Characterisation of Coal and Chars in Fluidised Bed Gasification

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Abstract

There is currently a gap in the understanding of the morphological transformations experienced by high ash and intertinite-rich coals undergoing conversion to char during atmospheric gasification. In this study, work has been carried to characterise residual char generated from some selected high-ash South African coals. The selected coals are different in rank, maceral and mineral matter composition. Pilot-scale fluidised bed gasification tests were carried out on the selected coals within a temperature range of 900 to 935^{o}C.

Char residual remaining after atmospheric gasification in a pilot plant bubbling fluidised bed reactor were analysed by petrographic techniques, X-ray diffraction, scanning electron microscopy (SEM), EDX, Raman spectroscopy, BET N2 surface and Hg porosity techniques. These techniques revealed key features in the transformation of these coals to char during gasification.

Key words Coal Char; Fluid bed Gasification, Char Morphology,

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 known as minerals. The mineral matters can exist separately or be associated with the carbonaceous materials (macerals) as well as dispersed elements attached to the organic part (Matsuoka *et al.*2006). The mineral matter could account for 50 wt% and it is distributed in various forms (Shiraz *et al.* 1995). The combustion or gasification of coal involves the devolatilisation of the organic matter and the mineral matter leaving solid residues behind. The volatile matter from the organic matter is combustible while the volatile matter from the mineral matter is incombustible. Some of the sources of volatiles in the mineral matter are clays (H_2O), carbonates (CO_2) and pyrites (SO_2). Subsequent processes include, the homogeneous reactions of the volatile species with the reactant gases, and also heterogeneous reactions of the char with the reactant gases during which the ash is formed.

The ultimate structure of a char plays a significant role in determining its reactivity during combustion and gasification. The mechanism of char structural formation is not that straightforward (Tang *et al.* 2005). Char formation involves the loss of volatiles, the development of fluidity (in some coals), and the structural rearrangements in the solid phase (Cousins *et al.* 2007). Both the organic components and the mineral matter could play an important role in the formation of the char structure. During the gasification, the organic and inorganic matters undergo various chemical and physical transformations. The chemical transformation involves the change in the organic chemical structure while the physical transformation involves a change in the char morphology and porosity. Particles with different organic (maceral) constituents generate different types of char structure. Gilfillan *et al* (1999) reported that maceral group containing liptinite or vitrinite generate porous char structure, while those containing inertinite generate dense char structures. These only holds for monomacerals coal particles. Reports in the literature have shown that there is a high likehood that some coal particles have a strong maceral association (Yu *et al.* 2003, Tang *et al.* 2005; Everson et al. 2008). Yu *et al.* (2003) further reported that it is quite difficult to quantify the proportion of pure vitrinite, vitrinite-dominated, or inertinite dominated particles because current petrographic analysis is not given on coal particle number basis. So the question is how much vitrinite content might be required to form a particular type of char structure.

Coal particles that have a mixture of different maceral components will produce an abnormal coal structure (Tang *et al.* 2005). The maceral association introduce some degree of heterogeneity in the coal particle. This suggests that the coal particle no longer behaves as a homogenous array of particles having the same average composition. Gibbins *et al* (1999) suggested that the proportion of unfused particles frequently found in mixed-maceral particles cannot be attributed to the inertinite group macerals only due to the wide range of particles type that could be found in mixed–maceral particles.

The wide range of particles could also contain some mineral matter. The mineral matter exists as pure mineral particles (excluded particles) and included minerals minerals (mineral-organic association). The degree of association between the mineral matter and organic matter can be divided into three classes based on the concentration of the ash content. Wigley *et al* (1997) reported that particles containing less than 10 wt % ash are classified as organic–rich particles, while particles with 10-90 wt % ash are classified as organic-included minerals and particles with more than 90 wt % are called excluded minerals. In the report of Gibbins and his co-workers reported that mineral matter are frequently associated with the inertinite macerals. The mineral matter could also have an impact on the physical structure of the residual char. Both studies (Wigely *et al* 1997 and Gibbins *et al.* 1999) indicated that there are anomalies when burning coals with high degree of heterogeneity such as mixtures of organic materials (maceral association) and mineral-organic association. Yu *et al.* (2003) observed that during pyrolysis the ash grains remain solid and this affected the thermoplastic properties of the whole particle. The absence of fluidity was attributed to the high intertinite and ash content. These coal particles did not exhibit any softening and swelling. They concluded that in addition to the role of macerals in char formation, the ash content also has impact on the physical structure of the residual char.

