Chapter 2

2. *LITERATURE REVIEW*

2.1   Introduction

In this chapter, a review of the relevant literature relating particularly to fuel bed behaviour in fixed bed gasification as well as lignite and coal properties relevant to fixed bed gasification are discussed.
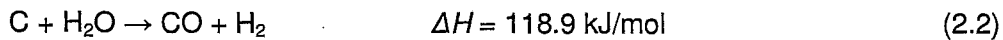
2.2   Coal Gasification

Coal gasification can be defined as the reaction of solid fuels with air, oxygen, steam, CO_2, or a mixture of these gases at a temperature of over 700 $^{\circ}$C to produce synthetic gas that is suitable for use either as a source of energy or raw material for synthetic liquid fuels, chemicals or other gaseous fuels (Higman and van der Burgt, 2003). The principal reactions occurring during coal/char gasification can be summarised as follows:-
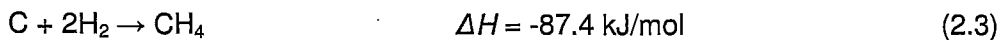
"True" gasification reactions
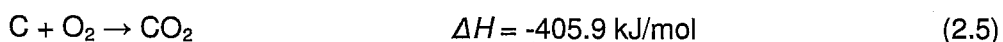
Gasification with carbon dioxide (Boudouard reaction)

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = 159.7 \text{ kJ/mol} \qquad (2.1)$$
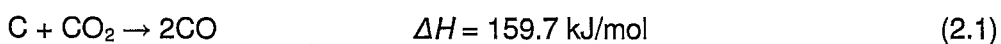
Gasification with steam (water gas reaction)

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = 118.9 \text{ kJ/mol} \qquad (2.2)$$

Gasification with hydrogen (hydro-gasification):

$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H = -87.4 \text{ kJ/mol} \qquad (2.3)$$

Combustion reactions

$$C + \tfrac{1}{2}O_2 \rightarrow CO \qquad \Delta H = -123.1 \text{ kJ/mol} \qquad (2.4)$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -405.9 \text{ kJ/mol} \qquad (2.5)$$
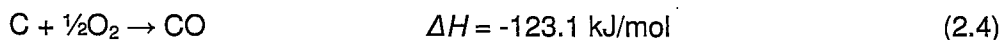
Gas phase reactions

Water gas shift reaction:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H = -40.9 \text{ kJ/mol}$$

(2.6)

Methanation:

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O \qquad \Delta H = -206.3 \text{ kJ/mol} \qquad (2.7)$$
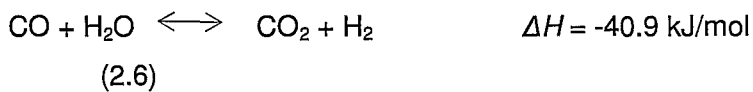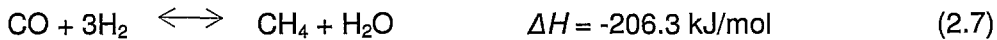
Prior to the above mentioned reactions that occur during gasification, pyrolysis of coal occurs at temperatures of over 300 °C, resulting in the formation of amongst others, tar, phenols and hydrocarbon gases. Depending on the type of gasification technology applied, these can either be further destroyed in the case of entrained flow gasifiers or released as by products in the case of fixed and fluid bed gasifiers.

2.2.1 Coal Gasification Technologies

Although there are various types of reactors used for the gasification process, the technology can be grouped into three main categories i.e. fixed/moving bed, fluid bed and entrained flow gasifiers. This study is based on fixed bed gasification technology (particularly the S-L FBDB) which will be discussed in detail in the following section.

In the fixed bed dry bottom gasifiers, lump coal (-100+5 mm) is fed in the top through the coal lock and the reactant gases (steam and oxygen) are introduced under pressure at the bottom of the gasifier and run counter-flow to the coal. As the coal descends, it is dried and devolatilized by the rising hot gas to form a char which is gasified in the reduction/gasification zone. The residual char is then burnt in the combustion zone which provides the heat for the entire reactor. For the dry bottom gasifier, the ash residue is removed by the grate and discharged through the ash lock (Slaghuis, 1993). For the slagging fixed bed gasifier, the molten ash is quenched and removed as solid slag.

The gas exit temperature is in the order of between 200 and 600 °C depending on the feed stock. The low gas outlet temperature is regarded as one of the advantages of fixed bed gasification technology as it allows the use of less costly gas cooling systems (Higman and van der Burgt, 2003).

In fluid bed gasifiers, coal particles (generally – 5+0.5 mm) are fluidised in the gas flow thus ensuring good mixing between feed and gasification agent. The fluid bed gasifiers operate at a temperature below the softening temperature of the coal ash to avoid mineral matter sintering. This can be a limitation to this type of technology as low operating temperatures result in low carbon conversion, particularly when gasifying less reactive coals (Higman and van der Burgt, 2003).

In entrained flow gasifiers, ultra fine coal (about 100 μm) is gasified (either dry or wet) concurrently with the gasification agent in an entrained fluid flow mode. The residence time in this process is very short (in the order of seconds) thus requiring high temperatures (in the region of 1200 – 1500 °C) for good conversion. The gasifiers operate above the ash flow temperature to ensure that the ash is removed in a molten form or as slag. Fluxing agents like limestone may at times be required to lower the ash melting temperature of the coal and this may have some economic implications. In addition, the fact that entrained flow gasifiers operate at higher temperatures can create a high oxygen demand. The reactors are nonetheless regarded as versatile since they can gasify both solid and liquid feed stocks (Collot, 2002).

2.2.2 Fixed Bed Gasification

The two commercially available fixed bed gasification technologies are British Gas Lurgi (BGL) as well as the S-L FBDB gasifiers. The BGL gasifier is a slagging gasifier that was developed by British Gas and Lurgi in the mid 70's. It is an extension of the Lurgi fixed bed dry bottom gasifier with the ash discharge designed for slagging conditions. The motivation behind this development was based on the desire to, amongst other things, increase CO and H_2 yields, accommodate coals with low ash fusion temperatures (AFT)

and reduce steam consumption and subsequent gas condensate production (Higman and van der Burgt, 2003). Although these have been achieved, the issues around availability and maintenance are still not resolved despite commercial operation at the now defunct Schwarze Pumpe plant in Germany.

2.2.2.1 *Sasol-Lurgi Fixed Bed Dry Bottom (S-L FBDB) Gasification Technology*

Formerly known as Lurgi dry ash, the S-L FBDB was first patented in 1927 and the first commercial scale plant built in 1936 at Hirsch-felde, Germany (Higman and van der Burgt, 2003). Since then, various commercial plants including *inter alia*, Sasol Synfuels (South Africa), Dakota Gasification Company (DGC, North Dakota, USA), Tianji Coal Chemical Company (Shanxi Province, China) and Yima Coal Gasification Company (Henan Province, China) were built. Very recently, seven gasifiers have been licensed to Jindal Steel and Power Limited (India) for the production of syngas to be used in the Direct Reduction of Iron (DRI) process. Table 1 summarises the major reference plants for the S-L FBDB technology (Turna, 2007). The operating S-L FBDB gasifiers at the plants listed in Table 1 amount to about 75% of the global coal gasification capacity (Turna, 2007).

Table 2.1. Major reference plants for the S-L FBDB gasification technology (Turna, 2007)

Plant	No. of Gasifiers	Coal rank	Location	Start -Up	Plant Capacity
Sasol Chemical Industries (now decommissioned)	17	Bituminous, Medium Rank C	Sasolburg, South Africa	1955	11×10^6 m^{3}N/day syngas for liquid fuels and chemicals
Sasol Synfuels	80	Bituminous, Medium Rank C	Secunda, South Africa	1979	80×10^6 m^{3}N/day syngas for liquid fuels and chemicals
Dakota Gasification Company (DGC)	14	Lignite	North Dakota, USA	1985	1450×10^6 m^{3}N/annum substitute natural gas
Shanxi-Tianji Coal Chemical Company	5	Low volatile matter, bituminous, Medium Rank A	Lucheng - Shanxi Province, China	1987	300 ktpa NH$_3$, 540 ktpa HNO$_3$, 900ktpa Nitro Phosphate and 200ktpa ammonium nitrate (explosive grade)
Yima	2	Sub-bituminous, Low Rank A	Yima City – Henan Province, China	2000	80 000 ton/annum methanol
Jindal	7	Sub-bituminous, Low-Rank A	Angul, Orissa, India	4th Q 2009	225 000 m^{3}N /h of syngas for direct reduction of iron (DRI)

SLTC offers three commercially proven standardised reactor sizes - see Figure 2.1. The MK III with a nominal internal diameter of 3 m can produce about 34 000 m^3N/h of crude gas. The MK IV and MK V gasifiers have internal diameters of about 4 and 5 m respectively and can produce about 65 000 m^3N/h and 90 000 m^3N/h of crude gas respectively. The MK VI version of the S-L FBDB gasifier with the capacity of 100 000 m^3N/h is currently under development (van de Venter, 2007).
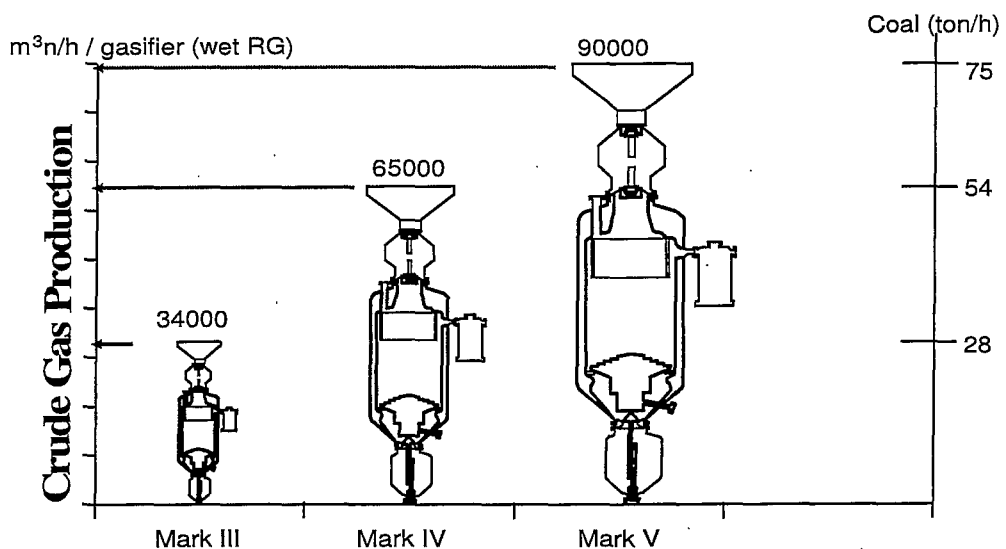

Figure 2.1. Schematic representation of MK III, MK IV and MK V S-L FBDB gasifiers showing hourly raw gas production and feed coal rate (Turna, 2007).

