

## **Chapter 4**

### **4. RESULTS AND DISCUSSIONS**

In this chapter, the reaction zones in “Albert” and “Bernice” gasifiers are identified using chemical properties of coal. The fuel bed behaviour as well as the chemical, physical, petrographic and mineral properties transformation in the identified reaction zones are discussed. Where possible, a comparison is made with the profiles of the Secunda GG41 MK IV gasifier which gasifies bituminous coal. The trend lines on most of the graphs presenting the data were drawn manually to guide the eye of the reader. Where the trend line joins the feed coal with the sample taken from the top of the gasifier, it should be noted that the trend is extrapolated. Detailed information on the graphs presented throughout this chapter can be found in Appendices 1&2.

#### **4.1. Chemical Properties and Identification of Reaction Zones**

As discussed in chapter 2, a fixed bed gasifier comprises of the drying zone, pyrolysis zone, gasification/reduction zone, combustion zone and the ash bed. The reaction zones explained in the literature are however ideal and in reality it is known that there are some overlaps between these reaction zones. The turn-out sampling methodology employed in this study, although providing only axial information, can provide an indication in terms of the level of the fire bed.

##### **4.1.1. Reaction Zones in the “Bernice” Gasifier**

###### **4.1.1.1. Drying Zone**

Proximate and ultimate analyses provide very important information with regard to reaction zones in the gasifier. Figure 4.1 illustrates the proximate analysis (dry basis) and reaction zones in the “Bernice” gasifier. From samples 27 to 19 no reactions related to gasification (i.e. carbon conversion or

volatile matter decrease) are observed. The only anomaly is a slight increase in volatile matter which can be attributed to the dusty tar recycling which is standard in the DGC operation unless the gasifier is “sick” (Baker, 2007a). This zone is therefore regarded as the drying zone. The same criterion for identifying the drying zone was also used by Bunt and Waanders (2008b). It should be noted that sample 32 was the feed coal, as sampled from the conveyor belt, and has therefore not been exposed to any form of heat from the gasifier. The line joining this data point is therefore just an extrapolation.

If each sample represents a slice of 0.26m as shown in Figure 3.3, then about 2.3 m (almost a quarter of the gasifier volume) of the gasifier is used to dry the coal, and given the high moisture content of the lignite (36% as received basis), this is not unexpected. In identifying the reaction zones in the pilot scale FBDB gasifier operating on bituminous coal, Krishnudu *et al.* (1989b) used the volatile matter to identify the drying and devolatilization zones. The authors therefore could not differentiate between these two zones. In this study, the drying zone is particularly important, given the high moisture content of lignite as well as the effects of this moisture on thermal fragmentation of the coal particles.

#### **4.1.1.2. Pyrolysis Zone**

The volatile matter as determined in the proximate analysis is a very good indication of the pyrolysis zone within the gasifier. The Fischer tar content serves as a confirmation of the pyrolysis zone position, particularly where fast pyrolysis occurs. In Figure 4.1, it can be seen that the volatile matter decreases sharply from sample 19 and stabilizes at about 10% (dry basis) from sample No. 7. Figure 4.2 illustrates, on a normalised basis (i.e. calculated per 100kg ash flow), the residual volatile matter and Fisher tar profiles in the “Bernice” gasifier. In this figure, a slight increase in volatile matter in the drying zone as well as a sharp decrease from samples 19 to 7 is clearly illustrated.

The Fischer tar content in Figure 4.2 decreases sharply from samples 19 to 11 and then slowly from sample 11 to 7. The end of Fischer tar production can be regarded as the end of organic volatile matter release from the gasifier bed. The 10% (dry basis) volatile matter content in the samples below No.7 as well as in the ash is therefore most probably inorganic in nature. Based on the volatile matter and Fischer tar profiles, the height from sample 19 to 11 and sample 11 to 7 can be regarded as fast and slow pyrolysis, respectively. Krishnudu *et al.* (1989b) as well as Bunt and Waanders (2008b) also used this criterion to determine the fast and slow pyrolysis/devolatilization zones in the FBDB gasifiers.

The pyrolysis zone in the “Bernice” gasifier is therefore between samples 19 and 7 which is about 3.4 m of the gasifier bed height. Combined with the drying zone, about 5.7 m (more than half of the reactor, or about two third of the reactor volume) of the total “Bernice” gasifier bed is used for devolatilizing of the lignite coal. This is a significant finding and clearly different from what was observed in the Secunda gasifiers that operate on bituminous coal as reported by Bunt (2006).

#### **4.1.1.3. Gasification, Combustion and Ash Bed Zones**

The beginning of an increase in the ash content on the residual ash content profile can provide an indication of the beginning of the carbon conversion process. This then has to represent the beginning of the gasification zone given that it happens in a reducing environment sometimes overlapping with the pyrolysis zone. In support of the criteria using an increase in ash content, a point where the normalised fixed carbon is equal to the normalised total carbon on the residual fixed carbon and residual total carbon profiles can also be used to determine the beginning of the gasification zone (Bunt *et al.*, 2008b and Krishnudu *et al.*, 1989b). However, experience has shown that this is not always easy to determine. This study therefore relies mainly on the residual ash content profile to determine the beginning of the gasification zone position.

In Figure 4.1, it is shown that the ash content begins to increase at sample No.13 (i.e. 4 m from the bottom of the gasifier) and hence overlapping with the pyrolysis zone. At the same point, (i.e. sample No. 13) the normalised total and fixed carbon contents are equal as depicted in Figure 4.3. In addition, the total carbon content (dry basis) begins to decrease at this particular height of the gasifier thus confirming the beginning of the carbon conversion process - see Figure 4.4.

It is always a challenge to identify the end of the gasification zone and the beginning of combustion and ash bed zones when a Turn-Out sampling method is used. However, the residual total oxygen profile, as shown in Figure 4.4, can provide an indication of the oxidation zone position. It is acknowledged that the results for total oxygen may be erratic as it is determined by difference in the ultimate analyses. However, in this study the trend is more important than the results of the individual samples.

As expected, the total oxygen content in Figure 4.3 decreases in the reducing environment (i.e. pyrolysis and beginning of the gasification zones). However, from sample No. 7 (i.e. the end of the pyrolysis zone), an increase in total oxygen is observed. This thus may be an indication of the beginning of an oxidizing environment. This sub-zone is therefore termed gasification and oxidation.

Further down the gasifier from sample No. 4, combustion seems to be dominating, given the very low amount of carbon remaining as well as a high ash and relatively high oxygen contents as illustrated in Figures 4.1 and 4.4. This is therefore regarded as the ash and combustion zones (i.e. between samples 4 and 1) from the bottom of the gasifier. The ash bed in the "Bernice" gasifier was therefore very short at about 1.7 m from the base of the reactor and this is in line with the low ash content of the feed coal (i.e. 4.7% as received basis).

Although the terms combustion, oxidation and fire bed can mean the same thing, they are used differently in the context of this study to be able to clearly

show the overlaps of the reaction zones in the gasifiers. For example, the gasification and oxidation sub-zone in Figure 4.1 shows the position where the gasification zone overlaps with the combustion zone. The fire bed position shows the height where oxygen is mainly consumed by the carbon in the gasifier.

According to the previous gasifier Dig-Out studies done by Glover (1988 and 1991) at Sasol, the position of the fire bed was observed at 70% carbon conversion. If this observation is applied to the DGC case studies, it can be seen in Figure 4.1 that the fire bed in the "Bernice" gasifier was between samples No. 5 and 6 which, according to Figure 3.3, are at about 2 m from the base of the reactor. The fact that the fire bed is in the oxidation zone may serve to support Glover's observation.

Although the carbon conversion occurred within a height of only about 3 m (i.e. a third of the gasifier bed height), the fixed carbon conversion (see Figure 4.4) in "Bernice" was >98%. The residual fixed carbon conversion profile in Figure 4.4 shows a very rapid conversion of carbon which is in line with the high reactivity of lignite chars (Slaghuis, 1993).

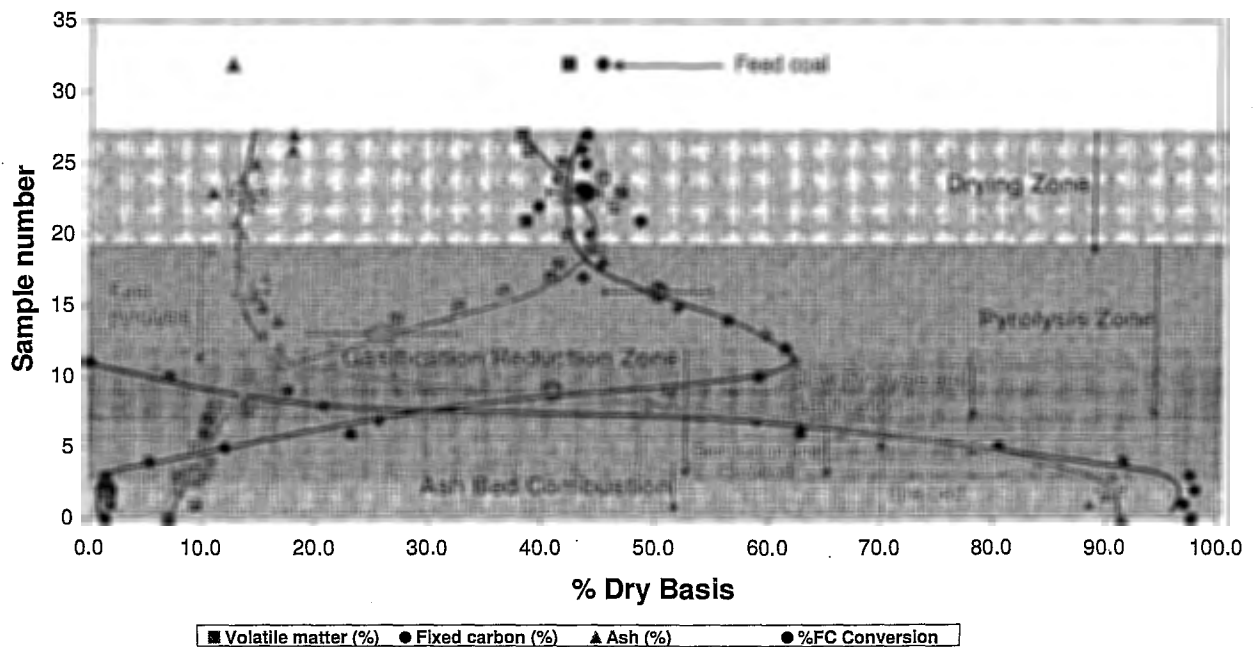


Figure 4.1. Profile of the proximate analysis (dry basis) in the "Bernice" gasifier.

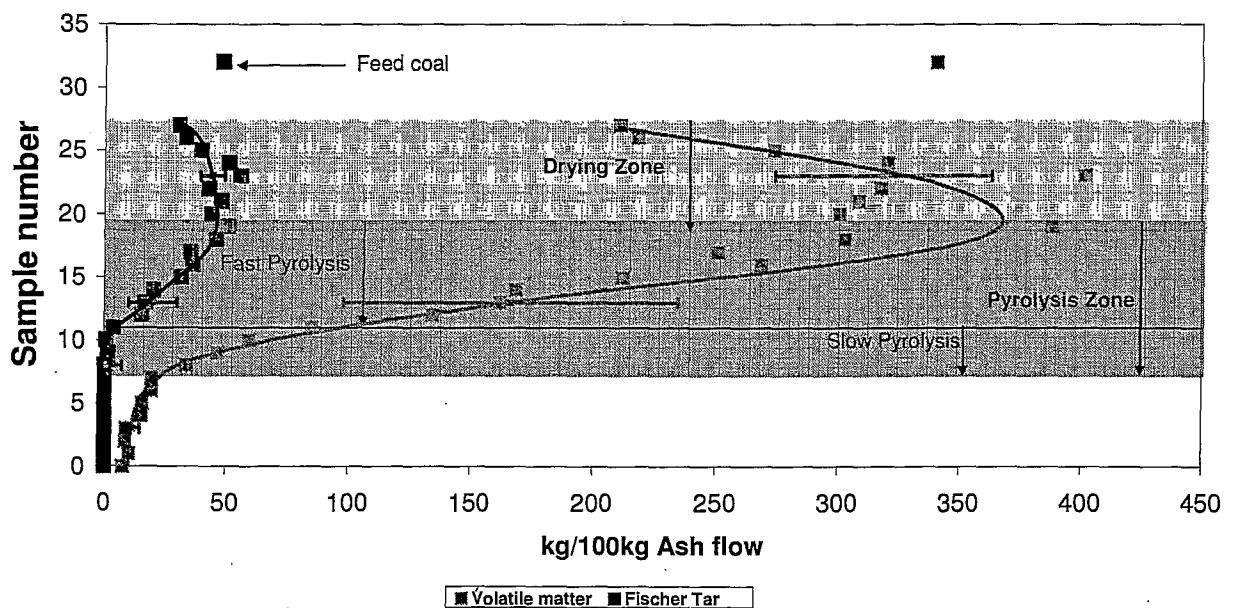


Figure 4.2. Residual volatile matter and Fischer tar profiles in the "Bernice" gasifier, normalised per 100kg ash flow.

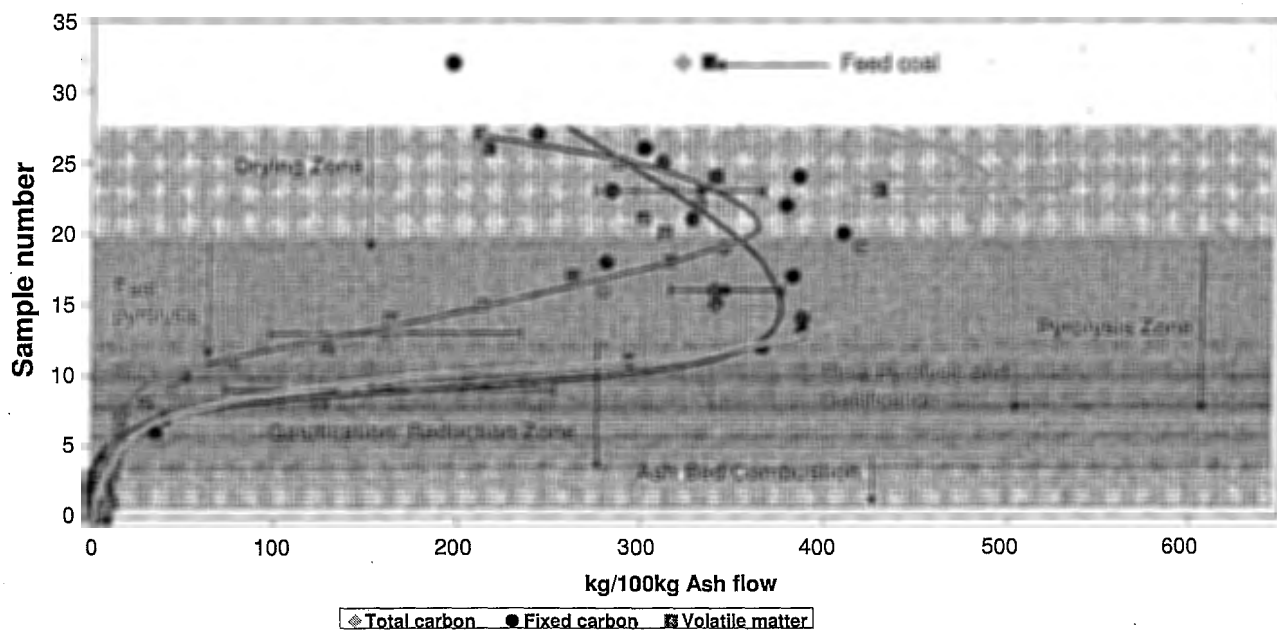


Figure 4.3. Residual fixed carbon, total carbon and volatile matter (VM) profiles in the "Bernice" gasifier, normalised per 100kg ash flow.

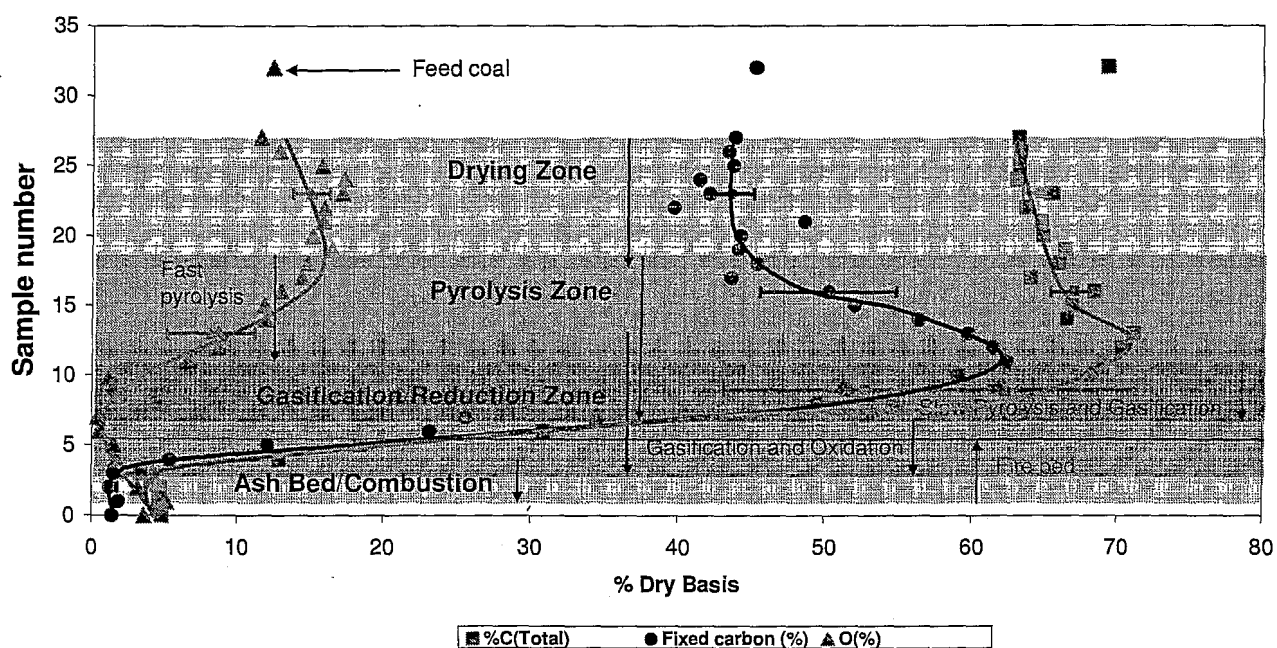


Figure 4.4. Residual carbon and oxygen profiles in the "Bernice" gasifier.

#### 4.1.2. Reaction Zones in the “Albert” Gasifier

The proximate analysis, volatile matter and Fisher tar as well as the carbon and oxygen profiles in the “Albert” gasifier are depicted in Figures 4.5 to 4.7. Using the same criteria as for the “Bernice” gasifier, the reaction zones in the “Albert” gasifier were identified. According to the DGC personnel, there was dusty tar recycling into the “Albert” gasifier prior to decommissioning (Baker, 2007b). The proximate analysis profile however proves the opposite with the ash, volatile matter and fixed carbon profiles in the drying zone being fairly stable as it would be expected when there is no tar recycling. In fact, dusty tar in the DGC operation is only recycled when the gasifier is stable (Baker, 2007a). With the “Albert” gasifier regarded as “sick”, it is likely that tar recycling was stopped prior to decommissioning.

The pyrolysis zone in the “Albert” gasifier ended at sample No. 9 (i.e. 3 m from the bottom of the gasifier) as compared to Sample No. 7 (i.e. 2.5 m from the bottom of the gasifier) in the “Bernice” gasifier. The gasification zone in the “Albert” gasifier began at sample No. 16 (i.e. 5 m from the bottom of the gasifier) which is higher when compared to sample No. 13 (4 m from the bottom of the gasifier) in the “Bernice” gasifier.

The ash bed and combustion zone began at sample No. 5 (i.e. 2 m from the bottom of the gasifier) which is slightly higher compared to “Bernice”. The position of the fire bed is also higher at sample No. 7, which was the end of pyrolysis zone in the “Bernice” gasifier. The fixed carbon conversion in the “Albert” gasifier was >99% and this may be attributed to the residence time of carbon in the hotter zones (i.e. taller ash bed and combustion zone in the “Albert” gasifier as compared to the “Bernice” gasifier).

A probable hot spot (i.e. a localised high temperature spot in the gasifier) which may be an indication of instability in the ash bed and combustion zone was observed in sample No. 5 (see Figure 4.5). As with the “Bernice” gasifier, the volatile matter in the ash from the “Albert” gasifier remained at about 10%



(dry basis). Although it is suspected to be emanating from the mineral matter (e.g. decomposition of carbonates), a mineralogical analysis will confirm its nature in this ash.

