined using the XRD pattern are: the aromatic layer stacking height or crystallite height, L_c ; average crystallite size or diameter, L_a ; and the inter-layer spacing or inter-planar distance (d_{002}) as annotated in Figure 2.6. Other parameters that can be determined from the XRD diffractogram include the carbon aromaticity and the fraction of amorphous carbon.

The aromatic layer stacking height and the distance between lamellae in the char depend on the rank of the parent coal; as the coal rank increases the crystallite height increases and the distance between lamellae decreases (van Krevelen, 1981; Marsh, 1989; Kabe *et al.*, 2004). The average crystallite lattice parameters (L_c and L_a) can be determined using the empirical equation first derived by Scherrer (Kashiwaya and Ishii, 1991; Davis *et al.*, 1995; Lu *et al.*, 2001; Feng *et al.*, 2003; Takagi *et al.*, 2004; Trejo *et al.*, 2007; Van Niekerk, 2008):

$$L_c = \frac{K\lambda}{\beta_{002} \cdot \cos \theta_{002}} \quad (2.1)$$

$$L_a = \frac{K\lambda}{\beta_{10} \cdot \cos \theta_{10}} \quad (2.2)$$

The interlayer distance between aromatic sheets, d_{002} , was calculated from the maximum of the (002) band using the Braggs Equation (Lu *et al.*, 2001; Takagi *et al.*, 2004; Van Niekerk, 2008):

$$d_{002} = \frac{\lambda}{2 \sin \theta_{002}} \quad (2.3)$$

The average number of crystallites in a stack N_{ave} , was calculated using the relation (Trejo *et al.*, 2007; Van Niekerk, 2008):

$$N_{ave} = \frac{L_c}{d_{002}} + 1 \quad (2.4)$$

If it is assumed that the area under the (002) band and the γ band (A_{002} and A_γ) are equal to the number of aromatic carbon and aliphatic carbon atoms respectively, then the aromaticity of the coal or char can be calculated using Equation 2.5 (Lu *et al.*, 2001; 2002a and 2002b; Kawakami *et al.*, 2006; Trejo *et al.*, 2007; Van Niekerk, 2008):

$$f_a = \frac{A_{002}}{A_{002} + A_\gamma} \quad (2.5)$$

The fraction of amorphous carbon can also be calculated from the reduced X-ray intensity of the d_{002} peak of the sample using the relation originally proposed by Franklin (1951) and used by Ergun and Tiensuu (1959) and Lu *et al.* (2001, 2002a and 2002b). These are discussed in detail in Section 3.6.4.

$$\frac{I - X_A}{1 - X_A} = \frac{0.0606}{s^2} \times \frac{\sin^2(N_{ave} d_{002} \pi \cdot s)}{N_{ave} \cdot \sin^2(d_{002} \pi \cdot s)} \quad (2.6)$$

2.5 Coal, Char and Gasification Reactivity

To be able to assess the suitability of coals for use in different gasification systems and to aid in the design of reactors to suit specific coal types, a comprehensive gasification model that can predict coal conversion levels under process conditions is necessary. The influence of the char gasification stage on the rate of conversion means that it is a significant variable in the development of such a model.

Char conversion rates are a function of many variables: the more significant of these are discussed in detail in later sections of this review. Some of these are physical effects, and can be modelled adequately with a thorough understanding of the gasification conditions and particle structure. Others relate more to the chemistry of the char; consequently predicting such variables requires experimental data on which models can be based.

The intrinsic reactivity of the char is such a property, and is the focus of much of the work in this research. The intrinsic reactivity of char is defined by kinetic data measured under conditions where chemical reactions alone control the conversion rates. Data are usually normalised to some measure of the total surface area of the char, so that they reflect the inherent nature of the carbon (and any influences of mineral matter and other impurities). Such data are required in order to understand conversion rates in processes that have some degree of chemical rate control, regardless of the extent of pore diffusion limitations. This is particularly relevant for the slower char- CO_2 and char- H_2O reactions under gasification conditions.

Chemical kinetics may also have some degree of controlling influence for combustion systems at the lower temperatures found in fluidised bed applications and for very fine particles in PF systems. Intrinsic reactivity is characterised by kinetic parameters determined from reaction rate measurements, both as measured (apparent or specific) and normalised to the char surface area (intrinsic), where measurement occurs under conditions where chemical processes alone control reaction rates. This usually necessitates the use of relatively low temperatures: for char- O_2 reactions, this is often below 500°C; while char- CO_2 and char- H_2O reactions are usually measured at between 800 and 1100 °C (Dutta *et al.*, 1977; Radovic *et al.*, 1985; Matsui *et al.*, 1987; Harris and Smith, 1990; Fu and Wang, 2001; Ochoa *et al.*, 2001; Sharma *et al.*, 2002).

The conditions under which intrinsic data are generated mean that they are more readily obtained than data generated under simulated process conditions. Intrinsic data are particularly useful in the modelling of the char gasification system. Combining intrinsic reactivity data with the appropriate diffusion, mass transfer and heat transfer calculations and char structural considerations will allow the development of a predictive process model that can be applied to the sample as it reacts under a variety of conditions. This is useful, as operating parameters of different gasifiers vary greatly. By understanding the factors that cause the intrinsic reactivity of a char to vary, particularly under the high pressure conditions that prevail in gasification applications, a more accurate predictive model is possible.

2.6 Factors Influencing Gasification Reactivity

In addition to the reaction conditions, the heterogeneous nature of coal means that there are a number of other factors that will affect the conversion rates of the subsequent chars. These are as follows:

- Parent coal properties
- Pyrolysis conditions
- Chemical structure and composition
- Changes in carbon crystallite properties
- Catalysis by mineral matter
- Physical structural properties of the chars

Different chars will be affected to different extents by the factors listed above, and the magnitude of these effects will depend on the parent coal properties as well as on the conditions under which it is reacting. For example, properties that affect the chemical rate of reaction but not the rate of diffusion, such as catalysis and available surface area, will be more important at lower temperatures than at higher temperatures, when chemical processes have more influence on the rate of conversion of the char.

Conversely, char porosity (which influences the rate of diffusion through the pores of the sample) will not have a large effect at low temperatures but become quite significant at higher temperatures.

2.6.1 Properties of the Parent Coal

The properties of parent coal have long been known to have some effect on the reactivity of the char produced after pyrolysis. Some of these properties that need consideration during gasification include: carbon content; volatile matter content; mineral matter content; and the petrographic properties of the parent coal.

2.6.1.1 Volatile Matter Content

The volatile matter content of coal depends on the maceral present. Cai *et al.* (1998) investigated some South African coals and reported that volatile matter content decreases in the order: liptinite > vitrinite > inertinite and influences both the quality and quantity of chars formed. The evolution and combustion of volatiles during devolatilisation affects the char porosity and hence the overall reactivity and can cause fragmentation of the coal particles (Kaitano, 2007). It is generally observed that the conversion rate during gasification is lower for chars that are produced from high-ranked coals. In practical and pilot-scale systems, this has usually been associated with the lower volatile content of the higher-rank coal, which results in a larger amount of char to be converted. The evolution rate of volatile matter in coal also depends on the particle temperature, operating pressure and composition of the volatiles as noted by Khairil *et al.* (2001).