2.2.2.1.1 The Gasifier Vessel and Down Stream Processes

A schematic representation of the S-L FBDB gasifier is depicted in Figure 2.2. In the gasifier, coal with particle size of preferably 5 – 50 mm is loaded from the bunker into an isolated coal lock which is then pressurized with raw syngas and opened to the gasifier. The coal is loaded into the gasifier in a batch mode. Almost all the gas used to pressurise the coal lock can be recovered during depressurization of the coal lock when loading it with coal from the bunker (Slaghuis, 1993; Higman and van der Burgt, 2003).

The gasifier itself is a double walled vessel. The Boiler feed water (BFW) level is maintained between the outer shell and inner wall (jacket) to protect the outer pressure-bearing shell from high temperatures. At the same time, saturated steam is generated in the jacket at a pressure similar to the gasification pressure (i.e. about 30 bars) from the heat lost through the reactor wall. This steam is added to the high pressure superheated steam used in the gasification process (Slaghuis, 1993; Higman and van der Burgt, 2003).

Coal from the coal lock is distributed across the area of the gasifier and descends slowly through the bed. A mixture of steam and pure oxygen (also referred to as the gasification agent) is injected at the bottom of the gasifier and distributed across the gasifier bed by the rotating grate assisted by the sintered ash (Slaghuis, 1993; Higman and van der Burgt, 2003). A "rabble finger", which helps to homogenize the sintered ash by breaking some clinkers and channels in the bed, can also be included in the design as in the case of DGC (Turna, 2008).

Some heat exchange occurs between the hot ash and the gasification agent. The ash is therefore cooled down to about 300 – 400 °C and discharged into the ash lock and subsequently to the ash sluiceway (Slaghuis, 1993; Higman and van der Burgt, 2003).
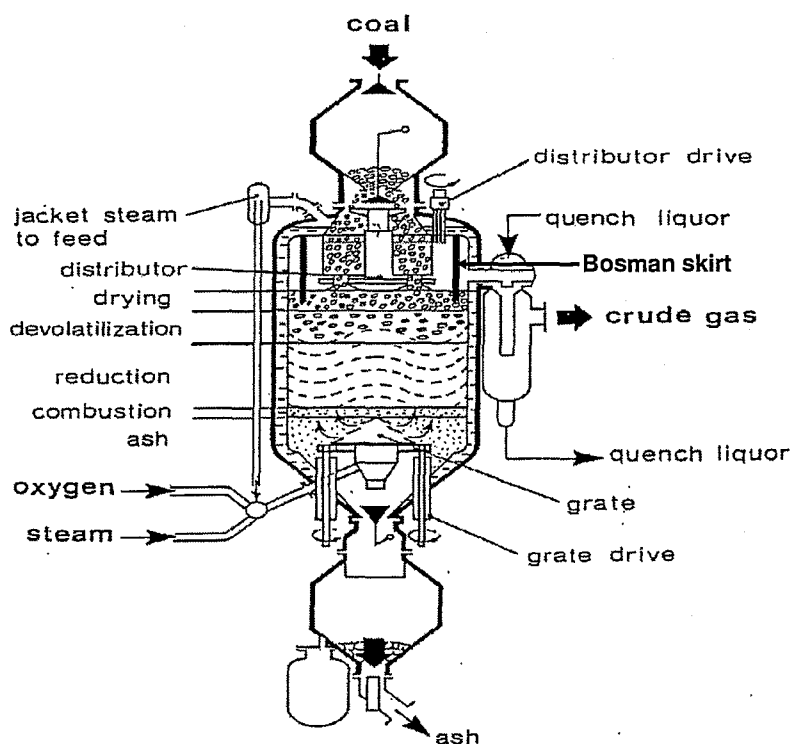
Figure 2.2. A schematic representation of a fixed bed dry bottom gasifier showing the various reaction zones (Hebden and Stroud, 1981).

The pre-heated gasification agent moves upwards into the combustion zone where the O_2 reacts with the char to form CO_2. The combustion zone is the hottest zone of the gasifier and hence provides heat for the upper zones where mainly endothermic reactions occur. As the hot gases (mainly CO_2 and steam) move up the gasifier, they reach the gasification/reduction zone where gasification reactions as shown in equations 2.1 and 2.2 occur. It is in this zone where most of the syngas is generated (Slaghuis, 1993; Higman and van der Burgt, 2003).

The gases continue to move upwards in the gasifier reaching the devolatilization zone where the descending coal is heated in an inert atmosphere and decomposes into a carbon-rich solid residue (char) and hydrogen rich volatile fraction consisting of gases, vapours and tar components (Tromp, 1987). The chemistry of pyrolysis is known to be very complicated. Figure 2.3 illustrates the simplified and summarised reactions which occur during pyrolysis of coal (Tromp, 1987).
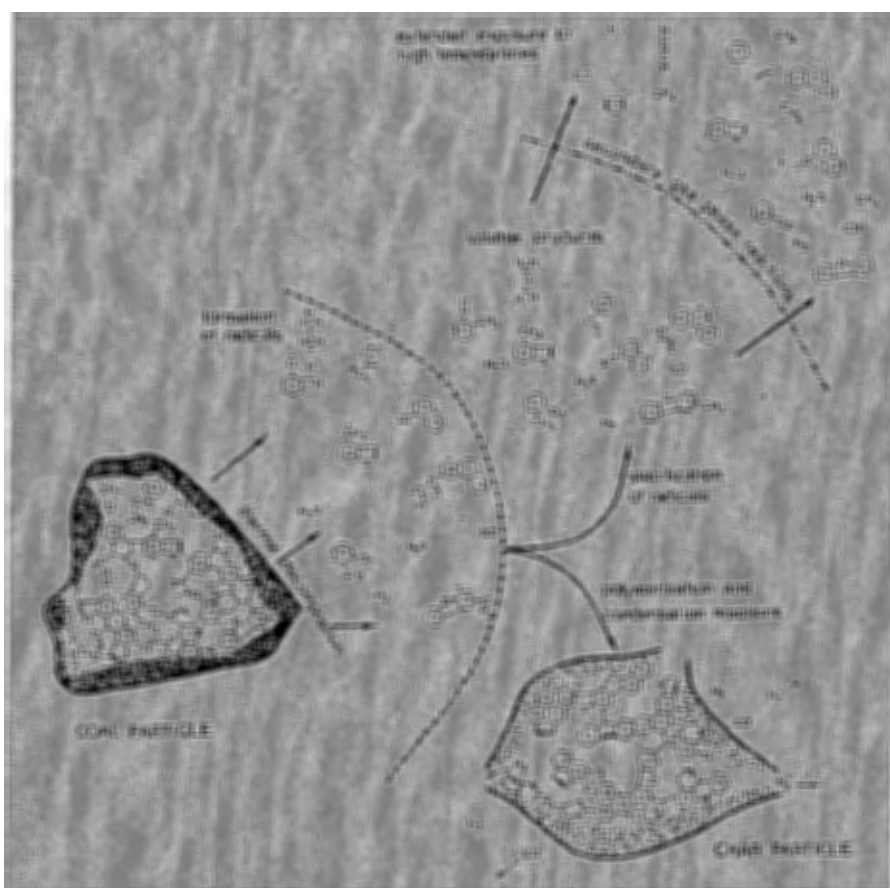
Figure 2.3. Reactions and processes occurring during pyrolysis of coal (Tromp, 1987).