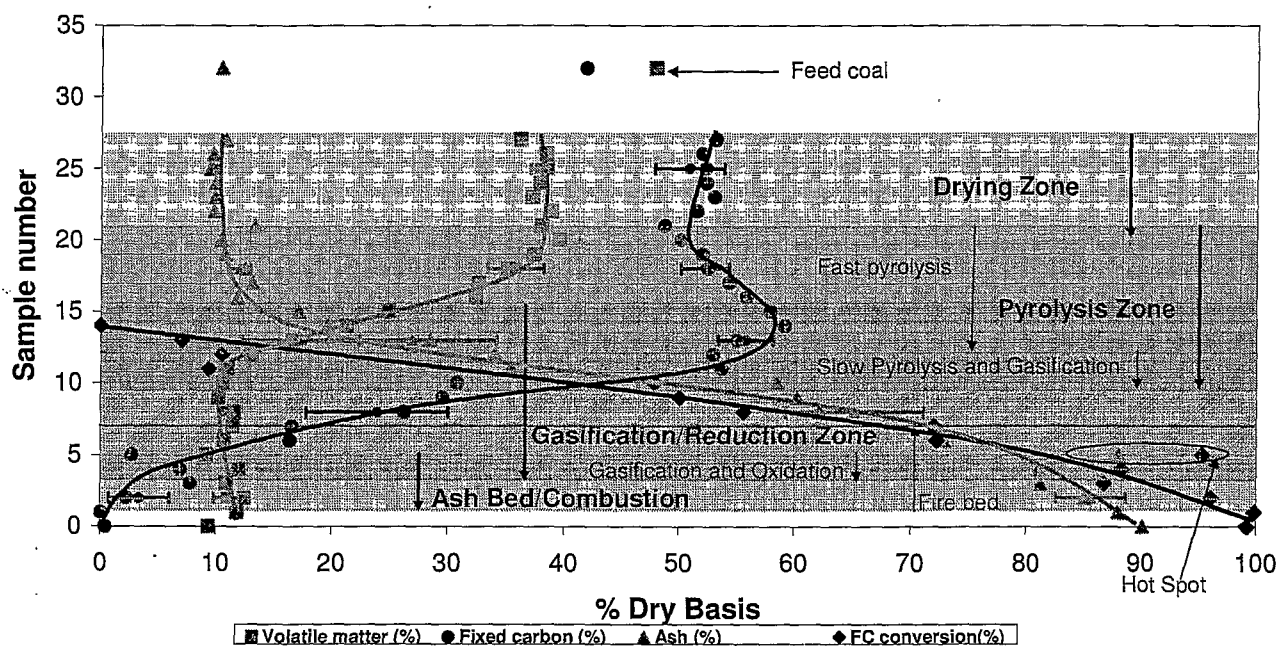


Figure 4.5. Profile of the proximate analysis (dry basis) in the "Albert" gasifier.

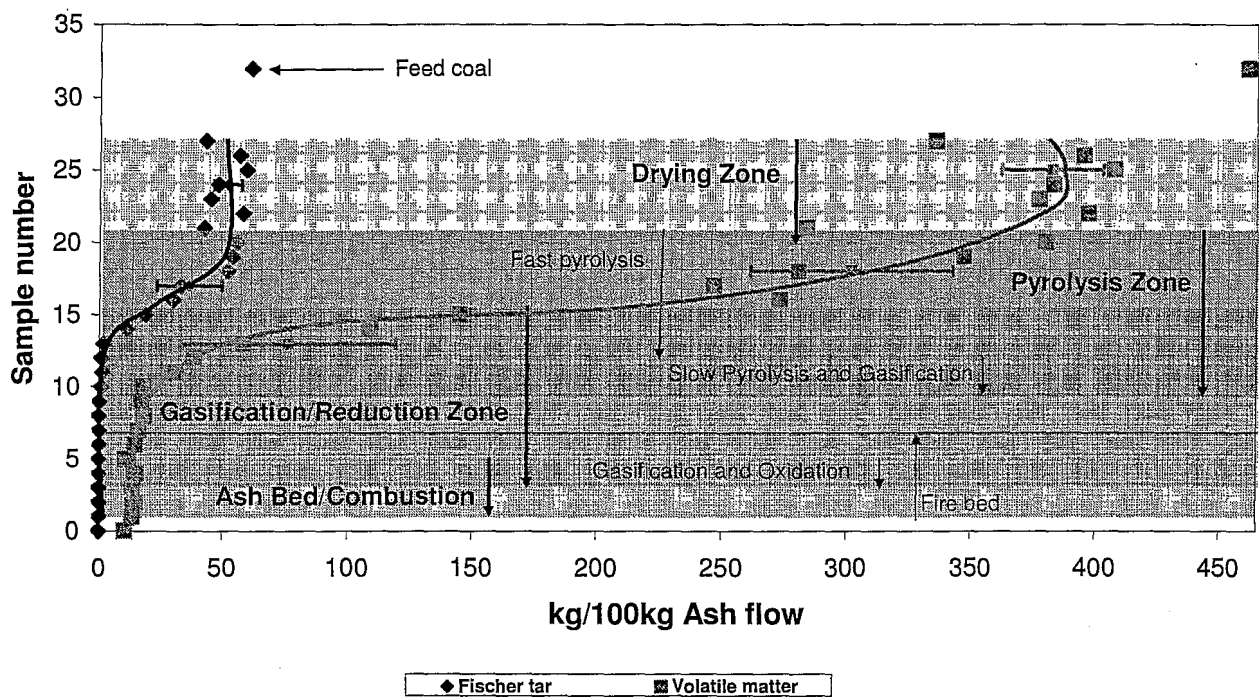


Figure 4.6. Residual volatile matter and Fischer tar profiles in the "Albert" gasifier, normalised per 100kg ash flow.

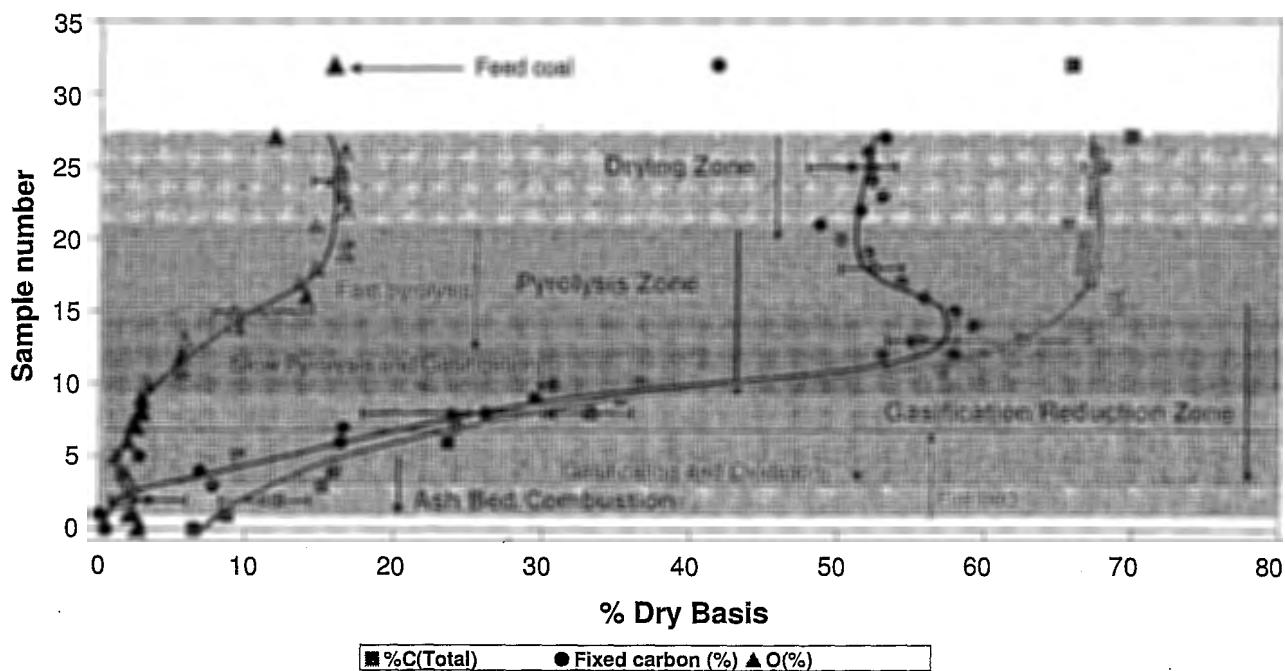


Figure 4.7. Residual carbon and oxygen profiles in the "Albert" gasifier.

#### **4.1.3. Comparison of Reaction Zones in “Albert” and “Bernice” Gasifiers with Secunda GG41 Gasifier**

In Figure 4.8 the reaction zones in “Bernice”, “Albert” and Secunda GG41 gasifiers are compared. Due to the high moisture content in the lignite, the pyrolysis zone in both “Albert” and “Bernice” gasifiers occurred lower/deeper in the bed as compared to the Secunda GG41 gasifier which gasifies bituminous coal. All the other reaction zones in the GG41 gasifier are also higher in the bed compared to “Albert” and “Bernice” gasifiers and this can explain the higher gas outlet temperature in the GG41 gasifier (i.e. 550 °C as compared to 222 °C in “Albert” and 232 °C in “Bernice”).

The taller gasification zone in the GG41 gasifier may be related to a relatively low reactivity of the Secunda bituminous coal when compared to the ND lignite tested. The overlaps between the various reaction zones are clearly illustrated in Figure 4.8 and proving the complexity of the gasifier fuel bed and the reactions and mechanisms occurring during the process.

At DGC, the recycled dusty tar as well as MEE (i.e. concentrate from the multiple effect evaporators, which process cooling tower blow down) are injected on top of the gasifier bed as per the design of the gasifiers. Looking at the identified reaction zones, it is clear that the tar is released again in the pyrolysis zone. Hence, if the aim is to convert the tar into syngas, then the recycling may not be optimal. However, if the aim of tar recycling is to crack the heavy molecules to produce oil, it may be serving the purpose, although the optimisation may be questionable. A deeper injection of tar into the hotter zone of the gasifier, preferably the fire bed, is therefore recommended. This may however be associated with some engineering challenges.

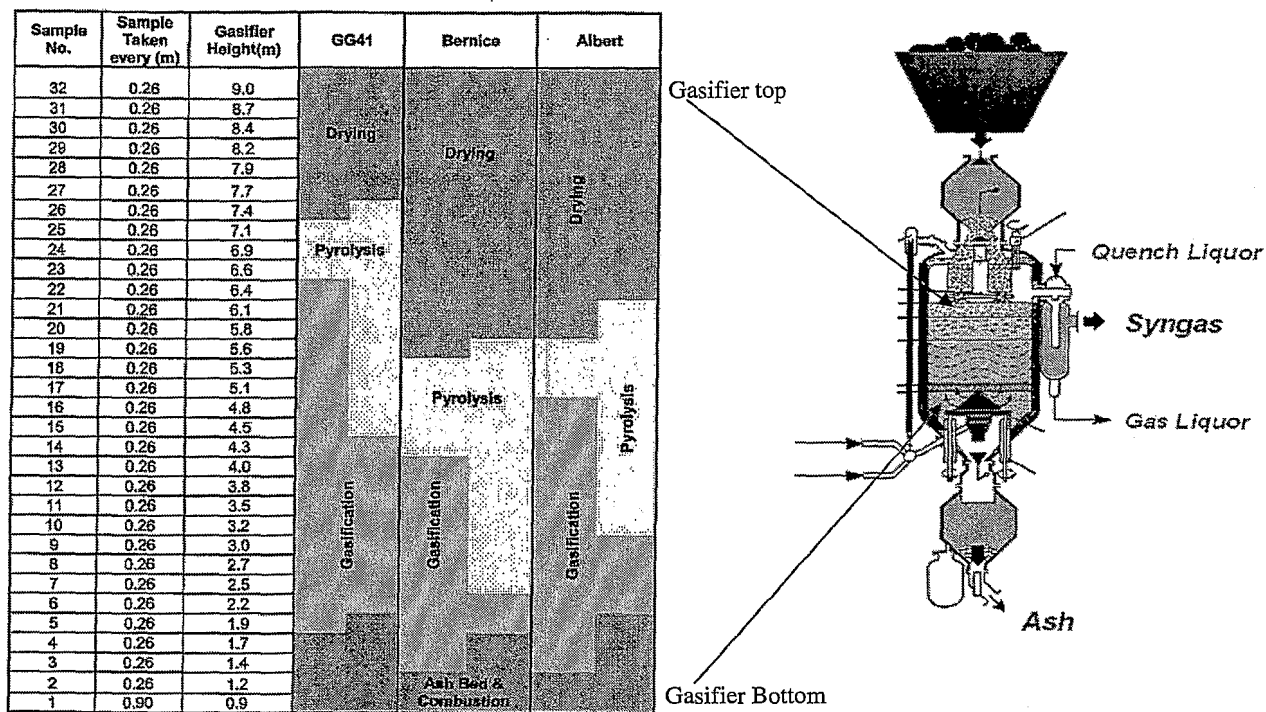


Figure 4.8. Comparison of reaction zones in the Secunda GG41 with DGC “Albert” and “Bernice” gasifiers. Step changes in the figure depict overlaps.

#### 4.1.4. H, N, and S Profiles

The profiles for residual hydrogen, nitrogen and sulphur in the “Albert”, and “Bernice” gasifiers are illustrated in Figures 4.9 and 4.10. The trends for these elements in the two gasifiers are similar. No reactions involving these elements are expected in the drying zone. However, in the drying zone, and in line with the volatile matter profile in the “Bernice” gasifier, a slight increase in hydrogen, nitrogen and sulphur content is observed. This can possibly be attributed to the dusty tar and MEE that were injected on top of the gasifier bed. This slight increase is however less significant in the “Albert” gasifier.

As expected, the three elements are volatilised mainly in the pyrolysis and gasification/ reduction zones as shown by the decreasing trend in Figures 4.9 and 4.10. Hydrogen is expected to be released in these zones in the form of  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$  (g),  $\text{H}_2$ , oil, tar and other hydrocarbon gases (Tromp, 1987; Bunt, 2006).

Nitrogen and sulphur are expected to be released in the pyrolysis and gasification/reduction zones mainly in the form of  $\text{H}_2\text{S}$ ,  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{COS}$  (Higman and van der Burgt, 2003). The trace amounts of nitrogen and sulphur remaining in the oxidation zone are expected to be released in the form of  $\text{NO}_x$  and  $\text{SO}_x$  (Bunt and Waanders, 2008c). These species are however not expected to survive in a hydrogen rich or reducing environment higher up in the gasifier (i.e. in the pyrolysis and reduction zones). The source of nitrogen in the oxidation zone of both "Bernice" and "Albert" gasifiers may be the absorption in the char of the nitrogen gas that was used to cool the gasifier prior to sampling and to preserve the samples during shipment prior to analysis.

A slight increase and/or stabilisation in the residual sulphur profile were observed in the oxidation zone of both "Bernice" and "Albert" gasifiers. This can be attributed to the ash chemistry of the ND lignite which is known to have high calcium content (Schobert, 1995). The calcium may be capturing the sulphur to form  $\text{CaSO}_4$  which should report in the ash. There may also be some more free calcium (either in the form of  $\text{CaO}$  or  $\text{CaCO}_3$ ) which may be available to capture excess sulphur. This may therefore be an opportunity for  $\text{H}_2\text{S}$  recycling but should be confirmed by further test work and a mineralogical study.

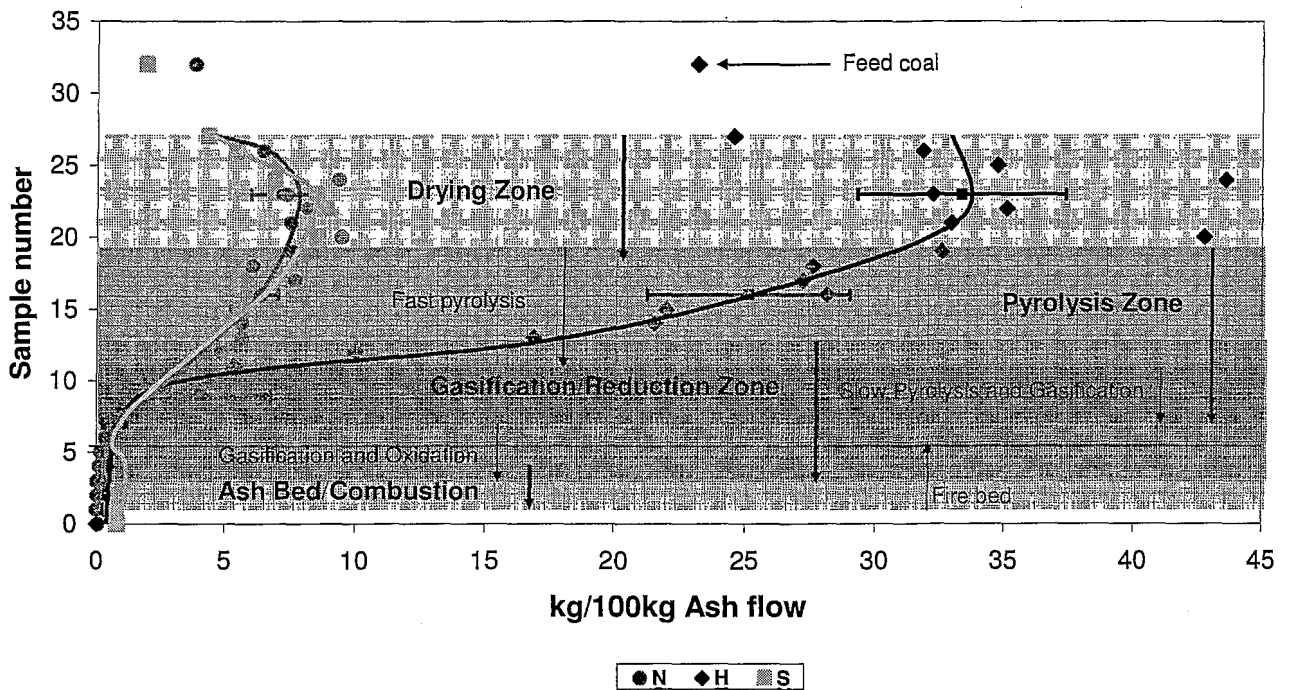


Figure 4.9. Residual hydrogen, sulphur and nitrogen profiles in the "Bernice" gasifier.

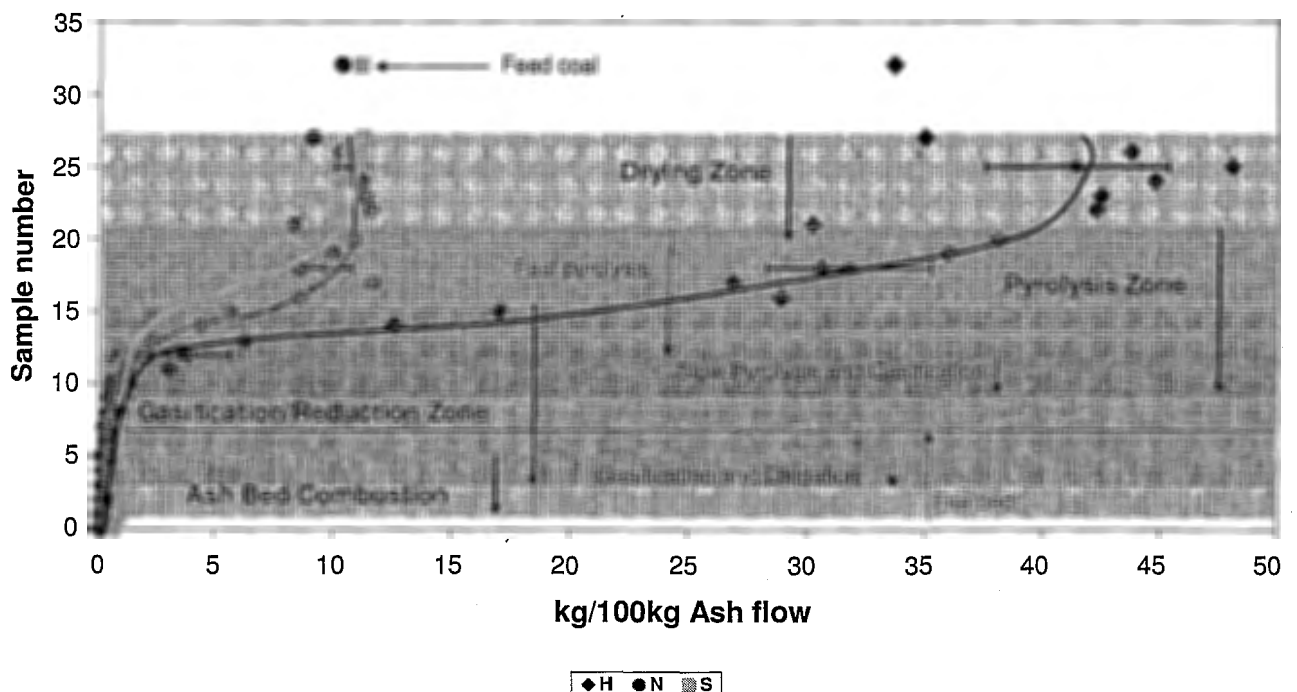


Figure 4.10. Residual hydrogen, sulphur and nitrogen profiles in the "Albert" gasifier.

#### 4.1.5. Reactivity

The char reactivity profiles in the “Bernice” and “Albert” gasifiers are illustrated in Figures 4.11 and 4.12. The reactivity of the feed coal to both “Albert” and “Bernice” gasifiers was  $38 \text{ h}^{-1}$ . As expected, this reactivity is significantly higher when compared to the Secunda coal with reactivity ranging from  $2 - 5 \text{ h}^{-1}$  (Van Dyk, 2001).

A very interesting and intriguing trend is observed in the residual char reactivity profile for the “Bernice” gasifier, where the residual reactivity of the char suddenly increases in the gasification or hotter zone of the gasifier- see Figure 4.11. Although not that clear in the residual char reactivity profile of the “Albert” gasifier, an increase in char reactivity in the gasification zone is also indicated – see Figure 4.12. Amongst the reasons for the not so clear trend in the gasification zone of the “Albert” gasifier is the fact that measurements were done only up to sample 8 as samples 6 and 7 did not have sufficient fixed carbon required for the reactivity test in a TGA. In the “Bernice” gasifier, there was sufficient fixed carbon to allow measurements in samples 6 and 7.

The very high reactivity of the feed coal as well as this sudden increase in reactivity of the chars obtained in the gasification zone can be part of the reason for the very high and rapid carbon conversion within only a third of “Albert” and “Bernice” gasifiers volume as shown in Figure 4.8. This is a significant finding.

