Study on the Structure and Gasification Characteristics of Selected South African Bituminous Coal in Fluidised Bed Gasification

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Abstract

The gasification characteristics of three South African bituminous coals were investigated in a bubbling fluidised bed reactor. The three coals are similar in rank, but two are inertinite-rich coals and the third has high vitrinite content. The microstructural characteristics of the parent coals and their resultant chars were determined using XRD, FTIR, Raman and petrographic analysis. The microstructural changes that occurred in the organic (maceral) and the inorganic (mineral) fractions of the selected coals were evaluated. The change in the carbon structure was correlated to the proportions of inertinite and vitrinite macerals in the coals. High vitrinite content resulted in an increase in the order of the disordered carbon structure after gasification and this lead greater graphitised ordered carbon structures. While a high inertinite content resulted in low or no structural transformation of the chemical structure. The transformation of inorganic mineral constituents of the coal was correlated to the amount of inerntinite present in the selected coals. Higher proportions of inertinite macerals and inertinitic chars resulted in higher proportions of melted minerals. This correlation could be well related to the fact that inertinites are known to burn at higher temperatures than vitrinites and for a longer time.

Key words: Inertinite-rich; Structure; Fluidised Bed Gasification,

Introduction

Coal is a heterogeneous material consisting of organic and inorganic matter. The organic matter is referred to as macerals while the inorganic matter is represented by minerals. The mineral matter occurs separately or is intimately associated with the carbonaceous materials (macerals) either as well as dispersed grains in various forms (Shiraz *et al.* 1995) or as inorganic elements within the organic structure (Matsuoka *et al.*2006). Mineral matter can account for up to 50wt% of a coal.

Coal gasification is a becoming attractive alternative for power generation since it offers higher efficiency and improved environmental performance than conventional pulverised fuel technology (Cousins *et al.* 2007). Fluidised bed gasifiers have the potential advantage that low-grade coals rich in ash and inertinites can be processed more efficiently than in conventional pulverised coal boilers. The higher efficiency that coal gasification offers could be used as a strategy for carbon abatement in the future.

A potential disadvantage of fluidised bed coal gasification is low carbon conversion in comparison to other types of gasifiers. This due to its low operating temperature (900-1050^{o}C) and rapid loss of reactivity (Collot, 2006 Cousins *et al.* 2007) The use of certain low grade coals characterised by high ash content and rich in inertinites presents a (further) challenge as a result of the presence of dense chars formed from the inert inertinites. In this type of gasifier, a better understanding of the forms of chars derived from inertinites and their reactivities at different operating conditions is clearly necessary.

The change in carbonaceous structure is stated to be one of the key factors that affect the rate of gasification (Sekine *et al.* 2006; Li, 2007). Also, given that the dispersion of mineral matter changes when there is a change in char structure and that minerals act as catalysts for coal gasification, these facts also impact upon the rate of gasification (Li, 2007). The change in carbonaceous structure is due to the modification of the organic and inorganic constituents of coal (Senneca *et al.* 1996;

Sekine *et al.*2006; Sheng, 2007). The different organic components present in coal react differently when gasified. Senneca *et al.* (1998) investigated the microstructural changes and loss of gasification reactivity of two types of coal, namely Ruhr coal (Ru) and a South African coal (SA) at different temperatures (900-1400^{O}C). These coal samples were similar in rank but different in the maceral composition. The Ruhr coal was reported to be vitrinite-rich and the South African inertinite-rich. The researchers observed that there were clear differences between the two coals and modification of their structures. They concluded that the cause could have been the difference in the inertinite and vitrinite content.

In addition to the organic component, Sheng (2007) and Jin *et al* (2009) observed that the inorganic component of coal can also have an effect on the evolution of the char microstructure. Jin *et al* (2009) reported that the melted minerals have a different structure relative to the parent coal. The structural alteration of melted minerals has a direct influence on carbon conversion. Carbon conversion is inhibited by aluminosilicate melts which cover the surface and block the pores of coal particles (Jin *et al.*2009). Melts with different structures have a different polymerisation degree which leads to different surface tension. The surface tension can be used to determine the contact of the melt and the char (Jin *et al*. 2009). A study showing the relationship between the organic (maceral-to-char) and inorganic (mineral-to-ash) components in coal including their structure and behaviour under various conditions will provide useful information on how to predict the behaviour of a particular coal/char submitted for fluidised bed gasification. Ultimately, it is anticipated that this would also assist in optimising gasifier operations.

For the above reasons, the current research seeks to explore the behaviour of three South African bituminous coals currently used as feed in local power stations and to establish their technical performance and structural changes in a fluidised bed gasifier. It is anticipated that this would provide new insights into the evolution of the typically high-ash inertinite-rich coals currently available on the South African domestic market. The study correlates the gasification performance of the selected coals and their derived chars against a range of chemical, physical and optical characteristics including mineral and maceral (and specifically inertinite) contents and their changes in chemical microstructures following gasification in a fluidised bed gasifier. Raman

spectroscopy and XRD analysis was used to examine the chemical carbon structure and minerals associated in the coal. FT-IR was used to determine the degree of polymerisation hence the contact between the chars and molten minerals. The relationship between the organic (maceral-to-char) and inorganic (mineral-to-ash) components in coal including their structure and behaviour was determined by a petrographic analysis.