2.6.1.2 Fixed Carbon Content

There is some evidence (Jenkins *et al.*, 1973; Miura *et al.*, 1989; de la Puente *et al.*, 2000) to suggest that the carbon in chars derived from high-rank coals is intrinsically less reactive than carbon in chars made from low-ranked coals. This can be due to the presence of more catalytically active mineral constituents in lower-ranked coals

(Miura *et al.*, 1989) or the difference in the fundamental structure of the carbon – low-rank coal chars have a structure with a higher degree of disorder which provide more ‘active sites’ for reaction, whereas the higher-rank coal chars have less surface area and a more ordered carbon lattice structure (Laurendeau, 1978) which may lead to less sites on which reaction can take place. Thus higher rank coals exhibit higher aromaticity and contains a lower fraction of carbon that is amorphous (Davis *et al.*, 1995; Lu *et al.*, 2001).

2.6.1.3 Petrographic Properties of Coal

There has been much research into the effects of the petrographic composition of the parent coals on the reactivity of the subsequent chars (Cai *et al.*, 1998; Megaritis *et al.*, 1999; Alonso *et al.*, 1999; Cloke and Lester, 1994). While there is experimental evidence that chars derived from inertinite-rich coals exhibit longer burning times than chars derived from coals that have a higher amount of vitrinite (Jones *et al.*, 1985; Sun *et al.*, 2004; Kaitano, 2007; Everson *et al.*, 2008a and 2008b), it is suggested that these differences are primarily due to the effects of the coal petrographic composition on the pyrolysis behaviour and the resultant char structure as demonstrated by Cai *et al.* (1998). However, Cloke and Lester (1994) noted that chars formed from inertinites (reactive- semifusinite and inertodetrinites) and micrinites associated with liptinites are indeed, as reactive as vitrinites. Suffice it to say that, not all inertinites are “inert”. Low reflecting inertinites are also more reactive than higher reflecting inertinites (Cloke and Lester, 1994); which suggests that inertinites from low ranked coals should be more reactive than their counterparts from higher ranked coals.

During pyrolysis, vitrinites readily soften and release volatile material (Tsai and Scaroni, 1987; Cloke and Lester, 1994; du Cann, 2008). This leads to chars with large pores (resulting in particles with a low carbon density) and a relatively low (yet accessible) surface area. Such morphology leads to particles that exhibit fast conversion rates under combustion and gasification conditions. Inertinites, conversely, have a tendency to not soften or release large amounts of volatile materials during pyrolysis (du Cann, 2008; Everson *et al.*, 2008b). Consequently, they are relatively carbon-rich and retain more of the parent coal’s microporosity.

The surface area of char made from inertinites is relatively high with a rather uncorresponding increase in char porosity (Friesen and Ogunsola, 1995; du Cann, 2008). Under process conditions, these pores are also inaccessible, leading to conversion rates that are low compared to chars made from vitrinite-rich coals. Bailey *et al.* (1990), Benfell *et al.* (2000) and Yu *et al.* (2004) have grouped the chars that result from the pyrolysis of coals rich in different macerals into 3 broad types: Group I (very porous, thin shelled) through group II to group III (dense, with limited porosity).

Everson and co-workers (2008b) and du Cann (2008) proposed a classification system for chars grouping the different resultant char carbon forms into seven broad groups (Groups A to F) and further delineated each broad group into different categories. A detailed discussion on these char carbon forms is presented in Section 3.7.6.

2.6.2 Pyrolysis Conditions and Heat Treatment

As well as determining the amount of char to be converted, the conditions of pyrolysis can affect the structure and morphology of the resultant char (Cloke and Lester, 1994). This in turn can influence the reactivity characteristics of the char during gasification reactions. Heat treatment of coals, the heating rates involved and the pressures at which it is done are all important issues that need to be considered when examining char reactivity.

When coal is heated to temperatures in the range of 400 - 900 °C in an inert atmosphere (pyrolysis), it decomposes into a hydrogen rich fraction (the volatiles), and a carbon rich solid residue (the char) (Laurendeau, 1978; Kristiansen, 1996). The pyrolysis reaction can be written as follows:



The hydrogen rich fraction consists of tars and gases. The resultant char mainly consists of fixed carbon and inorganic mineral matter (ash). The reactivity and the structure of the char depend on the coal type; the temperature of pyrolysis; the heating

rate; the particle size; the residence time or holding time of the coal particle in the reactor; and the pressure and the composition of the gas during pyrolysis. During pyrolysis, the microporosity (the volume fraction of pores with size <2 nm) largely increases (Laurendeau, 1978; Tsai, 1982). This is due to volatiles being released from previously inaccessible pores and to the restructuring of the aromatic clusters in the char (Jones *et al.*, 1999). The surface areas of mesopores (pore size, 2-50 nm) and macropores (pore size > 50 nm) increases as well, probably due to gasification (steam and carbon dioxide are produced in the pyrolysis process). Opening and coalescence of micropores (pore size, <2 nm) may also lead to more mesopores.

It is generally agreed that the production of the volatiles takes place by the following steps (Kristiansen, 1996):

- i. Depolymerisation of the coal macro molecule. This results in the ‘metaplast’; the fragments of the macro molecule.
- ii. Repolymerisation of the metaplast molecules.
- iii. Internal transport of molecules towards the surface and transport from the surface to the bulk gas.

Mass transport inside the particle takes place by convection and diffusion in pores when coal is non-softening. When the coal becomes plastic, the internal transport takes place by liquid-phase and bubble transport. Plasticity occurs in coals with carbon content between 81-92 % (Kristiansen, 1996), but this also depends on oxygen and hydrogen content, heating rate and particle size. When the heating rate is high, the repolymerisation reaction of the metaplast occurs very soon after the depolymerisation reaction and the coal cannot plasticise.

It is well known that chars that have endured higher temperatures during pyrolysis will generally exhibit a lower gasification reactivity indicated by slow conversion rates leading to longer burnout times (Jenkins *et al.*, 1973; van Heek and Mühlen, 1985; Davis *et al.*, 1995). Pyrolysis and post-devolatilisation heat treatment of coals reduces the number of heteroatoms and crystalline irregularities leading to increased aromaticity and crystalline carbon in the char, both of which play a role in

determining gasification reactivity (Russell *et al.*, 1999). Shim and Hurt (2000) investigated the effect of heat treatment on low temperature reactivity of char to O_2 . Their findings correlated well with published results, noting that the reactivity was observed to decrease with increasing heat treatment temperature, which was attributed to the annealing and structural ordering of the carbon in the char. The annealing was found to be very fast, such that the process could be assumed to occur simultaneously with char conversion. Wu *et al.* (2008) made similar findings in their CO_2 gasification of chars annealed up to 1400 °C.

It is not only the final temperature reached during pyrolysis, but also the residence time or holding time in a reactor at that temperature and the heating rate experienced by the coal particle during conversion to char that are important. Van Heek and Mühlen (1987) investigated the characteristic temperature at which a coal undergoing pyrolysis will drastically lose reactivity. Radovic *et al.* (1983) also investigated the reactivity of chars that were subjected to different residence times at a temperature of 1000 °C. The reactivity of the chars dropped after residence times of a few seconds and reached a minimum with a residence time of 5 minutes and could not be reduced further, even at a residence times of up to 1 hour.