As the gases continue to move upwards in the gasifier, the volatile components from the pyrolysis zone as well as the syngas are further cooled down in the upper part of the gasifier where the coal is preheated and dried. The gas then exits the gasifier at a temperature of between 200 and 650 °C depending on the feedstock (Slaghuis, 1993; Higman and van der Burgt, 2003). At the outlet of the gasifier, the bulk amount of unreacted products of pyrolysis such as tars, phenols, ammonia, and fine coal particles as well as other hydrocarbons are removed from the gas by means of a wash cooler. In the wash cooler, most of the hydrocarbons with high boiling point as well as dust are condensed and/or washed out with the gas liquor from the downstream condensation stage. The gasification (including gas cooling) process is illustrated in Figure 2.4 (Slaghuis, 1993; Higman and van der Burgt, 2003).
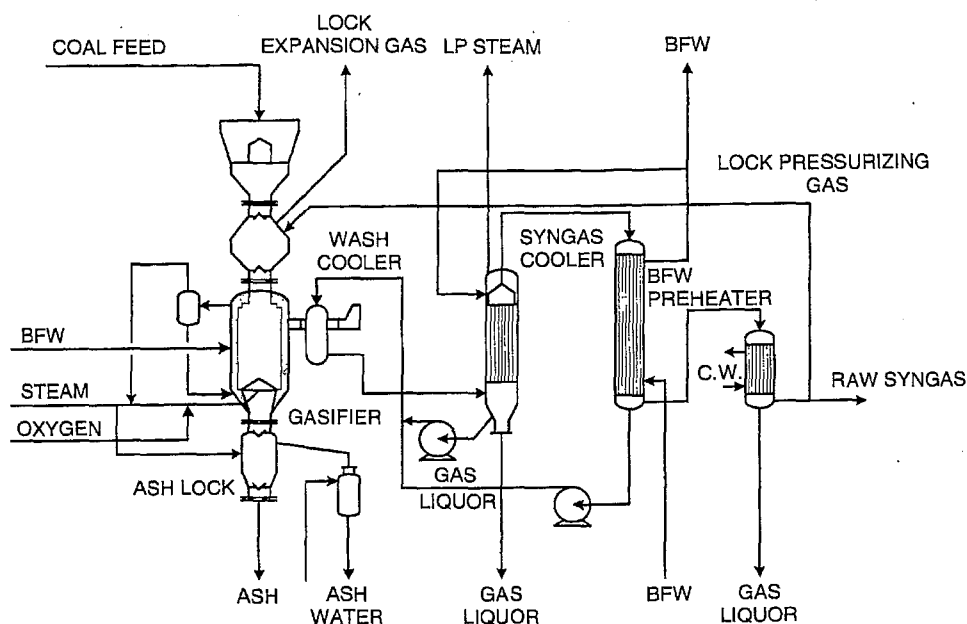
Figure 2.4. Process flow sheet of the S-L FBDB gasification process (Higman and van der Burgt, 2003).

The raw gas liquor can be processed by first removing the tar and oil using density separation. The tar can, depending on the application of the syngas, be recycled back into the gasifier to be cracked into lighter components which can either be combusted in the boilers to produce steam or sent to the refinery to produce high quality diesel in the case of a CTL application.

Once the tar and oils are removed, the gas liquor is further processed in the phenosolvan extraction process where raw phenols are recovered. The dephenolated gas liquor is then processed in the CLL (Chemie Linz-Lurgi) unit where sour gas and ammonia are selectively and separately stripped from the gas liquor. The stripped condensate is safe to be discharged to a biotreater. Pure anhydrous ammonia (99%) is produced as a by product (Higman and van der Burgt, 2003).

The cooled raw gas can be routed to the Rectisol unit which uses cold methanol wash to selectively remove lighter hydrocarbons, CO_2, HCN and volatile sulphur components. Depending on the site of deployment, CO_2 can either be vented to the atmosphere or be used for enhanced oil recovery as in

the case of the Great Plains Synfuels Plant (Fagerstrom, 2007). The H_2S rich Rectisol off gas stream is sent to the Sulphur Recovery Unit (SRU) comprising of an OxyClaus process and a Tail Gas Treatment unit. In the SRU, sulphur emissions are reduced to ppm levels by producing elemental sulphur (Higman and van der Burgt, 2003).

2.3 North Dakota Lignite and Coal Properties Relevant and Important to Fixed Bed Gasification

In a world where fossil fuels are the predominant source of energy, lignite, which accounts for about 50% of the remaining proven coal reserves, can be seen as one of the world's important primary energy sources. It is generally characterised by high moisture content, low heating values and low carbon content. In this section, the general coalification process, coal composition, a brief geological background of the ND lignite as well as the coal properties important in the fixed bed dry bottom gasification technology are discussed.

2.3.1 Coalification

During the coalification process, peat (a precursor of coal) is developed to lignite, sub-bituminous coal, bituminous coal, anthracite and then meta-anthracite (Stach *et al.*, 1982). As depicted in Figure 2.5, the coalification process occurs in three stages (aerobic decay, anaerobic decay and metamorphism/bituminisation) subsequent to the accumulation of plant debris under swamps (University of Wyoming, 2002).

The aerobic decay occurs in the very early stages of coalification by the action of aerobic bacteria which eventually die due to insufficient oxygen in the swamp. The decay process, which also produces acid, is then continued by the anaerobic bacteria until the pH is in the region of 4.0, where the bacteria eventually dies leaving the peat that has changed into a black, gel-like
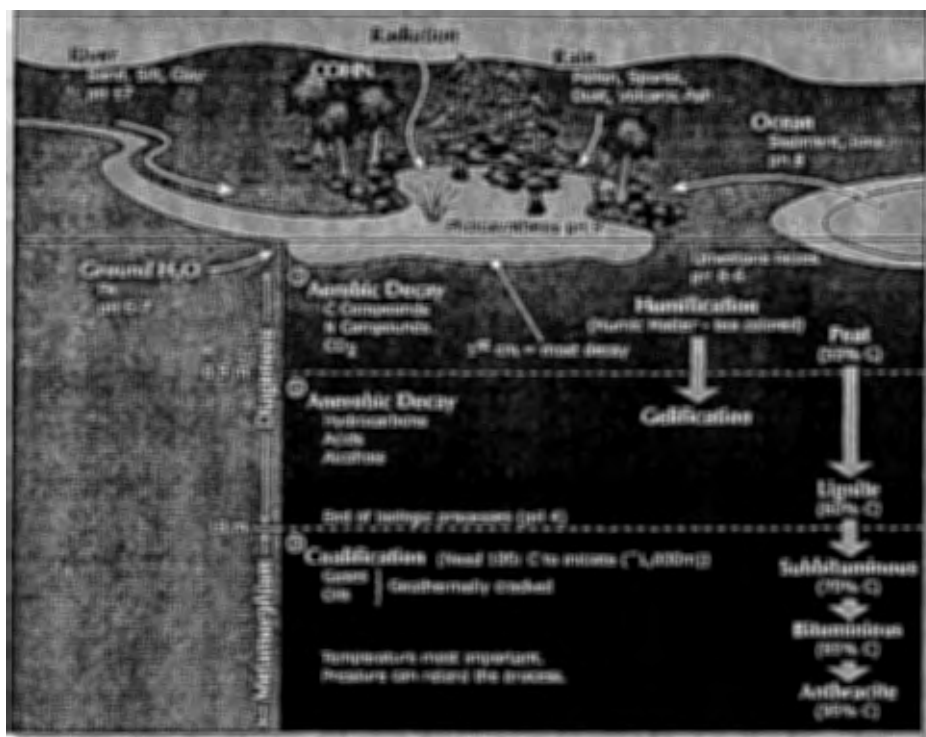
material called gytta. It is this material that is a precursor of coal (Falcon and Snyman, 1986; Stach et al., 1982).

Once the gytta/peat is formed in the biochemical stage, the thermal processes come into play for the final stages of coalification. The peat is then buried by an insulation blanket which forms the basis of the overburden during mining and retains the natural heat that rises to the earth's surface. The bituminisation process begins once the temperature reaches 100 °C and is a very slow process (University of Wyoming, 2002; Falcon and Snyman, 1986; Stach et al., 1982). Lignite was reportedly formed at temperatures of around 200 °C (Schobert, 1995).

Temperature and pressure continue to rise and the chemical reactions occur that drive off moisture, oxygen and hydrogen thus increasing the carbon content. The porosity also decreases as the overburden pressure increases with depth. The transition from peat to lignite takes place very gradually and it is therefore difficult to fix a precise boundary. However, in addition to a decrease in moisture content and an increase in carbon content, the absence of free cellulose and the difficulty in cutting can be used to differentiate lignite from peat (Stach et al., 1982).

As the bituminization process progresses, the volatile matter and moisture contents continue to drop, the distinguishable plant remains are lost (except microscopic ones) and the shiny black macerals are produced by the geochemical gelification of the humic substances. This culminates into sub-bituminous coal (Stach et al., 1982).

Further drop in moisture content culminates into high-volatile bituminous coal (>30% DAF). Aromatization of the humic complexes lead to a decrease in volatile matter and thus an increase in rank to bituminous coal (volatile matter of <30% - 10% DAF). Rapid decreases in the hydrogen content and atomic H/C ratio as well as a strong increase in reflectivity and optical anisotropy characterize the anthracite stage (Stach et al., 1982).

Figure 2.5. Schematic representation of the coalification process – anatomy of a swamp (University of Wyoming, 2002)

2.3.2 Coal Composition

2.3.2.1. Microscopic Composition

Microscopically, coal consists of macerals, mineral matter and microlithotypes (Falcon and Snyman, 1986). Macerals, which are the organic components, are fundamental in determining the nature of coal (i.e. rank and type) and its value in the utilization processes (Ward, 2002). Mineral matter (i.e. the inorganic components) on the other hand is a diluent to the more useful organic matter in coal (Ward, 2002).

Macerals

Macerals evolved from different organs or tissues of the initial coal-forming plant materials during the course of the first stage of carbonification (Falcon and Snyman, 1986). They are microscopically recognisable individual constituents and depending on their quantitative participation and association, they can control the chemical, physical and technological properties of a coal of given rank (Falcon and Snyman, 1986). The macerals with common properties are grouped into maceral groups and the three common ones are vitrinite (huminite in the case of lignite), inertinite and liptinite (Falcon and Snyman, 1986).

Huminite

Huminite is a precursor of vitrinite and represents a group of medium grey macerals having reflectances between that of the associated darker liptinites and lighter inertinites (Sýkorová *et al.* 2005). Huminite is generally isotropic and has a random reflectance (measured in oil) of between ~0.2% and 0.4% which is in the lignite range (Sýkorová *et al.* 2005). It is characterised by relatively high oxygen content when compared to the other maceral groups (Sýkorová *et al.* 2005). Huminite is derived from parenchymatous and woody tissues and the cellular contents of roots, stems, barks and leaves composed of cellulose, lignin and tannin (Sýkorová *et al.* 2005). It occurs in coal seams formed as a result of anaerobic preservation of lignocelluloses material in mires (Sýkorová *et al.* 2005).