The reasons for this intriguing phenomenon are not clear at this stage and hence, this calls for a more detailed investigation which is outside the scope of this study. However, the main difference between the chars formed in the gasification zone and the chars obtained higher up in the drying and pyrolysis zones of the gasifier is the fact that the latter had seen a higher temperature than the former and this may have changed the structure of the chars,

particularly the surface area as well as porosity which can affect the intrinsic reactivity of char particles (Smith *et al.*, 1993).

The chars in the gasification zone had higher ash content due to carbon conversion. The increased reactivity of the chars in this zone may also be due to the fact that the mineral matter, particularly the organically bound alkali and alkaline earth elements (e.g. Na, K, Mg and Ca) as well as Fe, which are known to catalyze gasification reactions, were concentrated in the chars and thus possibly catalyzing the reaction of the chars with CO<sub>2</sub> (Smith *et al.*, 1993).

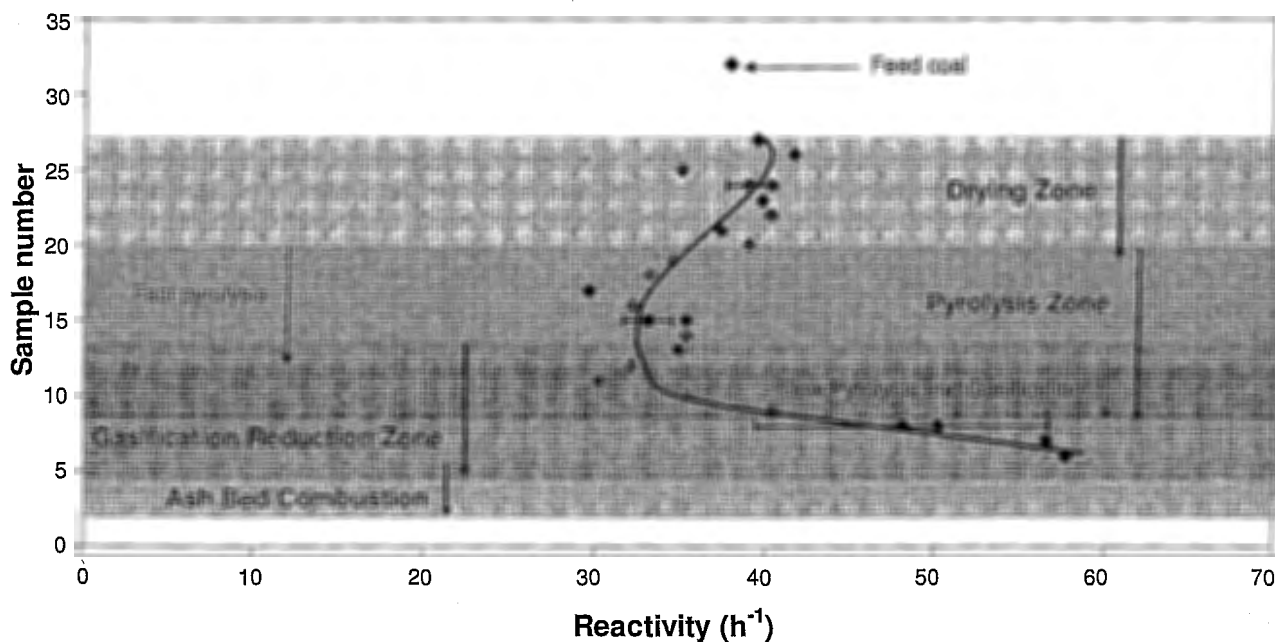


Figure 4.11. Profile of the residual char CO<sub>2</sub> Reactivity (h<sup>-1</sup>) in the "Bernice" gasifier measured at 1000 °C and 50% fixed carbon burn-off.



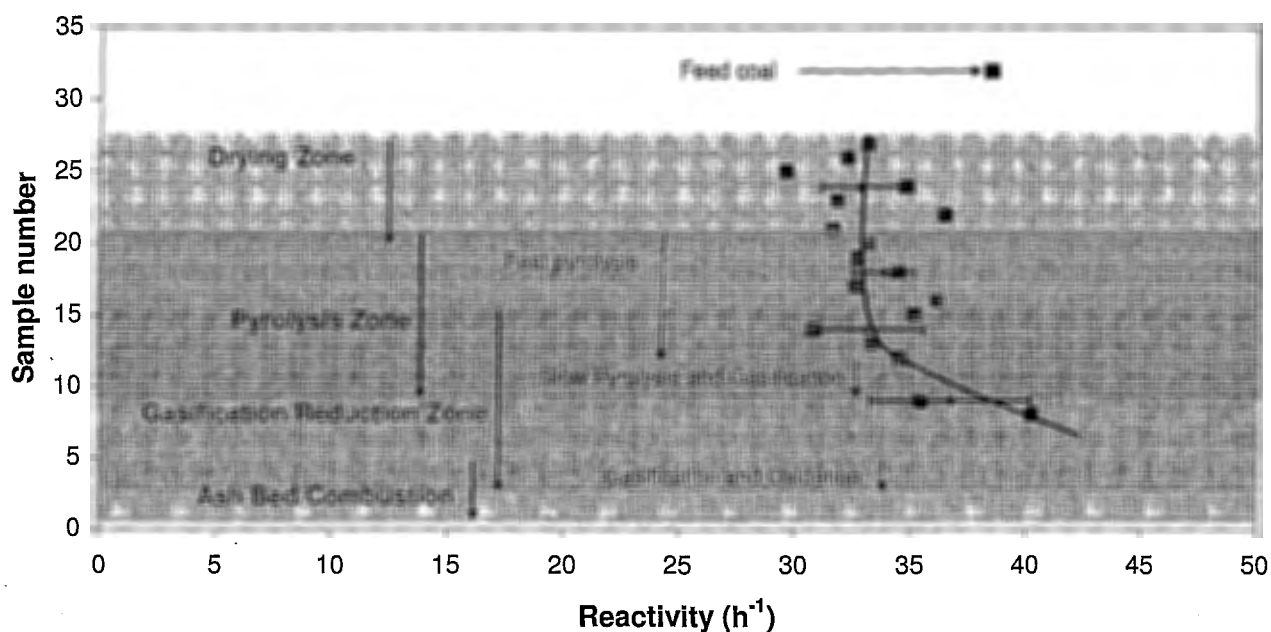


Figure 4.12. Profile of the residual char CO<sub>2</sub> Reactivity (h<sup>-1</sup>) in the "Albert" gasifier measured at 1000 °C and 50% fixed carbon burn-off.

## 4.2. Physical Properties

The reaction zones as well as the chemical properties transformation in the "Bernice" and "Albert" gasifiers were discussed in section 4.1. In this section, the physical properties transformations in the gasifiers are discussed. The properties include particle size distribution, density and AFT.

### 4.2.1. Particle Size Distribution (PSD)

Particle size distribution plays a crucial role during fixed bed gasification, particularly in terms of bed permeability. In Secunda and DGC, the feed coal to the gasifiers is commonly screened at 6 mm to remove the fine material (-6 mm) which is used for power and/or steam production. As mentioned in chapter 2, excess fine coal in the gasifier can have detrimental effects on the stability of gasifier operation. It is mainly for this reason why the feed coal to the S-L FBDB gasifiers is screened to remove the -6 mm material. However,

the PSD of the coal in the gasifier can, depending on the coal composition, be affected by thermal and mechanical fragmentation, caking and ash agglomeration.

Figures 4.13 and 4.14 depict the PSD profiles in the “Bernice”, and “Albert” gasifiers. The feed coal to the “Bernice” and “Albert” gasifiers contained about 3% of the -6.3 mm particles as per the common practice at DGC. However, the coal and char broke into about 90% of the -6.3 mm particles during drying and pyrolysis. This can be attributed to thermal fragmentation which seemed to begin in the coal lock as can be seen with a significant increase in the -6.3 mm particles from the feed sample (i.e. sample 32 with <5% of the -6.3 mm particles) to sample 27 (with about 35% of the -6 mm particles) which represents the top of the gasifier bed (i.e. below the Bosman skirt). This high thermal fragmentation is mainly due to the desiccation cracks that occur during the removal of the very high inherent moisture and volatile organic compounds (Schobert, 1995).

The 90% of -6.3 mm particles in the pyrolysis zone is in line with the relative thermal friability data for Beulah lignite (i.e. 89%) as reported in the literature (Schobert, 1995). The amount of the -6.3 mm particles shown in Figures 4.13 and 4.14 decreased in the gasification and combustion zones as the amount of the coarser particles (+25mm and the -25+6.3 mm) increased due to ash agglomeration.

Due to the diffusion effects (Smith *et al.*, 1993), the PSD in both the “Bernice” and “Albert” gasifiers can also be part of the reason for the very rapid and high carbon conversion within only a third of the gasifier volume as depicted in Figures 4.1 and 4.5. In addition, the fact that only 27 samples instead of 32 were obtained from both the “Bernice” and “Albert” gasifiers may be attributed to the packing density of the gasifier bed during decommissioning and subsequently the PSD and/or thermal fragmentation.

The low oxygen load in the DGC case as compared to Secunda (see Table 3.1) can also be attributed to this severe thermal fragmentation of the ND

lignite. With this severe thermal fragmentation, the DGC gasifiers cannot operate at higher loads due to the risk of fines carryover and subsequent blockages downstream (van Dyk *et al*, 2001; Turna, 2008).

Caking propensity, thermal and mechanical fragmentation of the gasifier bed samples could only be determined on the feed coal due to particle size limitations that resulted from the severe thermal fragmentation of the coal in the gasifiers. The thermal fragmentation (determined using the method developed at Sasol) of the feed coals to the “Albert” and “Bernice” gasifiers were reported as 45% and 42% respectively. These figures are two times lower when compared to the fragmentation that occurred in the gasifiers (i.e. ~90%) as well as the figures reported in literature (i.e. 89% as reported by Schobert (1995)). The Sasol method used to determine thermal fragmentation of feed coal to the S-L FBDB gasifiers, although applicable to Secunda bituminous coal, should therefore be modified to suit lignite.

As expected, and in line with the literature, the feed coal to “Bernice” and “Albert” gasifiers did not show any sign of caking (Schobert, 1995; Benson, 2007). The mechanical fragmentation of the feed coal was determined as 33% and 37% for “Albert” and “Bernice” respectively and these figures are higher than the figures of 11% reported in literature (Schobert, 1995). This difference in mechanical fragmentation can be attributed to the difference in moisture content of the samples tested as there is, particularly for the Beulah zap lignite, a direct correlation between an increase in friability with a decrease in moisture content (Schobert, 1995).

Based on the information in Figures 4.13 and 4.14, it is noted that both the “Albert” and “Bernice” gasifiers are basically gasifying “fine” coal. This is also a very significant finding. The fact that the reaction zones in these gasifiers have been successfully identified may therefore present an opportunity for extra fine coal injection in to the fire bed of the gasifiers. It is however acknowledged that this can be an engineering challenge but is nonetheless possibly worth investigating.

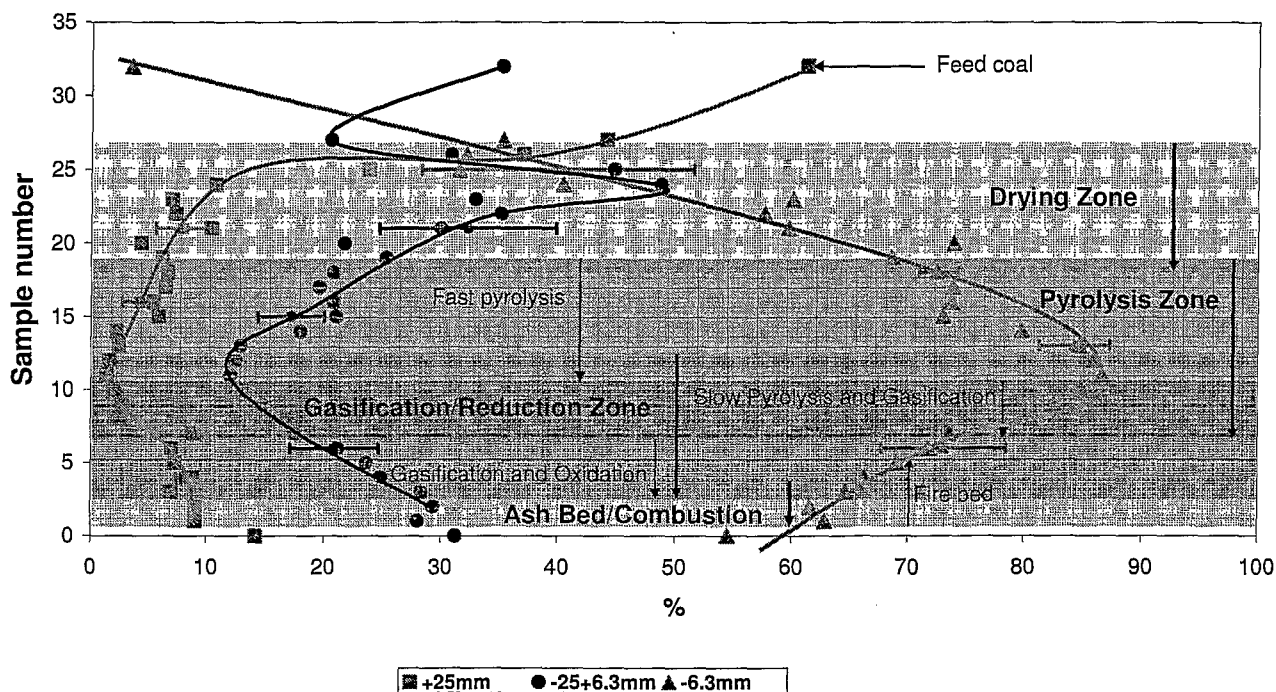


Figure 4.13. Particle size distribution profile in the "Bernice" gasifier.

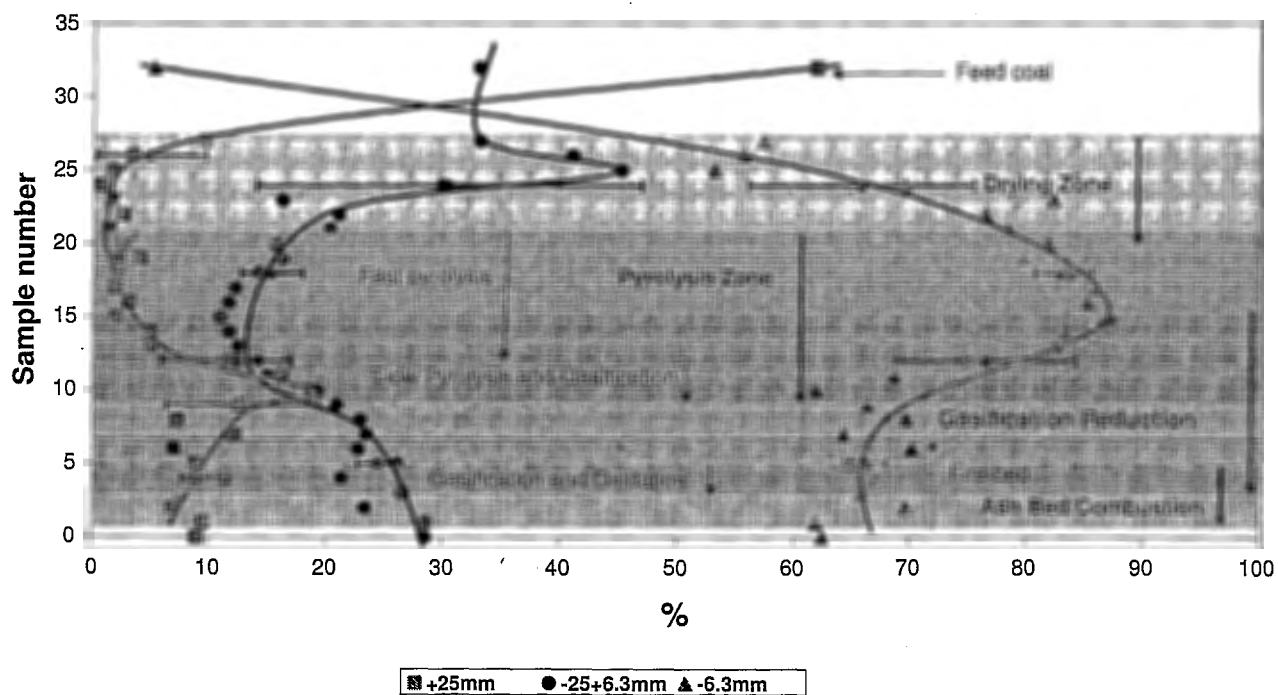


Figure 4.14. Particle size distribution profile in the "Albert" gasifier.

The mean Sauter diameter or the Ergun index (EI) which is basically the mean diameter of the particles (determined using equation 2.8) further demonstrates the severe thermal fragmentation of the feed occurring in the “Albert” and “Bernice” gasifiers. The profiles for the Ergun index (EI) in the “Bernice” and “Albert” gasifiers are shown in Figures 4.15 and 4.16. For “Albert” and “Bernice”, the profiles are similar, confirming fragmentation in the drying and pyrolysis zones and agglomeration in the hotter gasification and combustion zones.

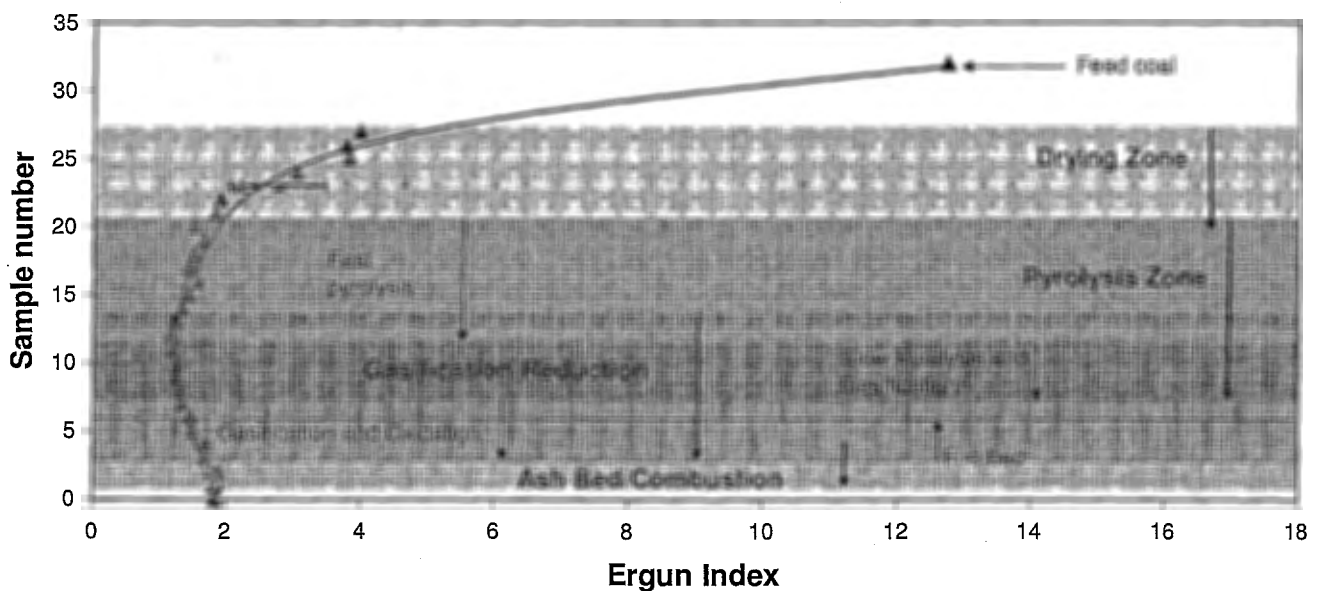


Figure 4.15. The Ergun index profile for the “Bernice” gasifier.

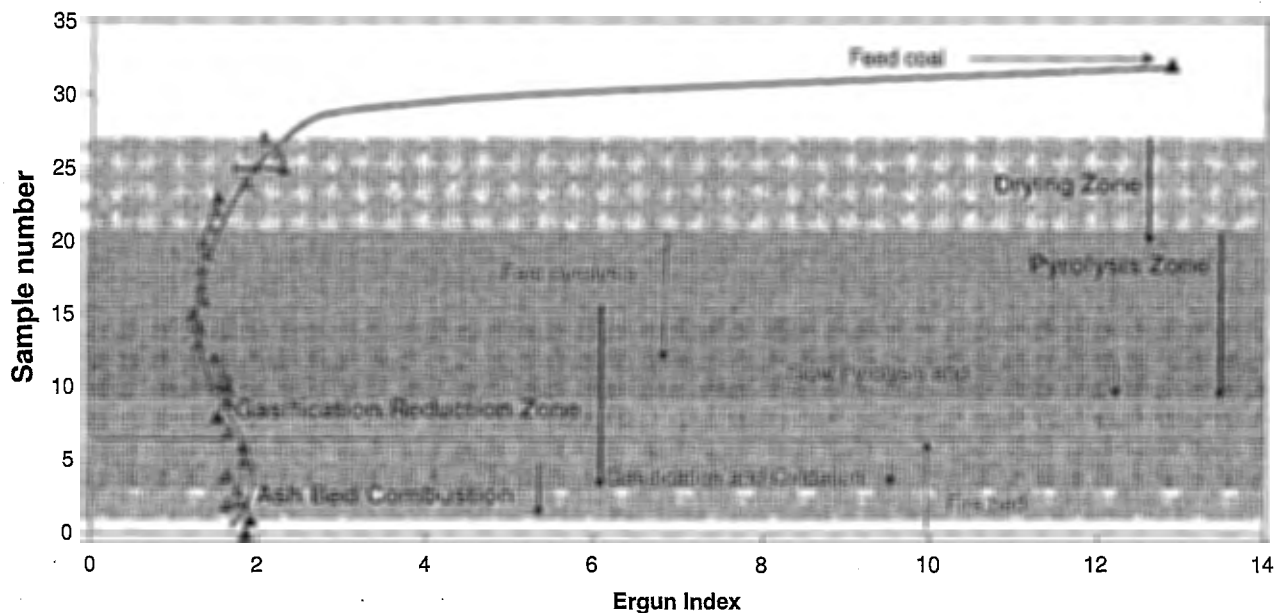


Figure 4.16. The Ergun index profile for the "Albert" gasifier.