This leads to the concept of a char being ‘dead burned’, meaning that the pyrolysis temperature caused the reactivity of the char to be substantially reduced and stabilised, in a very short residence time. This reduction in reactivity is attributed to the ordering of the carbon lattice in the char at higher temperatures, resulting in a decrease in the potential number of active reaction sites.

The heating rate of coal during the pyrolysis stage will also have effects on the reactivity of the resulting char. Hindmarsh *et al.* (1995) and Gale *et al.* (1996) studied the effects of heating rate on the low-temperature reactivity of the resulting char. Their results show a decrease in reactivity with both heating rate and pyrolysis temperature. An increase in both of these parameters results in an increase in the amount of volatiles released from the particles and hence in a decrease in subsequent char reactivity.

Different coals are, however, affected to different extents by heat treatment. Some coals undergo drastic changes in their chemical and physical properties during

pyrolysis. For some coals with strong coking properties this may include the formation of plastic intermediate phases. Coals that soften and also release large amounts of volatile matter will form chars that have structural properties quite different to the parent coal. On the other hand, coals such as anthracites have a solid structure that is less affected by carbonisation (Van Heek and Mühlen, 1987), and therefore are less likely to be affected by a variation in pyrolysis conditions.

The pressure at which the parent coal is devolatilised also plays an important role in the reactivity of the resulting char. Sha *et al.* (1990a) noted a significant decrease in the reactivity of the char as the pyrolysis pressure was increased, postulating effects on the pore structure as the cause. Two reasons for this are postulated, the first being that the compression of the pyrolysis products prevents the opening of the structure of the forming char, and the second being an indirect temperature effect. Such a temperature effect could arise from the exothermic hydrogasification reaction that may be occurring on the surface of the charring particle, following or simultaneous with the hydrolysis step. Cai *et al.* (1996) also found reactivity to decrease with hydrolysis pressures up to 40 atm and increased at pressures above this. The eventual increase in reactivity was the result of some char conversion by H_2 at the higher pressures exposing a fresh and enlarged carbon surface.

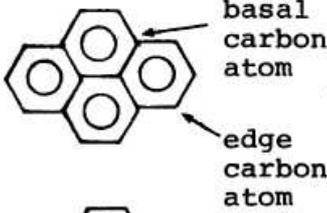
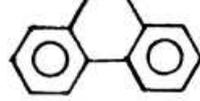
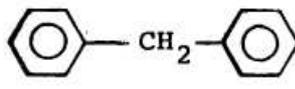
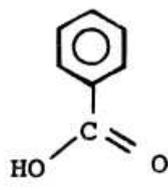
Lee *et al.* (1992) investigated the structure and reactivity of Illinois #6 coal char following pyrolysis at elevated pressures. They found that increasing the pyrolysis pressure slowed the rate of release of volatiles; increased the amount of char remaining after pyrolysis; and altered the composition of the volatile products. Their data also demonstrated how pressure hinders the development of the mesopore system that develops after the coal passes through the plastic phase of pyrolysis.

The increased fluidity that resulted from higher-pressure pyrolysis led to the enhanced ordering of carbon layers and the subsequent loss of gasification reactivity in the char residue. An interesting effect of pressure on the development of char structure during pyrolysis has been reported by Benfell *et al.* (2000), and Wu *et al.* (2000). Coal was devolatilised over a range of pressures and various structural parameters of the resulting char were analysed. They observed that as the pyrolysis pressure increases, the proportion of morphological Group I chars – the open structured, porous group – increases with a decrease in the proportion of Group II and III chars.

2.6.3 Chemical Structure and Composition of Coal and Char

The complex coal and char structures (Figures 2.2, 2.3 and 2.5) require analysis in terms of their characteristic functional groups (Laurendeau, 1978). These fundamental groups typifying the atomic species: *C*, *H*, *O*, and *S*, are summarised in Table 2.3.

Table 2.3: Basic structures and functional groups in coal (Laurendeau, 1978; Lahaye, 1998)

<u>Atomic Specie</u>	<u>Fundamental group</u>	<u>Typical example</u>
C	polynuclear aromatics	
	hydroaromatics	
H	aliphatics	
		
O	hydroxyl - OH	
	carboxyl - C(=O)OH	
	carbonyl >C=O	
N S	substituted aromatics	
	heterocyclics	

A typical coal structure consists of an aromatic/hydroaromatic cluster with an average of 4 to 10 rings per cluster loosely joined together by methylene, ether and sulphide

linkages that are 1 to 3 carbon atoms in length (Laurendeau, 1978). Given (1960) reported that the loose aliphatic groups allow cross-linking between clusters on different planes and hence the development of an extensive pore structure. He also noted that the aliphatic, hydroaromatic and heterocyclic bonds are quite susceptible to bond breakage at pyrolysis temperatures. This culminates in chars with less aliphatic and more aromatic carbon.

Chars are characterised by carbon-rich, poly-nuclear aromatic structures. Edge carbon atoms are at least one order of magnitude more reactive than are basal carbon atoms (Walker and Hippo, 1975). Increased reactivity at carbon edges is presumed to be due to the prevalence of unpaired σ electrons that are available to form bonds with chemisorbed species (Laine *et al.*, 1963). Furthermore, impurities that may catalyse some carbon reactions tend to diffuse and concentrate at crystallite edges (Walker and Hippo, 1975).

Enhanced activity found at defects in the char structure (such as vacancies) is probably due to geometric or charge imbalances (Thomas and Thomas, 1967). Laurendeau (1978) reported that oxygen and hydrogen sites on these functional groups also promote char reactivity since chemisorption usually favours non-aromatic sites over aromatic sites, noting that oxygen sites are thought to influence reactivity via electron exchanges. Hydrogen sites are presumed to increase char reactivity by preferential oxidation (Jenkins *et al.*, 1973; Laurendeau, 1978). Nitrogen and sulphur could promote ring structure attack since π electrons are most available at heterocyclic sites.

2.6.4 Changes in Carbon Crystallite Properties

The greater percentage of the organic portion of coal-derived char is composed of an imperfect arrangement of aromatic layers of varying sizes (Davis *et al.*, 1995). Various investigators (Sha *et al.*, 1990(b); Kashiwaya and Ishii, 1991; Davis *et al.*, 1995; Sharma *et al.*, 1999 and 2002; Feng *et al.*, 2003; Takagi *et al.*, 2004; Arenillas *et al.*, 2004) have been studied the effects of the changes that occur in these crystallites during devolatilisation and gasification reactions. Chemical properties of chars most

affected by these processes are the aromaticity and the fraction of amorphous carbon. Physical and structural lattice parameters such as inter-layer spacing; crystallite height; and diameter are also affected.

Char reactivity generally becomes low as the conversion increases. This has been attributed to the microstructural and microtextural changes that occur in the char crystallite and/or to the loss of catalytic activity of the minerals and inorganic matter. Davis *et al.* (1995), Russell *et al.* (1999), Sharma *et al.* (2002) and Arenillas *et al.* (2004) related the size and ordering of these layers to the reactivity of the carbon present in the char in three fundamental ways.

