Chapter 3

3. EXPERIMENTAL

In this chapter, the decommissioning and quenching procedure for the gasifiers prior to sampling is discussed. The sampling procedure as well as the methods used to characterise the fuel bed samples are also discussed.

3.1 Gasifier Quenching Procedure

Prior to sampling, it is critical that the gasifier be decommissioned and cooled sufficiently to avoid further reactions in the bed and most importantly for the safety of the sampling personnel. "Bernice" and "Albert" gasifiers were decommissioned and quenched by first stopping the flow of oxygen and coal, but continuing the flow of reaction steam to cool the bed. Once coal and oxygen flows were stopped, the gasifier outlet gas was piped to the start-up flare for disposal.

As the gas outlet temperature started to drop, the gasifier operating pressure was systematically ramped down to prevent condensation of steam inside the gasifier. Once the gasifier outlet temperature reached 110 °C, steaming was discontinued and replaced with a continuous flow of nitrogen which was continued until the gasifier outlet temperature dropped to about 38 °C. At this temperature, the gasifier was ready for sampling and therefore completely depressurised.

The quenching procedure was somewhat different to the method used by Bunt (2006) for sampling Secunda GG41 gasifier. In the case of GG41, the gasifier was steam cooled and depressurised. Start up air was then blown into the depressurised gasifier for about 16 hours to effect further cooling (Bunt, 2006). In the case of "Albert and "Bernice", nitrogen was used for further cooling due to the consideration of the higher reactivity and lower physical strength of lignite coal as well as the tendency of the lignite ash bed to form "mush" in the presence of liquid water.

The process conditions prior to decommissioning and sampling of the gasifiers are shown in Table 3.1. Comparison of "Albert" and "Bernice" gasifiers with Secunda GG41 is also made in the same Table 3.1. As expected, the oxygen load in the DGC gasifiers is lower when compared to Secunda. Due to higher operating pressure, the methane content in the DGC raw gas is higher when compared to Secunda. The gas outlet temperatures in the DGC gasifiers are also lower when compared to Secunda and this is also not unexpected for lignite gasification in a fixed bed gasifier. The trends of the process variables prior to and during decommissioning are depicted in Figures 3.1 and 3.2. Although the "Albert" gasifier was regarded as "sick" or unstable, the process conditions (i.e. the spikes on the graphs) show that the instability could be bearable.

Table 3.1. Process conditions prior to decommissioning and sampling of the gasifiers.

PROCESS VARIABLE	DGC – "Bernice"	DGC – "Albert"	[2]SECUNDA GG41
Coal feed rate (kg/h)	55 000	55 000	50 000
Steam flow (kg/h)	44 700	43 000	52 500
Oxygen flow (m^3N/h)	7 100	6 800	9 200
Blast temperature (°C)	329	332	344
Operating pressure (MPa)	3.16	3.15	2.85
Gas outlet temperature (°C)	232	221	550
Gas composition (vol %)			
CO_2	31.7	31.9	28.3
CO	15.1	14.4	23
H_2	41.0	40.8	39.7
CH_4	11.0	11.1	8.8
O_2	0.1*	0.2*	0
N_2 (by difference)	0.03	0.09	0.2
[1]Moisture in coal (wt %)	35.8	35.6	3.6
[1]Volatile matter in coal (wt %)	29.3	26.8	21.8
[1]Ash content in coal (wt %)	4.7	6.28	27.5
[1]Fixed carbon in coal (wt %)	30.2	31.3	47.1
Volatile matter (wt % DAF)	49.2	46.1	31.6
Rank	Lignite	Lignite	Bituminous
Steam (kg):Oxygen (m^3N/h) ratio	6.3	6.3	5.7
Coal (kg):Steam (kg) ratio	1.23	1.3	0.95

[1] Air dry basis for GG41 and as received basis for "Albert" and "Bernice"
[2] After Bunt (2006)
* May be associated with argon