#### 4.2.2. Density

Figures 4.17 and 4.18 illustrate the bulk density profiles in the "Bernice" and "Albert" gasifiers. The profiles for the particle density (calculated from the bulk density by multiplying with a factor of 0.6) are also illustrated in the same figures. Although the conversion is normally done for indication purposes, it is interesting to note that the calculated particle density of the feed coals is in line with the data obtained in literature (i.e. 1.23 and 1.18 g/cm<sup>3</sup> for the feed coal to "Bernice" and "Albert" respectively versus 1.22 g/cm<sup>3</sup> for the Beulah Zap coal as reported by Schobert (1995)).

At a constant particle size, the bulk density is expected to decrease in the drying and pyrolysis zones due to the expected mass loss associated with the processes. However, due to thermal fragmentation, as shown by the Ergun index profile in the same Figures 4.17 and 4.18, a slight increase in bulk

density is observed in the drying zone. In the fast pyrolysis zone where most of the organic volatiles are removed, the bulk density seems to stabilise in line with the slowing thermal fragmentation process, showing that the organic volatiles have little effect on the density of coal. As expected, in the gasification and combustion zones, the bulk density increased in line with carbon conversion and subsequent increase in ash content. This trend can be a sign of plug flow during sampling.

As with the Ergun index profiles in both the “Albert” and Bernice” gasifiers, the “noise” in the data obtained from “Albert” is observed in the bulk density profile, particularly in the ash bed – see Figures 4.17 and 4.18. For the bulk density, the standard deviation in the ash bed of the “Bernice” gasifier is 0.1 versus 1.8 in the “Albert” gasifier. This may confirm the ash homogenisation effect of the rubble finger which in the “Albert” gasifier was bent as per the information obtained from the DGC personnel (Baker, 2007c). The bent rubble finger may have been the cause of “instability” in the “Albert” gasifier.

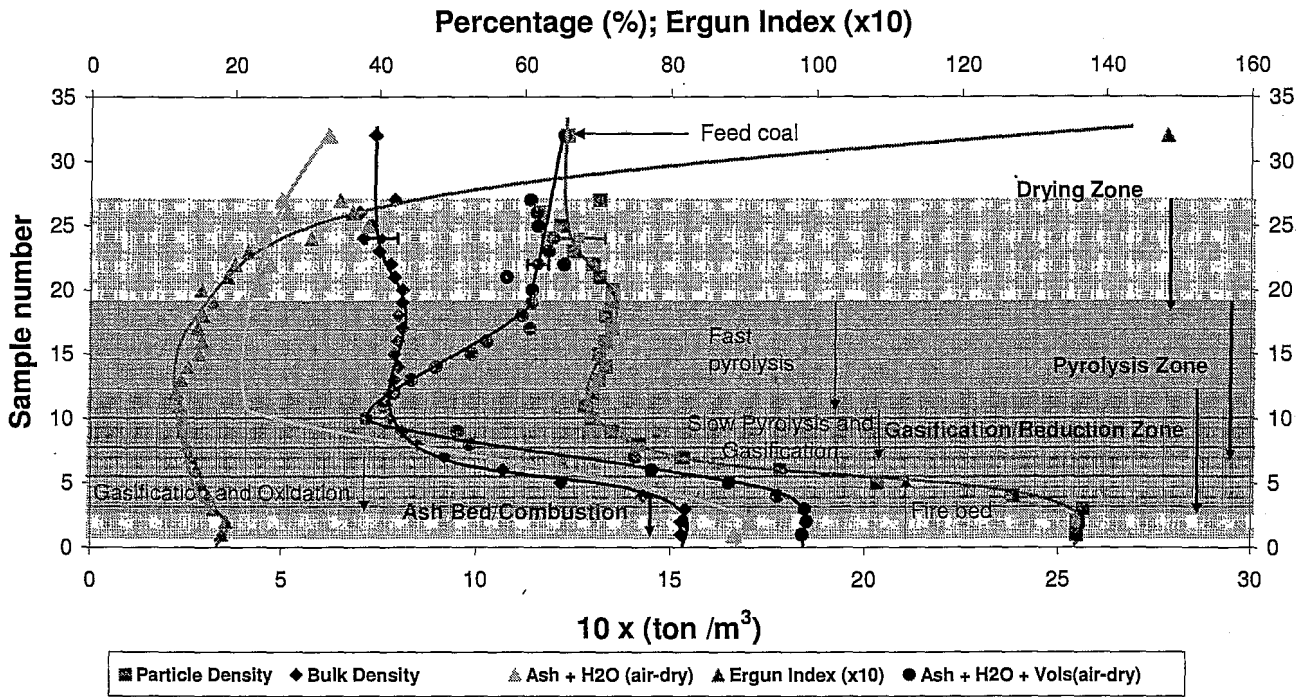


Figure 4.17. Density profile in the “Bernice” gasifier and relation with ash, moisture, particle size and volatile matter.

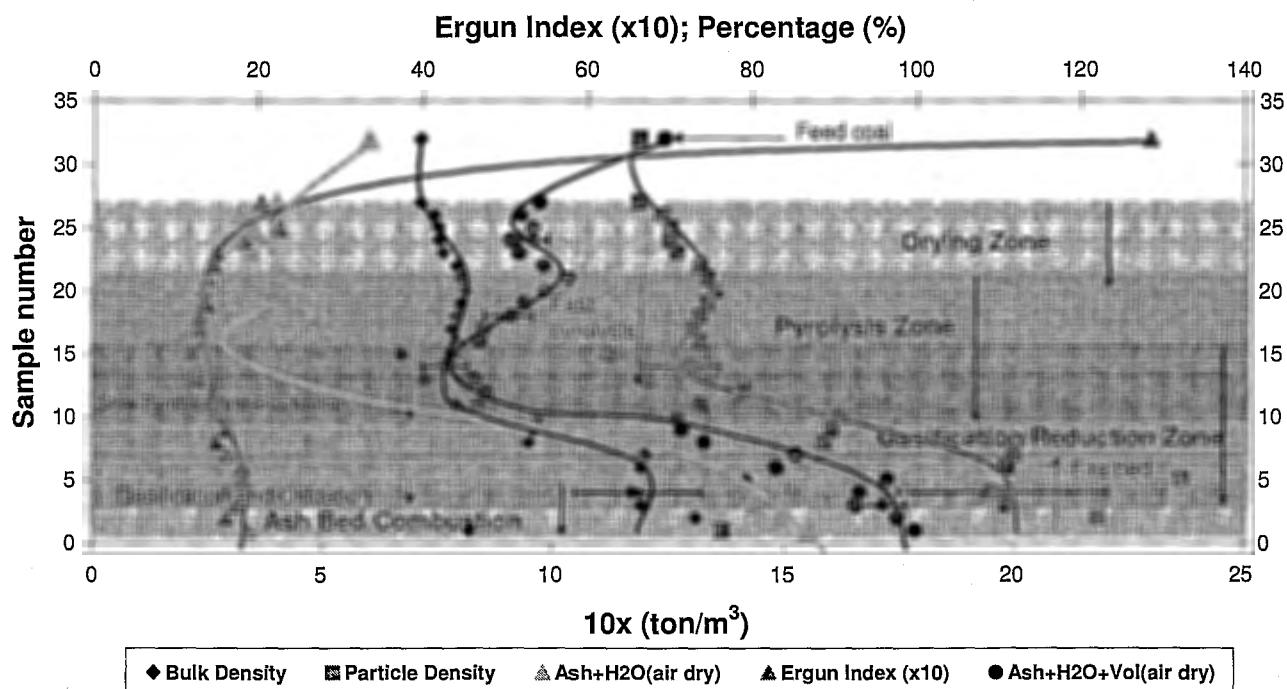


Figure 4.18. Density profile in the “Albert” gasifier and relation with ash, moisture, particle size and volatile matter.

#### 4.2.3. Ash Fusion Temperatures (AFT)

Although designed to operate with a dry ash, the S-L FBDB gasifier requires a certain degree of ash agglomeration/sintering to assist with the agent (i.e. steam and  $O_2$ ) distribution. The sintering should however be minimal to avoid ash removal problems. The ash fusion temperature (AFT) test is a generally accepted method used for assessing the ash melting properties. As mentioned in Chapter 2, the S-L FBDB gasifiers are commonly designed to operate between the initial deformation temperature and the flow temperature of the ash.

The profiles of the residual AFT (measured in both reducing and oxidising atmospheres) for both the “Bernice” and “Albert” gasifiers are illustrated in Figures 4.19 to 4.22. The trends of the profiles throughout the gasifiers for the AFT measured in an oxidizing environment are characterised by a decrease,



from top to bottom, in the initial deformation (DT) and flow temperatures (FT) of the ash as shown in Figures 4.19 and 4.20. The most noticeable is the AFT of the feed coal which is significantly higher when compared to the samples taken from the gasification and combustion zones of the gasifiers.

The trends in the AFT profiles for the “Bernice” and “Albert” gasifiers measured in a reducing atmosphere are illustrated in Figures 4.21 and 4.22. Due to different mineral matter transformations during heating in oxidising and reducing environments, the AFT profiles measured in a reducing atmosphere do not follow the same trend as with the profiles measured in an oxidising environment. This is not unexpected given the fact that mineral matter transformation in both atmospheres is different (Alpern *et al.*, 1984). However, common to the profiles, particularly in the “Bernice” gasifier, is the decreasing AFT’s in the gasification and combustion zones of the gasifiers.

As mentioned in Chapter 2, the operation window for the S-L FBDB gasifiers is between the initial deformation and flow temperatures of the ASTM ash which is prepared under carefully controlled conditions. For the ND lignite tested, this may be misleading as the AFT’s of the ash in the ash bed and combustion zones of both “Albert” and “Bernice” gasifiers are lower when compared to the feed coal. This may be due to the effect of organically bound cations, Ca, Na and Mg in particular, which are known to complicate the mineralogy of lignites (Schobert, 1995; Ward, 2002). A detailed mineralogical study is required to further understand and model the behaviour of the ash formed from the coals tested.

The opposite is true in the case of Secunda GG41 as shown in Figure 4.23 (Bunt, 2006). In this case the operation window between the initial deformation and flow temperatures holds true, and this can be attributed to the different mineralogy of the Secunda bituminous coal when compared to the ND lignite.

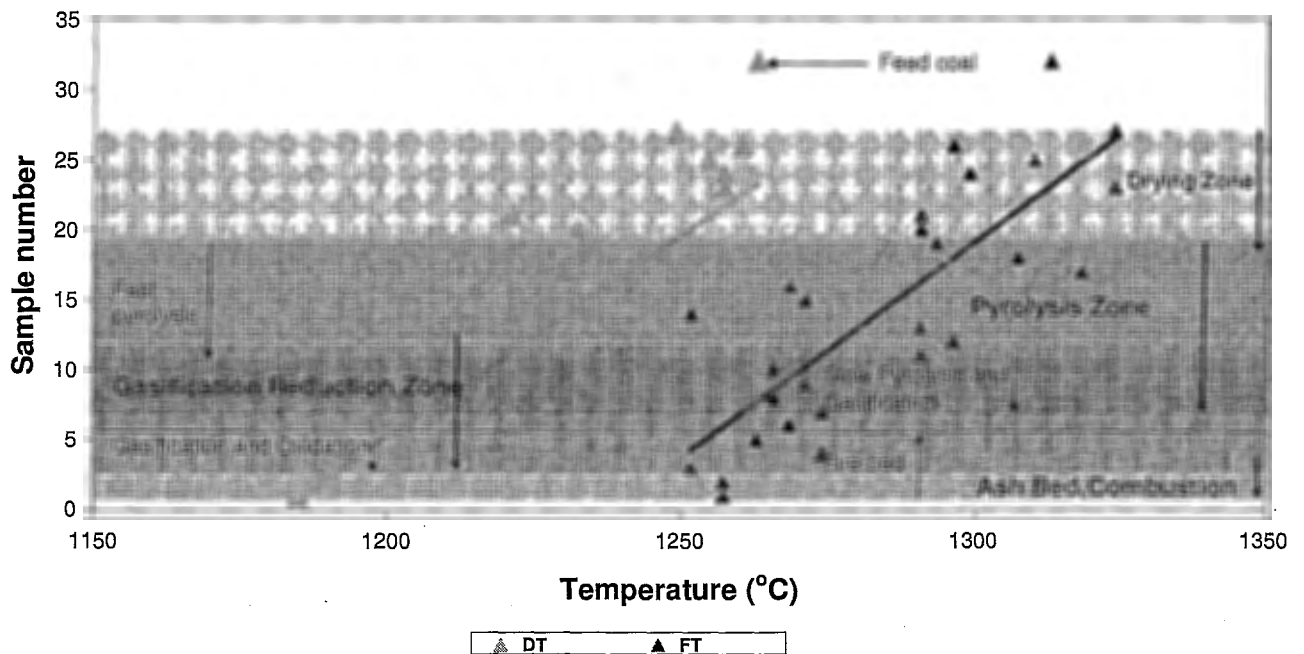


Figure 4.19. Ash fusion temperature (AFT) profile in the "Bernice" gasifier, measured in an oxidising environment.

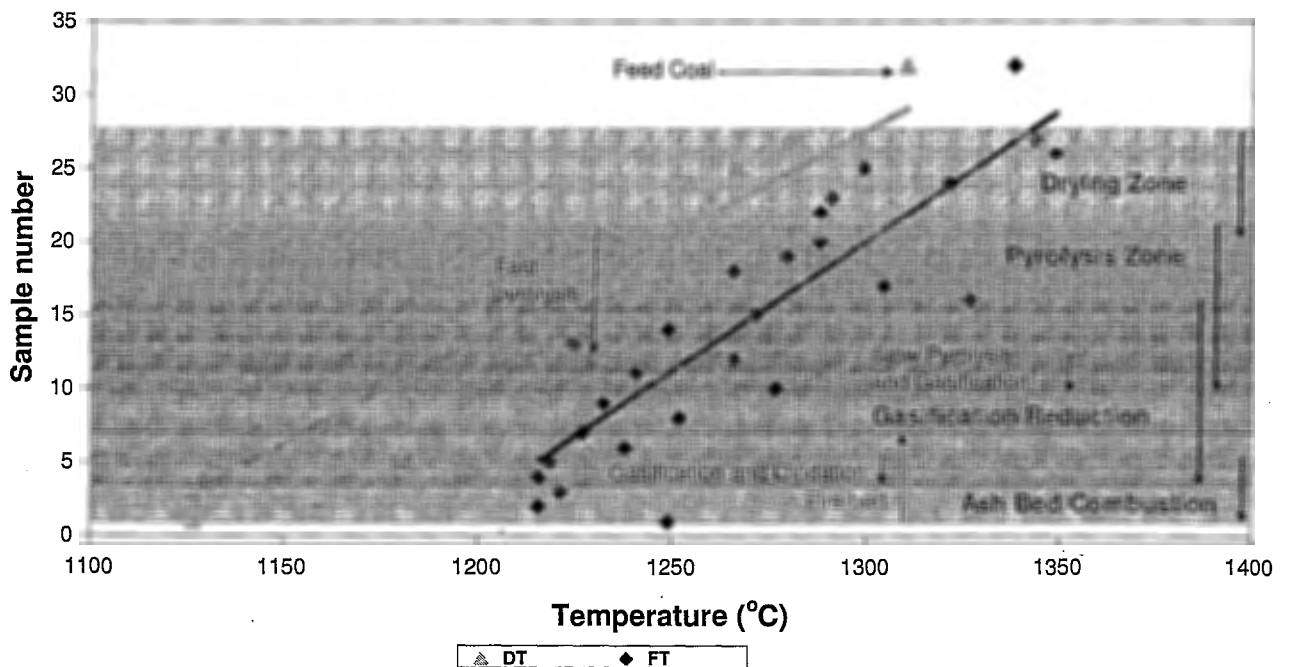


Figure 4.20. Ash fusion temperature (AFT) profile in the "Albert" gasifier, measured in an oxidising environment.

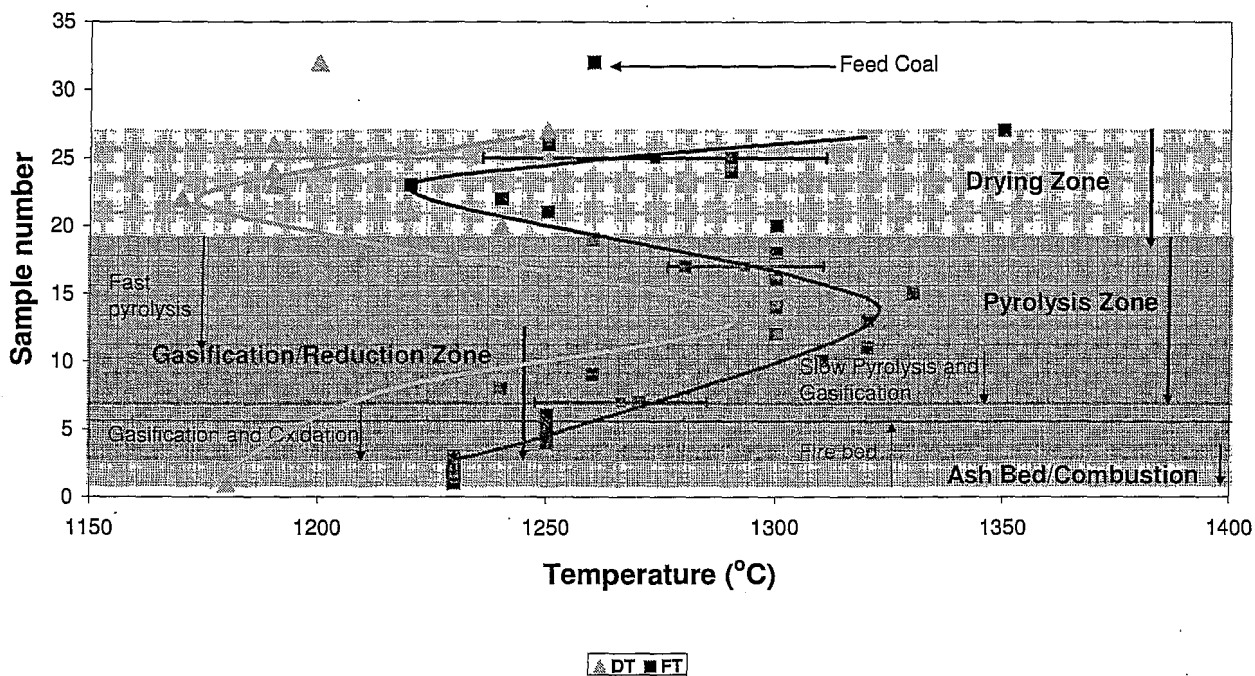


Figure 4.21. Ash fusion temperature (AFT) profile in the "Bernice" gasifier, measured in a reducing environment.

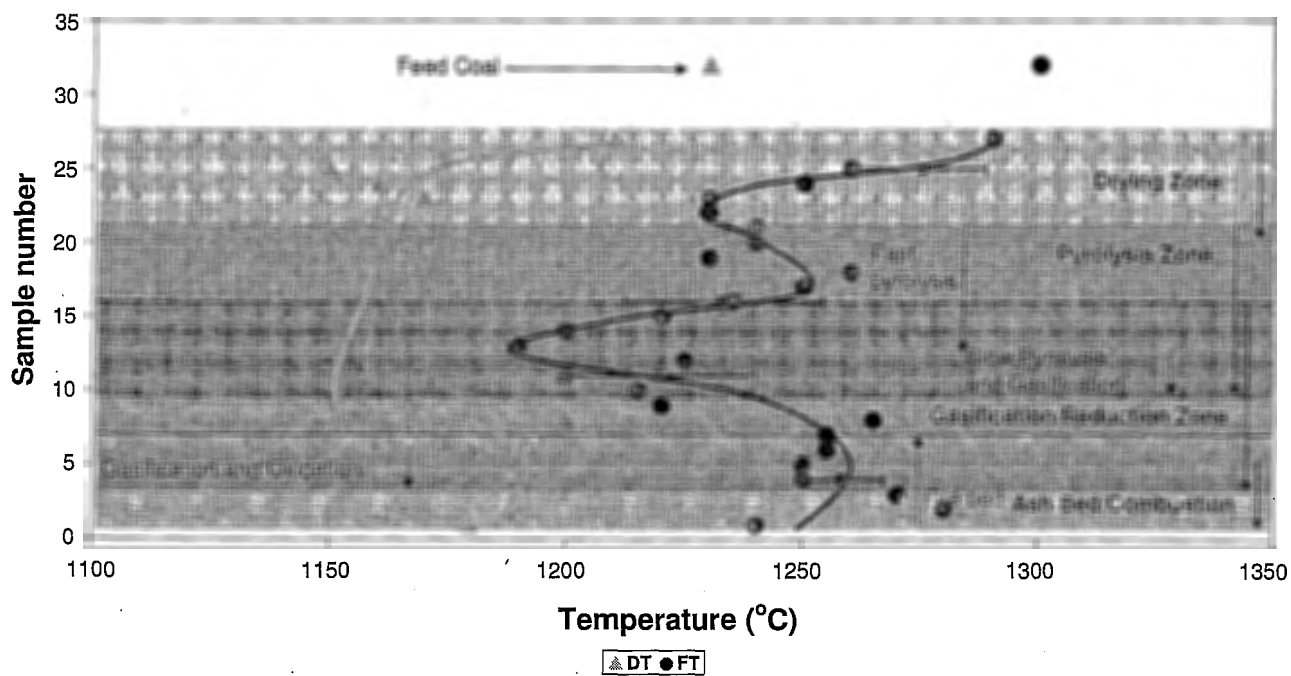


Figure 4.22. Ash fusion temperature (AFT) profile in the "Albert" gasifier, measured in a reducing environment.