- First, as the crystallite size changes, the amount of hydrogen and the ratio of reactive edge sites to unreactive interior sites decreases, thus, carbon aromaticity increases.
- Second, as the individual layers approach a more perfectly graphitic arrangement of aromatic units, active sites associated with defects, heteroatoms (non-sp²-hybridized or π carbons) are lost, hence, the fraction of amorphous carbon decreases.
- Third, as the aromatic layers reach a more compact stacking arrangement, the microscopically available surface area decreases.

Although the relationship between reactivity and crystallite ordering is more complex than this simple scheme suggests, reactivity in general decreases as the degree of orderliness across the spectrum of carbon materials increases (Kashiwaya and Ishii, 1991; Davis *et al.*, 1995; Russell *et al.*, 1999; Sharma *et al.*, 2002; Feng *et al.*, 2003; Arenillas *et al.*, 2004; Wu *et al.*, 2008). The increasing degree of orderliness usually results in an increase in aromaticity, a corresponding increase in the fraction of crystalline carbon, and a decrease in the fraction of amorphous carbon (Franklin, 1951; Hirsch, 1954; Schoening, 1983; Davis *et al.*, 1995; Lu *et al.*, 2001, 2002a and 2002b; Maity and Mukherjee, 2006; Wu *et al.*, 2008).

The reduced reactivity of subsequent chars may also be explained by: a lower surface area of carbon available for reaction; a lower intrinsic reactivity (the reaction rate per unit area of pore surface in the absence of any mass transfer restriction); or a lower

number of active carbon sites (Smith, 1978). As the most reactive carbon atoms are located at the edges of the lamellae and not on the layer planes (basal planes), the density of accessible layer edges depends on the molecular orientation domain (*MOD*) size. Therefore, the smaller the *MOD* size, the greater the free edge density (Rouzaud *et al.*, 1988). Essenhigh (1981) and Tomita (2001) however noted that, reactivities at the carbon active sites located on different edges such as armchair and zig-zag are different.

Kashiwaya and Ishii (1991) designed an experiment to observe the difference in reactivity of carbon atoms located on the basal plane and the edges of the polyaromatic layers. They measured the aromatic layer stacking height, L_c , and average crystallite diameter, L_a , of a metallurgical coke at different temperatures under inert gas (*Ar*) and reaction gas mixtures of *Ar-CO-CO₂*. They found out that crystallite stacking height L_c , was affected only by temperature with no significant difference between the L_c of both the annealed and reacted cokes, implying that the reaction is very slow on the basal plane. The crystallite diameter L_a , of both annealed and reacted cokes also showed an increase with temperature, but the reacted coke had a lower L_a , than the annealed coke at similar temperatures, indicating that the reaction occurs at the edges of the polyaromatic layers.

Sharma and co-workers (1999 and 2002) studied the structure of coal char during low-temperature gasification using High-Resolution Transmission Electron Microscopy (*HRTEM*). Different coal chars show different behavior in the change of ordering with conversion. Chars from Pocahontas #3 low volatile bituminous coal contained both ordered and disordered crystallites at the initial stage, and the ordered crystallites were dominant after gasification (dry ash-free basis). Beulah-zap lignite chars mainly consisted of a higher fraction of amorphous carbon, and the crystallite ordering increased upon gasification. On the other hand, chars from high volatile bituminous coal, Illinois #6, and all the demineralised chars from these coals, did not show a large change before and after gasification.

Feng *et al.* (2003) determined the crystallite size of a char sample during reaction with carbon dioxide at a constant temperature (800 °C) up to 90% carbon conversion. Crystallite height (L_c) did not change significantly below approximately 60% carbon conversion but it decreased at greater conversion levels. Crystallite diameter (L_a), however, decreased during gasification, even at an early stage. They assumed that

initially the reaction occurs predominantly at the edges of the polyaromatic layers, which implies a decrease of the crystallite diameter, while the entire polyaromatic layers are consumed only at the later stages of reaction. This correlates to the findings of Kashiwaya and Ishii (1991).

The aromaticity of chars has been found to increase and the fraction of amorphous carbon to decrease during conversion processes. In the investigations of Lu *et al.* (2001, 2002a and 2002b) chars produced at between 900 °C and 1500 °C were characterized accordingly for various crystallite properties and subjected to combustion reactivity tests. Their findings on the chars are similar to published results, showing an increasing aromaticity and a decreasing fraction of amorphous carbon at increasing pyrolysis temperatures. Their reactivity results also show that increased aromaticity and decreased fraction of amorphous carbon impacts negatively on reactivity.

Recent research on CO_2 gasification of chars prepared at temperatures ranging from 950 °C to 1500 °C corroborates the above findings (Wu *et al.*, 2008). Their characterisation results show that the fraction of amorphous carbon decreases with increasing charring temperature while the reactivity results show that chars prepared at 950 °C have a higher fraction of amorphous carbon and are more reactive than chars prepared at higher temperatures. They also found that reactivity increases with increasing inter-layer spacing. Chars pyrolysed at 950 °C have a higher inter-layer spacing value and were more reactive when compared with their counterparts devolatilised at 1200 °C and 1400 °C.

2.6.5 Catalysis by Mineral Matter

Coals contain a variety of inorganic mineral constituents that are left behind as ash after coal conversion processes. Inorganic impurities in coal occur in the form of both mineral matter and trace elements. Mineral matter in raw coal consists of four major types:

- i. Alumino-silicates (clays), such as kaolinite- $Al_3Si_2O_5(OH)_4$ and illite- $KAl_3Si_3O_{10}(OH)_2$.

- ii. Oxides, such as lime- CaO , quartz- SiO_2 and hematite- Fe_2O_3
- iii. Carbonates, such as calcite- $CaCO_3$, siderite- $FeCO_3$, dolomite- $CaCO_3 \cdot MgCO_3$ and ankarite- $2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$.
- iv. Sulphides and sulphates, such as pyrite- FeS_2 and gypsum- $CaSO_4 \cdot 2H_2O$.

Typically, mineral matter is randomly distributed in coal as inclusions about 2 micron in diameter (Wigley *et al.*, 1997). During pyrolysis, gasification or combustion, mineral matter undergoes transformation causing the mineral phases in the chars to be entirely different to those in the precursor coal (Van Alphen, 2009). Some 20 to 30 trace metals are also distributed throughout the coal structure. These are either organically bound to the coal molecule (for example boron); or inorganically bound to mineral matter (for example zirconium, manganese); or occur in both organic and inorganic forms such as copper. Typical concentrations of trace metals in coal are between 5 and 500 ppm, although some elements such as- *B, Ba, Sr, Cu, Mn, Sn* and *Zr* often appear in the 500 to 1000 ppm range (Laurendeau, 1978).

Although Tomita (2001) and Lee (2007) confirmed that the mechanism of catalysis by mineral matter in the gasification systems is not straightforward, Walker, *et al.* (1968), reported that catalysts might affect gasification in several ways.

- i. It may affect both steps of the oxygen-exchange mechanism of the gasification reaction by either increasing the number of active sites or lowering the overall activation energy of the reaction.
- ii. It may induce pits in the carbon basal plane and expose additional edge planes for reaction.
- iii. It may also bypass the oxygen-exchange mechanism of the gasification reaction completely.