Vitrinite

As with huminite, vitrinite is a group of grey macerals having reflectances between that of the associated darker liptinites and lighter inertinites (Falcon and Snyman, 1986). The original material is also the same as for huminite. It has a random reflectance (measured in oil) of between 0.4% and 0.5% in sub-bituminous coals, 0.5% - 2.0% in bituminous coals and more than 2% in anthracite (Falcon and Snyman, 1986). At any given rank of coal, the carbon and hydrogen contents of vitrinite are intermediate between the inertinite and liptinite group macerals (Falcon and Snyman, 1986).

Inertinite

Inertinite is a maceral group that comprises macerals whose reflectance in low- and medium-rank coals and in sedimentary rocks of corresponding rank is higher in comparison to the macerals of the vitrinite and liptinite groups (ICCP, 2000). The original parent material for inertinite is the same woody and cellular constituent from which vitrinite was formed (Falcon and Snyman, 1986). The inertinite macerals have however undergone aerobic decomposition (i.e. macerals were exposed to a strongly oxidizing environment) during coalification (ICCP, 2000). The inertinite macerals have the highest carbon and lowest hydrogen contents of all the other maceral groups (ICCP, 2000).

Liptinite

Liptinite group macerals are derived from waxy, lipid-rich and resinous parts of plants like spores, cuticles and resins (Falcon and Snyman, 1986). The macerals are darker when compared to vitrinite in the low and medium rank coals (Falcon and Snyman, 1986). However, in higher rank coals (i.e. at a vitrinite reflectance of >1.3%) the liptinite group macerals are difficult to distinguish from vitrinite and inertinite (Falcon and Snyman, 1986). In any given coal, liptinite has the highest relative hydrogen content and the lowest relative carbon content of all the other macerals (Falcon and Snyman, 1986). Liptinite macerals produce the highest percentage of volatile matter, followed by vitrinite (Falcon and Snyman, 1986).

Mineral Matter

As with the macerals, the abundance and composition of mineral matter in coal is determined by the conditions of coalification (Falcon and Snyman, 1986). Mineral matter in coal occurs in the form of discrete inorganic particles (crystalline or non-crystalline) representing true mineral components and as non-mineral inorganics which include dissolved inorganic salts and other inorganic substances in the coal's pore water as well as inorganic elements incorporated within the organic compounds of the coal macerals (Gary *et al.*

1972; Harvey and Ruch, 1986; Finkelman, 1994; Ward, 2002). The most common terms used for categorising mineral matter in coal are extrinsic and intrinsic mineral matter (Falcon and Snyman, 1986).

The non-mineral inorganics are more common and prominent in low rank coals (i.e. lignite and sub-bituminous coals) and contribute significantly to ash formation during utilisation (Benson and Holm, 1985 and Ward, 2002). Removal of moisture and some volatile matter, as well as changes in the chemical structure of the organic matter during the advance in rank in the coalification process, led to the removal of most of the non-mineral inorganics (Ward, 2002). Higher rank coals (i.e. bituminous and anthracite) therefore contain relatively low quantities of non-mineral inorganics (Ward, 2002).

The non-mineral inorganics form part of the intrinsic/inherent inorganic matter which was present in the original living plant tissue (Falcon and Snyman, 1986). The inherent mineral matter is intimately associated with the coal macerals and cannot be effectively removed using the conventional coal preparation techniques (Ward, 2002). The most common organically bound or non-mineral inorganics in lignite are Ca, Na, Mg and S (Benson and Holm, 1985, Schobert, 1995 and Ward, 2002).

Discrete inorganic particles, or minerals, may occur in both lower and higher rank coals and, in the absence of non-mineral inorganics, they are the dominant if not the sole component of the mineral matter in higher-rank coal deposits (Ward, 2002). They form the better part of the extrinsic/ introduced mineral matter which can be primary or syngenetic i.e. arising from the material washed or blown as detrital fragments into the accumulating peat deposit (Falcon and Snyman, 1986 and Ward, 2002). They can also be secondary or epigenetic i.e. deposited by percolating waters into fractures, cavities and pores within the coal seam long after initial accumulation of the peat (Falcon and Snyman, 1986).

The extrinsic minerals can to a certain extent be effectively removed by coal preparation processes (Falcon and Snyman, 1986). The common minerals in

coal include clay minerals (e.g. kaolinite, illite etc.), quartz, carbonates (e.g. calcite, dolomite etc.), sulphides like pyrite, phosphates like apatite etc. (Ward, 2002).

Microlithotypes

Microlithotypes are microscopic layers (>50 µm in width) formed by a combination, in various forms, of inorganic and organic constituents of coal. In reality, macerals are not scattered randomly throughout coal but are generally grouped in layers in which one or another maceral predominates. The fact that microlithotypes composition determines the macerals and/or maceral-minerals associations makes them even more useful during coal utilisation (Falcon and Snyman, 1986).

The organic microlithotypes include monomaceral, bimaceral and trimaceral which are distinguished based on their compositions and depending on whether they contain macerals of one, two or three maceral groups (Falcon and Snyman, 1986). Examples of monomacerals include vitrite, inertite and liptite microlithotype groups which are constituted by >95 vol% (mineral free) of vitrinite, inertinite and liptinite group macerals, respectively (Falcon and Snyman, 1986). The bimacerals include clarite (i.e. vitrinite + liptinite >95 vol%, mineral free), vitrinertite (i.e. vitrinite + inertinite >95 vol%, mineral free) and durite (i.e. inertinite + liptinite >95 vol%, mineral free) microlithotype groups (Falcon and Snyman, 1986). The trimacerite microlithotype group which is constituted by vitrinite, inertinite and liptinite group macerals adding up to >95 vol%, mineral free, is an example of a trimaceral (Falcon and Snyman, 1986).

The association of mineral matter (in proportions of >20 vol% or >5 vol% in the case of pyrite) and macerals (irrespective of the number of maceral groups present) forms the carbominerite microlithotype group (Falcon and Snyman, 1986). Examples of carbominerites include carbopyrite (coal + 5-20

vol% sulphides), carbosilicate (coal + 20 -60% quartz) carbagillite (coal+20 – 60% clay minerals) etc (Falcon and Snyman, 1986).

The chemical properties of microlithotypes are similar to those of the predominant macerals (Falcon and Snyman, 1986). The physical properties are however dependent also on the combined effect of the associations (Falcon and Snyman, 1986).

2.3.2.2. *Macroscopic Composition*

Macroscopically coal comprises of lithotypes. The lithotypes are distinguished on the basis of lustre, fracture pattern, colour, texture and type of stratification (Falcon and Snyman, 1986). They are related to maceral types and hence to precursor plant matter (Falcon and Snyman, 1986). Lithotypes may be divided into sapropelic and humic coals. Sapropelic coal lithotypes are non-banded, dull and compact with an even granular surface and conchoidal fracture. They originated in open or deeper water and are formed from the accumulation of algae and fine wind- or water-borne detrital organic matter. They include cannel coals, boghead coals and oil shales (Falcon and Snyman, 1986).

Humic coal lithotypes are banded with alternating fine layers of varying brightness. These lithotypes originate from the accumulation of the abundant humic matter within the original peat swamp (Falcon and Snyman, 1986). The four main lithotypes within the humic coals are vitrain (bright coal), clarain (banded bright coal), durain (dull coal) and fusain (fibrous coal) (Falcon and Snyman, 1986). Attritus lithotype occurs as dull to moderately bright lignite with vitrain and fusain lenses (Schobert, 1995). As it would be expected, inertinite and huminite macerals in the Beulah-zap lignite are more abundant in the fusain and vitrain lithotypes respectively (Schobert, 1995). Liptinite is not particularly related to any lithotype in lignites (Schobert, 1995).

2.3.3 Brief Geological Background of the North Dakota Lignite

The ND lignite is part of the Fort Union lignite field which is reportedly the second largest lignite field in North America (Ruppert *et al.* 2002). It is of Paleocene age as the peat from which this lignite formed was deposited in swamps 55 to 65 million years ago (Murphy, 2005). The lignite deposits of ND cover an area of 83 000 km^2 with only about 28 000 km^2 recoverable by surface mining (Schobert, 1995). The overburden on most of the lignite is rich in sodium which is most probably the source of sodium in the lignite itself (Schobert, 1995). North Beulah, South Beulah and Zap are the three separate lignite fields in the Beulah–Zap deposit in Mecer and Oliver counties. The Beulah-Zap bed is also found in some parts of the Dunn County (Schobert, 1995).

The Freedom mine which supplies lignite to the DGC's Great Plains Synfuels plant and the Antelope Valley power station was established on the Beulah-Zap bed. The seam in the mine is 4 – 6 m thick and is located 15 – 46 m below surface (The Coteau Properties Company, 2008).

The Beulah-Zap bed was reportedly deposited in a marsh environment. The deposition started in moderately deep water and vegetation growth was halted twice by major increases in water level that also increased the deposition of clay and silt in the southern portion of the basin. Deposition ended with a major drying episode, followed by extensive flooding that terminated peat accumulation throughout the basin. The lower seam formed in deep water with a gradually but steadily shallowing water level (Schobert, 1995).

The middle seam was initially formed in relatively shallow water, the level of which later increased throughout the depositional basin to moderate to deep. The depositional environment of the uppermost Beulah-Zap seam was unstable, with the majority of deposition occurring in moderate to shallow water with an overall shallowing trend preceding the end of deposition. Humification was the most predominant coalification process in the formation of the Beulah-Zap lignite and this is manifested by the dominance of huminite macerals in the lignite (Schobert, 1995).