In summary, the distinct burnout characteristics of coals could be attributed to the differences in the macerals and microlithotypes compositions, and mineral matter distribution (Gibbins *et al.* 1999; Cloke *et al* 2003; Choundhury *et al.* 2008).Hence, there is a need to understand the formation of char structure from coals with a strong maceral association and also with the presence of some significant amounts of mineral matter.

In this study, the physical and chemical transformation of char/ash residue generated from fluidised bed gasification test of several South African high-ash and inertinite-rich coal was characterised by scanning electron microscopy (SEM), coupled with energy dispersive X-ray analyser for particles chemical analysis, maceral/mineral combinations were analysed with a coal petrographic microscope. Raman spectroscopy and X-ray diffraction (XRD) to examine the carbon structure and mineral associated with the char/ash residue in order to understand the role of mineral matter in the structural reorganisation in the solid char.

Experimental

2.1Materials

Coal samples used in the gasification tests are some of the coal types used for power generation plants in South Africa. The selected coals are currently used as fuel for the Lethabo(New Vaal coal), Matla, Matimba(Grootegeluk coal) and Duhva power stations

2.2 Test facility

The fluidised bed gasifier consists of six main parts: (1) Coal feeding system (2) air and steam supply and preheated system (3) cyclone (4) gas sampling system (5) furnace; (6) gas distributor. A schematic diagram of the pilot plant is shown in Figure 1.