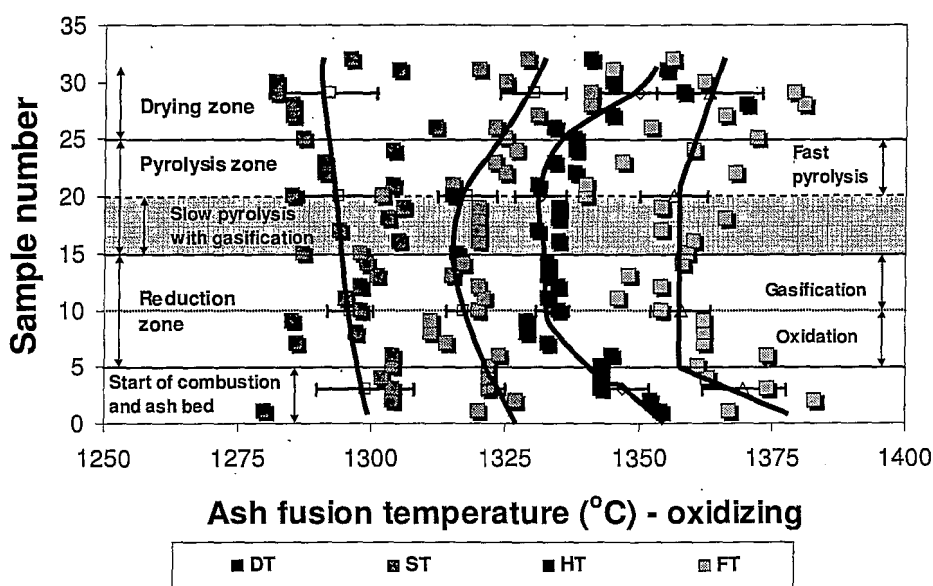


Figure 4.23. Ash fusion temperature (AFT) profile in the Secunda GG41 gasifier, measured in an oxidising environment (Bunt, 2006).

### 4.3 Petrographic Properties

The effect and application of coal petrography in fixed bed coal gasification was discussed in Chapter 2. In this section, the maceral composition and rank of the feed coals to the “Bernice” and “Albert” gasifiers are discussed. The carbon particle type transformations as well as the temperature profile in the gasifiers are also discussed.

#### 4.3.1. Maceral Composition and Rank

The petrographic properties of the feed coals to both the “Bernice” and “Albert” gasifiers are shown in Table 4.1. With the random vitrinite reflectance (Rr%) of 0.25 and 0.23 respectively, the feed coal to “Bernice” and “Albert” is as per the ISO 11760 (2005) standard classified as, Low Rank B (Lignite B), high huminite, and low ash coal. The lignite coal tested, both feeds to “Bernice” and “Albert”, is characterized by high huminite content of over 80% (vol).

Compared to the data in literature (Schobert, 1995) as shown in Table 2, the ulminite reflectance (Rr%) and maceral composition are different and this may

be attributed to the different mining areas which change with time. Also, maximum instead of mean random reflectance was measured in the data from the literature (Schobert, 1995).

The huminite particles in the lignites tested in this study differ from the huminite particles described in Sýkorová *et al.*, (2005) in the fact that they did not fluoresce. This has therefore made classification difficult. The inertinite content of 8.5% (vol) in the feed coal to “Bernice” was mainly fusinite.

Table 4.1. Petrographic composition of the ND coals studied

Sample	PETROGRAPHIC COMPOSITION (Volume %)				RANK Rr%
	Vitrinite/ Huminite	Liptinite	Total inertinite	Visible Minerals	
Feed to “Bernice”	86.2	2.1	8.5	2.8	0.25
Feed to “Albert”	94.4	1.9	3.2	0.6	0.23
Freedom Mine*	67	11	17	3	0.36

\* Data from the literature (Schobert, 1995)

#### 4.3.2. Petrographic Carbon Particle Types

The coal particle conversion profiles for both the “Albert” and “Bernice” gasifiers are illustrated in Figures 4.24 and 4.25. Clear trends are apparent in both gasifiers where the coal/lignitic particles decrease from top to bottom of the gasifier bed as it would be expected. In line with an increase in fixed carbon content, the char particles increased very rapidly in the pyrolysis zones of both gasifiers.

In the gasification and combustion zones, the heated minerals increased rapidly in line with the ash content, whilst the char particles decreased rapidly and again in line with the fixed carbon content. The probable hot spot in sample No.5 of the “Albert” gasifier, which was observed in the proximate analysis profile (Figure 4.5), is again observed in the coal particle conversion profile. The fact that the petrography data shows an excellent match with the other results obtained using different methods of analysis may further prove plug flow during sampling as was observed on a 1 ton/hour pilot fixed bed dry bottom gasifier (Madhusudhan *et al.*, 1989).

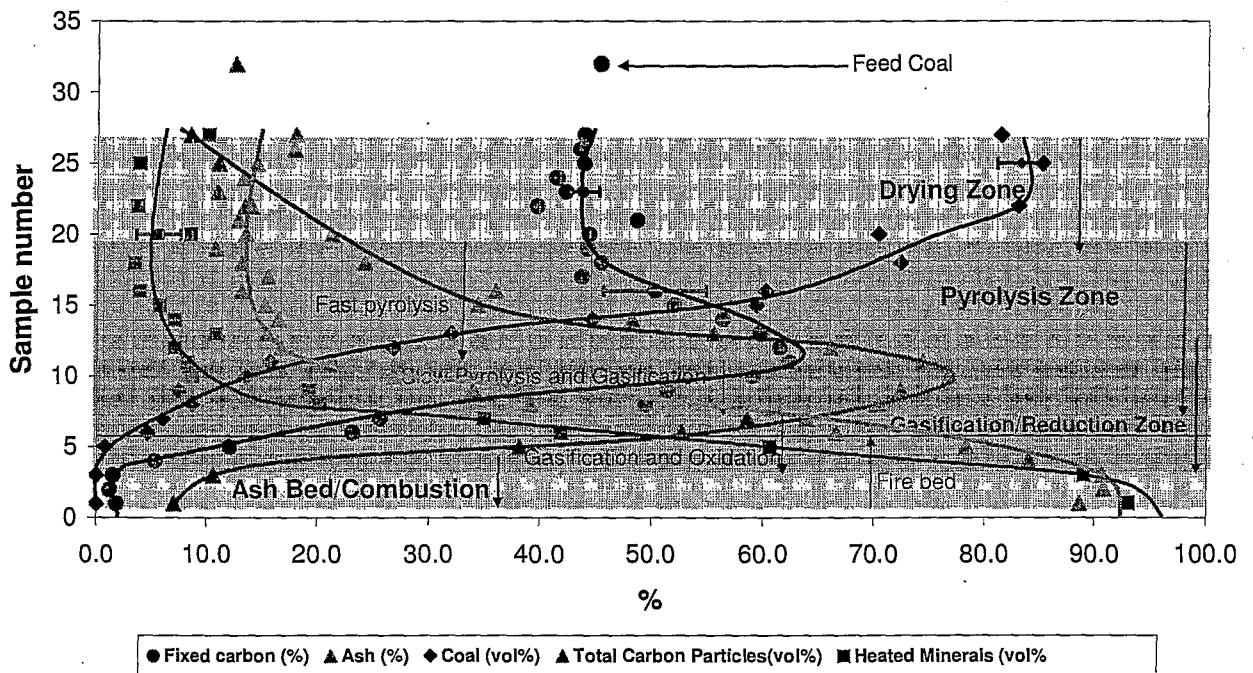


Figure 4.24. Coal particles conversion profiles in the "Bernice" gasifier.

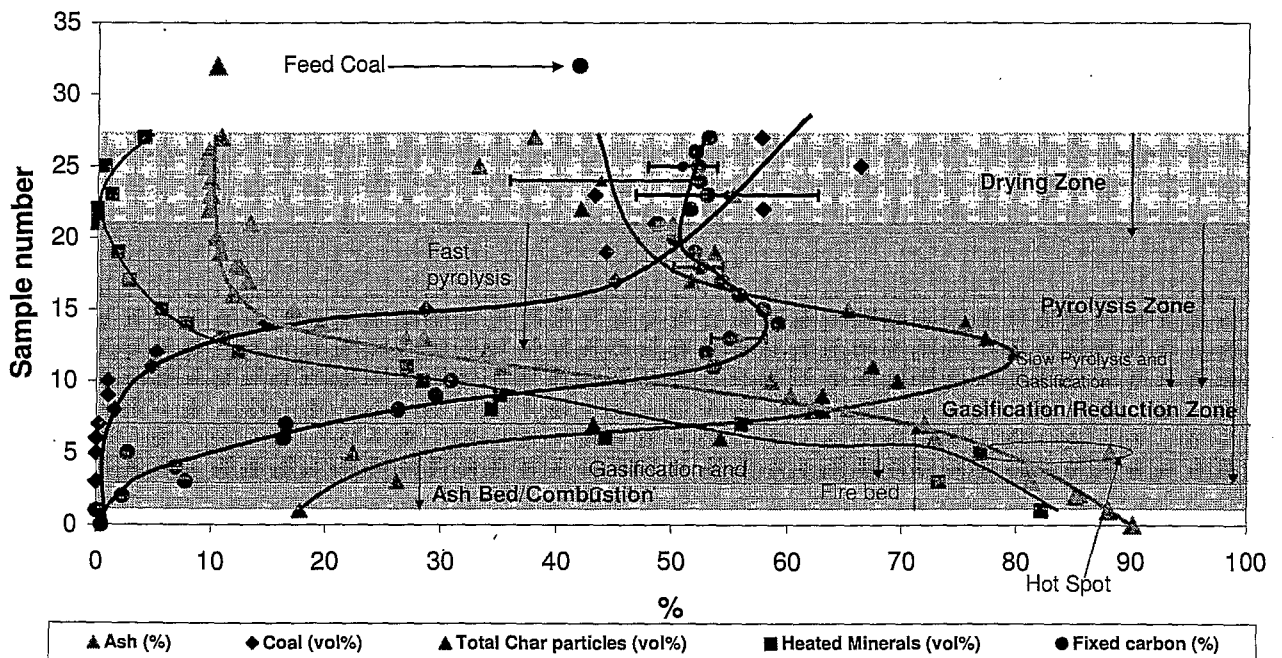


Figure 4.25. Coal particles conversion profiles in the "Albert" gasifier

The residual char particles conversion profiles in “Bernice” and “Albert” gasifiers are illustrated in Figures 4.26 and 4.27. The chars formed in both gasifiers are dominated by the dense char, the formation of which peaked in the gasification zones of both gasifiers (i.e. at sample No. 9 in “Bernice” and between samples 10 and 12 in “Albert”). Dense chars are commonly formed from inertinite macerals. However, in the case of “Albert” and “Bernice”, this is less likely as the coals were rich in huminite (a precursor of vitrinite).

The devolatilized coal present in “Bernice” peaked at sample No. 12 which is the beginning of carbon conversion. In “Albert”, the devolatilized coal peaked in the drying zone at sample No. 23. This is very uncommon as the temperature in the drying zone is expected to be low. There is therefore a strong possibility that this anomaly may be related to the stability of the gasifier and a possible bed fluidisation process. It may also possibly be related to the dusty tar recycling process. Generally, the trends are clearer in “Bernice” when compared to “Albert”.

As mentioned in Chapter 3, the devolatilized coal particles comprised of porous particles as well as particles which showed a reflectance change. An interesting observation in the particles showing reflectance change was that the structure and texture typical of lignitic coals became insignificant in some particles; i.e. certain particles essentially changed rank from huminite to vitrinite typical of bituminous coals (artificial coalification) – see Figure 4.28. This is not unexpected but observed for the first time in the S-L FBDB gasifier.

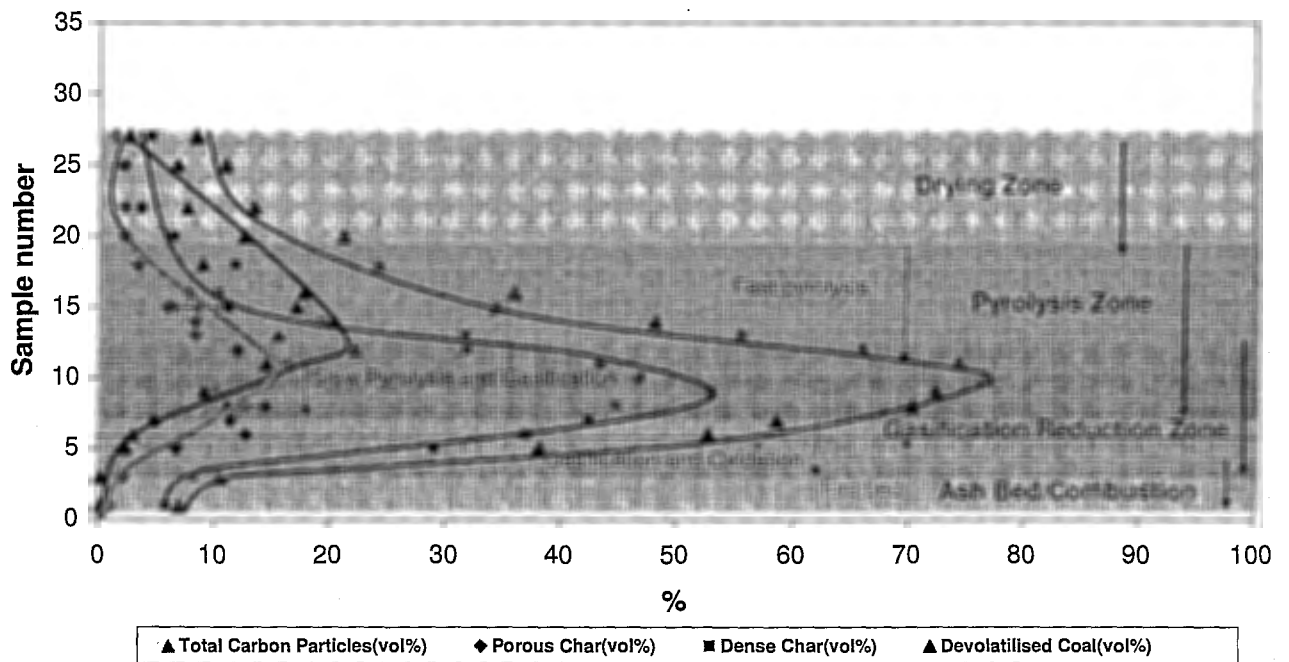


Figure 4.26. Char particles conversion profiles in the "Bernice" gasifier

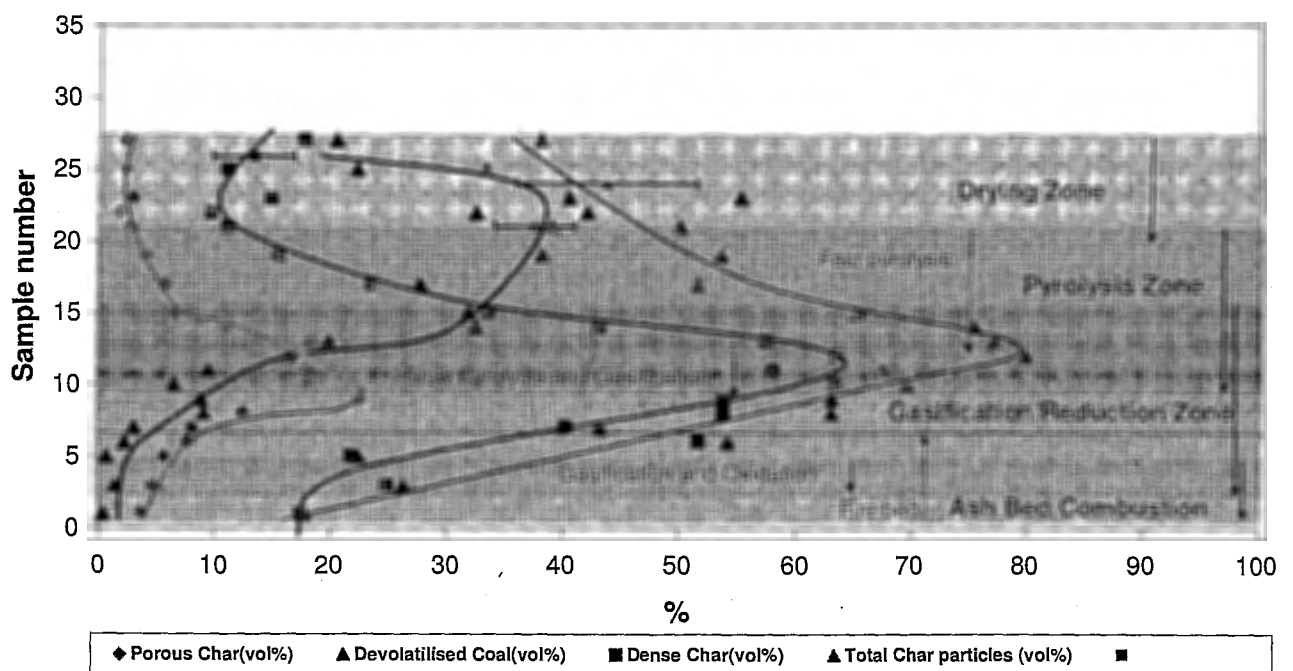


Figure 4.27. Char particles conversion profiles in the "Albert" gasifier





A huminite (telohuminite) particle in the feed coal to "Bernice" gasifier

A "vitrinite" particle in sample No.11 from "Bernice" gasifier

Figure 4.28. Comparison of the synthetic vitrinite particle from the gasifier with the huminite from the feed coal.

#### 4.3.3. Temperature Profile

A calibration curve generated from the reflectance measurements of the chars prepared at various temperatures is shown in Figure 4.29. The solids temperatures in the gasifier were interpolated from the calibration curve using reflectance values measured on the chars from the fuel bed. Due to the shape of the calibration curve, temperatures below 300 °C and above 1100 °C cannot be accurate as they were extrapolated outside the range of the calibration curve.

Figure 4.30 shows the solids temperature profile in the “Bernice” gasifier. The trend in the estimated average solids temperature profile is in line with the expectations as the temperature increases in the drying, pyrolysis, gasification and combustion zones. The average solids temperature seems to be too low, with a value of about 700 °C in the combustion zone. The peak temperature in the combustion zone was estimated at about 1100 °C which is well below the AFT and in fact too low. The peak and surface temperatures of about 800 °C measured on the particles in the drying and pyrolysis zones may be attributed to carryover of fine ash/ char particles as well as dusty tar recycling. It should be noted that the data point at the bottom of the graph (i.e. temperature of the ash) was taken from the agent temperature and not measured from the char.

A confidential and proprietary thermodynamic model used by SLTC in designing the FBDB gasifiers predicted the maximum temperature (i.e. temperature at the end of the combustion zone where all the oxygen has reacted with the carbon) of 1258 °C, and gas outlet temperature of 247 °C. The temperature at which the water gas shift reaction (equation 2.6) was forced into chemical equilibrium was predicted at 741 °C.

Given that the solids temperature is expected to be lower than the gas temperature in the gasification zone, the data estimated experimentally (particularly the average solids temperature which is in line with the predicted temperature at which the water gas shift reaction was forced into chemical equilibrium) in this study is not that far out. Although this method has its own limitations (e.g. reading high reflectance and subsequent high temperatures in the drying zone due to possible fines carryover, dusty tar recycling or channeling) it may be used for indication purposes.

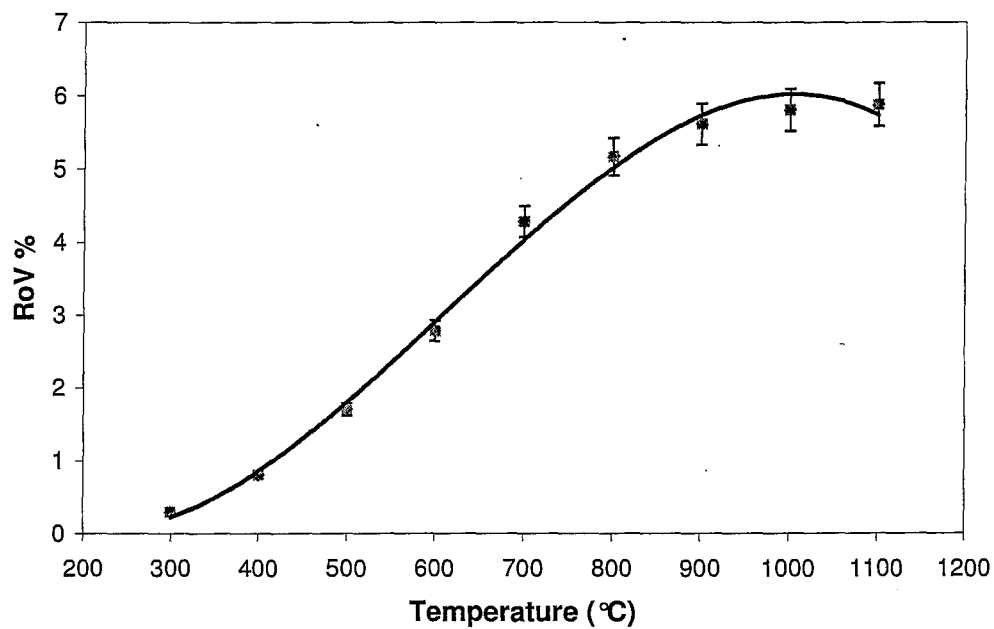


Figure 4.29. Calibration curve for the temperature profile in the "Bernice" gasifier.