The ND lignite is mainly brown but may appear black and lustrous in some deposits depending on the level and severity of weathering (Schobert, 1995). In most of the locations the lignite appears woody and sometimes flattened trunks or branches are found in the lignite structure (Schobert, 1995). The lignite shrinks and crumbles on drying and/or heating and the high moisture content (in the region of 28 – 45% on an as received basis) may have a high impact on this (Schobert, 1995 and Ruppert *et al.* 2002). During storage the lignite may also be liable to spontaneous combustion (Schobert, 1995).

The average ash content in the ND lignite is in the region of 6% (as received basis) and the calorific value in the region of 28 MJ/kg on a dry ash free (DAF) basis (Schobert, 1995 and Ruppert *et al.* 2002). The sulphur content ranges from 0.3% to 4%, with an average of 1.1% on a daf basis (Schobert, 1995). The CaO content in the ash averages 31%, whilst the Na_2O content can range from 0.1% to 27% (Schobert, 1995). The Na_2O and CaO contents are high and may hence lead to low ash melting temperatures which have adverse effects on the S-L FBDB gasification process. The average SiO_2 content in the ash is, although variable, in the region of 26% (Schobert, 1995). Al_2O_3 and Fe_2O_3 are on average in the region of 14% and 12% respectively (Schobert, 1995).

2.3.4 Some Properties of Coal Relevant and Important to the S-L FBDB Gasification Technology

2.3.4.1 *Petrographic Properties*

Petrographic analyses permit determination of coal rank by vitrinite reflectance as well as maceral, microlithotype and mineral composition of coal by optical examination and modal analyses in reflected light (Falcon and Snyman, 1986). Subsequent to analysis, classification of coal can be done in accordance with the ISO 11760 (2005) standard, as summarised in Figure 2.6.

As in any other process involving the utilization of coal, the rank and petrographic composition play an important role in gasification. In fact, most of the other coal properties measured for most of the processes (e.g. caking, fragmentation, grindability, volatile matter, reactivity etc. - to be discussed in the later sections) are highly influenced by the petrographic composition (Falcon and Snyman, 1986). Of particular importance to the S-L FBDB gasifiers is the rank of the coal (determined using vitrinite reflectance) which forms an integral part of the gasifier design as it affects the reactivity of coal (Slaghuis, 1993, Smith *et al.* 1993).

The maceral composition, reactive macerals (total of vitrinite and liptinite) content in particular, is important when dealing with caking coal which is known to have a high composition of these macerals, particularly vitrinite (Tromp, 1987). Fischer tar yield, which is particularly important in the CTL process, is also dependent on these reactive macerals, particularly liptinite and vitrinite (Tromp, 1987). The maceral and microlithotype composition also affect the type of chars that can be formed in the pyrolysis zone of the gasifier. This in turn may affect the reactivity of the particular coal (Smith *et al.* 1993).

	Low rank			Medium rank				High rank		
	C	B	A	D	C	B	A	C	B	A [a]

Vitrinite, % by volume, mineral-free [c]

100 — High vitrinite

80 — Moderately high vitrinite

60 — Medium vitrinite

40 — Low vitrinite

20

0

75 35 0,4 0,5 0,6 1,0 1,4 2,0 3,0 4,0 6,0

Bed moisture (% ash free)   Vitrinite reflectance ($\bar{R}_r$ %)

Lignite/Brown coal			S'bit [b]	Bituminous				Anthracite		
C	B	A	D	C	B	A	C	B	A

[a] At upper limit for High Rank A, $\bar{R}_{v,max} < 8\%$ preferred to $\bar{R}_r < 6\%$.

[b] Sub-bituminous.

[c] Reproducibility: $\bar{R}_r$ 0,08% ; vitrinite content 9%.

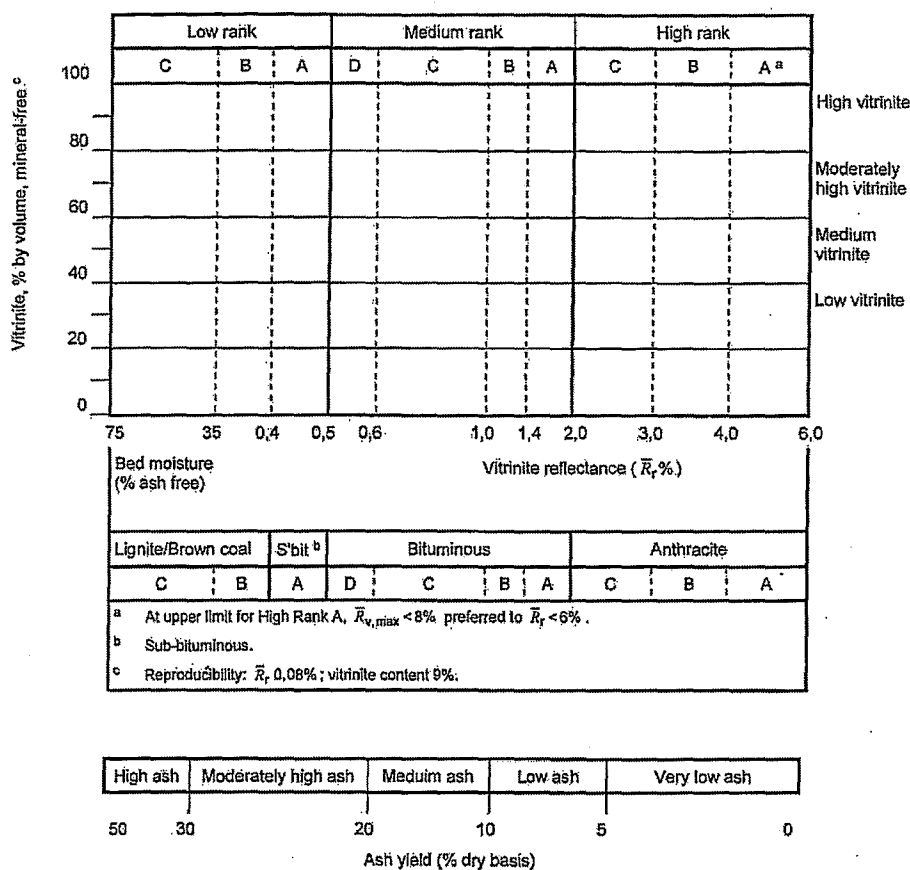| High ash	Moderately high ash	Medium ash	Low ash	Very low ash
50	30	20	10	5	0

Ash yield (% dry basis)

Figure 2.6. Summary of coal classification (ISO 11760, 2005)

The H_2 yield in the raw syngas, which can influence the H_2/CO ratio required for particular applications (e.g. DRI, CTL etc.), can also be influenced by high liptinite content in the coal due to the fact that liptinite macerals are rich in hydrogen (Falcon and Snyman, 1986 and Turna, 2008). For completeness and to be able to understand the behaviour of particular coal feedstocks in the S-L FBDB gasifiers, it is therefore important to perform petrographic analyses.

The ND lignites from the Freedom mine reportedly have a vitrinite or huminite reflectance (R_{max}) in the order of 0.36% (Schobert, 1995). On a mineral matter free basis the huminite content was reported to be 70% (vol), liptinite 12% (vol) and inertinite 18%(vol) (Schobert, 1995). The macerals at this rank or level of maturity are known to behave very differently in various coal utilization processes when compared to medium and high rank coals (Stach *et al.*, 1982). Hence, given this significant difference in rank and maceral composition, the Freedom mine lignite, in the S-L FBDB gasification process,

is expected to behave in a totally different way when compared to the South African bituminous coals.

The South African coals mined in the Witbank and Highveld coalfields, some of which are gasified on a commercial scale in the S-L FBDB gasifiers in Secunda, have a mean random vitrinite reflectance (Rr%) of 0.5 – 0.7 % and are hence classified, according to ISO 11760, as bituminous, Medium Rank C (Pinheiro *et al*, 1999). On a mineral matter free basis, the run of mine (RoM) coals typically have an average vitrinite content in the region of 30% (vol), liptinite of 5% (vol), and reactive semifusinite of 25% (vol) and inert inertinite of 45% (vol) (Pinheiro *et al*, 1999).

2.3.4.2 *Proximate Analyses*

The proximate analysis of coal describes its composition in terms of the relative amounts of moisture, volatile matter, ash and fixed carbon content which is calculated by difference. Although very basic, the proximate analysis is a very practical, less costly and quick method to assess the quality of coal (Slaghuis, 1993).

Determination of moisture in the analysis sample allows for the expression of the results of other analyses on a dry basis. This moisture is determined in accordance with SANS 5924 (1978) standard method. ISO 5068 (2007) is used particularly for lignite.

The total moisture gives an indication in terms of the amount of gas liquor/liquid condensate that will be generated during gasification in the S-L FBDB gasifiers. Although there are technologies to treat it to some acceptable levels in terms of environmental performance, the liquid condensate/liquor is known to be a nuisance. It is therefore preferable to have as low the moisture content in the feed coal as possible. During gasification of lignite, which is known to have very high moisture content, the total moisture content on an as received basis is particularly important. ISO 589 (2008) and ASTM D3302

(2007) standard methods are used for the determination of total moisture in coal.

Compared to bituminous coal and anthracite, lignite typically has a very high moisture content which is reportedly very difficult to measure (Schobert, 1995). The moisture contents of the ND, Texas and California lignite, on an as received basis, were reported as 34.7%, 35.8% and 37.7% respectively and between 14 and 26% on an air dry basis (Schobert, 1995). South African bituminous coals on the other hand have on average about 3% moisture on an air dry basis (Pinheiro et al, 1999). The feed coal to the gasifiers in Secunda has total moisture content in the region of 10% and this is due to wet screening.