Mineral matter and trace metals, particularly calcium, iron, and manganese compounds, can provide direct catalytic activity (Tomita, 2001; Lee, 2007). Laine *et al.* (1963) reported findings that as little as 100 ppm *Fe*, can increase carbon- CO_2 gasification reactivity by a factor of about 150. Kayembe and Pulsifer (1976) found

that 10% by weight of K_2CO_3 reduced the activation energy of the steam gasification of Bear coal chars from $254 \text{ kJ}\cdot\text{mol}^{-1}$ to $145 \text{ kJ}\cdot\text{mol}^{-1}$ at atmospheric pressure and at temperatures between 600-850 °C.

Different metals show different catalytic influences during coal gasification. Ye *et al.* (1998) ranked four of the more prominent catalytically active materials as: $Na > K > Ca > Ni$, and found that their effect on reactivity is not additive since the expected effect of the combined activity of several cations was less than the sum of their individual effects. They also reported that the activity of Ca in particular was dependent on the form it took in the char structure: Ca^{2+} cations chemically associated with the carboxyl groups are active, whereas cations that are not chemically associated have only a slight effect on the reactivity.

Hüttinger and Nattermann (1994) investigated the rates of steam and carbon dioxide gasification as a function of burn-off, and observed, particularly the catalytic effects of the inorganic mineral constituents Ca and Fe . They found, for a range of coal ranks, that the average rate over the extent of burn-out did not correlate well with the molar ratio of Ca in the char. They did find that Fe was three times more active than the Ca , and that its effects were additive with Ca . This is particularly relevant for chars derived from low-ranked coals as it has been reported by many investigators that their reactivity is very dependent on the presence of mineral matter (Laurendeau, 1978, Miura *et al.*, 1989; Huang *et al.*, 1991; Czechowski and Kidawa, 1991; Kyotani *et al.*, 1993; Ye *et al.*, 1998; Samaras *et al.*, 1996; Hüttinger and Nattermann, 1994; Tomita, 2001; Kabe *et al.*, 2004; Lee, 2007).

Huang *et al.* (1991) prepared chars from vitrinite- and inertinite-rich fractions from a low rank coal (34% volatile matter). The vitrinite-rich char was more reactive than the inertinite-rich char but after demineralisation the former was less reactive. The surface area of the micropores and mesopores of the inertinite-rich char was greater than that of the vitrinite-rich char. They concluded that the catalytic effect of the mineral matter on the reaction rate is greater than the surface area effect. Czechowski and Kidawa (1991) made similar observation in their study. They assumed that the greater concentration of the elements: Ca , K and Na in the ash of the vitrinite-rich char is responsible for its higher reactivity relative to the inertinite-rich char.

Other salts found to have catalytic effects during low temperature gasification were in decreasing order of effectiveness: $NaCO_3 > Li_2CO_3 > KCl > NaCl > CuO$ (Miura *et al.*, 1989; Samaras *et al.*, 1996; Hüttinger and Nattermann, 1994; Tomita, 2001; Lee, 2007).

Tomita (2001), and more recently, Lee (2007), noted that the catalytic activity of inorganic substances containing *Na*, *Ca*, *K*, *Fe* species etc., depends not only on the cation specie, but also on the degree of its dispersion in the coal or char; and on the gasification conditions. Kyotani *et al.* (1993), however, observed that the catalytic effects of minerals are less significant at higher temperatures. This might be expected because, at higher temperatures, chemical processes and their catalytic effects have less influence on the reaction rate.

2.6.6 Physical Structural Properties of Chars

2.6.6.1 Total Surface Area

Considering the adsorption-desorption mechanism which is widely accepted for heterogeneous char-gas reactions (Laine *et al.*, 1963; Thomas and Thomas, 1967; Walker, *et al.*, 1968; Radovic *et al.*, 1983; Kyotani, *et al.*, 1988; Tomita, 2001, Arenillas *et al.*, 2004), reaction rate would be expected to increase relative to an increase in a particular sample's total carbon surface area. Attempts to correlate the observed 'apparent' or 'specific' reactivities to the total surface area of the char sample have been met with mixed success. Reports of two chars with equal total surface areas having different reactivities, and two chars with similar reactivities having different surface areas exist (Radovic *et al.*, 1985). Nonetheless, the normalisation of measured reactivities to the total surface area of the char can help to differentiate between physical and chemical effects on the reaction rates. The objective of such an exercise is not to use surface area as an explanation for the kinetic behaviour of the char, but to attempt to remove the influences of the physical structure of the char and leave behind the effects of the 'intrinsic' chemical properties of the sample.

Total surface area is commonly measured using two techniques: adsorption of nitrogen gas onto the surface of the sample at 77 K, and adsorption of carbon dioxide onto the surface of the sample at 273 K, sometimes lower than 273 K (Anderson *et al.*, 1965; Walker *et al.*, 1988; Micromeritics, 2006). Often these two techniques will give different results and the interpretation of these results can provide a lot of information regarding the structure of the char. In chars with an extensive micropore network (generally $< 2\text{ nm}$), adsorption of nitrogen does not always reveal the surface area attributed to these micropores (Anderson *et al.*, 1965; Walker *et al.*, 1988). As the CO_2 adsorption experiment is performed at higher temperatures (usually 273 K as opposed to 77 K) the CO_2 molecules have a higher average kinetic energy. This increased average energy means that the gas molecules are more likely to penetrate the smaller pores. Thus samples with high CO_2 areas and low N_2 areas indicate an extensive micropore network, while chars with similar N_2 and CO_2 surface areas are believed to have larger pores (Walker *et al.*, 1988).

2.6.6.2 Active Surface Area

The fact that reactivity does not always correlate well with the total surface area of a char led some researchers to investigate the proportion of this total surface that was actually available for chemical reaction (Laine *et al.*, 1963; Radovic *et al.*, 1983; Arenillas *et al.*, 2004). This so-called ‘active surface area’ (ASA) is attributed to surface defects, heteroatoms (ring structures containing *O*, *N*, etc.), mineral matter and disordered carbon atoms or carbon edges. It rarely includes the entire surface of the char. Reliable measurement of the ASA is difficult, and this is reflected in the lack of consistency between different researchers’ results and a lack of reproducibility of individual techniques. ASA is usually determined using temperature programmed desorption (TPD), according to the following procedures (Laine *et al.*, 1963; Radovic *et al.*, 1983; Kyotani *et al.*, 1988; Arenillas *et al.*, 2004): Oxygen is adsorbed onto the surface of the char at low temperatures (≈ 200 to $300\text{ }^\circ\text{C}$) and allowed to equilibrate. This equilibration time varies and can take up to 12 hours. The sample is then heated in an inert environment at a known and constant rate and the desorbing surface complexes are measured as the carbon-containing gases CO and CO_2 . By assuming

that the oxygen chemisorbed to all the active sites is available for reaction, the amount of desorbed product is believed to be proportional to the active surface area.

This technique has enjoyed only limited practical success (Lizzio *et al.*, 1990; Lahaye, 1998). The major problem with the process appears to be the time allowed for adsorption of oxygen. Though, an equilibrium between the char and the O_2 is required, it is often not reached within a practical time-frame and consequently an arbitrary adsorption period is allocated. This leads to inconsistencies between investigators.