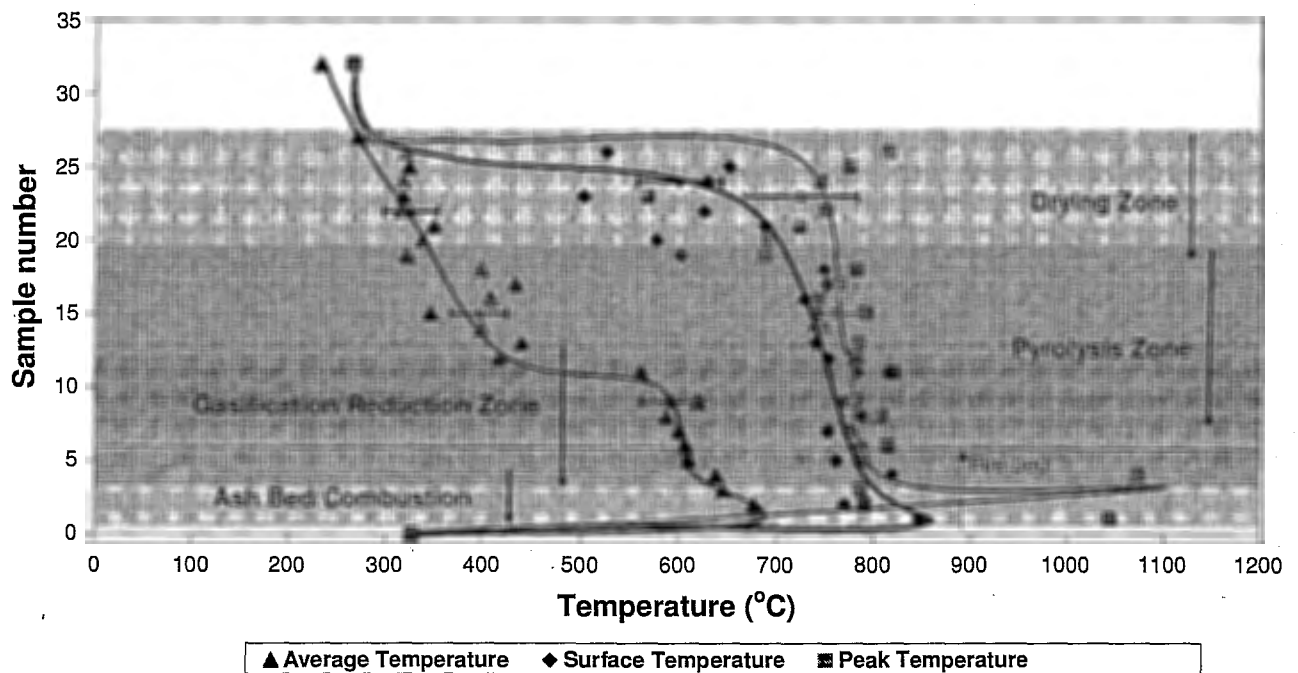


Figure 4.30. Estimated solids temperature profile in the "Bernice" gasifier.

## 4.4 Mineralogical Properties

Profiles of the mineralogical properties, determined using XRD, CCSEM and SEMPC, within the gasifier fuel bed are discussed in this section. Mineral matter transformation in the gasifier fuel bed is also related to the other coal properties investigated in this study.

### 4.4.1. XRD Results

The profiles of the minerals determined using XRD in the selected samples from the Bernice gasifier are illustrated in Figures 4.31 – 4.33. The profiles of the major minerals that were present in the feed coal are shown in Figure 4.31.

As depicted in Figure 4.31, quartz ( $\text{SiO}_2$ ) seems to have survived the chemical attack in the gasification and combustion zones. This is not unexpected as quartz is generally regarded as non reactive during combustion and/or gasification (Nankervis and Furlong, 1980; Van Alphen, 2005). A slight decrease is however observed in the hotter zones of the gasifier.

Quartz transforms at 573 °C to  $\alpha$ - quartz and  $\beta$ -quartz which at 870 – 1470 °C can be transformed to  $\beta$ -tridymite and to  $\beta$ -cristobalite at 1470 – 1713 °C (Nankervis and Furlong, 1980; Unsworth *et al.*, 1987). These polymorphs can only melt at temperatures in the region of 1700 °C (Unsworth *et al.*, 1987). However, the structure of  $\beta$ -tridymite and  $\beta$ -cristobalite can open and react with alkali ions (Watt, 1969). This is probably the reason for the slight decrease in quartz in the gasification and combustion zones.

Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), a clay mineral, started disappearing in the pyrolysis zone and was completely transformed in the gasification zone as shown in Figure 4.31. When exposed to high temperatures, kaolinite starts to lose its hydroxyl water at a temperature of between 400 and 525 °C, the process of

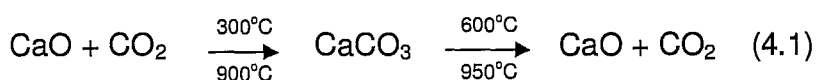
which completes at 800 °C to form metakaolinite - an amorphous material (Alpern *et al.*, 1984; Unsworth *et al.*, 1987). The final products from kaolinite transformation during heat treatment are gamma-alumina ( $\text{Al}_2\text{O}_3$ ), mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and cristobalite ( $\text{SiO}_2$ ) with a silicon spinel ( $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ) occurring as an intermediate phase (Unsworth *et al.*, 1987). These final products are formed at 950 – 1000°C but will during gasification react with the fluxing elements, particularly Ca and Na, to form new phases with lower melting points (Nankervis and Furlong, 1980; Schobert, 1995; Matsouka *et al.*, 2006).

Illite ( $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})$ ), also a clay mineral, was one of the minor phases in the feed coal and was not detected in the pyrolysis zone but as shown in Figure 4.31, illite was detected in the gasification and combustion zones. At a temperature of 1127 °C illite loses its crystalline structure and completely melts to form a potassium aluminosilicate glass (Srinivasachar *et al.*, 1990a). Its presence in the ash is probably due to the short residence time in the hotter combustion and gasification zones, given their small height in the “Bernice” gasifier as shown in Figure 4.8 and the temperature profile in Figure 4.30. In addition, illite may have been concentrated with an increase in the ash content of the fuel bed in the hotter zones of the gasifier. Its presence in the combustion zone may also confirm the peak temperature of 1100 °C in the combustion zone of the “Bernice” gasifier as per the temperature profile shown in Figure 4.30.

Calcite ( $\text{CaCO}_3$ ) seemed to increase in the beginning of gasification zone, towards the end of pyrolysis zone, and decreased in the hotter combustion zone – see Figure 4.31. At a temperature of 600 – 700 °C, calcite in coal decomposes to CaO and  $\text{CO}_2$  (Nankervis and Furlong, 1980; Alpern *et al.*, 1984). In the case of “Bernice” gasifier, a formation of calcite is observed.

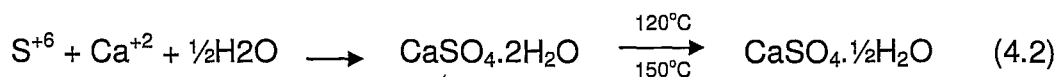
Lancet and Curan (1982) produced  $\text{CaCO}_3$  from the reaction of CaO and  $\text{CO}_2$  in a fluidised bed reactor gasifying wood at a temperature below 845 °C and a pressure of below 13 bars. The exothermic reaction of  $\text{CaCO}_3$  formation (equation 4.1) was used to maintain the desired reaction temperature in the

reactor (Lancet and Curan, 1982). The calcite formed in the “Bernice” gasifier was therefore most probably formed from the carbonation of CaO from the organically bound Ca (Quann and Sarofim, 1986) with the CO<sub>2</sub> in the raw syngas. The formed calcite has probably survived complete decomposition in the hotter combustion zone due to the short residence time, given the small height of this zone as was shown in Figure 4.8. The mechanisms for the formation and decomposition of calcite are shown in equations 4.1.



The formation of calcite in the beginning of the gasification zone is in line with the temperature profile shown in Figure 4.30 and actually further proves the lower temperatures associated with lignite gasification in the S-L FBDB gasifiers. The fact that calcite survived in the hotter combustion zone may also be an opportunity for *in situ* capturing of excess CO<sub>2</sub> in the DGC gasifiers.

Bassanite (CaSO<sub>4</sub>·½H<sub>2</sub>O) was only detected in the samples that were subjected to low temperature ashing (LTA) – see Figure 4.31. This mineral is not necessarily in the original coal, but is derived from interaction of organically associated Ca with organic sulphur and water during the plasma ashing process – see equation 4.2 (Nankervis and Furlong, 1980; Alpern *et al*, 1984; Ward, 2002). The proportion of bassanite in the LTA decreased in line with a decrease in volatile matter from top to bottom of the gasifier. The samples evaluated without plasma ashing showed no bassanite. An XRD scan conducted on a char sample with 34% ash (i.e. sample No.9) without low temperature ashing showed no traces of bassanite and this further proves the fact that bassanite formed during the LTA process.



The crystalline phases forming in the gasification and combustion zones of the gasifier as shown in Figures 4.32 and 4.33 were mainly bredigite (Ca<sub>7</sub>Mg(SiO<sub>4</sub>)<sub>4</sub>), gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>), glauberite (Na<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and anhydrite

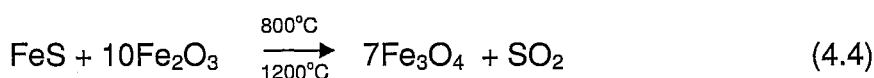
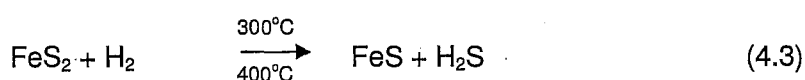
(CaSO<sub>4</sub>). The hydrated sulphates like gypsum and melanterite in the gasification and combustion zones may have formed from the hydration of the anhydrite during the steam quenching of the gasifier prior to sampling.

Bredigite and gehlenite seemed to be the dominating species in the gasification and combustion zones. As shown in Figure 4.32, bredigite in the "Bernice" gasifier, started forming as early as the pyrolysis zone and the concentration increased in the hotter gasification and combustion zones. This mineral is known to form in a melt at temperatures between 850 – 1450 °C and its formation is favoured more in the coals with low (<7% Na<sub>2</sub>O) sodium content (Nankervis and Furlong, 1980). In the "Bernice" gasifier, bredigite is most probably formed from the reaction of CaO and MgO (formed from the decomposition of the Ca and Mg organic salts in the coal (Quann and Sarofim, 1986)) with the reactive SiO<sub>2</sub> present in the system from the decomposition of kaolinite.

As with bredigite, gehlenite in the "Bernice" gasifier started forming as early as the pyrolysis zone and the concentration increased in the hotter gasification and combustion zones – see Figure 4.32. Gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) in coal ash forms at about 900 °C but was also observed in the laboratory at 750 °C (Goblirsch *et al.*, 1984; Unsworth *et al.*, 1987; Schobert, 1995). In the "Bernice" gasifier, gehlenite was probably formed from the reaction of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (from kaolinite and probably submicron quartz) with CaO which was formed from the decomposition of the Ca organic salts in the coal. The fact that gehlenite is commonly found in slags, particularly if CaO content is greater than Al<sub>2</sub>O<sub>3</sub> (Nankervis and Furlong, 1980) as is the case with ND lignite, may mean that ash melting began in the pyrolysis zone.

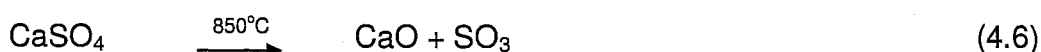
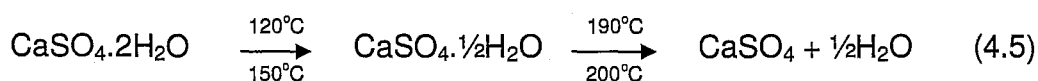
Magnetite, in the "Bernice" gasifier, formed in the pyrolysis zone and the concentration increased in the hotter gasification and combustion zones as shown in Figure 4.32. This mineral phase is also commonly found in lignite slags (Schobert, 1995). In the ND lignite ash, magnetite forms in the region of 800 to 1200 °C (Nankervis and Furlong, 1980).

The source of Fe in the case of the “Bernice” gasifier is most probably the included, sub-micron pyrite (which could not be detected by XRD) as well as the organically associated Fe. These are expected to form pyrrhotite (FeS) and hematite (Fe<sub>2</sub>O<sub>3</sub>) respectively in the pyrolysis zone. The pyrrhotite can then react with hematite to form magnetite in the hotter gasification and combustion zones – see equations 4.3 and 4.4 (Nankervis and Furlong, 1980; Alpern *et al*, 1984). The SO<sub>2</sub> formed in the reaction is not expected to survive the highly reducing environment of the gasifier.



The profiles of the sulphur bearing minerals (sulphates in particular) formed in the “Bernice” gasifier are illustrated in Figure 4.33. The species detected by XRD are gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), anhydrite (CaSO<sub>4</sub>), glauberite (Na<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>) and melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O). Except for melanterite which peaked in the combustion zone, the sulphate minerals started forming in the drying zone, peaked in the pyrolysis zone and decreased, probably due to decomposition, in the gasification and combustion zones.

The mechanisms for the formation of calcium sulphates involves first the formation of bassanite and/or gypsum from the organically bound sulphur and calcium – see equation 4.1 (Nankervis and Furlong, 1980; Alpern *et al*, 1984). The bassanite will dehydrate at about 200 °C to form anhydrite which may decompose at a temperature of above 850 °C to form CaO which can in turn form calcium silicate phases at higher temperatures – see equation 4.5 and 4.6 (Nankervis and Furlong, 1980; Alpern *et al*, 1984).





The formation of glauberite is also expected to be from the organically associated Na, Ca and S and its formation was probably in competition with the calcium sulphates discussed above (Goblirsch et al., 1984; Schobert, 1995). In addition to the organically associated Fe and S, melanterite in the combustion zone was probably formed from the oxidation of pyrrhotite and subsequent hydration with steam during quenching.

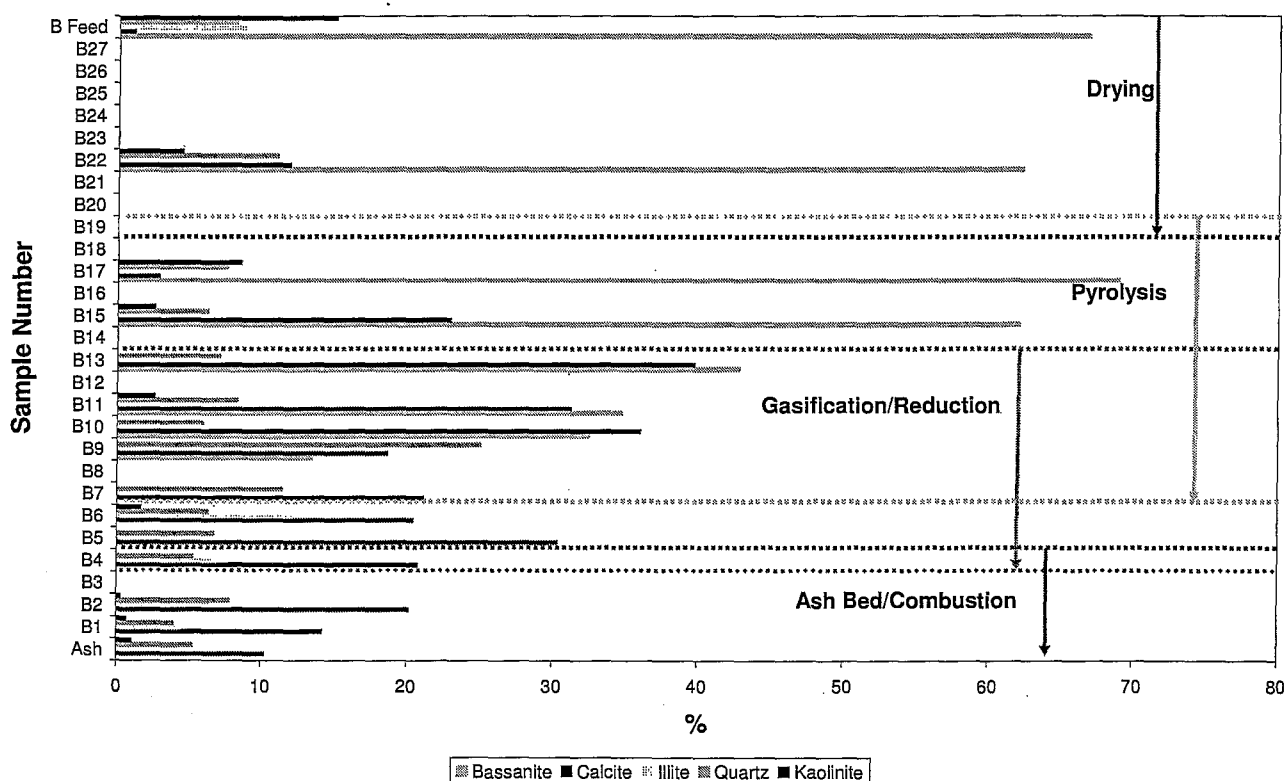


Figure 4.31. Profiles of the minerals present in the feed coal.

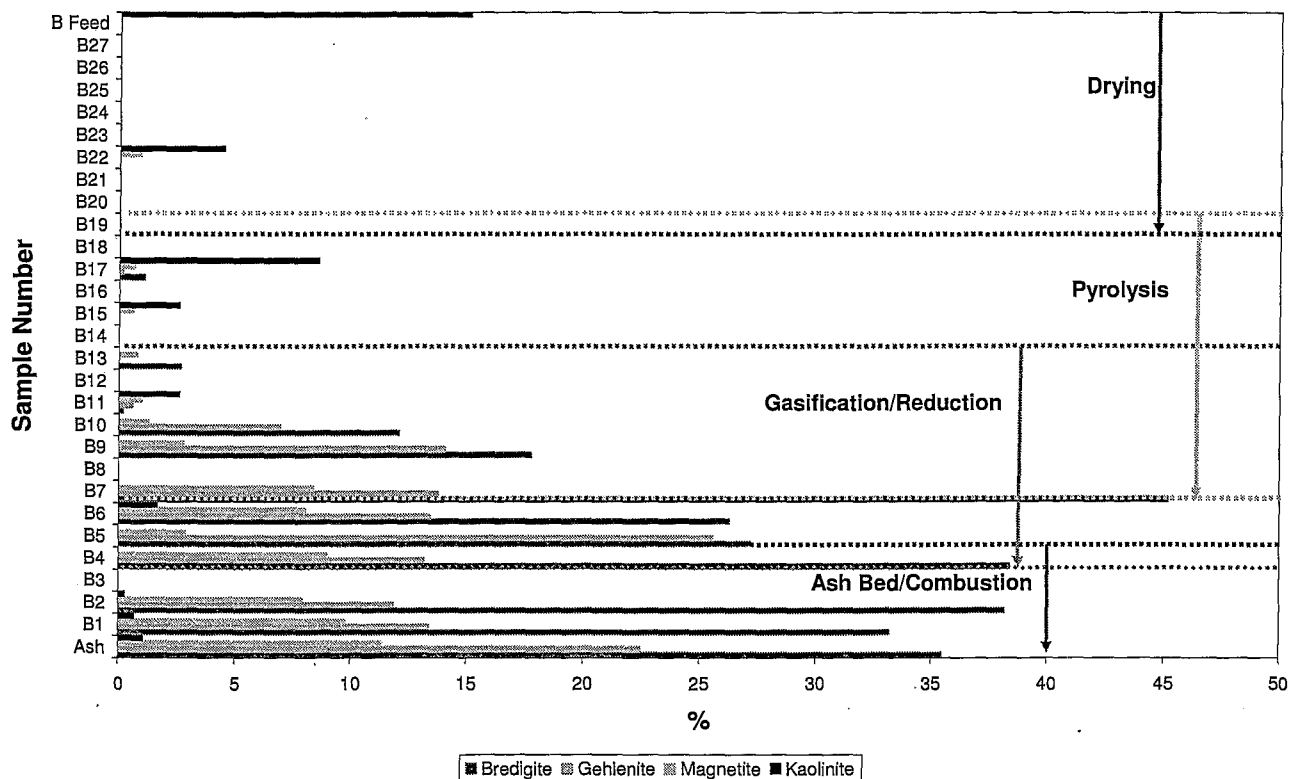


Figure 4.32. Profiles of the minerals formed during gasification

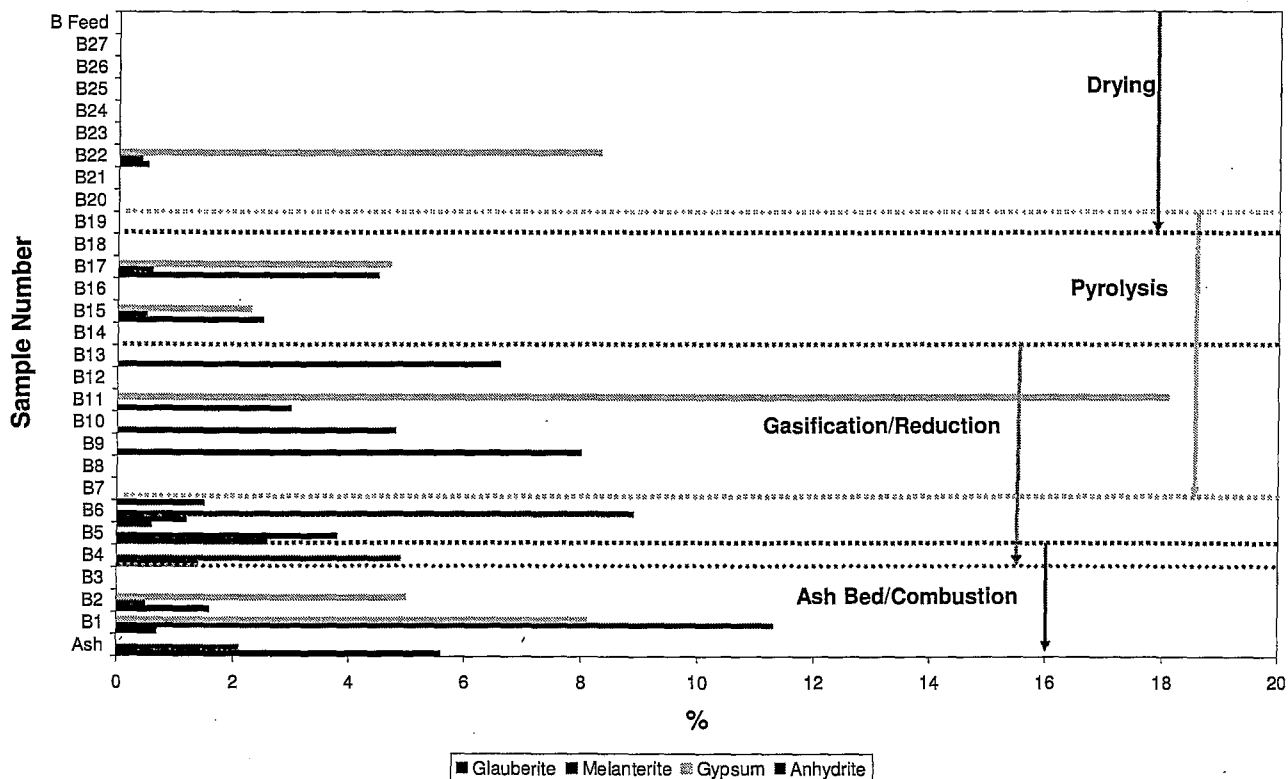


Figure 4.33. Profiles of the sulphur bearing minerals formed during gasification

#### 4.4.2. CCSEM and SEMPC Results

In addition to the species determined using XRD, the profiles of other mineral species identified in the Turn-Out samples using CCSEM and SEMPC are depicted in Figure 4.34. It should be noted that due to their matrix, samples from B Feed to B9 and from B7 to B Ash as shown in Figure 4.34 were analysed using CCSEM and SEMPEC techniques respectively.