The volatile matter provides an indication of the reactivity of coal, as well as the amount of tar and oils that might be produced during gasification (Slaghuis, 1993). Although not that accurate, the volatile matter may also give an indication in terms of the rank of the coal (i.e. for the coals with similar reactive macerals content – vitrinite, liptinite and reactive inertinite, the volatile matter (dry ash free basis) will decrease with an increase in rank from peat to anthracite). The volatile matter is determined in accordance with ISO 562 (1998) standard method.

The ash content gives an indication of the amount of impurities present in the coal. During gasification in the S-L FBDB gasifier, ash is produced as a by product and the proximate analyses gives an indication of the amount of ash to be handled. Although they are diluents to the coal, the S-L FBDB gasifiers can accommodate up to 50% of total moisture plus ash content and this is one of the advantages of this technology (Turna, 2007). The ash is determined in accordance with ISO 1171 (1997) standard method.

The S-L FBDB gasifiers are perfectly suited to lignite gasification as the process includes drying and devolatilization prior to gasification and combustion as shown in Figure 2.2. Drying of lignite prior to feeding into the gasifier will not only increase operating costs but also create an excessive

amount of fines which unless agglomerated will be very difficult to handle and feed into the fixed bed gasifiers (Higman and van der Burgt, 2003).

2.3.4.3   Ultimate Analysis

The ultimate analysis is the determination of C, H, N, S and O (calculated by difference) which are present in the organic structure of coal. The mass balance of the gasification process is based partly on the ultimate analyses expressed on a dry ash free basis. The ultimate analysis therefore plays a very crucial role in the design of gasifiers. Carbon, Hydrogen, and Nitrogen are determined in accordance with ASTM D5373 (2002), Sulphur determined according to ASTM D4239 (2002) and oxygen determined by difference.

Carbon in the ultimate analysis represents the total carbon in the coal. Sulphur in coal can occur in three forms namely pyritic, sulphate and organic. During gasification the sulphur is released mainly in the form of H_2S and COS whilst some of the sulphur is retained in the ash. The gaseous sulphur species are not environmentally friendly and it is preferable to gasify the coal with as low total sulphur content as possible (Slaghuis, 1993).

The nitrogen in the coal is released mainly in the form of NH_3 and HCN during gasification. These species are expected to report in the raw gas liquor, and NH_3 in particular, serves to regulate the pH of the gas liquor thus reducing corrosion on the equipment (Turna, 2008). A particular minimum amount of nitrogen in the coal is therefore required for gasification in the S-L FBDB gasifiers (Turna, 2008).

2.3.4.4   Fischer Assay

The Fischer Assay is performed in accordance with the South African standard method number SANS 6073 (1984) and measures the amount of tar, water, gas and char which form during coal pyrolysis at atmospheric pressure. These products are an indication of the species that may be formed in the pyrolysis section of the S-L FBDB gasifier (Slaghuis, 1993).

Tar may represent total tar, naphtha and oil which are particularly important in a CTL facility as mentioned in section 2.3.4.1. The measured moisture is used to determine the gas condensate produced. The amounts of condensable liquids provide an indication of the load on the cooling system in a plant. The data can however not be related directly to that from a commercial plant, since the effect of various variables (such as pressure, temperature, heating rate, the use of steam in the plant etc.) cannot be simulated effectively in the laboratory.

On an air dry basis, the Secunda coals produce a Fischer tar yield of between 3% and 5 %, char (including ash) of 82% − 85%, water of 8% -10% and gas/ losses of 2% − 6% (Bunt, 2006). Although substantial amount of work was done on pyrolysis of lignite (Schobert, 1995), no specific Fischer assay data on the ND lignite could be found in the literature.

2.3.4.5   Particle Size Distribution

As mentioned in section 2.2.1, the S-L FBDB gasifiers are coarse coal gasifiers. Particle size distribution (PSD) therefore plays a crucial role during the operation of these gasifiers. The main issue associated with PSD of the feed coal is the stable operation of the gasifier due to pressure drop effects. These can manifest themselves in a variety of ways including grate traction loss (due to bed fluidization), channel burning (leading to unacceptable gas outlet temperatures) and solids elutriation or carry-over (Slaghuis, 1993).

Coal particle size also affects other properties of coal that influence gasifier operation e.g. reactivity, fragmentation, bed homogeneity, etc. A bottom to top size ratio of 1:10 is therefore preferred for the S-L FBDB gasifiers (Bunt, 2006). This however, only holds true for higher rank coals which are known to be less friable when compared to lignite (Schobert, 1995).

Screening at various particle sizes is used to determine the PSD of the feed coal to the S-L FBDB gasifiers. However, the mean Sauter diameter ($\overline{d_p}$) or the Ergun index, as defined by equation 2.8 below, is a very useful parameter for measuring/determining the PSD that can result in an unstable gasifier operation. The $\overline{d_p}$ is influenced more by the amount of fines in the distribution and for the Secunda operation, experience has showed that PSDs with the $\overline{d_p}$ of below 7.5 result in unstable gasifier operation (van Dyk et al., 2001).

$$\overline{d}_p = \frac{1}{\sum\limits_i \left(\dfrac{x_i}{d_{p,i}} \right)} \quad \text{-------------- (2.8)}$$

where i = screen number, x_i = fraction (mass %) on screen i, and $d_{p,i}$ = diameter (mm) of screen i.

2.3.4.6   Caking Properties

Caking of coal particles can be described as the thermoplastic property of coal, which causes particles to agglomerate when heated in the absence of oxygen (Tromp, 1987). Caking of coal within the S-L FBDB gasifier can cause pressure drop fluctuations and channel burning, resulting in unstable gasifier operation (Slaghuis, 1993). In a worst case scenario, oxygen may break through the bed and cause some explosion risks down stream of the gasifier (Slaghuis, 1993). Excessive caking of coal in a fixed bed gasifier may also lead to operation failures resulting from an impermeable bed. However, caking does assist with the agglomeration of the coal particles that fragment in the gasifier as a result of thermal shock (see section 2.3.4.7).

A proprietary caking test method is used at Sasol. Caking behaviour is measured by pyrolyzing a pre-screened coal sample at gasification temperature and pressure in an inert atmosphere. The percentage caking or caking propensity is determined by the mass of particles agglomerated after the test.

The S-L FBDB gasifier can safely accommodate coal with a caking propensity of <30% as was observed in the Secunda operation (van Dyk et al., 2001). Beyond this level, coal can be blended to reduce the caking propensity to acceptable levels. Highly caking coals with propensity of 80% and more can also be accommodated by the inclusion of mechanical, water cooled and hard faced coal distributor and stirrer in the design. This has been proven in many plants like Tianji Coal Chemical Company in Shanxi, China which has been operating for more than 20 years (Li, 2004).

The ND lignite does not exhibit thermoplastic properties upon heating (Benson, 2007). Generally, caking does not seem to be an issue with most of the lignites (Benson, 2007). However, some Canadian lignites tested at Sasol Technology R&D exhibited a caking propensity of up to 80% (Mangena, 2006). The reason for this is not clear but it is suspected that it may be due to different types of huminite macerals.

2.3.4.7   Mechanical and Thermal Fragmentation

Due to the specification on the top to bottom size ratio as well as the allowable amount of fines in the feed coal to the gasifier, screening of the coal prior to gasification is very critical. However, even after screening, mechanical fragmentation during handling can still occur and thus change the PSD of the feed coal. To be able to accommodate this fragmentation in the design of the coal handling and preparation equipment, it is important to measure its extent.

At Sasol, mechanical fragmentation is measured by a change in mean Sauter diameter subsequent to tumbling a pre-screened coal sample in a micum drum (van Dyk et al., 2001). It is affected by various properties of coal including amongst others mineralogical composition, maceral composition, and microlithotypes composition and weathering (Stach et al, 1982). For Secunda coals, the mechanical fragmentation is in the region of 35% (van Dyk et al., 2001).

Thermal fragmentation occurs when the coal is exposed to the heat at the top of the gasifier, particularly in the drying and devolatilization zones. This can also change the PSD of the coal thus causing pressure drop problems as explained in section 2.3.2.5. In addition, thermal fragmentation can lead to load restrictions (van Dyk et al., 2001).

At Sasol, thermal fragmentation is measured by the change in mean Sauter diameter of a pre-screened coal sample that is heated at a rate of 12 °C/min to a temperature of 700 °C under nitrogen. Thermal fragmentation is highly affected by moisture content in the coal (van Dyk et al., 2001, Schobert, 1995). This therefore makes lignite to be even more prone to thermal fragmentation. The thermal and mechanical fragmentation of the Secunda coals is about 30% (van Dyk et al., 2001).

The methods used at Sasol are not the only methods that can be used for thermal and mechanical fragmentation determination. However, tumbling in a micum drum and subsequent screening is the common method used in the coal industry. For low rank coals, Beulah-Zap lignite in particular, mechanical fragmentation increases sharply with the amount of drying prior to tumbling (Schobert, 1995). This is most probably due to the desiccation cracks that are expected to occur during drying, given the high moisture content in the lignite. The same explanation may hold true for thermal fragmentation which is expected to be aggravated by the release of volatiles.

When measured by the amount of -13 mm particles remaining after tumbling (mechanical fragmentation), heating to 540 °C (thermal fragmentation) or both (combined mechanical and thermal friability), the Beulah-Zap lignite (19x13 mm) gave values of 38%, 86% and 97% for mechanical, thermal and combined mechanical and thermal friabilities respectively (Schobert, 1995). This is not unexpected as it was also observed with lignites from other parts of the world (Mangena, 2006).

2.3.4.8 Reactivity

Compared to thermodynamics, the kinetics of coal gasification, although it has been and still is a subject of intensive investigation, is not yet well developed. This is mainly due to the complexity of the heterogeneous gasification reactions as well as the mass transfer limitations (Higman and van der Burgt, 2003).