The concept of active sites and more importantly the concentration of activated surface complexes present during the reaction is a fundamental issue behind the understanding of the behaviour of the gasification reactions over a wide range of conditions. The ability to measure the amount of reaction intermediates or surface complexes at any stage of gasification would therefore be an extremely useful tool (Hüttinger, 1990; Hüttinger and Nill, 1990).

2.6.6.3 Surface Complex Concentration during Reaction

Investigations into char- CO_2 gasification reactions have measured the amount of surface complexes present on the surface of the char during gasification (Hüttinger, 1990; Hüttinger and Nill, 1990; Köhl *et al.*, 1992). During these investigations, the sample was gasified to a pre-determined level of conversion and quenched rapidly, leaving the adsorbed surface complexes on the surface of the char. By heating the sample slowly in an inert gas environment, the amount of desorbed carbon products can be measured and used to estimate the amount of adsorbed surface complexes. This is a very useful approach for the analysis of the processes involved in the gasification reactions. It is not, however, a means by which an active surface area can be measured for the purposes of characterising a char because of the nature of the measurement. This is due to the fact that the number of surface complexes present during reaction is dependent on the reaction conditions of temperature and reactant partial pressure. Thus, the so-called 'reactive surface area' will be a function of the reaction conditions.

2.7 Methods of Measuring Gasification Reactivity

There are several methods by which the reactivity parameters that apply to char gasification can be measured. These vary in their methods of particle suspension and the conditions under which the sample reacts. Because different approaches are more suited to a particular task than others, it is important to match the desired outcomes of a set of experiments to the type of apparatus used in order to ensure that the data generated are appropriate.

Many methods for the measurement of the reactivity of coal and char during gasification are available from laboratory and pilot scale through to test-rig facilities. These include: entrained flow reactors (EFR) (Chitsora *et al.*, 1987; Hampartsoumian *et al.*, 1993); fluidised bed gasifiers (Hüttinger and Nattermann, 1994); drop tube furnace (DTF) simulating entrained flow gasifiers (Megaritis *et al.*, 1999; Liu *et al.*, 2000; Kajitani *et al.*, 2006); horizontal tube reactors (HTR) (Harris and Smith, 1990, Lizzio *et al.*, 1990; Sinağ *et al.*, 2003); and thermogravimetric analysers (TGA) (Dutta *et al.*, 1977; Matsui *et al.*, 1987; Mühlen *et al.*, 1985; Miura *et al.*, 1990; Huang *et al.*, 1991; Czechowski and Kidawa, 1991; Ochoa *et al.*, 2001; Kaitano, 2007; Everson *et al.*, 2006 and 2008a) In this investigation, a TGA was used.

2.7.1 Thermogravimetric Analysers

TGA is one of the more common techniques used for the analysis of heterogeneous reaction kinetics. In investigations using TGAs, the char sample is held in a basket, in a furnace, and the gasifying medium flows through the furnace where it encounters the sample in the basket. The sample holder is attached to a sensitive balance and the mass of the sample is monitored as a function of time and/or temperature. Derivatives of the mass versus time and the reaction rate(s) can be calculated.

The details of individual TGA designs vary, with some having reference sample holders while others have thermocouples underneath the sample holder, both to aid in accurate temperature change measurements.

Some TGAs have a horizontally-orientated reaction tube. The majority are, however, vertical. While they are one of the most common means by which attempts are made to measure kinetics, TGAs are limited by the sensitivity of the balance mechanism employed; by the means for estimating the temperature of the sample; and by the means of ensuring intimate gas-sample contact. Since any physical contact with the sample by the thermocouple will disturb the balance reading, the sample thermocouple is usually situated a few millimetres below the basket, which introduces some uncertainty in the sample temperature measurement. It therefore needs to be confirmed that the amount of sample used in the experiment is small enough so that the thermodynamics of the reaction being studied make negligible contributions to the discrepancies between the actual and the measured sample temperatures (Feng and Bhatia, 2002; Patnaik, 2008).

TGAs have been used extensively in the past for studies of the kinetics of gas-solid reactions (Dutta *et al.*, 1977; Matsui *et al.*, 1987; Mühlen *et al.*, 1985; Mühlen and Sulimma 1987; Miura *et al.*, 1990; Huang *et al.*, 1991; Czechowski and Kidawa, 1991; Ochoa *et al.*, 2001; Kaitano, 2007; Everson *et al.*, 2006 and 2008a). There are pressurised TGA instruments commercially available, with the latest ones capable of 100 *atm* pressure and 1600 °C sample temperature. Increasing the system pressure does introduce problems, such as increased effects of drag, variations in buoyancy and large heat transfer from the furnace walls to the gas. State of the art TGA designs and the use of suitable control software is able to counter these effects, and provide smoothed and corrected differentiation of the raw TGA data (Mühlen and Sulimma, 1987).

In contrast to fixed-bed reactors, where the reaction rate can be directly measured from the product gas concentration and the gas flow rates, TGAs produce an integral of the rate data. These data are usually expressed as mass (or fractional mass loss) versus time. Derivative calculations on the data generated by the TGA are required to generate results that are representative of the reaction rate. Such calculations can produce rate versus time or burn-out curves that have a poor signal to noise ratio. The differentiation of corrected mass versus time data and the plotting of this function against conversion gives us data that follow the reaction rate as the gasification of the sample proceeds.

The use of TGAs in the investigation of heterogeneous reaction kinetics needs to be accompanied by a thorough understanding of the limitations of such a system. TGAs are unsuited to the simulation of the extreme conditions that prevail in combustion and gasification technologies. This is due primarily to the unreliability of the measurement of the sample temperature at such high temperatures, but also has to do with the static presentation of the sample and the associated problems of reactant diffusion through the bed. Using TGAs under well-defined, well-controlled conditions, however, produces data that are both applicable and reliable (Patnaik, 2008).

TGAs are particularly suited for the measurement of Regime I kinetics (chemical reaction controlled kinetics), which necessitate the use of low sample temperatures, and which by definition should be independent of the sample presentation such as particle size, gas flow rates, and mass of sample. Such data can then be used as the basis for kinetic models, or can be combined with structural data to estimate high-temperature reactivity.

2.8 Char- CO_2 Gasification Reactions

This section of the review presents the mechanisms by which chars react with CO_2 . The kinetics of these reactions, which have been reported in the literature, is also discussed.

2.8.1 Char- CO_2 Reaction Mechanism

Char- CO_2 reactions occur via reactant adsorption, surface reaction and product desorption. From an experimental point of view, CO_2 gasification reactions are easier to study than combustion reactions as they are much slower and the chars do not have the tendency to ignite, as the reactions are endothermic. A widely accepted mechanism for the char- CO_2 reaction is the reversible oxygen-exchange mechanism (Ergun and Mentser 1968; Turkdogan and Vinters, 1969; Hüttinger, 1990; Hüttinger and Nill, 1990; Kashiwaya and Ishii, 1991; Hampartsoumian *et al.*, 1993; Kristiansen, 1996; Lee, 2007):



It was observed by Turkdogan and Vinters (1969) and corroborated by Hüttinger and Nill (1990), that the desorption reaction (Equation 2.9), is the rate-determining reaction for the overall process, at least at atmospheric pressure. The adsorption reaction influences the reaction rate by determining the number of adsorbed surface complexes, $C(O)$, through the forward reaction of Equation 2.8.