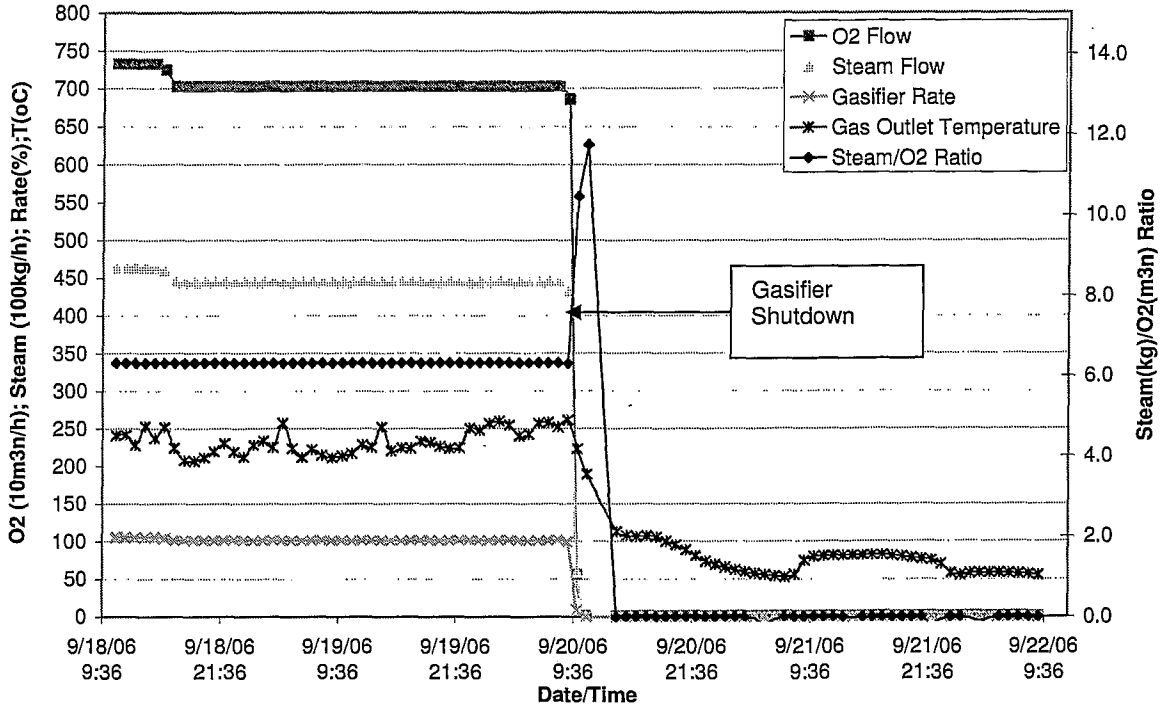

Figure 3.1. "Bernice" gasifier process variables (hourly averages) prior to and during decommissioning.