Sampling, Methodology and Experimental work

Samples

Coal samples were taken from three different mines in South Africa and are typical of feed coal used in certain South African power stations. The coal samples are Matla, Duhva and Grootegeluk. The chemical, physical and petrographic properties of the coal samples are presented in Table 1

Table 1: Properties of the different coal samples

Sample	Matla	Duhva	Grootegeluk
Coal Proximate (wt%)			
Ash	44.00	39.20	35.70
Moisture	3.50	2.00	2.00
Volatile matter	19.90	19.60	27.30
Fixed Carbon(Calculation)	32.10	39.10	35.00
Coal Ultimate (wt%)			
C	39.09	46.93	49.20
H	2.90	2.87	3.87
N	0.92	1.10	0.97
O(Calculation)	8.60	6.38	6.79
S	0.66	1.42	1.47
Ash analysis			
SiO_2	58.91	53.08	68.60
Al_2O_3	28.76	20.18	20.05
Fe_2O_3	2.13	7.41	5.59
TiO_2	1.33	1.35	0.72
CaO	2.99	4.65	0.71
Na_2O	0.35	0.12	0.12
K_2O	0.76	0.89	1.25
SO_3	1.17	3.31	0.57
P_2O_5	0.22	0.73	0.08
Macerals analysis			
Vitrinite content %	36	24	83

Liptinite content %	4	4	5
Inertinite content %	59	71	12
Total reactives macerals %	56	55	96
Mean reflectance %	0.64	0.76	0.67
Microlithotype analysis			
Vitrite %	10	7	24
Liptite %	0	0	0
Inertite %	8	14	29
Intermediates %	22	24	23
Carbominerite %	29	24	18
Minerite %	17	28	23

Methods

The gasification experiments were performed at atmospheric pressure in a bubbling fluidised bed reactor. The apparatus had an operating limit of 950^{o}C and atmospheric pressure. The tests were conducted well within this limit. Details of the experimental plans and condition have been reported elsewhere (Engelbrecht, 2008).

Analysis of raw coal and char

The examination of the chemical carbon structure and minerals associated in the coal and char was carried out by XRD (X-ray Diffraction) in a Siemens D5000 powder diffractometer using Cu Kα radiation. The mineral phase was identified using the reference intensity ratio (RIR). RIR values were determined from PDF-2 date base (JCPDS-ICDD PDF-2, 2003). The chemical structure of the raw coals and chars was characterised by FT-IR (Fourier Transform Infrared) technique. FT-IR spectra were obtained with a Bio-Rad FTS-165 spectrometer. The relationship between the organic (maceral-to-char) and inorganic (mineral-to-char) components in coal including their structure and behaviour was determined by detailed petrographic analysis.

Results and Discussion

Carbon form analysis

In order to determine the gasification properties of the selected coals, a petrographic analysis was performed on the both the selected coals and their resultant chars, i.e. on the two inertinite-rich (Matla and Duhva) and the one vitrinite-rich (Grootegeluk) coals. The results are presented in Table 2.

The petrographic analyses conducted on the chars indicated that there is a far higher organic-matter-derived carbon content in the Grootegeluk char with little or no indication of melted minerals whilst the reverse is the case in the other two samples, namely, both Matla and Duvha chars showed low carbon contents and high proportions of melted minerals. The char-to-mineral matter proportions (organic constituents versus visible mineral matter as determined by volume in percentage terms) indicate that Grootegeluk has 64% organic matter (char) and only 20% melted/sintered minerals with 16% unchanged minerals. The other two samples, Duhva and Matla both have very low proportions of organic matter (chars, 16% and 6% respectively) and very high proportions of melted/sintered minerals (74 and 75% respectively), with 10-19% of unchanged minerals. Borrego *et al* (1997) and Wang *et al* (2009) reported similar results for inertinite-rich coals when exposed to ~~at~~ higher temperatures during pyrolysis and combustion tests undertaken between the temperatures of 600-1100^{o}C. The gasification temperature (900-950^{o}C) used in this study falls within this range.

Further analysis showed much higher proportions of melted minerals found in the two coals having higher inertinite contents (Duvha and Matla). Grootegeluk on the other hand has very low inertinite (12% relative to 59 and 71% in Matla and Duvha respectively) and very low melted minerals (20% relative to 74 and 75% in Duvha and Matla respectively). These results indicate a close correlation between the inertinite content and amount of melted minerals in the relevant chars.

From the microlithotypes analysis in Table 1, an attempt was made to correlate the proportion of the melted minerals in the various chars to the amount of minerals (and ash content?) in the parent coal. The results indicated a poor correlation (not shown). This suggests that there is little or no impact of mineral matter (or ash content?) on melted products but a significant relationship was found between the transformation of the organic fraction (maceral) and the inorganic fraction (mineral matter) during gasification. The effect of this relationship on the carbonaceous structure was investigated further.