Experimental evidence has shown that carbon monoxide, the product of the CO_2 gasification reactions, inhibits the desorption reaction of Equation 2.9 (Ergun and Mentser, 1968). This inhibition by carbon monoxide can be accounted for, by the dynamic equilibrium shifts in the above oxygen-exchange mechanism of Equation 2.8. There are data to support this mechanism in the review by Ergun and Mentser (1968) which has been confirmed by the results of Hampartsoumian *et al.* (1993). This mechanism is currently the accepted mechanism for CO_2 gasification of carbonaceous materials at atmospheric pressure. Hampartsoumian *et al.* (1993) also suggest that CO inhibition in gasification reactions is less important at high temperatures (up to 1527 °C), suggesting that as the temperature increases the rate of formation of CO decreases.

2.9 Heterogeneous Char-Gas Kinetics

2.9.1 Reaction Rate Models

There are two ways by which the variations of char gasification rates with temperature and pressure can be represented. These are:

- i. Rate equations based on stepwise reaction mechanisms (the so called Langmuir-Hinshelwood equations, with stepwise rate constants that vary in Arrhenius form with temperature)

- ii. An n th order approximation to this rate equation- the power rate law (an overall Arrhenius-type representation).

By taking the reaction mechanisms proposed earlier (Section 2.8.1; Equations 2.8 and 2.9) and applying standard kinetic theory, the rates of each of these two reactions would be:

$$r_{(1)} = k_1 [C_f] y_{CO_2} - k_2 [C(O)] y_{CO} \quad (2.10)$$

$$r_{(2)} = k_3 [C(O)] \quad (2.11)$$

Assuming that the rates of reaction: $r_{(1)}$ and $r_{(2)}$ are equal at equilibrium and given that:

$$[C_f] = [C_t] - [C(O)] \quad (2.12)$$

an expression for the number of adsorbed surface complexes in terms of the gas partial pressures and the total concentration of available carbon sites can be evaluated using Equation 2.13:

$$[C(O)] = \frac{[C_t] k_1 y_{CO_2}}{k_1 y_{CO_2} + k_2 y_{CO} + k_3} \quad (2.13)$$

The char- CO_2 reaction rate is believed to be determined by the rate of desorption of surface complexes (Hüttinger and Nill, 1990). Therefore the reaction rate can be written as:

$$r_{CO_2} = k_3 [C(O)] \quad (2.14)$$

By substituting Equation 2.13 into Equation 2.14, the rate equation for the char- CO_2 reaction can be expressed as follows (Blackwood and Ingeme, 1960; Smith *et al.*, 1991):

$$r_{CO_2} = \frac{[C_t]k_1y_{CO_2}}{1 + \frac{k_2}{k_3}y_{CO} + \frac{k_1}{k_3}y_{CO_2}} \quad (2.15)$$

Equation 2.15 is the Langmuir-Hinshelwood rate equation for atmospheric CO_2 gasification. There is the possibility that reactions not discussed here become significant in the mechanism at high pressures (which is not within the scope of this investigation).

By considering the reaction as an overall rate expression, an n^{th} order approximation of the rate equation can be used to describe the reaction rate. This is often called an Arrhenius-type representation or the n^{th} order rate equation (power rate law). Such an expression is essentially empirical, relating the intrinsic reaction rate (which can be the combination of several individual steps) in terms of a rate constant and the concentration of reactant gases (expressed as concentration, partial pressure or mole fraction) raised to an order, m (Smith *et al.*, 1991):

$$r_s = ky_{CO_2}^m \quad (2.16)$$

The rate constant, k , is exponentially dependent on the reaction temperature, T , through the relationship:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (2.17)$$

Thus,

$$r_s = A \exp\left(\frac{-E_a}{RT}\right) y_{CO_2}^m \quad (2.18)$$

Many chemical reactions obey this type of relationship, and generally the gasification reactions (steam and CO_2) are no exception within a limited range of conditions (Dutta *et al.*, 1977; Laurendeau, 1978; Harris and Smith, 1990; Smith *et al.*, 1991; Murillo *et al.*, 2004 and 2006). Kaitano (2007) reported that the power rate law is

generally more applicable at lower partial pressures of gasifying agent. This is predominately due to the inability of the values of the kinetic parameters to apply over extremes of pressure and temperature conditions. At higher pressures, the Langmuir-Hinshelwood rate equation is more applicable as it accounts for both the CO_2 partial pressure as well as the formation of the product gas (CO).

It is likely, however, that in measuring such kinetic parameters over such a variety of conditions, the influences of a number of other processes such as mass transfer, gas-film diffusion, or product inhibition on the reaction rates are also measured. In order to be able to quantify reaction rates at high temperatures and pressures, the influences of pore and bulk diffusion must be accounted for, separate from the chemical processes, either by mathematical estimation or experimental measurement.

2.9.2 Overall CO_2 Gasification Kinetics

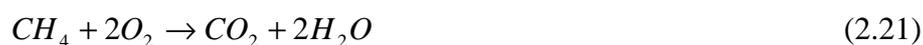
The rate of the char- CO_2 reaction is several orders of magnitude slower than the char- O_2 reaction (Harris and Smith, 1990). Due to these slower reaction rates, the processes limiting gasification with CO_2 under process conditions are expected to be a combination of chemistry and diffusion through the pores of the char, even at the high temperatures experienced in practical gasification systems. There have been many investigations into the reactivity to CO_2 of chars produced from a variety of coal types both at atmospheric and higher pressures with reported activation energies ranging from 100 to 280 $MJ \cdot mol^{-1}$ (Dutta *et al.*, 1977; Radovic *et al.*, 1985; Matsui *et al.*, 1987; Miura *et al.*, 1990; Ochoa *et al.*, 2001; Everson *et al.*, 2006 and 2008a; Murillo *et al.*, 2006; Kajitani *et al.*, 2006; Kaitano, 2007). Measured activation energies for the char- CO_2 reaction are usually greater than those for char- O_2 reaction.

Overall reaction orders, however, are similar. The accepted value for the reaction order for the char- CO_2 reaction is in the range 0.5 - 0.7 (Laurendeau, 1978; Harris and Smith, 1990; Kaitano, 2007; Everson *et al.*, 2008a), which is similar to the value reported for the oxygen reactions. This may be expected because the surface adsorption-desorption mechanism is similar for the oxygen and carbon dioxide reactions (Radovic *et al.*, 1983). There is some experimental evidence for this provided by Hüttinger (1990); Hüttinger and Nill (1990); and Zhang and Calo (1996).

They performed experiments at atmospheric pressure, in which the partial pressure of CO_2 was varied. The experiments were ‘frozen’ at a known level of conversion, and the sample was then heated at a known heating rate in an inert gas. The adsorbed surface complexes, which remained on the surface when the reaction was stopped, then desorbed and were able to be measured as evolved CO . They found that the amount of adsorbed complex increased with the partial pressure of CO_2 . Hüttinger and Nill (1990) however observed that the reaction rate normalised to the amount of adsorbed complex is constant.