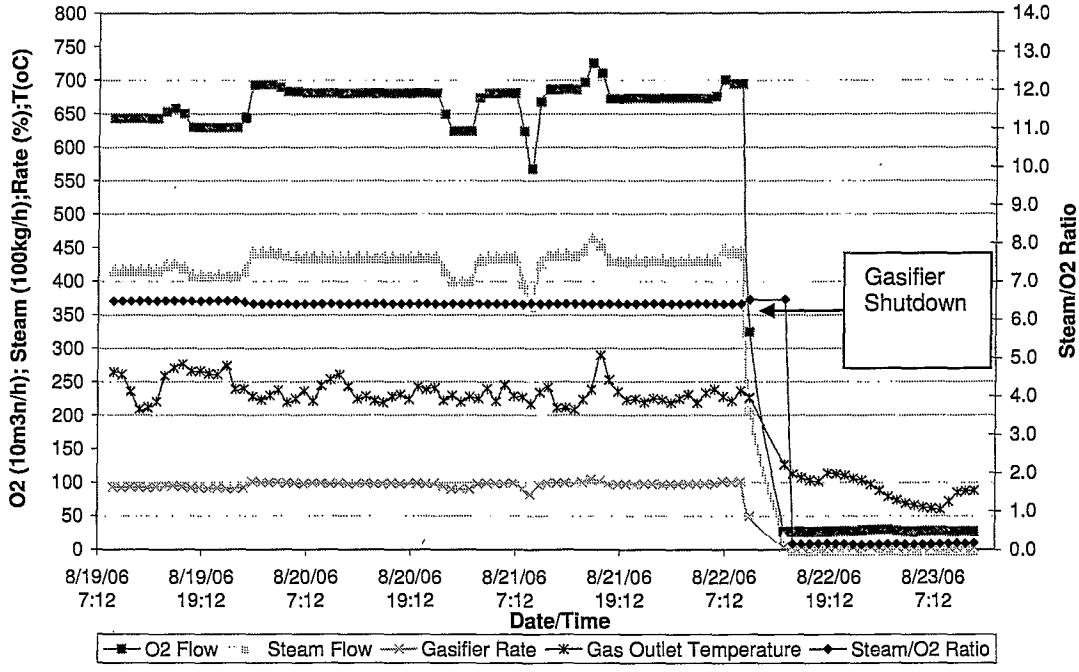

Figure 3.2. "Albert" gasifier process variables (hourly averages) prior to and during decommissioning.

3.2 Gasifier Sampling Method

The gasifier sampling methods (i.e. Dig-Out and Turn-Out) were discussed in chapter 2. A Turn-Out sampling methodology was however used in this study. A total of 27 samples were obtained from a quenched gasifier by running out the material in the gasifier bed through the grate into a 3 m^3 shovel/front end loader bucket. The sampling time increments were maintained at 30 minutes. The 27 x 3 m^3 increments were sub-sampled as for truck sampling into 200 litre drums under nitrogen gas.

The same method was used for sampling of the Secunda GG41 gasifier and although the dimensions of the gasifiers are the same, 32 samples were obtained in the Secunda GG41 case correspondent with the height of the MK IV gasifier (Bunt, 2006). However, 27 samples were obtained in the cases of "Bernice" and "Albert" gasifiers respectively, and this was most probably due to the difference in the packing density of the gasifier fuel beds. Figure 3.3 shows the relationship between the sample number and gasifier height. It can be seen in the figure that sample 1 relates to the bottom of the gasifier and sample 32 (or 27 in the case of "Bernice" and "Albert" gasifiers) relates to the top of the gasifier bed. Samples of the feed coal and ash were sampled prior to decommissioning of the gasifiers. The samples obtained from the "Bernice" and "Albert" gasifiers are depicted in Figures 3.4 and 3.5.

3.3 Characterization of the Samples

The samples were shipped to South Africa, split and prepared for analysis at the SABS laboratories in Secunda. The standard chemical, physical and petrographic analyses were conducted at the SABS, Sasol Technology R&D and DGC using the standard methods shown in Table 3.2. The CO_2 reactivity, thermal fragmentation, caking propensity and mechanical fragmentation of the samples were conducted at Sasol Technology R&D using the methods described and discussed in Section 2.3.4.

Sample No.	Sample Taken every (m)	Gasifier Height(m)
32	0.26	9.0
31	0.26	8.7
30	0.26	8.4
29	0.26	8.2
28	0.26	7.9
27	0.26	7.7
26	0.26	7.4
25	0.26	7.1
24	0.26	6.9
23	0.26	6.6
22	0.26	6.4
21	0.26	6.1
20	0.26	5.8
19	0.26	5.6
18	0.26	5.3
17	0.26	5.1
16	0.26	4.8
15	0.26	4.5
14	0.26	4.3
13	0.26	4.0
12	0.26	3.8
11	0.26	3.5
10	0.26	3.2
9	0.26	3.0
8	0.26	2.7
7	0.26	2.5
6	0.26	2.2
5	0.26	1.9
4	0.26	1.7
3	0.26	1.4
2	0.26	1.2
1	0.90	0.9