Table 2: Petrographic Composition of Chars

CHAR	GROOTEGELUK 903°C	MATLA 935°C	DUHVA 918°C
Carbon form analysis - Total %			
Organic constituents/visible mineral matter			
Total organic material %	64	6	16
Relatively unchanged visible minerals %	16	19	10
"Melted" minerals % - penetrating/surrounding carbon	4	19	16
"Melted slag" minerals % - separate bodies	16	56	58
Total %	100	100	100

Structural characteristics of raw coals and chars

Aromaticity

Borrego *et al.* (1997) stated that the active site concentration in the molecular structure of chars depends on the aromaticity and the degree of molecular ordering in the parent maceral structure. The aromaticity factor was obtained from the expression in Equation 1 reported by Wang *et al.* (2009).

$$f_a = \frac{1200x(100 - V_{daf})}{1240xC_{daf}} \qquad \textbf{Equation 1}$$

Where f_a is aromaticity, V_{daf} is volatile matter on air dry basis and C_{daf} is carbon on air dry basis. The results are presented in Table 3. The results showed that Matla and Grootegeluk coals had the highest and the lowest aromaticity factor respectively. The results also showed there was an increase in aromaticity after gasification. This result correlates with the conversion level reported as total organic material in the chars in Table 2. These results are in agreement with those published for combustion by Lu *et al.* (2000).

These results also indicate that inertinite-rich coals are more aromatic than vitrinite-rich coals. Similar results have been reported by this Sun *et al*. (2003) and Wang (2009). However Duhva coal with higher inertinite contents (71%) had a lower conversion and lower aromaticity factor (1.66) in it chars than the Matla derived char (1.98) with 59% inertinite content and an aromaticity factor of 1,98. This might be due to difference in rank Although it was assumed that all coals were similar in rank,

their mean random vitrinite reflectances (Rov) were not exactly equal but spanned over the interval 0.64-0.76%. This suggests that for Matla and Grootegeluk with similar RoV values of 0.64% and 0.67% respectively, the high inertinite contents is the main factor that contributed to the higher aromaticity and high burnout level, while for Matla and Duhva with 0.64% and 0.76% Rov values, both the rank and inertinite content playing a role in the carbon conversion with the rank reducing the level of burnout.

Table 3: Aromaticity of the different coals and chars

Samples	Parent Coal	Char
Matla	1.98	57.88
Duhva	1.66	16.23
Grootegeluk	1.42	4.24

Coke Forms

The formation of coke indicates changes in the carbon structure of the coal/chars. Coke are graphitised ordered carbon. From the petrographic analysis carried out to determine the various types of chars, Grootegeluk coal formed a higher proportion of isotropic coke (50%), as compared to Matla and Duhva coals (28 % and 22% respectively).

Raman Analysis

The Raman spectra of the chars produced from the three different coal samples are presented in Fig 1-3. In all the Raman measurements the G and D bands were dominant and a weak 1124 cm^{-1} band was apparent. Qualitatively, the spectra for Duvha and Grootegeluk char are similar while spectra of the Matla char are different. The G band for both Duvha and Grootegeluk char is weaker than D band in contrast to that for the Matla char. A comparative study of the peak position, intensity and bandwidth of the three bands obtained after curve fitting is presented in Table 4. The parameters were used to evaluate the changes in the microstructure of the coal during gasification.

The D bandwidth of the three coal samples decreased after gasification thereby suggesting an increase in reordering of the amorphous carbon (Dong *et al*.2009).The most significant change was observed in Grootegeluk char. The D bandwidth decreased by 72cm-1, while that of the Duhva and Matla chars decreased by 20cm-1 and 5cm-1 respectively. These results indicate that increased ordering of the amorphous region can be correlated to the proportions of inertinite and vitrinite macerals in the coals. The Grootegeluk coal sample with high vitrinite content had the highest degree of ordering while the Duhva and Matla coals with high inertinite contents had low degrees of ordering. These results are in agreement with those reported by Sun et al (2003) and Wang et al (2009). They reported that inertinite macerals have higher thermal stability than vitrinite

On the other hand the G-band width which is related to the crystalline component in the coal shows that there was a decrease in the G-ban width of Grootegeluk coal after gasification but relatively no change for Duhva and Matla coal. This indicates that there was no significant growth in the crystalline component for Duhva and Matla chars however there was an increase in crystalline component for the Grootegeluk coal.