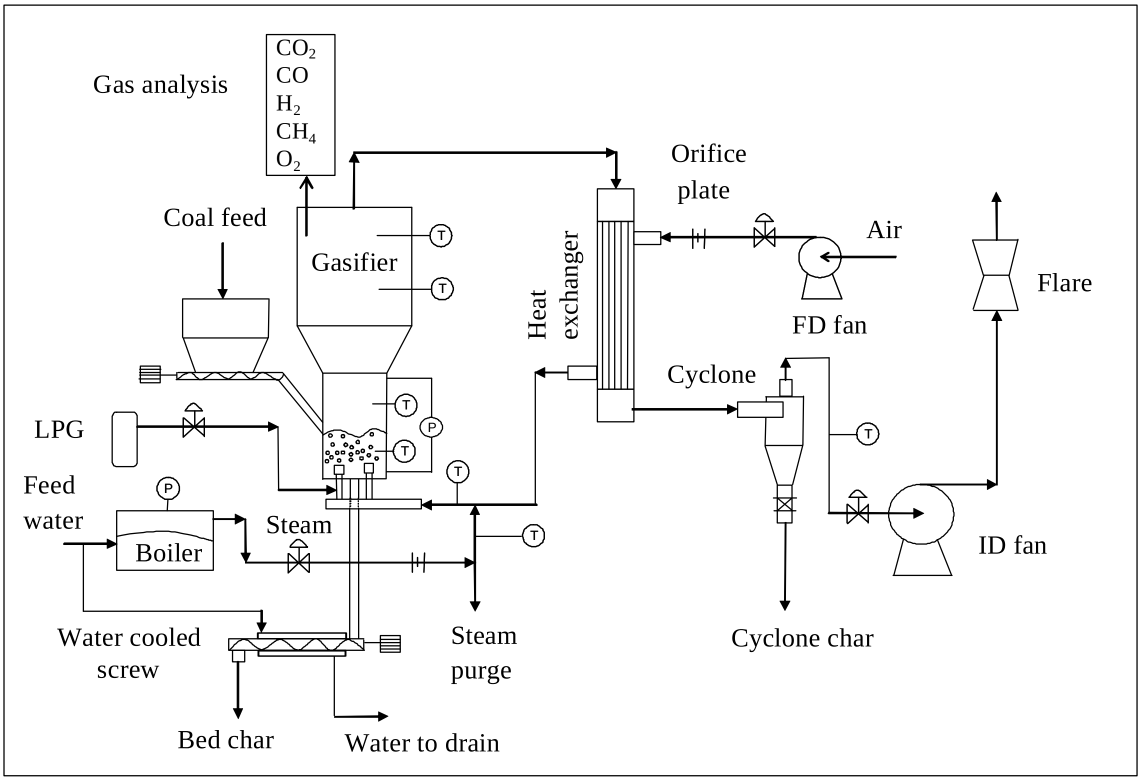


Figure 1. A schematic diagram of FBG pilot plant

Gasification of coal

Briefly, the gasifier is a refractory-lined reactor and has a 0.2 m x 0.2 m bed section, which expands to a 0.55 m x 0.55 m freeboard section. Full details of gasifier are presented in Table 1. While the operating conditions for the gasification tests are summarised in Table 2. Two different runs were carried for the different types of coal. Coal particles that enter the furnace via the coal feed chute drop into the fluidised bed section and start the conversion to gas and char. The char particles move rapidly up and down between the gasification and combustion zones in the bed. The combustion zone is limited to the lower 10-15 % of the bed above the air and steam distributor and is rich in oxygen. The bed temperature is controlled by increasing or decreasing the steam flow. If the steam flow drops below a minimum value (determined by the air/steam ratio), the air/coal ratio is adjusted. A minimum steam flow is required in order to prevent hot spots in the bed. The bed height is controlled by removing char. Char is removed from the bed (bed char) by means of a water-cooled screw conveyor and from the gas (cyclone char) by means of a cyclone which is placed after the gas cooler. The de-dusted gas is combusted (flared) before it is vented to atmosphere. All the char samples generated from the FBG were characterised by using a range of analytical tools including using X-ray diffraction, petrographic microscope, scanning electron microscopy (SEM)/EDX, Raman spectroscopy, BET analysis

Maceral,microlithotype analyses and reflectance measurements were carried out using Zeiss Universal microscope at a magnification X500 with oil immersion. Physical structural characterisation of char samples was carried out by nitrogen adsorption at 77k to determine the pore volume, surface area and pore size. All samples were degassed for a period of 8h at 25^{0}C prior to sorption experiments. Coal char morphology and cross-sections were examined analysis using JEOL JSM-840 and Philips XL30 scanning electron microscopes. SEM images were taken using a 20Kev accelerating for collecting images and collection of EDS spectra. For char morphology a small amount of char samples were mounted on adhesive tape and examined under the microscope. Samples for cross-sectional images were prepared by placing them into epoxy resins and polished for high image quality. The examination of the chemical carbon structure and minerals associated in the coal char was carried out by XRD (X-ray Diffraction) in a Siemens D5000 powder diffractometer using Cu Kα radiation. The change in the crystalline structure of the coal during conversion was quantified using a Raman spectroscope. Raman experiments were conducted with a Jobin Yvon Labram HR800 spectrometer using an Ar-ion laser as a source

Table 1: Specifications of the FBG pilot plant

Operating pressure	**Atmospheric**
Bed dimensions (m)	0.2 × 0.2 (square)
Freeboard dimensions (m)	0.55 × 0.55 (square)
Furnace height (m)	4 (2 m bed & 2 m freeboard)
Fluidised bed height (m)	< 0.6
Coal feedrate (kg/h)	18 - 30
Coal particle size (mm) (d_{50})	1 - 2.5
Coal CV (MJ/kg)	> 10
Air flowrate (Nm^3/h)	40 - 60
Steam flowrate (kg/h)	5 - 12
Bed temperature (°C)	850 - 950
Air temperature (°C)	155 - 210
Fluidising velocity (m/s)	1.5 - 2.5

Table 2: Gasification operating conditions

Coal	Bed temperature (°C)	Mean residence time of char (min)	Mean particle size (mm)[1]	Fluid-ising velocity (m/s)	Absolute pressure (kPa)	Gasification agents
Matla	935	36 - 37	1.6	1.9 - 2.2	90	O_2 & steam
Grootegeluk	903	45 - 46	1.9	1.9 - 2.2	90	O_2 & steam
Duvha	918	35 -36	1.7	1.9 - 2.2	90	O_2 & steam