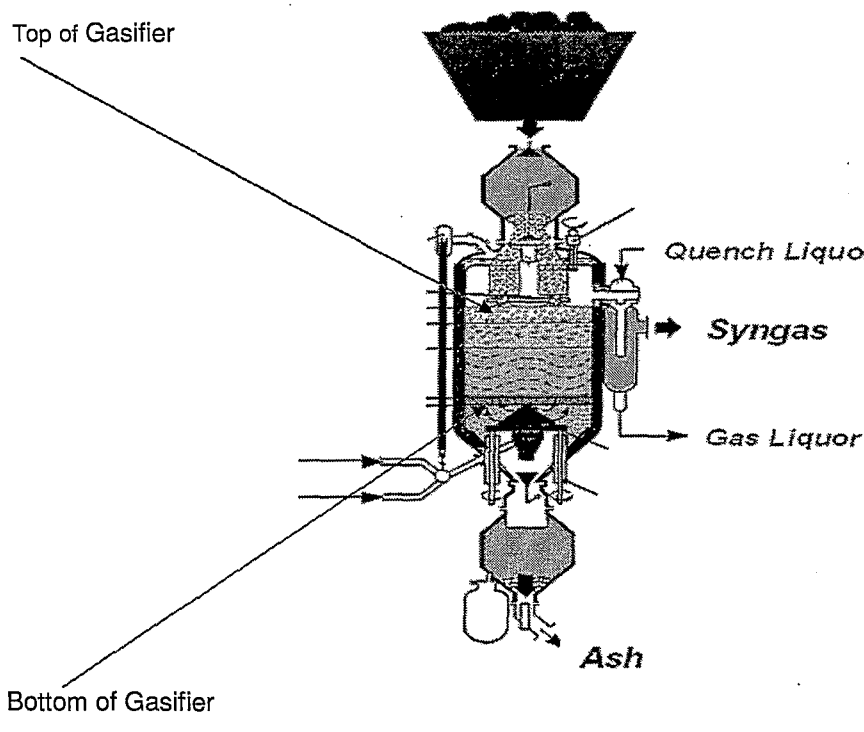

Figure 3.3. Relationship between sample number and the height of the MK IV S-L FBDB Gasifier (Bunt, 2006).

Table 3.2. Standard methods used for characterisation of samples obtained from the quenched gasifiers.

Coal Property	Standard Method
Proximate Analyses	
Moisture in analysis sample	SANS 5924 (1978)
Volatile Matter	ISO 562 (1998)
Ash	ISO 1171 (1997)
Fixed Carbon	By Calculation (FC= 100-(ash+Vol +Moisture)
Ultimate Analyses	
Carbon, Hydrogen, Nitrogen	ASTM D5373 (2002)
Total Sulphur	ASTM D4239 (2002)
Oxygen	By Difference (O = 100-(Moisture+Ash+C+H+N+S))
Fischer Assay	SANS 6073 (1984)
AFT	ASTM D1857 (2004)
Ash Composition	ASTM D3682 (2001) and ASTM D5016 (2003)
Particle Size Distribution	ASTM D4749 (1987)
Preparation of Petrographic Blocks	ISO 7404-2 (1985)
Maceral Group Analyses	ISO 7404-3 (1984)
Coal rank – vitrinite reflectance	ISO 7404-5 (1994)