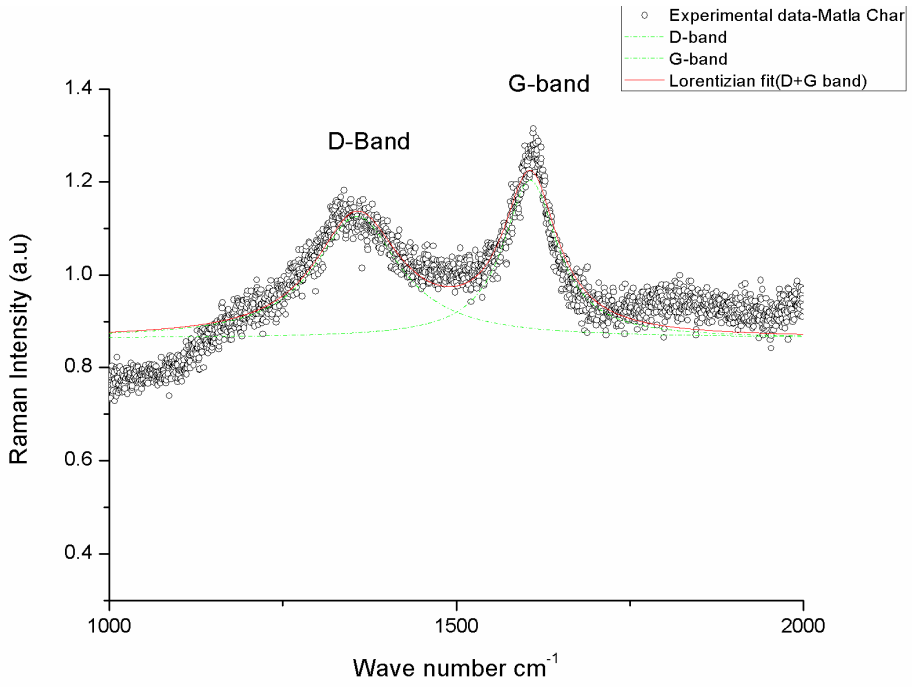


Figure 1: Raman spectra of Matla char with corresponding curve fitted bands

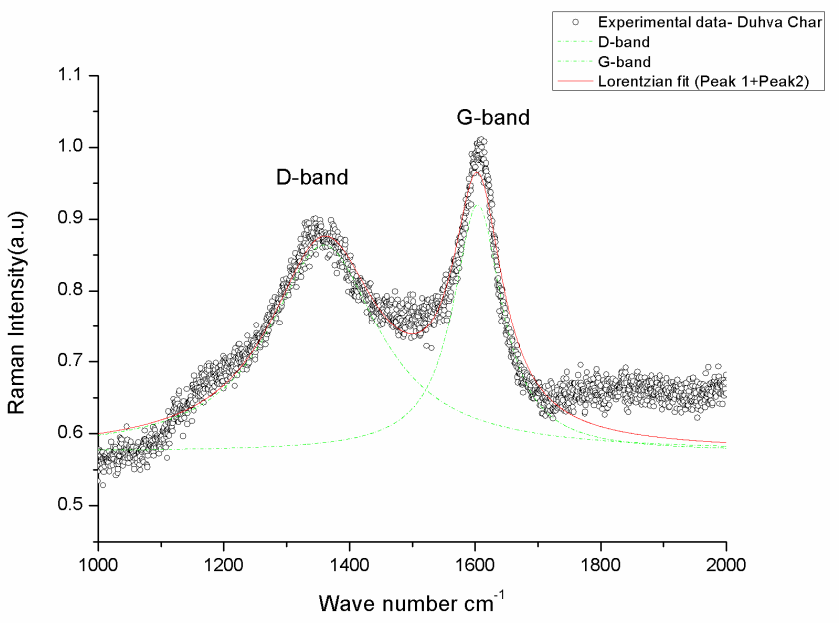


Figure 2: Raman spectra of Duhva char with corresponding curve fitted bands

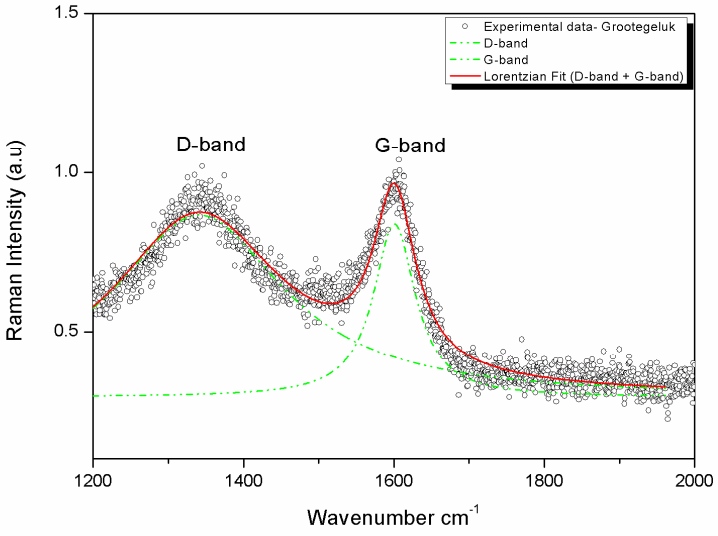


Figure 3: Raman spectra of Grootegeluk char with corresponding curve fitted bands

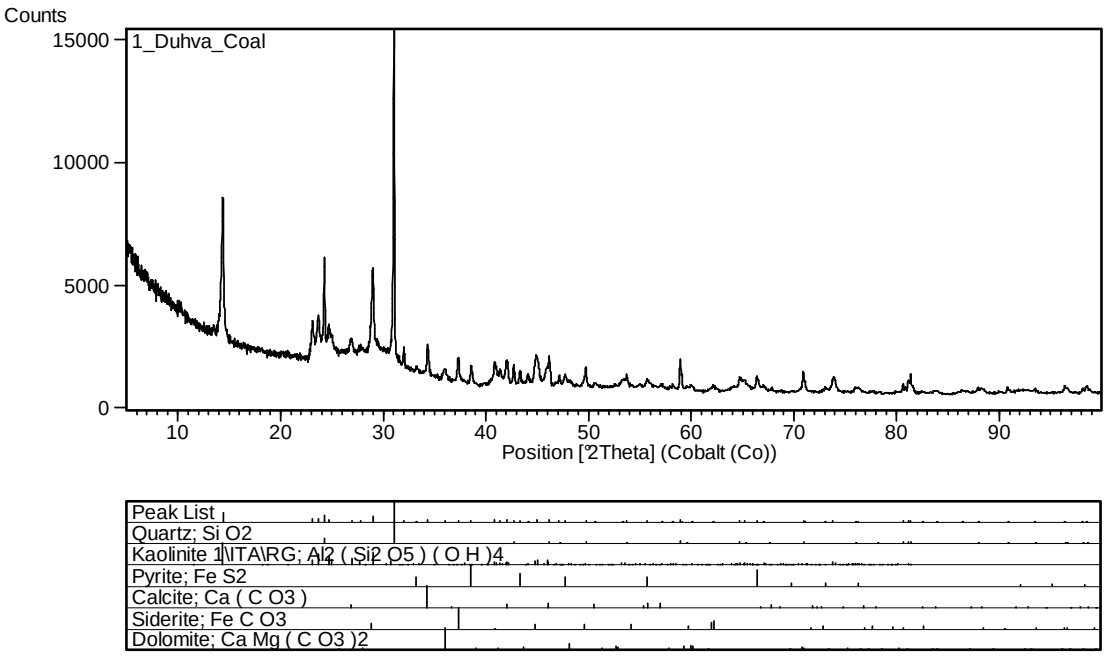
Table 4: Raman spectroscopic parameters obtained after curve fitting the experimental by using two-lorentzian bands (D and G).