Pyrite in the feed coal was detected by CCSEM and as expected, it seemed to decrease from the top to the bottom of the gasifier. This mineral transformed completely in the pyrolysis zone, where pyrrhotite started to appear. Pyrrhotite transformed completely at the start of the gasification zone. According to the CCSEM and SEMPC results, iron oxide started to form only in the gasification zone, and this is in line with the XRD results which showed an increase of magnetite in the gasification and combustion zones as shown in Figure 4.32. According to Alpern *et al.* (1984), pyrrhotite forms from the reduction of pyrite at temperatures of 300 to 400 °C – see equation 4.3. This is therefore expected in the pyrolysis zone of the S-L FBDB gasifier. The iron oxide detected by SEMPEC is most probably magnetite, as reported in the XRD results above, and may result from the oxidation or decomposition of pyrrhotite (Srinivasachar *et al.*, 1990b).

Akermanite ( $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ ) and nepheline ( $\text{NaAlSiO}_4$ ) were also detected in the gasification and combustion zones of the “Bernice” gasifier. Akermanite in coal ash forms at about 900 °C but was also observed in the laboratory at 750 °C (Goblirsch *et al.*, 1984; Unsworth *et al.*, 1987; Schobert, 1995). In the “Bernice” gasifier, akermanite was probably formed from the reaction of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , from kaolinite and part of quartz, with CaO and MgO which were formed from the decomposition of the Ca and Mg organic salts in the coal.

Nepheline forms at about 800 °C as a recrystallisation product of the sodium rich aluminosilicates (Goblirsch *et al.*, 1984; Unsworth *et al.*, 1987; Schobert,

1995). The source of Na in the case of the “Bernice” gasifier is most probably the organic salts of sodium (e.g. sodium carboxylates) whilst the Al and Si are probably from the clays. As mentioned in the literature review, nepheline formation in the gasifier has detrimental effects and at DGC its formation is minimised by blending the coal to reduce the Na content to <8% (Dittus and Johnson, 2001).

The unclassified phase (also referred to as the glass phase) increased with an increase in ash content from the top to the bottom of the gasifier. The formation of this phase is even more pronounced in the gasification and combustion zones of the gasifier where melting and interaction of ash species occur. The chemical composition (expressed as weight percent equivalent of the oxides) of the unclassified phase in the gasification and combustion zones is shown in Table 4.2. In these reaction zones, this phase forms a major component of the ash in all the samples tested.

The unclassified phase consists mainly of alkali and alkaline earth aluminosilicates, with some iron as can be seen by the high amount of Si, Al, Ca, Mg, Na and Fe. According to Benson (1987), this is a key phase associated with slag formation from the utilization of Fort Union lignite. The composition is definitely different to the ash composition of the feed coal to the gasifier. In fact, this phase may be associated with the melt/clinkers that formed in the gasifier as shown by the increase in particle size of the bed in the gasification and combustion zones – see Figure 4.13 and 4.15. It is highly likely that the fluxing elements in the dominating unclassified/glass phase are responsible for the low AFT of the ash from the gasifier when compared to the feed coal as discussed in Section 4.2.3.

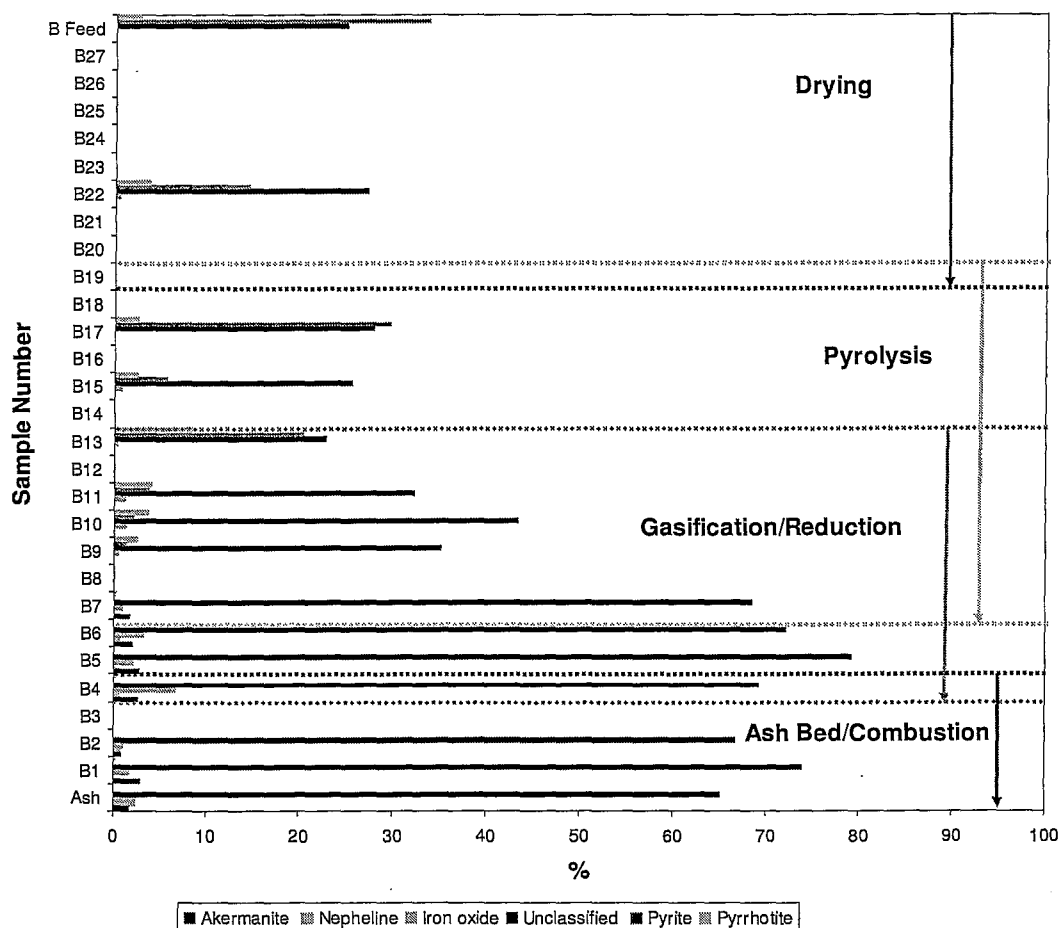


Figure 4.34. Profiles of other mineral species in the "Bernice" gasifier as determined using CCSEM and SEMPC.

Table 4.2. Average chemical composition (wt %) of the unclassified/glass phase, based on X-ray analysis results from the SEMPEC analysis.

Sample No.	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	BaO
B Feed	4.7	6.0	8.6	17.5	0.3	28.0	-	0.6	17.7	0.3	-	15.9	0.4
B7	6.2	9.1	15.4	26	0.2	0.5	0.2	0.6	30.7	0.5	0.4	9.1	1.0
B6	6.4	8.3	16.0	29.0	0.1	0.9	0.4	0.6	27.1	0.5	0.4	9.3	0.9
B5	6.8	8.7	15.4	26.4	0.2	1.1	0.3	0.5	31.2	0.4	0.5	7.5	1.1
B4	6.9	6.3	14.4	27.8	0.1	0.7	0.4	0.7	33.2	0.4	0.2	8.0	0.9
B2	6.5	6.2	17.1	28.3	0.1	1.9	0.7	0.6	26.8	0.6	0.4	8.9	1.7
B1	8.3	7.8	15.8	27.0	0.2	1.4	0.4	0.5	29.5	0.4	0.3	7.4	1.0
B Ash	6.8	9.9	16.6	25.7	0.3	1.2	0.4	0.5	29.7	0.5	0.3	6.9	1.2

Figures 4.35 and 4.36 depict the backscattered electron micrographs of the feed coal as well as the sample in the ash/combustion zone showing the analysis points and areas. It should be noted that the carbon peaks in the

spectrum were excluded during quantification of the inorganic elements in the organic matrix.

The profiles of the inorganic elements determined in the organic matrix of the Turn-Out samples are illustrated in Figure 4.37. As with the unclassified species in the mineralogical analysis, the inorganic elements in the organic matrix are mainly Si, Al, Ca, Mg, Na and Fe. These species appeared in the organic matrix throughout the gasifier bed and were dominated by Ca and Si, followed by Al, Mg and Fe. Sodium showed a significant appearance in the ash bed and this is in line with the appearance of nepheline – see Figure 4.37. The organic sulphur decreased significantly in the pyrolysis zone, probably reacting with the organically bound calcium to form calcium sulphates.

A chemical fractionation study by Benson and Holm (1985) found that 38% Ba, 76% Ca, 20% K, 90% Mg, 30% Mn, 84% Na and 87% Sr were present in the ND lignite as ion exchangeable cations. Should they not be ion-exchangeable, Si, Al and Fe determined in the organic matrix of the coal studied may be present as submicron minerals (Ward, 2002).

Given that the ash content of the feed coal was only 4.7% (as received basis), it may be concluded that these organically bound inorganic elements formed the building blocks of the ash in the gasifier. This is supported by the fact that the unclassified/amorphous ash species, which formed the better part of the ash minerals as shown in Figure 4.34, consisted mainly of alkali and alkaline earth aluminosilicates, with some iron. The better part of bredigite and gehlenite, which were the dominating crystalline phases in the gasification and combustion zones, as determined by XRD analysis, also resulted from the interaction of these organically bound inorganic elements with the clays.

Profiles of the inorganic elements determined in the included minerals of the Turn-Out samples from the “Bernice” gasifier are illustrated in Figure 4.38. Silicon is still the dominating element and its appearance with aluminium is typically an indication of the presence of clay minerals. The Si measured in sample 9 is most probably in the form of quartz and this is in line with a spike

of quartz in sample 9 as depicted in Figure 4.31. The Ca and Mg are most probably associated with the calcite and dolomite cleats, particularly in the feed coal. The sodium once again is more pronounced in the ash bed. The appearance of S and Fe in the feed coal and pyrolysis zone may indicate the presence of pyrite and pyrrhotite respectively.

As illustrated in Figure 4.39, the ash/excluded minerals in the drying and pyrolysis zones were minimal and this is not unexpected for the ND lignite (Schobert, 1995). The excluded minerals probed in the feed coal as well as the pyrolysis zone consisted mainly of Si and Al indicating the presence of clay minerals. Ash particles/minerals started appearing in the beginning of the gasification zone. This is in line with the coal particles conversion profile determined using petrography – see Figure 4.24. Agreement of the chemical, physical, petrographic and mineralogical properties of the “Bernice” gasifier bed samples and plug flow of solids during sampling is therefore further confirmed.

The ash particles probed, once again were dominated by Ca and Si followed by Al, Fe, Mg and Na which confirmed the role played by the organically bound inorganic elements in the formation of aluminosilicates.

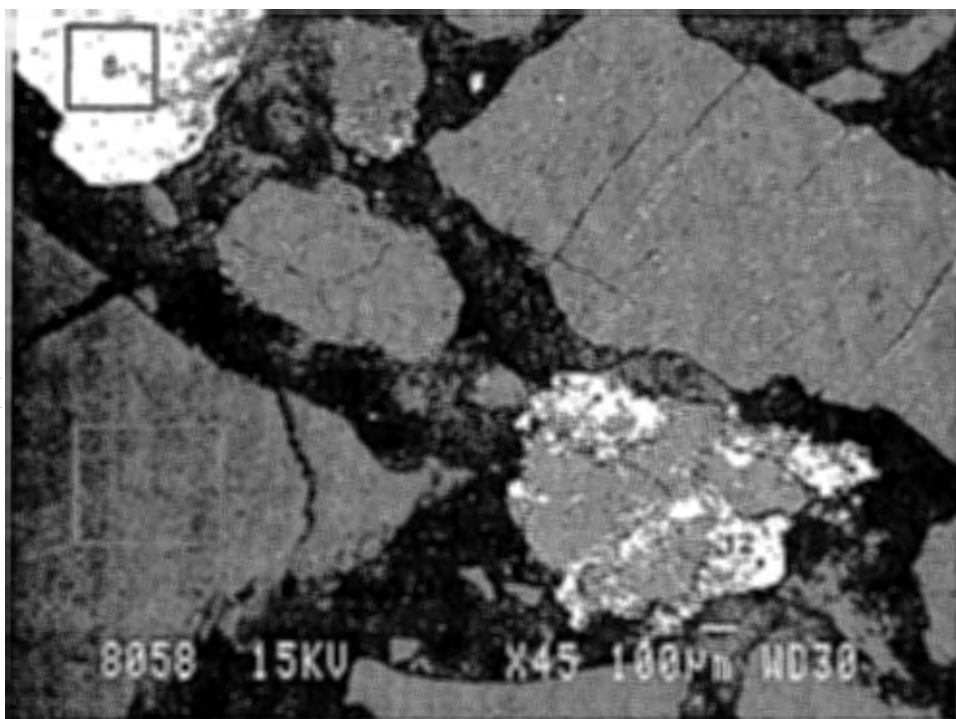


Figure 4.35. Backscattered electron micrograph of the "Bernice" feed coal sample showing analysis points on coal matrix (7), excluded mineral (8 &9) and included mineral (10, 11 and 12).

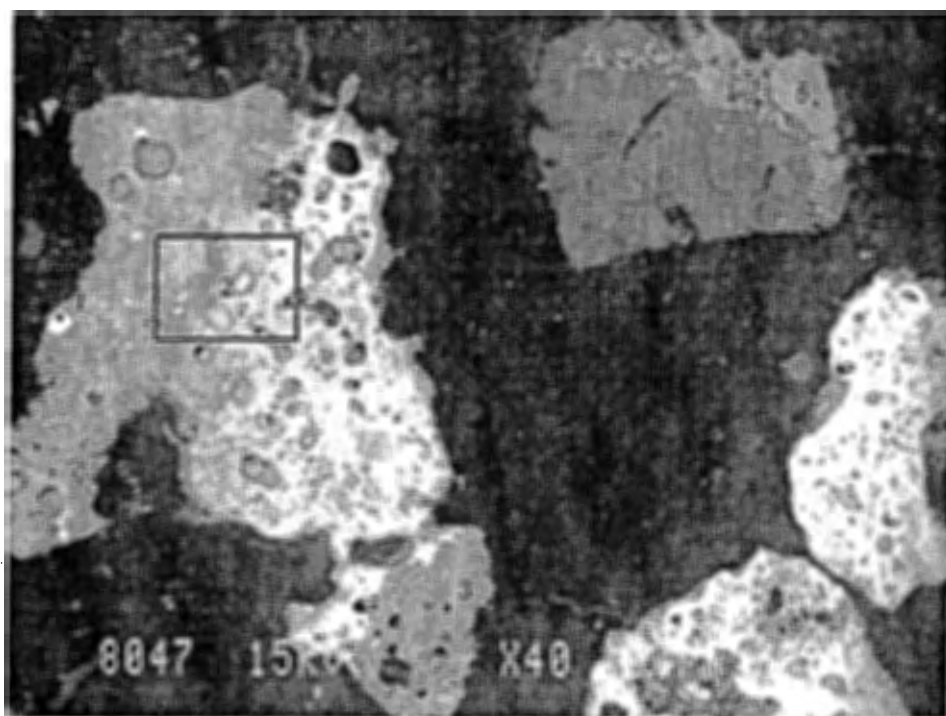


Figure 4.36. Backscattered electron micrograph of the "Bernice" ash bed sample No.4, showing analysis points on the organic (i.e. char) matrix (4), ash particle (1, 2 and 3) and included mineral (5).



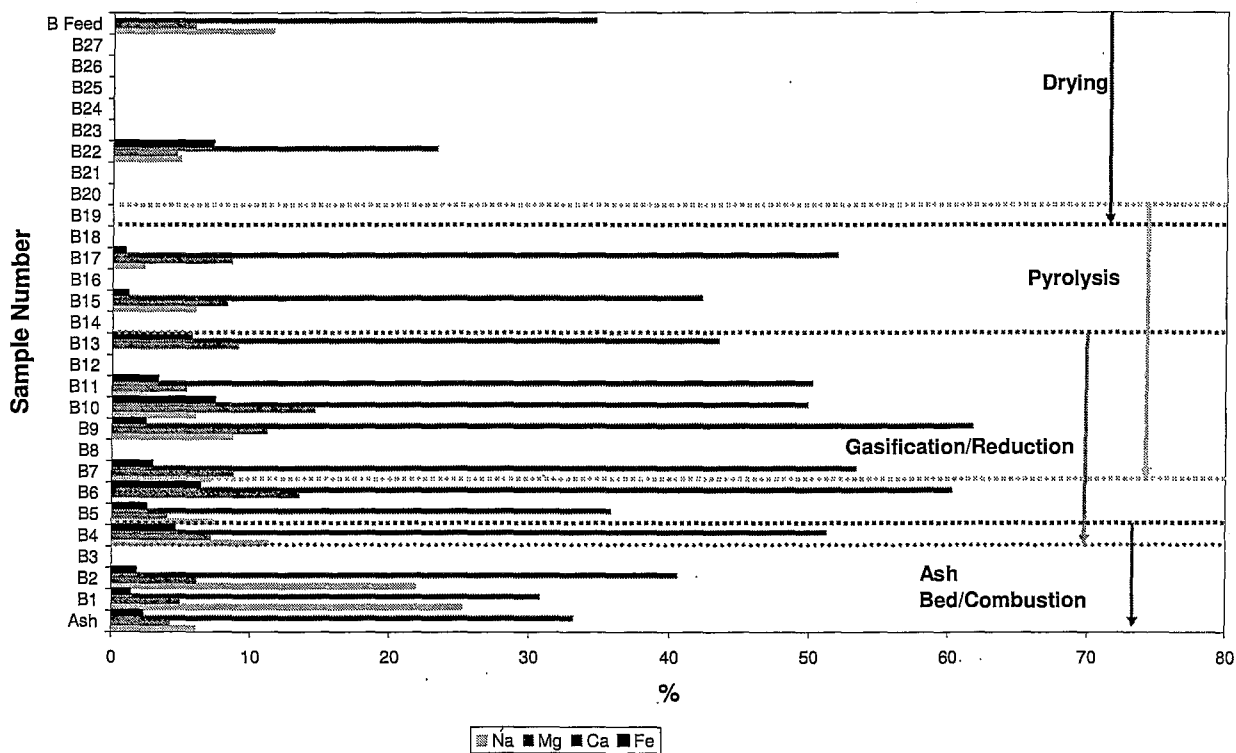
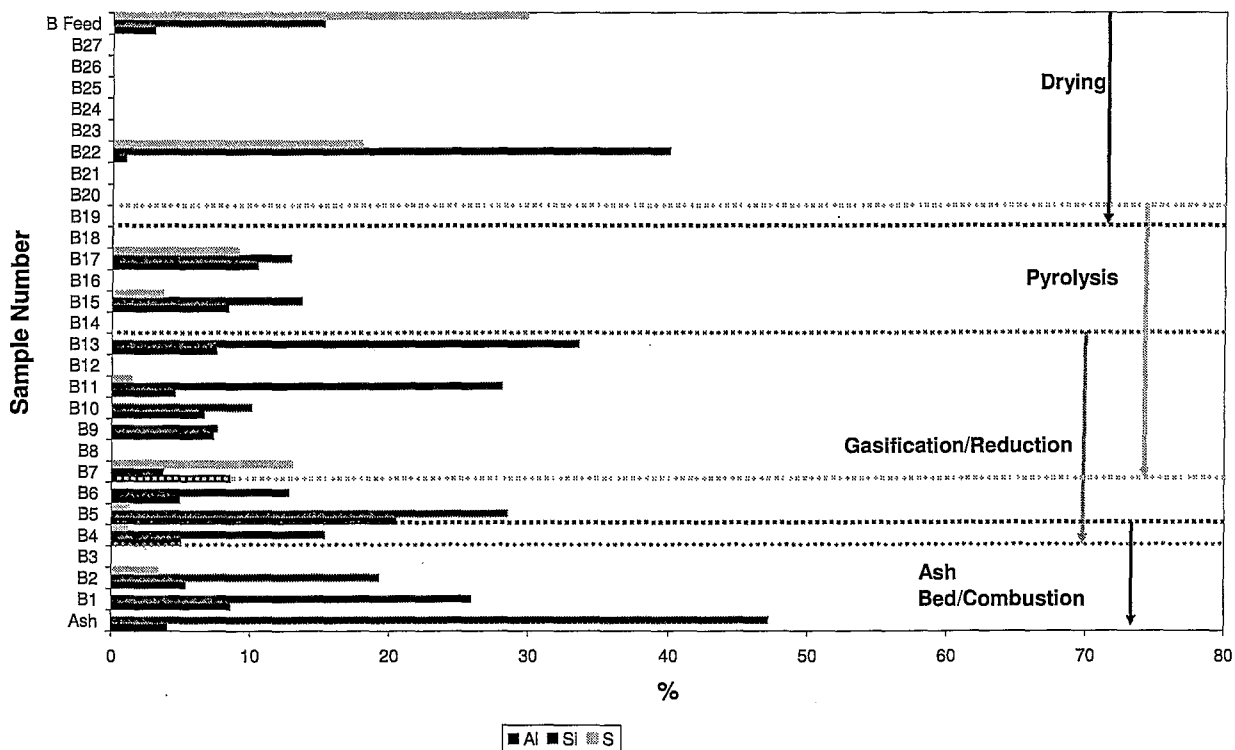


Figure 4.37. Profiles of the elements determined in the organic matrix (i.e. on the pure coal and char particles) of the Turn-Out samples from the "Bernice" gasifier.