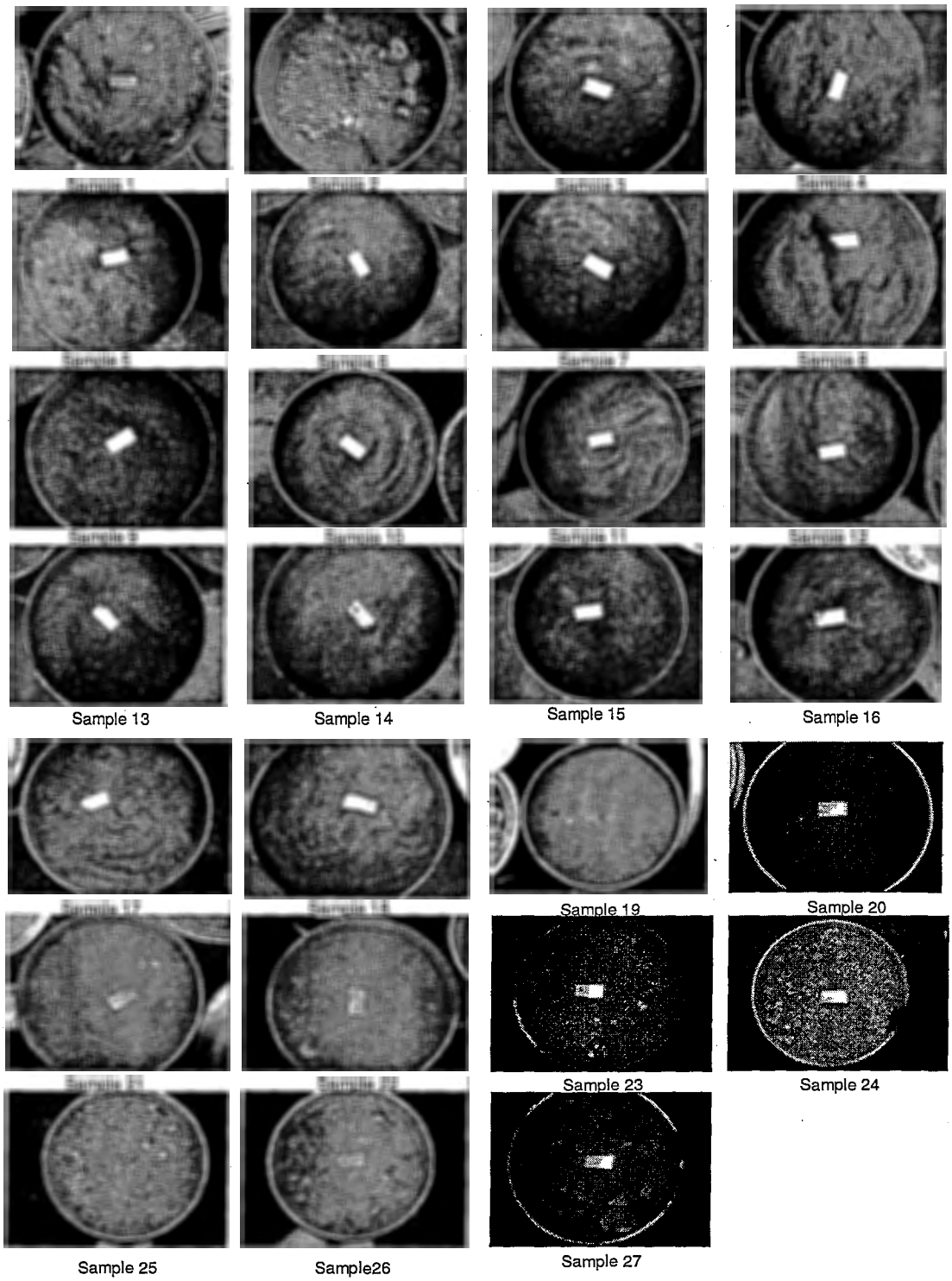

Figure 3.4. Pictures of the samples obtained from the "Bernice" gasifier.