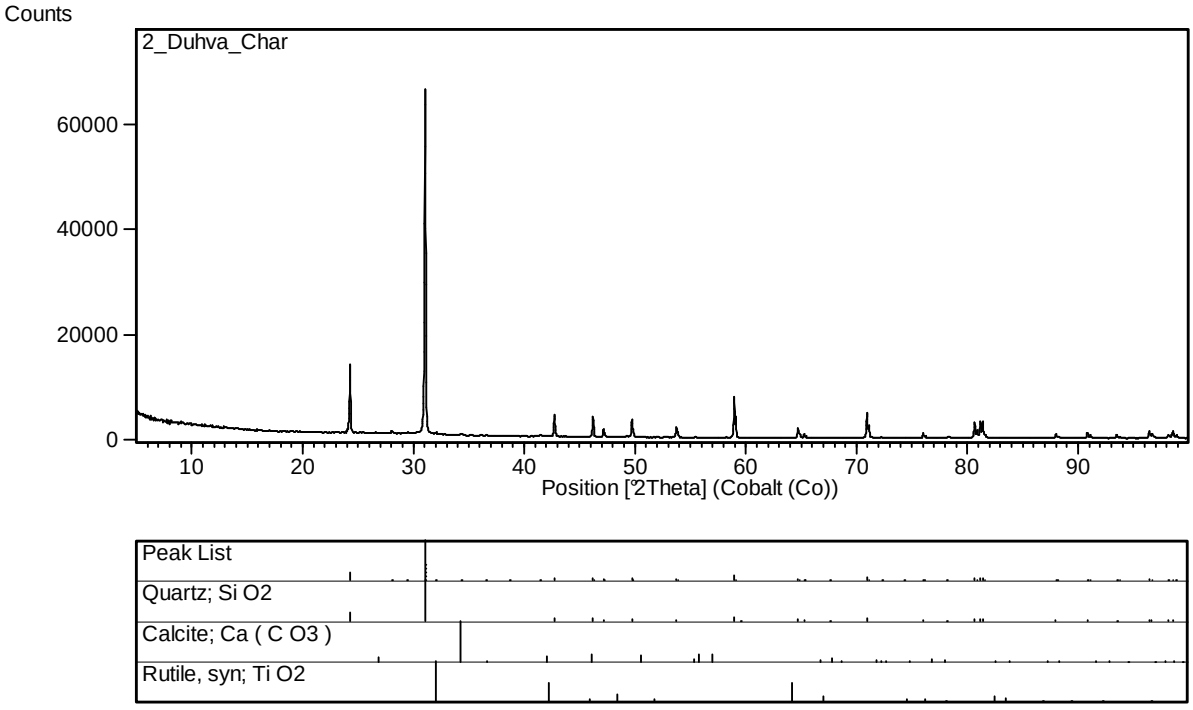
Samples	Peak position (cm-1)	Band width (cm-1)
Matla		
Coal		
D	1363	153.71
G	1604	92.39
Char		
D	1357	149.09
G	1606	94.57
Grootegeluk		
Coal		
D	1370	260.56
G	1597	87.10
Char		
D	1349	188.32
G	1600	69.54
Duhva		
Coal		
D	1348	224.61
G	1598	84.15
Char		
D	1359	204.42
G	1603	92.61