Results and Discussion

Analysis of char yield

Table 3 shows the amount and particle size of the char that was generated from the different types of coal. From the results obtained, higher amount of char was collected from the cyclone. Cyclone chars accounts for 43-70% of the total char collected for the different types of coal was the bed. The results are consistent with the results reported by Xiao *et al*. (2007), they obtained 42- 62% of fly ash and while remaining char was collected from the bed during the partial gasification of high-ash Chinese coal in a pilot plant. The data also shows that the mean particle sizes of the various residual char were smaller than the feed coal and the particle size of the bed char were higher than the particle of the cyclone char. The chars from the cyclone were mainly fines. Thermal shattering and attrition of the coal in the bed could results in the generation of fines that are eventually elutriated from the gasifier. There was no direct relationship with the percentage of char elutriated to the cyclone and the fixed carbon conversion, but further analysis on the amount of carbon in the elutriated char suggest there is a relationship between the loss of carbon–rich fines and carbon conversion. This is also agreement with report of Xiao *et al.* (2007).

The highest percentage of the unconverted char on a carbon basis in the bed was observed for the Grootegeluk coal and while the lowest percentage was generated in the Malta coal. Similar results were obtained for the char recovered from the cyclone.

While there are reports in the literature that shows that the fixed carbon conversion of the lower-rank coals is higher than for the higher-rank coals. Although in this study the lowest rank coal (Matla) had the highest carbon conversion, the results obtained in this study suggest that there is no a direct relationship with the value of the vitrinite random reflectance and the fixed carbon conversion. Duvha coal higher in rank than Grootegeluk produced almost the same carbon conversion. Possible reason for this might be the difference in the maceral composition (Further discussion will be provided in the petrographic analysis section).

Table 3: Analysis of char yield

	New Vaal		**Matla**		**Grootegeluk**		**Duvha**	
Test number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Coal particle size – d_{50}			1.3	1.3	2.1	2.1	1.4	1.4
Char residence time (min)			37.4	37.6	41.7	41.7	36.	36.6
Carbon in bed char (%)			2.0	2.0	24.8	24.4	12.	12.0
Bed char particle size			0.4	0.4	1.1	1.0	0.6	0.6
Carbon in cyclone char			12.3	12.0	31.0	27.0	38.	38.9
Cyclone. char particle size			0.05	0.07	0.07	0.07	0.0	0.08
Char elutriated to cyclone			52.8	53.6	42.1	42.6	67.	67.9
Fixed carbon conversion (%)			89.4	89.0	66.2	67.0	69. 0	69.7

Proximate and ultimate analysis

Results consisting of proximate and ultimate analyses together calorific value of the parent coals and chars are presented in Table 4. The ash content of the different coal samples ranges from 33.4- 40.4 wt %, the calorific value was between 15.1-7 and 21.1 MJ/kg and the volatile matter varies from 19- 24.90%. The Results shows that the selected coals have low calorific values and high ash contents, and are therefore low in grade (Grade D). Also, the inherent moisture and oxygen contents indicate that the coals are bituminous in rank.

One of the key factors that determine the formation of char is the amount of volatile matter released. From the results presented in Table 4, there was a significant reduction of volatiles in all the chars. The total volatile yield was about 96%. Although there no significant difference in the total volatile yield for the three chars (94-96%), there was a significant difference in the morphology of the chars. Possible reasons for this will be provided in the Char morphology Section.