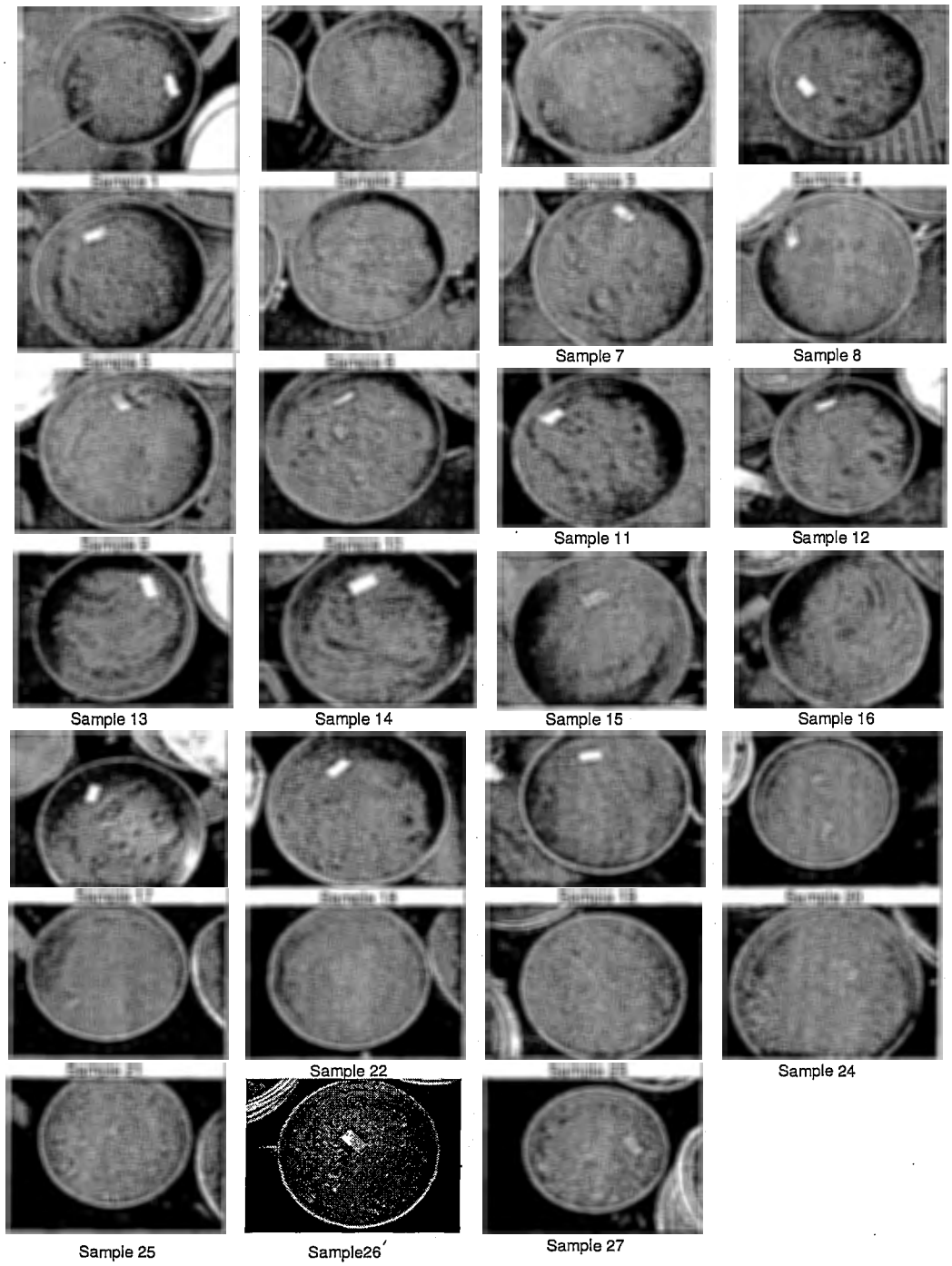

Figure 3.5. Pictures of the samples obtained from the "Albert" gasifier.

3.3.1 Char Morphology and Temperature Profile

Char morphology or carbon particle type analysis was conducted at the University of Witwatersrand (Wits). The petrographic blocks were prepared in accordance with ISO 7404-2 (1985). The particles in the samples were divided into two categories (coal/lignite and char) each of which had some sub categories as defined below (Wagner, 2007). The particles were then counted as per a normal petrographic analysis.

Lignite/ Coal Particles

I. Humite:

Conventional terms were applied to ***monomaceral*** *particles (>95% in particle/ 50 x 50 µm field of view (f.o.v.)). Subcategories:*
telohumite,
detrohumite,
gelohumite.