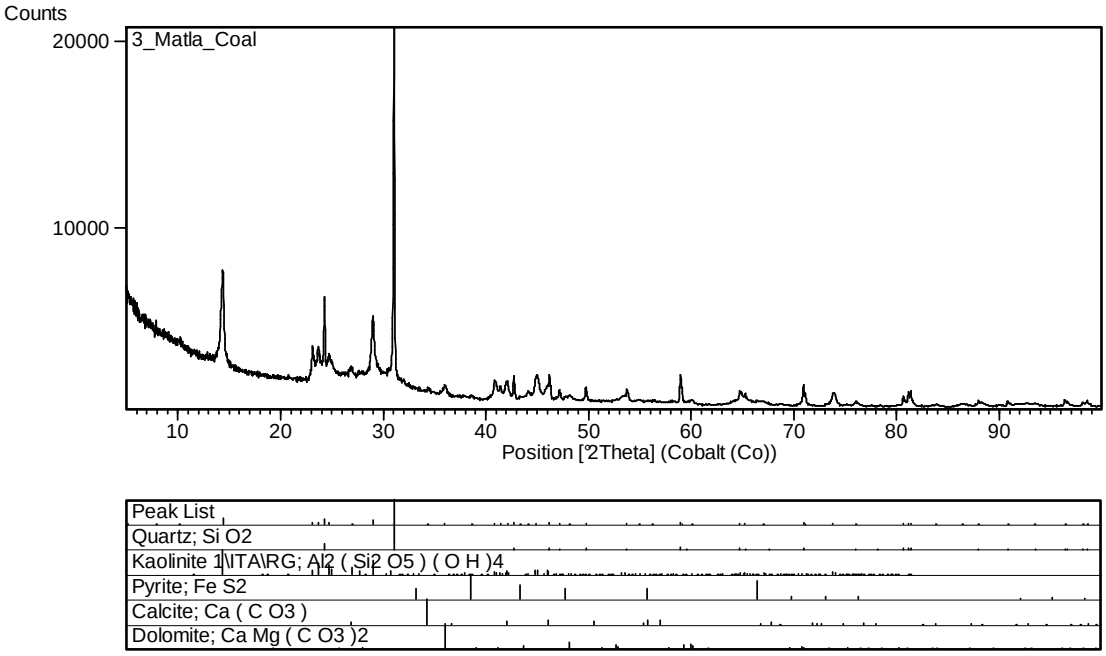
X-ray diffraction (XRD)

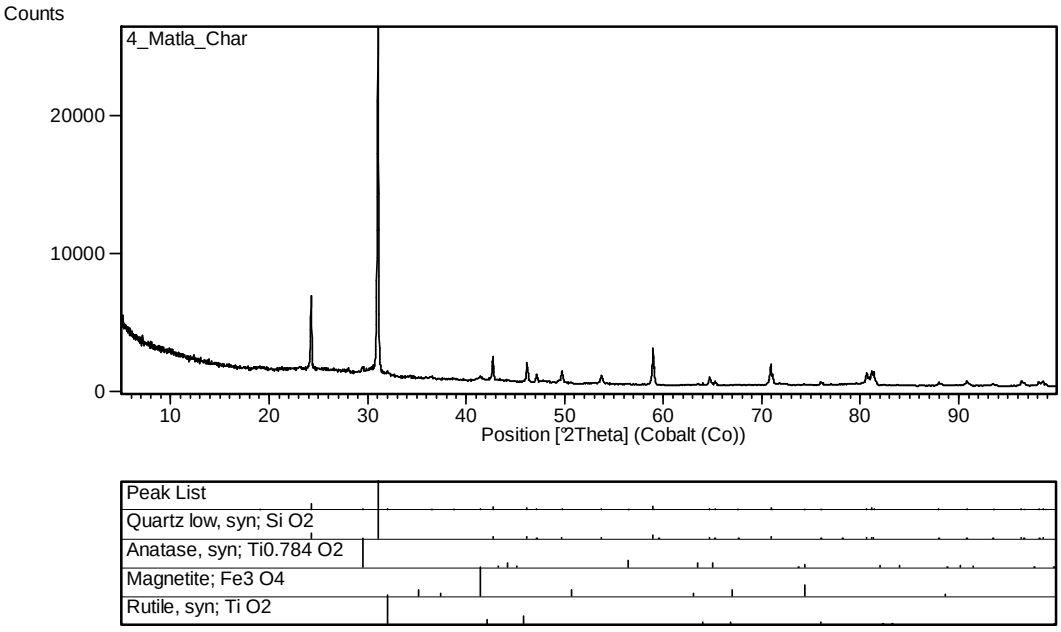
Some minerals appear to have melted and been transformed into molten ash. We need to investigate this matter further to see what minerals have changed. According to the XRD scans of the coals presented in Figure 4, The coals contain quartz, kaolinite, calcite, siderite, pyrite, and dolomite. After, gasification, all these minerals with the exception of quartz and siderite disappear from the spectra. The major transformation would appear to be the decomposition of the crystalline aluminosilicate minerals such as kaolinite to amorphous aluminosilicates. This observation is in agreement with Grigore *et al* (2008) who stated that amorphous aluminosilicates are produced from the dehydroxylation of kaolinite. Jin *et al* (2009) reported that the determination of the alteration of crystalline minerals to their melted forms can be used to indicate the amorphous phase of minerals after gasification

These observations are in agreement with the petrographic analyses of the chars as reported earlier, i.e. petrographic analysis reported that certain minerals had melted and been transformed into molten ash with some molten matter penetrating into cracks and pores in the chars. The presence of such mineral matter or “slag” which bordered, penetrated or engulfed carbon fragments accounted for 15% to 20% in the Matla and Duhva chars respectively, whereas only 5% was observed in the Grootegeluk char. Such inert mineral boundaries may be expected to severely reduce the ability of the carbon to further react.