Table 4: Proximate and ultimate analysis and calorific value

Coal		New Vaal	Matla	Grootegeluk	Duvha
Proximate analysis	Standard				
Ash content (%)	ISO 1171	40.40	33.40	36.40	40.00
Inherent moisture (%)	SABS 925	5.80	3.50	2.00	2.10
Volatile matter (%)	ISO 562	19.20	21.00	27.80	20.10
Fixed carbon (%)	By diff.	34.60	42.10	35.60	39.10
Calorific value					
Calorific value (MJ/kg)	ISO 1928	15.07	18.60	19.80	21.10
Ultimate analysis					
Carbon (%)	ISO 12902	42.58	50.66	51.96	58.70
Hydrogen (%)	ISO 12902	2.19	2.65	3.15	3.33
Nitrogen (%)	ISO 12902	0.89	1.07	0.99	1.27
Sulphur (%)	ISO 19759	0.69	0.74	1.50	1.10
Oxygen (%)	By diff.	7.54	7.97	5.85	3.14
Bed Char		**New Vaal**	**Matla**	**Grootegeluk**	**Duvha**
Proximate analysis	Standard				
Ash content (%)	ISO 1171			75.10	93.60
Inherent moisture (%)	SABS 925			2.10	0.60
Volatile matter (%)	ISO 562			0.90	1.00
Fixed carbon (%)	By diff.			23.50	5.30
Calorific value					
Calorific value (MJ/kg)	ISO 1928				
Ultimate analysis					
Carbon (%)	ISO 12902				
Hydrogen (%)	ISO 12902				
Nitrogen (%)	ISO 12902				
Sulphur (%)	ISO 19759				
Oxygen (%)	By diff.				
Cyclone Char		**New Vaal**	**Matla**	**Grootegeluk**	**Duvha**
Proximate analysis	Standard				
Ash content (%)	ISO 1171			69.10	52.90
Inherent moisture (%)	SABS 925			1.70	2.40

Volatile matter (%)	ISO 562	1.50	2.40
Fixed carbon (%)	By diff.	28.80	42.40
Calorific value			
Calorific value (MJ/kg)	ISO 1928		
Ultimate analysis			
Carbon (%)	ISO 12902		
Hydrogen (%)	ISO 12902		
Nitrogen (%)	ISO 12902		
Sulphur (%)	ISO 19759		
Oxygen (%)	By diff.		

Petrographic analysis

The reflectance and type of macerals present in the parent coal could have an effect on the char properties (Jones *et al.* 1985). The results of reflectance properties and the petrographic composition for the selected coals and its char are presented in Tables 5 and 6.

Reflectance properties

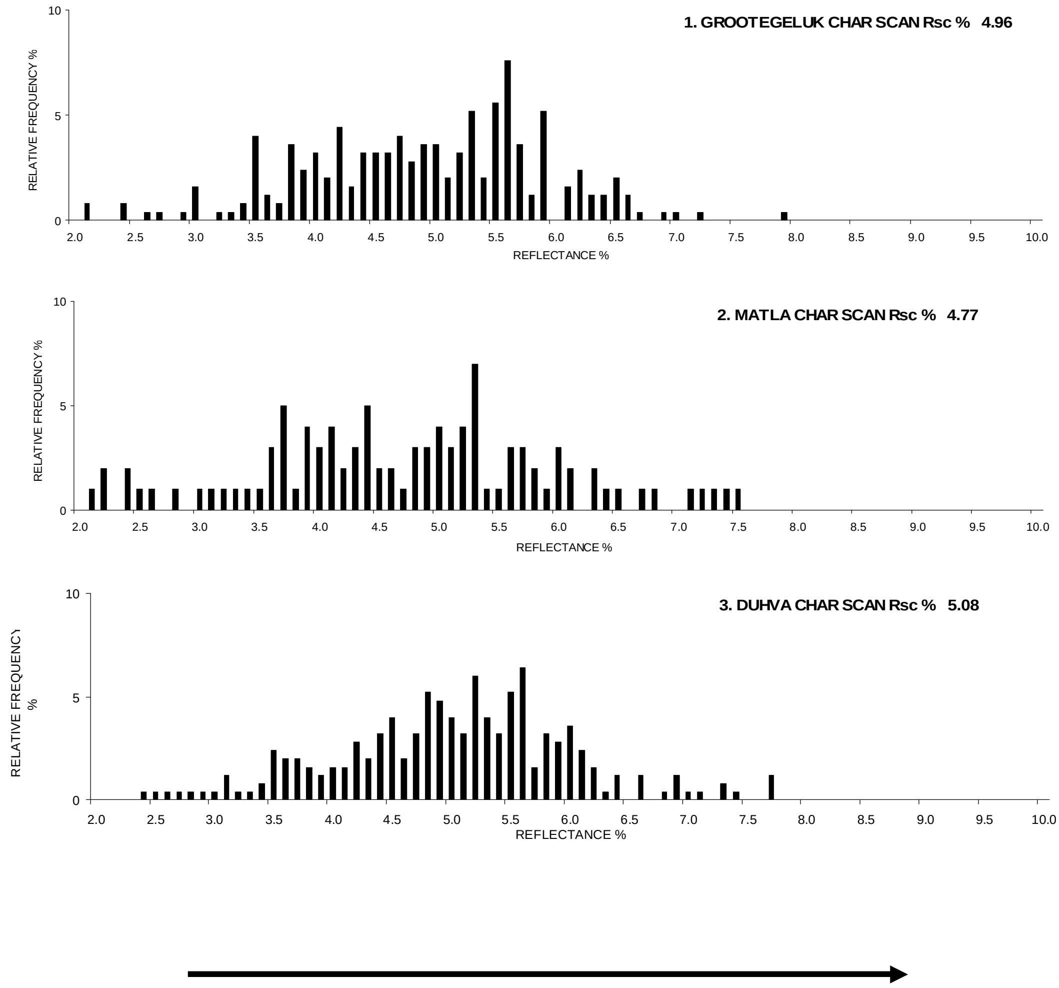
The vitrinite random reflectance data showed that, according to the ISO 11760 - 2005 Classification of Coals, the 3 original parent coals were characterized as bituminous, Medium Rank C coals, with mean random reflectance values within the range of 0.64% up 0.76% Rr. In order to asses the reactivity of the organic constituents during the char forming process, reflectance measurements taken on the all the organic char components. The results are shown in Figure 2. The mean reflectance increased from 0.67 to 4.96% for the Grootegeluk char, for Malta char it increased from 0.64 to 4.77 and Duhva from 0.76 to 5.08 5 . Overall mean scan reflectance values had shifted dramatically towards substantially higher ranges of the order of 5% Rr as a result of the temperatures applied. Approximately 15% to 30% of carbon particles exhibiting substantially lower levels of reflectance representing partially consumed char were encountered.