2.10 Homogeneous Gas-Phase Reactions

Although the heterogeneous char-gas reactions are important when considering the burnout times for char during gasification, there are also homogeneous gas-phase reactions that are important in determining the composition of the fuel or synthesis gas produced in the gasification process. If there is oxygen in the gasifier, it dominates the gas-phase reactions. These include:



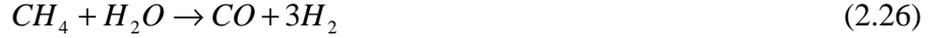
Gas-phase reactions that occur after oxygen is removed are also important as they influence the composition of the fuel/synthesis gas. In the presence of steam, the water-gas shift reaction has a dominant influence on the resulting CO/H_2 ratio:



And the methanation reaction (important at higher pressures) increases the calorific value of the fuel gas (Lee, 2007):



Jüntgen *et al.* (1981) also reported that methane can also react with steam as follows:



which will affect the final ratio of hydrogen to methane. The sulphur species present may also undergo the following homogeneous reactions with hydrogen and steam:



The formation of nitrogen oxides also occurs, but this is readily reduced (*in-situ*) so that the form of nitrogen in the exit stream of a gasifier is principally molecular nitrogen, N_2 with some NH_3 (Watkinson, 1991). The kinetics of these gas-phase reactions are not discussed in this review. The focus is on the heterogeneous char- CO_2 reactions.

2.11 Structural Kinetic Models

The overall reaction rate for char-gas reactions depends on the intrinsic surface reaction r_s and the structure of the char particles (structure factor, $f(X)$). These are determined by various factors including coal properties, devolatilisation conditions and the reaction conditions (See section 2.6). This can be expressed as follows:

$$\frac{dX}{dt} = r_s(T, C)f(X) \quad (2.30)$$

The surface of char particles is both physically and chemically heterogeneous. It is expected, therefore, that different parts of the surface will behave differently under varying conditions. Considering this, there is no single technique that can be used to consistently remove all effects of the surface of the char from a reactivity measurement. Thus, a measure of the true intrinsic reactivity of char is rather hard to achieve. Instead, a value of the total surface area is introduced as a useful measurement that can be used to get a reactivity parameter that is representative of the average reactivity of the char particle.

As conversion progresses and the reactions remove carbon from the surface of the pores, the surface area of the char changes. An understanding of how the coal char surface evolves and, more importantly, how we can predict its behaviour is an important part of the knowledge required for successful modelling of gasification reactions. To this end, a number of models predicting the evolution of surface area have been developed. Most of these models are based on the development of various pore structures in the solid reactant in this case coal char. Some of these models incorporating structural evolution during the reactions are: the volume reaction model (Dutta *et al.*, 1977; Murillo *et al.*, 2004 and 2006; Wu *et al.*, 2008); the shrinking core model (Levenspiel, 1972; Bhatia and Perlmutter, 1980 and 1981; Mühlen *et al.*, 1985; Mühlen and Sulimma, 1987; Murillo *et al.*, 2004; Everson *et al.*, 2006; Zhang *et al.*, 2006); and the random pore model (Bhatia and Perlmutter, 1980 and 1981; Radovic *et al.*, 1985; Matsui *et al.*, 1987; Miura *et al.*, 1990; Hampartsoumian *et al.*, 1993; Ochoa *et al.*, 2001; Sinağ *et al.*, 2003; Kajitani *et al.*, 2006; Zhang *et al.*, 2006; Kaitano, 2007; Everson *et al.*, 2008b; Sangtong-Ngam and Narasingha, 2008).

2.11.1 The Volume Reaction Model

The volume reaction model (VRM) is the simplest model that takes into account structural changes that occur during the reactions and was proposed by Dutta *et al.* (1977) to describe char reaction with CO_2 (Murillo *et al.*, 2004 and 2006; Wu *et al.*, 2008). The VRM assumes uniform gas diffusion in the entire solid particle and simplifies the heterogeneous char- CO_2 reaction by assuming that the gas is reacting homogeneously with the char. The kinetic expression for the reaction rate is (Dutta *et al.*, 1977; Murillo *et al.*, 2004):

$$f(X) = k_v(1 - X) \quad (2.31)$$

and the reaction rate expression is given by (Bhatia and Perlmutter, 1980):

$$\frac{dX}{dt} = \frac{k_v C_g}{1 - \varepsilon_o} (1 - X) \quad (2.32)$$

The limitations of the model are that it only predicts a monotonically decreasing reaction rate whereas most gasification systems have been known to exhibit maximum reaction rate.

2.11.2 Shrinking Core Model

The Shrinking core model (SCM) considers reaction(s) as occurring on the surface of a shrinking non-reacted core within the solid particle (grain). The shrinking surface can leave behind a layer of ash, which may offer resistance to the transport of reactant and product gases. Under these conditions, it is assumed that there is negligible penetration for the reaction in the core and that the reaction occurs within a very thin layer on the surface of the shrinking particle. Levenspiel (1972) assumed that a porous particle with negligible diffusion between individual grains consists of an assembly of uniform non-porous grains and that the shrinking core behaviour is confined to these grains. Most investigators, however, considered this behaviour applicable to the whole particle and have used it to effectively predict heterogeneous coal char-gas reaction kinetics (Levenspiel, 1972; Everson *et al.*, 2006). For a shrinking core model, with the surface chemical reaction controlling and the particles assumed to be spherical, the structure factor is given below (Mühlen *et al.*, 1985; Mühlen and Sulimma, 1987; Murillo *et al.*, 2004; Zhang *et al.*, 2006; Everson *et al.*, 2006; Bhatia and Perlmutter, 1980 and 1981):

$$f(X) = \frac{S_o (1 - X)^{2/3}}{(1 - \varepsilon_o)} \quad (2.33)$$

And the overall reaction rate can be expressed as:

$$\frac{dX}{dt} = r_s \frac{S_0}{(1 - \varepsilon_0)} (1 - X)^{2/3} \quad (2.34)$$

It encompasses the initial structural properties of the char in terms of the initial porosity and external surface area, but fails to predict a maximum behaviour observed for some gasification experiment (Hashimoto *et al.*, 1979). The SCM, however, does not account for structural changes (surface area and porosity) occurring during reaction of the char.

2.11.3 Random Pore Model

The Random pore model (RPM) can describe gasification systems that show maximum reaction rate as well as those that do not. According to Bhatia and Perlmutter (1980) and (1981), this model considers a transformation from non-overlapped cylindrical pores to overlapped ones during gasification and assumes that pores are of random sizes and orientations and may adjust for intersections. The model's structural factor is given by (Bhatia and Perlmutter, 1980):

$$f(X) = \frac{S_0(1-X)\sqrt{1-\psi \ln(1-X)}}{1-\varepsilon_0} \quad (2.35)$$

where,

$$\psi = \frac{4\pi L_0(1-\varepsilon_0)}{S_0^2} \quad (2.36)$$

Several investigators (Bhatia and Perlmutter, (1980) and (1981); Kaitano, (2007); Everson *et al.*, (2008b)) have successfully used RPM and its various modifications in modeling char's gasification and other heterogeneous reaction kinetics in gasification systems. A detailed discussion on RPM is presented in chapter 6.