At Sasol, the Boudouard reaction (see equation 2.1) in a thermo gravimetric analyser (TGA) is used to measure coal char reactivity. This is often done for comparison purposes, but the information is sometimes useful in design as it provides an indication of the expected rate of gasification in the gasifier. The method applied at Sasol measures the mass loss of 5 mg fixed carbon in the coal char (300x150 μm, prepared at 1200 °C and heating rate of 50 °C/min under a nitrogen atmosphere) at a gasification temperature of 900 °C in a CO_2 atmosphere until the carbon is completely burned off. The reactivity is then calculated at 50% burn-off and expressed in h^{-1} units (Slaghuis, 1993).

For the S-L FBDB gasifiers, the limitations for reactivity are not known as coals with reactivities ranging from as low as 0.5 to 40 h^{-1} are gasified successfully on a commercial scale (van Dyk et al., 2001). Secunda blended coal typically has a reactivity of 2 -5 h^{-1} whilst ND lignite has a reactivity of >25 h^{-1} (Slaghuis, 1993 and van Dyk et al., 2001).

2.3.4.9 Mineralogical Properties and Ash Melting Properties

During fixed bed gasification, the mineralogical properties of coal play an important role with regard to the ash melting properties. The S-L FBDB gasifiers are, as per the name, designed for a dry bottom/ash removal operation. Severe clinkering can therefore cause serious problems with regard to ash removal. In addition, clinkering can cause channel burning, pressure drop problems and unstable gasifier operation (Slaghuis, 1993 and van Dyk et al., 2001).

Although there are other methods like slag viscosity for measuring ash melting properties, the ash fusion temperature (AFT as measured according to ASTM D1857, (2004)) is a good measure for ash agglomeration and clinkering in the S-L FBDB gasifiers. The gasifiers are designed to operate between the initial deformation and flow temperatures of the ash to ensure an enhanced distribution of the gasification agent (steam and oxygen) in the ash bed and to avoid excessive clinkering or slagging (i.e. complete melting of the mineral matter particle) of the ash. The ash flow temperature of <1200 °C is regarded as low, >1200<1450 °C intermediate and >1450°C high (Slaghuis, 1993).

High ash melting temperatures are regarded as beneficial to fixed bed gasification. With coals displaying high ash melting temperatures, a low H_2: CO ratio gas can normally be produced (van Dyk, 2006). This reduces the overall steam consumption of the gasifiers and increases the carbon efficiency by lowering the CO_2 content of the product gas (van Dyk, 2006).

The mineral matter in coal can be in the form of organically associated inorganic species and minerals (Ward, 2002). Due to the lack of homogeneity in the S-L FBDB gasifiers, the effect of mineral matter on the AFT is dependent on the association of these inorganic species (Matjie et al., 2006). In addition, due to the difference in mode of occurrence the behaviour of mineral matter in lignite is expected to differ from that of the bituminous coals.

X-ray diffraction (XRD), chemical fractionation, computer-controlled scanning electron microscopy (CCSEM), SEM and microprobe analyses are some of the techniques used for qualitative and quantitative analyses of mineral matter in coal. These are however advanced and expensive and are mainly used in particular cases where a detailed understanding of ash behaviour is required. The major minerals in the Secunda coals are kaolinite (~35%), quartz (~30%), illite/muscovite (~13%), calcite (~8%), dolomite (~9%) and pyrite (~4%) (Matjie et al. 2006).

The minerals encountered in the ND lignite include quartz, kaolinite, pyrite, illite, montmorilonite, calcite, gypsum, and dolomite (Morgan et al., 1980; Schobert, 1995; Benson, 2007). Although these minerals can be found in the ND lignite, mineral matter in this coal is also mainly in the form of organically bound/ion exchangeable cations (e.g. Na, Ca and Mg) which complicate the transformation of mineral matter during combustion and gasification (Nankervis and Furlong, 1980; Benson and Holm, 1985; Quann and Sarofim, 1986; Schobert, 1995).

Chemical ash composition analysis is most commonly used as an approximate guide to predict the behaviour of inorganic species of a particular coal during gasification. However, this analysis has limitations in that it measures the average ash composition, which as mentioned earlier, does not reflect the processes occurring in the S-L FBDB gasifier. Nonetheless, this gives an indication particularly with regard to the basic oxides (i.e. CaO, MgO, Na_2O, Fe_2O_3 etc.) which are known to have fluxing effects.

In the ND lignite, the CaO content in the ash averages 31% (Schobert, 1995). Electron microprobe scans as well as X-ray absorption fine structure spectroscopy (EXAFS) showed that Ca in this lignite is predominantly organically bound and dispersed as salts of carboxyl groups (Huggins et al., 1983 and Schobert, 1995). This is also supported by chemical fractionation results where 76% of the Ca in the ND lignite was removed by ammonium acetate and hence ion exchangeable (Benson and Holm, 1985). In Secunda (South Africa) RoM coals, the CaO content is less than 10% and is found mainly in the form of calcite and dolomite (Pinheiro et al. 1999 and Matjie et al. 2006).

The Na_2O content in the ND lignite can range from 0.1 to 27% (Schobert, 1995). As with Ca, the Na in this lignite is organically bound and dispersed as salts of carboxyl groups (Huggins et al., 1983, Benson and Holm, 1985 and Schobert, 1995). The Na_2O content in Secunda coals is in the region of <1% and the Na is mainly associated with the water (Pinheiro et al. 1999 and Matjie et al. 2006).

The sodium content in the feed coal is particularly important for the Great Plains Synfuels Plant. At this plant, the Na content of >8% leads to the formation of clinkers that fill up to 20% of the gasifier bed (Dittus and Johnson, 2001). When this happens, the gasifier has to be shut down and jackhammers used to break up the clinkers so that they can be removed. The feed at this plant is therefore blended accordingly to provide a constant feed with 6 - 8% (max) Na content (Dittus and Johnson, 2001).

The Fe_2O_3 content in ND lignite is on average in the region of 12% and the Fe in the species is mainly in the form of pyrite although some may be organically bound (Schobert, 1995). In Secunda it is mainly in the form of pyrite (Matjie *et al.* 2006). Magnesium in the ND lignite is mainly organically bound (Schobert, 1995, Huggins *et al.*, 1983 and Benson and Holm, 1985). In Secunda coals it is mainly in the form of dolomite (Matjie *et al.* 2006).

2.4 The Great Plains Synfuels Plant

The Great Plains Synfuels Plant started operating in 1984 and is the only commercial plant in the United States (US) producing synthetic natural gas from coal via the gasification route. It is owned and operated by DGC (a subsidiary of Basin Electric Power Cooperative (BEPC)), and gasifies about 18000 tons of lignite daily in the S-L FBDB MK IV gasifiers to produce about 4500 km^3N (about 160 million cubic feet) of Synthetic Natural Gas (SNG) and other by-products (Fagerstrom, 2007).The lignite is supplied from the nearby Freedom mine. The fines (-6 mm) from the coal handling facility are sent to the Antelope Valley Power Station which is also owned by BEPC.

The process flow diagram for the plant is depicted in Figure 2.7 (Fagerstrom, 2007). In the process, sized coal (>6 mm) is gasified in 14 S-L FBDB MK IV gasifiers to produce raw syngas, which is first cooled in the waste heat boiler that generates steam which is used elsewhere in the plant. The gas is then sent to the additional waste heat recovery and cooling water unit where it is further cooled down to 35 °C. About 80% of the cooled gas is sent to the shift

conversion process to adjust the H_2 : CO ratio by converting some of the CO and H_2O to CO_2 and H_2 through the water gas shift reaction as shown in equation 2.6.

The shifted gas is then mixed with the cooled raw gas and sent to the Rectisol process where acidic gases, particularly CO_2 and volatile sulphur compounds as well as naphtha, are removed by a cold methanol wash. The gas from Rectisol is sent to the methanation process for the production of SNG which is compressed, dried and sent to the pipeline. Part of the processed syngas is diverted to the ammonia plant for the production of anhydrous ammonia. Some of the acid gas is used as boiler fuel whilst the rest is sent to the CO_2 compression unit where it is compressed and piped to Canada to be used for enhanced oil recovery (Fagerstrom, 2007).

The condensate or gas liquor from the cooling process is processed by first removing dusty tar by gravity separation methods and recycling it back into the gasifiers. The oils are also separated by gravity and used as boiler fuel. Phenols and ammonia are recovered in the Phenosolvan and CLL processes, respectively (Fagerstrom, 2007).
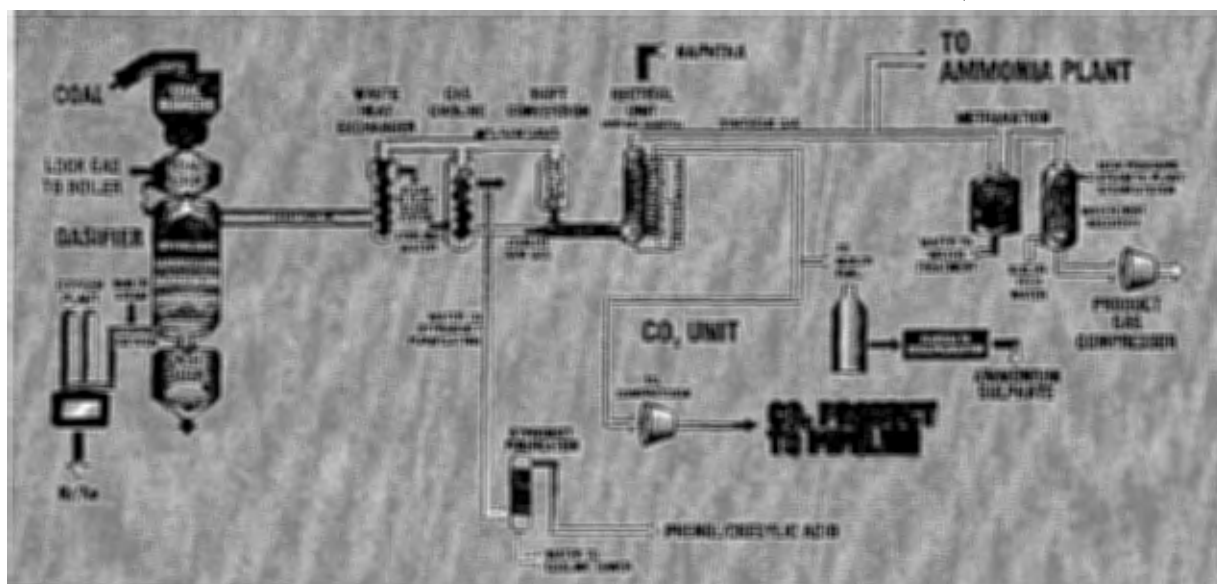

Figure 2.7. Great Plains Synfuels plant/DGC process flow (Fagerstrom, 2007).