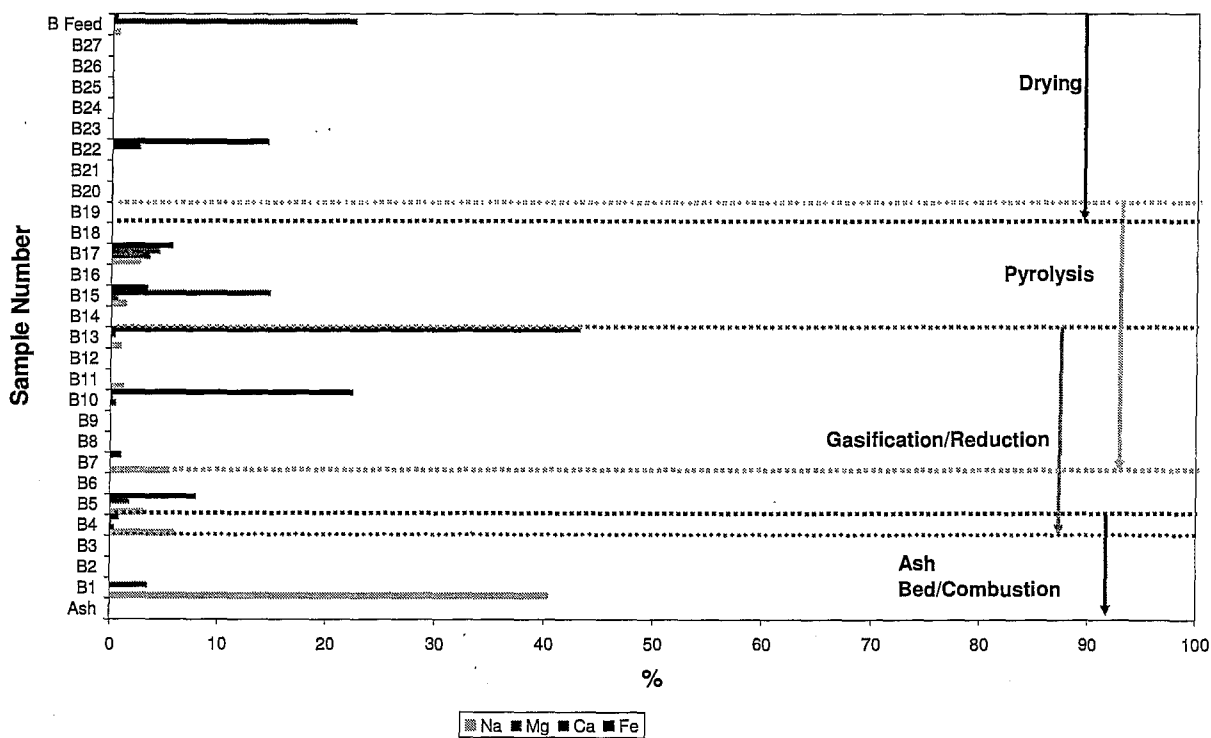
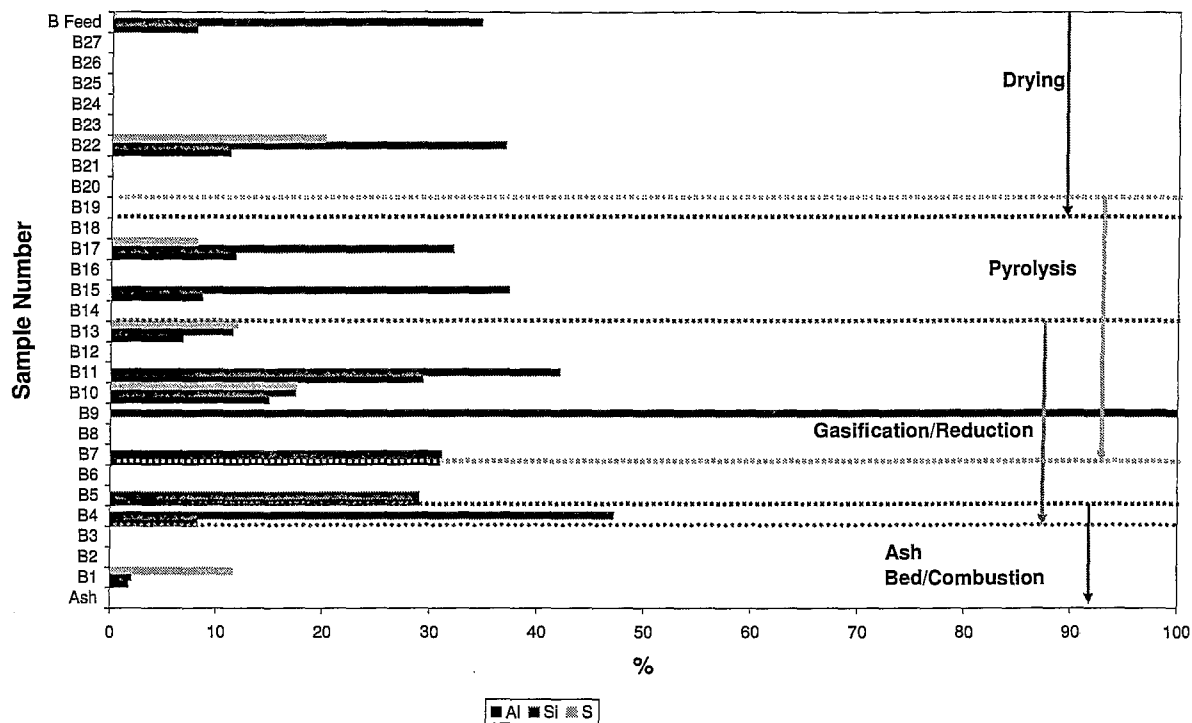


Figure 4.38. Profiles of the elements determined in the included minerals of the Turn-Out samples from the "Bernice" gasifier.

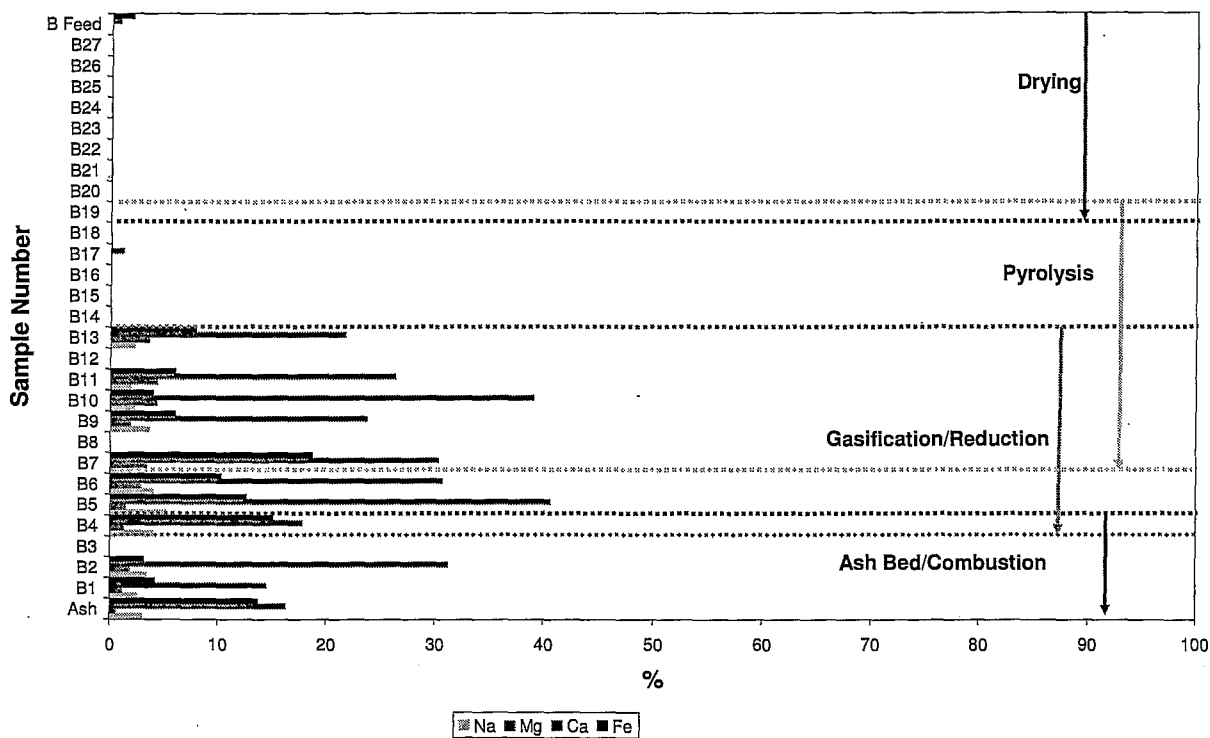
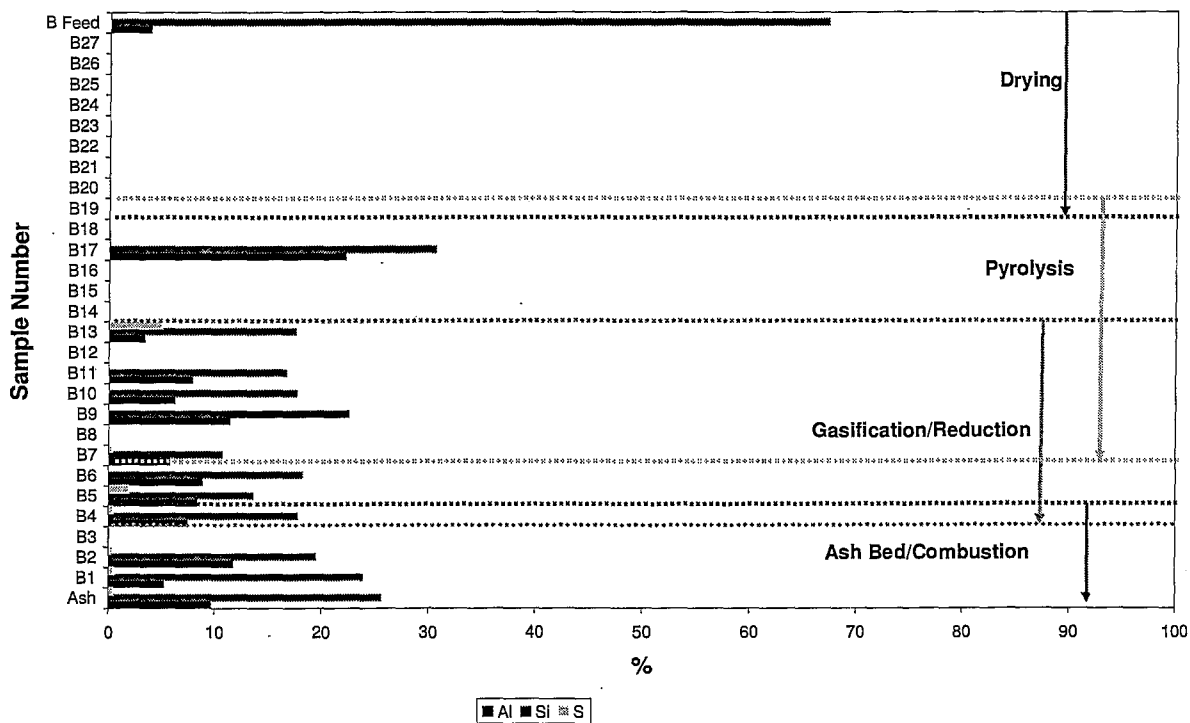


Figure 4.39. Profiles of the elements determined in the ash/excluded minerals of the Turn-Out samples from the "Bernice" gasifier.

#### **4.4.3. Mineral Matter Transformation in Relation to other Coal Properties and their Behaviour in the “Bernice” Gasifier**

In this section, an attempt is made to explain, using the mineral matter transformation in the gasifier, the behaviour or profiles of volatile matter and CO<sub>2</sub> char reactivity. An opportunity to investigate *in-situ* sulphur capture is further explained and so is the phenomenon of oxygen scavenging in the gasifier.

##### **4.4.3.1. Volatile Matter**

The residual volatile matter profile in both the “Bernice” and “Albert” gasifiers showed a stabilization at about 10% (dry basis) in the ash bed see Figures 4.1 and 4.5. The fact that the pyrolysis zone in “Bernice”, defined in terms of tar removal, ended at sample 7 may indicate that the volatile matter in the ash bed was originating from the inorganic species. The XRD analysis of the samples in the ash bed showed the presence of calcite (CaCO<sub>3</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O).

Calcite is expected to decompose at a temperature of about 700°C to form CaO and CO<sub>2</sub> as shown in equation 4.1 (Alpern *et al*, 1984). In a neutral atmosphere, gypsum is expected to lose the water of crystallisation at about 200 °C to form anhydrite – see equation 4.5 (Alpern *et al*, 1984). At about 900 °C, anhydrite can decompose to CaO and SO<sub>3</sub> – see equation 4.6 (Alpern *et al*, 1984). Melanterite is also expected to lose the crystal water during heating.

During the determination of volatile matter using ISO 562 (1998), a coal sample in a crucible with a close fitting lid is heated to a temperature of 910 °C. At this temperature, the reactions showed in equations 4.6 to 4.8 are not impossible. It is therefore suggested that the volatile matter in the gasification ash of the ND lignite is mainly from the minerals. Studies should be conducted to determine the leachability of this ash in order to quantify the environmental impacts during storage.

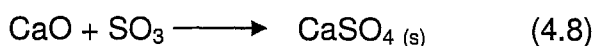
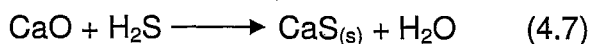
#### 4.4.3.2. Reactivity

It was mentioned in Section 4.1.5 that the organically bound Na, K, Ca and Fe may be catalysing the gasification reactions in the gasification zone thus leading to the observed increase in char reactivity – see Figures 4.11 and 4.12. Ca in particular, was concentrated in the chars from the gasification zone. Although there may be other factors (e.g. pore structure, active sites, surface area etc.) contributing to this phenomenon of an increasing reactivity in the gasification zone (Smith *et al.*, 1993), catalysis by the organically bound Ca cannot be excluded.

In fact, for the ND lignite, Ca, which was added as calcium acetate to the coal that was demineralised with HCl and HF and pre-treated/ion exchanged with ammonium acetate, proved to be catalysing the char/CO<sub>2</sub> reaction (Radovic *et al.*, 1984).

#### 4.4.3.3. In Situ Sulphur capturing and H<sub>2</sub>S Recycling

In situ sulphur capturing is a well documented subject and is practiced mainly in coal combustion processes, particularly fluidised bed (Boardman and Smoot, 1993). The process involves the addition of sorbents, preferably limestone (CaCO<sub>3</sub>) and hydrated lime (Ca (OH)<sub>2</sub>) in the fluid bed (Boardman and Smoot, 1993). These materials decompose on heating to form CaO which can react with the gaseous sulphur species to form CaSO<sub>4</sub> and/or CaS (see equation 4.7 and 4.8) that can be disposed of safely with the ash (Boardman and Smoot, 1993).



XRD analysis of the “Bernice” gasifier fuel bed samples showed the formation of calcite in the gasifier. The fact that not all the calcite formed in the pyrolysis zone has decomposed or reacted in the hotter zones may present an opportunity for H<sub>2</sub>S recycling. The formation and survival of calcium sulphates

in the gasifier may also mean that the temperature in the ash/combustion zone may be below 900 °C where species like anhydrite begin to decompose. The challenge with this idea may be corrosion issues associated with the acidic H<sub>2</sub>S. However, it is possibly worth investigating.

#### 4.4.3.4. Oxygen Scavenging

Oxygen gas is one of the major cost items during fixed bed dry bottom gasification (Higman and van der Burgt, 2003). It has been shown by various authors, using Fact Sage thermo-equilibrium simulation, that mineral matter in the coal can, during fixed bed dry bottom gasification, capture some of the oxygen fed to the gasifier (Bunt and Waanders, 2008c; van Dyk *et al.*, 2008 and van Dyk, 2008). This occurs due to the formation of complex species containing a high number of oxygen molecules (e.g. anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), margarite CaAl<sub>4</sub>Si<sub>2</sub>O<sub>10</sub>(OH)<sub>2</sub>, cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>), ferro-cordierite (Fe<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>) in the gasification and combustion zones of the gasifier (Bunt and Waanders, 2008c; van Dyk *et al.*, 2008).

The residual oxygen profile in both the “Bernice” and “Albert” gasifiers was used to determine the beginning of the oxidation/combustion zone in these gasifiers – see Figure 4.4 and 4.7. In both cases, oxygen was found to increase in this reaction zone. Mineralogical characterization of the “Bernice” gasifier bed samples revealed the formation of oxygen containing species like bredigite (Ca<sub>7</sub>Mg(SiO<sub>4</sub>)<sub>4</sub>), gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>), akermanite (Ca<sub>2</sub>Mg (Si<sub>2</sub>O<sub>7</sub>)), nepheline ((Na,K)AlSiO<sub>4</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) etc. In addition, the glass phase which was found to be the dominating phase in the gasification and combustion zones composed mainly of alkali and alkaline earth aluminosilicates, with some iron – see Table 4.2. These aluminosilicates can also contain oxygen thus adding to the scavenging of the oxygen added as agent to the gasifier.

According to the results obtained using Fact Sage thermo-equilibrium simulation, between 12 and 20% of the oxygen fed to the gasifier as agent is captured in the ash minerals formed during the gasification of ND lignite

investigated in this study (van Dyk, 2008). The quantification is based on the increase in mass flow of the ash minerals (including the slag phase) in the gasification and combustion zones when compared to the devolatilization zone (van Dyk, 2008). The main crystalline phases reported by Fact Sage at 1150 °C in the combustion zone were found to be merwinite ( $\text{MgOCa}_3\text{O}_3\text{Si}_2\text{O}_4$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) (van Dyk, 2008). These species were found to be minor in the gasifier bed samples investigated in this study using XRD and SEMPC analysis. The accuracy of the quantification of oxygen scavenging using Fact Sage may therefore be questionable. However, it may be useful for indication purposes.

The plant/process data presented in Table 3.1 showed the steam and oxygen flows of 44700 kg/h and 7100 Nm<sup>3</sup>/h respectively. This amounts to a steam (kg): oxygen (Nm<sup>3</sup>) ratio of 6.3. When using this steam (kg):oxygen (Nm<sup>3</sup>) ratio to simulate the DGC gasification process with the proprietary and confidential thermodynamic model used at SLTC to design the gasifiers, a maximum temperature of 1389 °C in the gasifier is calculated. At this temperature, which is about 90 °C more than the flow temperature of the ash, slag formation and subsequent operational problems can be expected in the gasifier.

The expected steam (kg): oxygen (Nm<sup>3</sup>) ratio for the DGC gasifiers, determined using the SLTC proprietary thermodynamic model, is 7.5 with the gas composition presented in Table 3.1 and a maximum temperature of 1257 °C, which is within the operating window for the coal in question. Based on the steam (kg): oxygen (Nm<sup>3</sup>) ratio of 7.5 and 6.3 for the expected and the actual cases respectively, a simple calculation revealed a surplus of 1140 Nm<sup>3</sup> (i.e. 16% more) of oxygen that is fed to the gasifier as agent. This is most probably to compensate for the oxygen scavenged by the minerals. Coincidentally, the value of 16% falls within the 12 – 20% range of oxygen captured as determined using Fact Sage (van Dyk, 2008). Oxygen scavenging by the ash minerals therefore seems to be real in the case of the DGC operations. Further laboratory and plant investigations on different coals are therefore

recommended to validate these observations and to develop more accurate prediction tools for quantifying the oxygen capture phenomenon.

The SLTC proprietary gasification model does not take the ash composition/minerals interactions into account. Accurate quantification of oxygen capture can therefore help to improve this model.