Table 5: Summary of the Major Petrographic Properties of the Parent Coals

	GROOTEGELUK	MATLA	DUHVA
PARENT COAL			
RANK (degree of maturity) **ISO 11760-2005 Classification of Coals**	**Bituminous Medium Rank C**	**Bituminous Medium Rank C**	**Bituminous Medium Rank C**
Mean random reflectance of vitrinite %	**0.67**	**0.64**	**0.76**
Vitrinite-class distribution Standard deviation, □	**V 5 to V 8** **0.067**	**V 5 to V 9** **0.078**	**V 5 to V 10** **0.090**
Abnormalities	**None observed**	**None observed**	**None observed**
PETROGRAPHIC COMPOSITION (% by volume) **Maceral analysis (mineral matter-free basis)**			
Total reactive macerals %	**91**	**56**	**55**
Vitrinite content % Liptinite content % Total inertinite % Heat altered (coke, char etc.) %	**83** **5** **12** **0**	**36** **4** **59** **1**	**24** **4** **71** **1**
Maceral analysis - Total %	**100**	**100**	**100**
Microlithotype analysis (mineral matter basis) Vitrite % Liptite % Inertite % Intermediates %	 **24** **0** **8** **22**	 **10** **0** **14** **24**	 **7** **0** **29** **23**
Visible minerals Carbominerite % Minerite %	 **29** **17**	 **24** **28**	 **18** **23**
Microlithotype analysis - Total %	**100**	**100**	**100**
Condition analysis "Fresh" coal particles % Cracks and fissures % Severely weathered % Heat altered (e.g., coke/char) %	 **84** **14** **2** **0**	 **78** **19** **2** **1**	 **83** **15** **1** **1**
Condition analysis - Total %	**100**	**100**	**100**