2.5 Previous Work Done on Fixed Bed Dry Bottom Gasifier Fuel Bed Analysis and Evaluation

In Sasol, the initial study on the physical and chemical processes occurring within the MK-IV S-L FBDB gasifier was pioneered by Glover (1988 and 1991) with the inspiration from similar developments in blast furnace technology that is used in the iron and steel industry (Pistorius, 2006). Glover (1988 and 1991) used two methods of sampling (i.e. Run-Out/Turn-Out and Dissection/Dig-Out) to study the gasifiers in both the Sasolburg and Secunda operations.

In a Run-Out/Turn- Out sampling methodology, the complete gasifier contents run continuously out through the ash lock by the action of a rotating grate. A sampling device is then periodically located into the falling stream of contents to capture a predetermined quantity of the sample (Glover, 1988). In a Dissection or "Dig-Out" sampling methodology, the contents of the gasifier are cooled sufficiently to allow safe access into the reactor. The coal lock is removed and the samples taken out of the gasifier using shovels. A pre-determined sampling grid scheme is used to ensure that the samples can be related back to their corresponding position in the gasifier (Glover, 1988).

A Turn-Out sampling programme takes about 2 days to complete and about 34 samples are obtained (Glover, 1988 and Bunt, 2006). Although it does not show the finer details of the fuel bed, it is adequate to gauge the axial ash bed height as well as other properties of the bed like reaction zones (Bunt, 2006). In a situation where a commercial gasifier is used for the studies, this method is ideal as it consumes less production time.

A Dig-Out sampling programme takes about two weeks to complete and a total of about 244 samples are obtained from 22 levels of a MK IV gasifier. As it can be expected, a greater degree of details pertaining to the axial, radial and tangential behaviour of the fuel bed can be obtained (Glover, 1988). The method is however better suited for a dedicated test unit as it is more time consuming. Despite the limitations due to production disturbances, Glover

(1988 and 1991) managed to do 3 Dig-Outs (1 in Sasolburg and 2 in Secunda) and 2 Turn-Outs (1 in Sasolburg and 1 in Secunda).

From the studies conducted by Glover (1988 and 1991), gas flow maldistribution within the gasifier was found to be the major factor affecting its performance (Glover, 1988). Coal reactivity, feed coal particle size distribution, ash content of the coal, fixed carbon of the coal, ash melting properties, devolatilization behaviour of the coal as well as the mechanical properties of the coal were found to be the macroscopic properties of the coal that significantly affect reactor behaviour.

Caking of the char in the fuel bed was observed for the first time in Secunda but was not observed in Sasolburg (Glover, 1998). The observed char cake was mechanically strong but friable. On the sides of the gasifier, closer to the jacket, discrete particles were observed and according to Glover (1988), this might lead to preferential gas flow or channelling. Asymmetrical ash beds and isolated wall channels rooted to the ash bed were also observed in the gasifiers, and this may be an evidence of thermal channelling.

Glover's (1988 and 1991) studies led to the design and implementation of a new coal feeding mechanism (i.e. "unifeeder") that ensures uniform coal feeding with less segregation into the gasifier. Although the coal properties important in the gasifier were identified, there are still some gaps in the coal properties that may require some further fundamental studies e.g. the minerals and their effect on the ash fusion properties and clinker formation, trace elements behaviour etc. In addition, the behaviour of the coals studied will not be the same as that of the lignite coal.

A 1 ton of coal/h Lurgi FBDB pilot gasification plant was commissioned at the Indian Institute of Chemical Technology in 1993 to study utilization potential of the high ash Indian coals (Madhusudhan et al., 1989 and Krishnudu et al., 1989a). A study with the objective of developing a flow model for the FBDB gasification reactor was initiated (Madhusudhan et al., 1989).

The initial study was aimed at examining the flow behaviour of solids within the gasifier (Madhusudhan *et al.*, 1989). Mullite pebbles were used as tracers and a known weight was charged along with the coal (6x25 mm) into the continuously operating gasifier. The ash was discharged in batches and the tracers in the ash recovered and weighed. Vessel dispersion numbers were calculated, assuming that a continuum of flow elements exists in the flow of solids as in the case of fluids, and found to be nearly zero for the test that was done in triplicate (Madhusudhan *et al.*, 1989). The authors therefore concluded that the gasifier behaved like an ideal plug flow reactor with no back mixing of solids and no stagnant regions inside (Madhusudhan *et al.*, 1989).

Although there may be scale-up issues from a pilot scale gasifier with internal diameter of 1.13 m to a commercial MK IV gasifier with internal diameter of about 4 m, this conclusions may hold true for commercial scale gasifiers (Bunt, 2006). This may however require some testing in future.

The study on the flow behaviour was followed by the determination and prediction of reaction zones in the pilot scale gasifier (Krishnudu *et al.*, 1989b). A Turn-Out method was used to sample the gasifier sequentially after quenching it by cutting off the oxygen and steam. The samples were analysed for proximate, ultimate and Gray-King assay. From these analyses, particularly volatile matter, ash content and tar yield from the Gray-King assay, three reaction zones (i.e. fast devolatilization, slow devolatilization with gasification and gasification) were determined. It was found that two-thirds of the total fuel bed height of 3.5 m was for devolatilization and the rest for gasification and combustion and ash zones (Krishnudu *et al.*, 1989b). This information is important during design of the gasifiers.

A temperature profile in the gasifier was also predicted using the residual volatile matter remaining in the samples. The maximum temperature in the bed was found to be 1100 °C and as expected this was observed in the combustion zone (Krishnudu *et al.*, 1989b). This temperature is in line with the process conditions (e.g. steam (kg): O_2 (m^3N) of 6.1, 33% of CO_2 in the raw

gas and gas outlet temperature of 350 °C), which do not seem to be optimal given the high ash flow temperature (>1400 °C) of the coal tested.

In an attempt to take Glover's work further, Bunt (2006) designed a new controlled dissection methodology for sampling a full MK IV S-L FBDB gasifier after shutdown. The method is similar to a Run-Out/Turn-Out method applied by Glover (1988) and Krishnudu *et al.* (1989) but included a more controlled and stable gasifier operation prior to shut down and incremental sampling as well as a sub-sampling method similar to the one used for sampling trucks (Bunt, 2006).

The samples tested provided a clear residual internal profile of the gasifier which allowed the development of a "pan-cake" model that shows the axial distribution profiles of most of the coal properties investigated (Bunt, 2006). Optimisation opportunities around char type responsible for carbon loss, oxygen scavenging effect of minerals, volatile matter re-condensation in the cooler zone of the gasifier, and reduction of top size of the feed coal to a "thermally stable" size were identified (Bunt, 2006, Bunt and Waanders, 2008a).

Reaction zones in a commercial MK IV S-L FBDB gasifier operating on bituminous coal were identified in one of the studies using the proximate, ultimate, Fischer assay and CO_2 char reactivity analyses (Bunt and Waanders, 2008b). The authors observed that the top half of the reactor volume was required for drying and devolatilizing the coal leaving the other half for gasification, combustion and ash bed zones (Bunt and Waanders, 2008b). The reaction zones were also found to overlap and this is in contradiction with what is depicted in Figure 2.2.

Bunt *et al.* (2008) also developed a temperature profile of the commercial scale S-L FBDB gasifier using a vitrinite reflectance of the chars obtained from the Turn-Out samples. The profile was found to be in line with the literature and the temperature peaked at about 1200 °C in the combustion zone as it would be expected (Bunt *et al.* 2008). This temperature is below the ash flow

temperature of the coal studied (i.e. 1350 °C) and hence within the operating window. The authors however concluded that the peak temperature observed was a hot spot that may be caused by localised oxygen concentration due to lack of uniformity in agent distribution. Homogenisation of the bed was suggested as the potential solution to this hot spot anomaly (Bunt *et al.* 2008).

Other investigations on fuel bed behaviour were conducted by Lurgi and British gas in the BGL slagging fixed bed gasifier retrofitted with a coal distributor and stirrer to enable operating on caking coal. The information is however confidential to the owners of the BGL gasification technology and could not be accessed. Nonetheless, the Lurgi personnel who were involved in the studies confirmed that the methodology used at Sasol is more advanced and detailed when compared to the BGL studies (Turna, 2008).

The information obtained in all the studies reviewed is undoubtedly useful for the optimization and modelling of the gasifiers. However, fuel bed behaviour in the FBDB gasifier is expected to be coal dependent. Hence, the majority of the information and knowledge generated in the reviewed studies cannot be directly used in a lignite FBDB gasification operation.