Counts
1_Duhva_Coal
15000
10000
5000
0
10
20
30
40
50
60
70
80
90
Position [°2Theta] (Cobalt (Co))
Peak List
Quartz; Si O2
Kaolinite 1\ITA\RG; Al2 (Si2 O5) (O H)4
Pyrite; Fe S2
Calcite; Ca (C O3)
Siderite; Fe C O3
Dolomite; Ca Mg (C O3)2


Counts
2_Duhva_Char
60000
40000
20000
0
10
20
30
40
50
60
70
80
90
Position [°2Theta] (Cobalt (Co))
Peak List
Quartz; Si O2
Calcite; Ca (C O3)
Rutile, syn; Ti O2


Counts
3_Matla_Coal
20000
10000
10
20
30
40
50
60
70
80
90
Position [°2Theta] (Cobalt (Co))
Peak List
Quartz; Si O2
Kaolinite 1\ITA\RG; Al2 (Si2 O5) (O H)4
Pyrite; Fe S2
Calcite; Ca (C O3)
Dolomite; Ca Mg (C O3)2


Counts
4_Matla_Char
20000
10000
0
10
20
30
40
50
60
70
80
90
Position [°2Theta] (Cobalt (Co))
Peak List
Quartz low, syn; Si O2
Anatase, syn; Ti0.784 O2
Magnetite; Fe3 O4
Rutile, syn; Ti O2

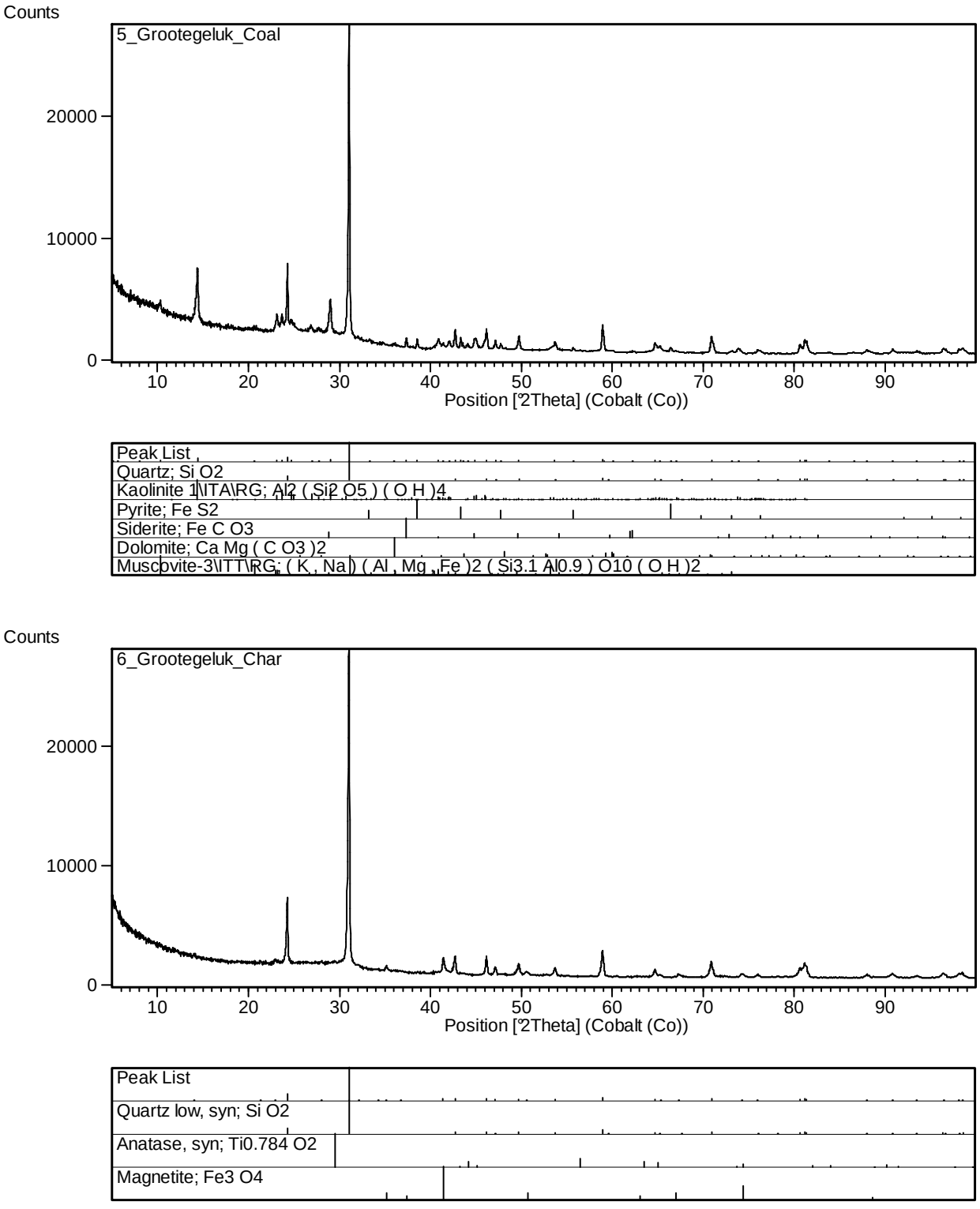


Figure 4: XRD pattern for the different coals and their chars

FT-IR Analysis

The alteration of molten mineral structure can be determined by the FT-IR technique (Sun *et al*. 1996; Jin *et al*.2009). Minerals in an amorphous phase have a higher degree of polymerisation and increased surface tension of the molten form. This determines the interaction between the char and the molten minerals (Jin *et al*.2009).