Intermediate *particles, or* ***bi-maceral*** *particles (<95% in particle / 50 x 50 µm f.o.v), exhibiting both telohuminite and gelohuminite (that is distinct cell wall structure infilled with gelified material) were termed* ***telogelohumite,*** *and* ***tri-maceral*** *particles (telo-, gelo-, detrohuminite) were termed* ***tri-humite.*** *Corpohuminites were apparent in these particles.*

II. Inertite

Mono-inertinite particles were termed ***inertite,*** *and mixed or intermediate particles with inertinite + huminite were termed* ***huminertite, or mixed coal.***

III. Mineral matter

Carbominerite particles*: 20 – 60% mineral matter bound within the organic structure in a particle / f.o.v*
Rock*: >60% mineral matter in f.o.v. / particle.*

Char particles

I. Devolatilized coal:

***Porous particles**: those particles exhibiting degassing as noted by the occurrence of pores within the organic structure, but where the particle does not exhibit a white shade typical of a char. In many instances the particle remains a comparable shade to the feed material, simply exhibiting pores, or swelling.*

***Reflectance change**: those particles which clearly show a change in the shade of the particle to a lighter shade relative to the particles in the feed sample, but not as white as a char particle. These particles do not show any degree of degassing in terms of pores, but are clearly being affected by the process.*

II. Char:

***Porous**: particles exhibiting thin walls, large pores, even sized pores.*
***Honeycomb**: particles exhibiting pores, wall thickness & pore size may vary through the particle.*
***Dense:** a significant proportion of the chars observed in the ND gasifier samples were observed to be dense particles. Hence this category was further subdivided.*

<20% pores is applied to particles which are essentially dense particles, but do show some degree of degassing / pore formation. These pores are generally small (<10 μm), dispersed in the particle, but only making up a small fraction of the particle (>25%). This category was created to differentiate between true dense particles, and dense particles that have potentially degassed to a small extent.

Solid is applied to dense char particles that show no signs of alteration due to heating beyond the change in shade of grey to white. The inherent coal structure is still visible, although the individual macerals are no longer distinct.

Cracked is applied to particles where distinct cracks (typically tapered, up to 20 µm thick, 50 µm long within a particle) are apparent. The particle has cracked most likely due to stresses from heating, but not swelled or degassed to form pores. Some cracks may open further during carbon conversion.

***Oxidised**: applied to particles where the whole charred particle has a yellowish or grey tinge, clearly distinct from the typical white char particles. These particles may or may not exhibit cracking, and or some degree of porosity. Zones are apparent around pores within these particles. The origin and behaviour of these particles is not yet understood.*

***Consumed char**: based on the previous work conducted, this term was applied to char particles showing a skeletal structure, which is almost completely consumed (Bunt, 2006).*

III. Mineral:

***Carbominerite:** 20 – 60% mineral matter bound within the organic structure in a particle/ f.o.v.*

***Heated minerals**: >60% mineral matter in f.o.v./particle showing clear signs of having been heated, i.e. change in colour, texture, structure, formation of crystal laths.*

The solids temperature profiles in the "Bernice" gasifier were estimated using the optical reflectivity of the chars (Bunt, Joubert and Waanders, 2008). A calibration curve was first constructed by heating, in a TGA, the feed coal samples to temperatures ranging from 100 °C to 1200 °C and thereafter measuring their reflectance. The reflectance of the char samples obtained from different heights of the gasifier bed was then measured and the temperatures intrapolated from the calibration curve.

The average temperature was determined from about 50 to 100 reflectance measurements per sample whilst the surface temperature (i.e. temperature on the surface of the particle) was determined as the mean of 15% of the highest reflectance measurements per sample. The peak temperature was determined as the highest reflectance measurement in a set of 50 to 100 reflectance measurements in a sample. Due to the cost and complexity of the measurements, only the samples from the stable "Bernice" gasifier were used for the determination of the temperature profile.