The FTIR spectrums of the coals under investigation and their chars are shown in Fig 5. The shift of the Si-O-Si band at 1000 cm-1 and the Si-O band at 845cm-1 represents the degree of polymerisation of the aluminosilicates. The graphs illustrate that the fine crystalline structure of the aluminosilicate minerals (between? 1000-600cm-1) weakened after gasification due to polymerisation and the presence of a non-crystalline phase. The Si-O symmetric vibration band moves to lower wave number and the Si-O-Si asymmetric stretching band moves to a higher wave number.

These observations indicate that the degree of polymerisation is higher (intensity virtually unchanged and therefore remains the same) in Grootegeluk char than in Matla and Duhva char thereby suggesting that the amount of molten minerals spreading on the char surfaces is lowest in the Grootegeluk char. This is in agreement with results obtained from petrographic analysis which showed 15% to 20% penetration of melted minerals in the Matla and Duhva chars and only 5% in Grootegeluk Char.

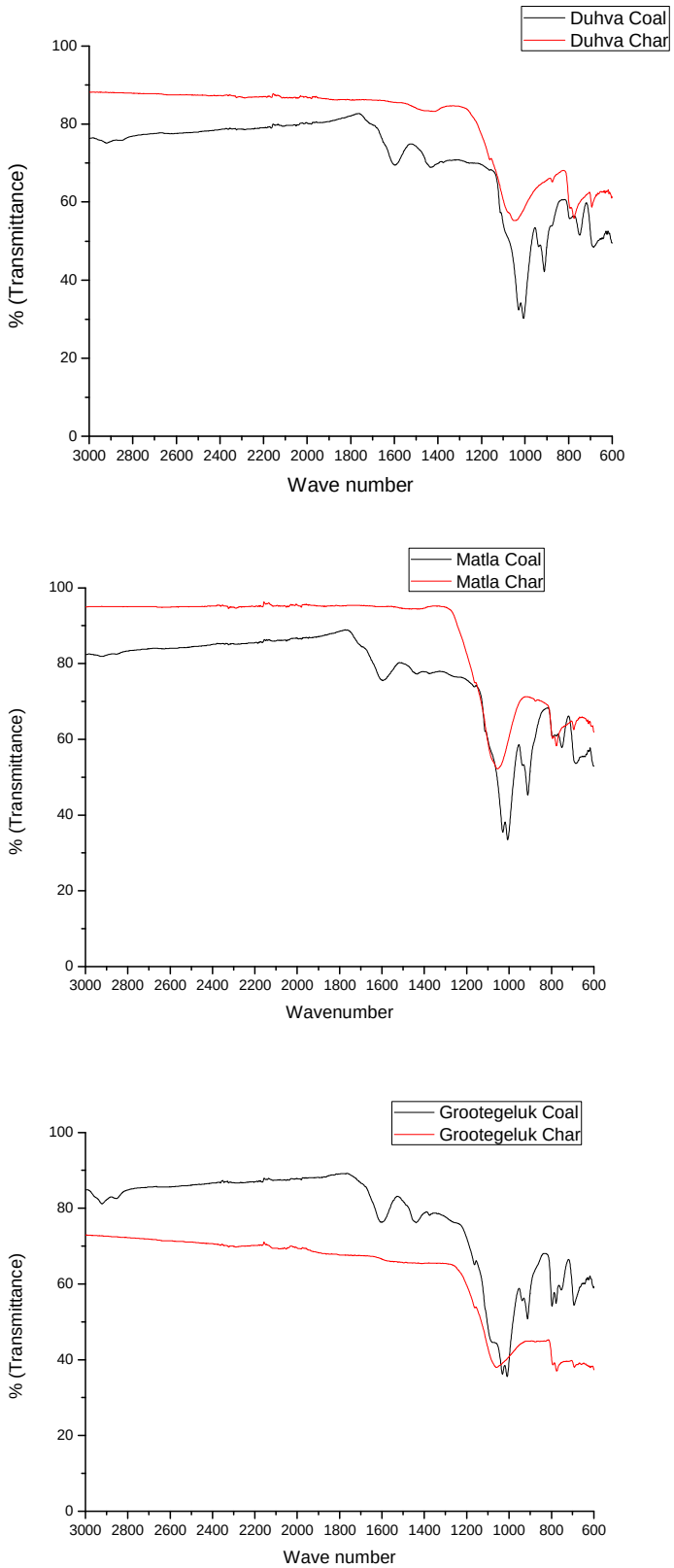


Figure 5 : FT-IR Spectra for the three coals and chars

Conclusion

The results of this study indicate that inertinite-rich coals experienced a greater degree of structural transformation into the disordered forms of char whilst the vitrinite-rich coal indicated that the vitrinite also became more graphitised during gasification.

In addition, the structural transformation of the crystalline form of the clay mineral, kaolinite, into an amorphous form as well as the disappearance of the carbonate minerals in all three coals after gasification correlated to the amount of inertinite present in the coals; i.e. the higher the proportion of inertinite in the parent coal, the higher the proportion of melted minerals in the char. This correlation supports the contention noted elsewhere (Falcon pers comm, 2009) that inertinites burn at higher temperatures than vitrinites and for a longer time resulting in the transformation of kaolinite to amorphous forms.

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