3.3.2. Mineralogical Analyses

The mineralogical characterisation was conducted at Microbeam Technologies Inc. (MTI) in ND, USA and the University of New South Wales (UNSW) in Australia. Given the cost of advanced mineralogical analyses, only 15 samples representing all the reaction zones in the "Bernice" gasifier (i.e. the more stable gasifier) were selected for characterisation.

XRD analyses were conducted by the University of New South Wales and to do the analysis, representative portions of 8 coal (lignite)/char samples (i.e. feed coal, samples 22, 17,15, 13, 11, 10 and 9) and 7 char/ash samples (i.e. samples 1,2,4,5,6,7 and ash) were pulverized to fine powder (<75 μm). The powdered coal samples were subjected to low-temperature oxygen-plasma ashing using an IPC 4-chamber asher and the mass percentage of low-temperature ash (LTA) determined in each case (Gluskoter, 1965). Each LTA, and also each of the pulverized char/ash samples, were analysed by X-ray powder diffraction using a Philips diffractometer with CuK-alpha or CoK-alpha radiation. Quantitative analyses of mineral phases in each LTA were made from the X-ray diffractograms using Siroquant™, commercial interpretation software written by CSIRO (Taylor, 1991) based on the Rietveld XRD analysis technique.

The other mineralogical analyses were conducted by MTI on the same samples analysed by XRD at UNSW. For morphological and automated SEM

analysis, each of the 16 samples was prepared and mounted. Mounting for morphological analysis involved mixing two grams of as-received sample with three grams of melted carnauba wax. This mixture was poured into a small rubber mold and, after solidifying, was topped off with epoxy. The epoxy was allowed to cure overnight, and the mounted sample was then polished to a one-micron grit. The polished samples were cleaned and coated with carbon to improve conductivity in the electron microscope. The samples were mounted in the carnauba wax because un-reacted coal particles are more discernable from the mounting medium than they are from epoxy.

The 7 char/ash samples (i.e. samples 1,2,4,5,6,7 and ash) were prepared for SEMPC (scanning electron microscopy point counter) analysis by crushing the sample material to a smaller and more consistent particle size (about <75 μm) and mounting the crushed sample in epoxy. These sample mounts were polished as previously described. SEMPC analysis is an automated SEM technique, in which X-ray spectra are obtained at points along a grid pattern on the surface of the polished sample. The size of the grid, and spacing between analysis points, is set up by the SEM operator; the remainder of the analysis proceeds automatically. Only the mounted deposit is analyzed; the epoxy mounting medium that surrounds and penetrates the deposit is excluded from the analysis automatically.

The data produced by the SEMPC technique consists of up to three hundred chemical analyses that correspond to specific locations on the grid. The SEMPC data is reduced using a database of the most commonly-occurring chemical phases in deposits. The reduced data is then used to report on the frequency (or weight percent) of chemical phases (including quartz, calcium silicate crystalline phases, carbonates, sulphates, and mixed aluminosilicate amorphous phases).

The 8 coal/char samples (i.e. feed coal, samples 22, 17,15, 13, 11, 10 and 9) were prepared for CCSEM (computer-controlled scanning electron microscopy) analysis by grinding to a -250 μm particle size, and then mounting the ground sample in carnauba wax as previously described. The

prepared coal/char samples were analyzed to determine size, composition, and abundance of mineral or ash grains using CCSEM. The elemental compositions and mineral sizes determined with CCSEM analysis were used to categorize individual coal mineral particles by size and type.

Scanning electron microscopy (SEM) morphological and point count (SEMPC) analyses were performed on the samples. Morphological analyses were performed to obtain high magnification images and chemical compositions of selected features in the samples. Such features might include: coatings on bed or ash particles; entrained metals; fine-sized bonding material; liquid bonding material; and other features of interest. Chemical compositions were obtained by performing X-ray analysis on the features identified; the X-ray spectra were quantified using reference files of standard analyses.