Table 6: Summary of the Major Petrographic Properties of the Chars

CHAR	GROOTEGELUK 903°C	MATLA 935°C	DUHVA 918°C
REFLECTANCE PROPERTIES			
Mean scan random reflectance %	**4.96**	**4.77**	**5.08**
Range of readings %	**2.1 - 7.9**	**2.1 - 7.5**	**2.4 - 7.7**
Standard deviation, □	**1.001**	**1.230**	**0.993**
Percentage of measurements Rr < 4%	**18**	**27**	**15**
Percentage of measurements Rr > 4%	**82**	**73**	**85**
PETROGRAPHIC COMPOSITION (% by volume)			
Carbon form analysis			
Isotropic coke - thin walled, very porous %	**22**	**18**	**16**
Isotropic coke - thick walled, porous %	**28**	**10**	**6**
Mixed porous %	**14**	**16**	**21**
Relatively unchanged inertinite %	**12**	**27**	**33**
Partially consumed carbon %	**18**	**20**	**11**
Organic/inorganic associations % (minerals 25%-50%)	**6**	**9**	**13**
Carbon form analysis - Total %	**100**	**100**	**100**
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**
Char particles size (microns)			
< 10 %	**12**	**15**	**15**
10 - 25 %	**11**	**10**	**8**
25 - 50 %	**11**	**21**	**5**
50 - 100 %	**11**	**18**	**7**
100 - 200 %	**9**	**12**	**18**
> 200 %	**46**	**24**	**47**
Total %	**100**	**100**	**100**



Increasing reflectance, decreasing volatiles, expected Increase in ignition temperature and time for burn-out

Figure 2; Coal/Char total maceral reflectance histogram

Petrograhpic composition

The results revealed that the char's samples represented different mixtures of partially reacted coal, "char', coke and visible mineral.

- **PARTIALLY CONSUMED CARBON**

Photomicrographs of partially consumed carbon are presented in Figure 3. This material was of reflectance levels above those of the original parent coal vitrinites, but substantially lower than those of the bright "clean" carbons. These darker appearing particle edges and inner zones had been partially "eaten away".

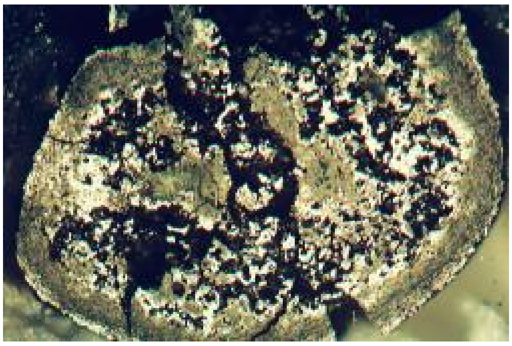


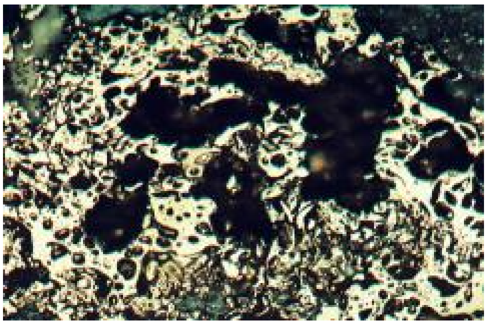
Figure 3: Partially consumed carbon body with darker borders and zones

- **CHAR FORMS**

Photomicrographs of mixed porous from reactives-rich coal particle and inertinite showing extensive cracking Figures 4a and b.

a) Mixed porous – derived mainly from intermediate microlithotypes in the parent coal. Those networks which had developed from reactives-rich coal were fine-walled and had "opened up" to varying extents, providing high internal surface areas. Thicker-walled and less porous networks had formed from inerts-rich parent coal particles.

b) Relatively unchanged Inertinites - derived from inert coal macerals in the parent coal which had not softened, expanded and “opened up” to any very appreciable extent on processing, largely retained their original coal maceral shape and form. These carbons were also commonly pitted with tiny open pores, providing some fine porosity.



(a) **(b)**

Figure 5a Mixed porous from reactives-rich coal particle and (b) inerts-rich coal particle

- **COKE FORMS**

They are derived mainly from “pure” vitrinite, i.e., vitrite, in the parent coal. Typical features of isotropic coke forms are shown in Figures 5a. When heated during the charring process, the vitrinites and other reactive coal macerals soften and degasify, creating pores. As the released gases within the pores increase in volume, the softening walls expand and the material increases in volume and surface area. The "coke" in these samples was represented by isotropic forms, sometimes pitted with very fine–sized open pores. Some coke particles were thin walled and very porous, displaying well-developed devolatilisation vesicles, while others had quite thick coke walls with relatively smaller gas pores.

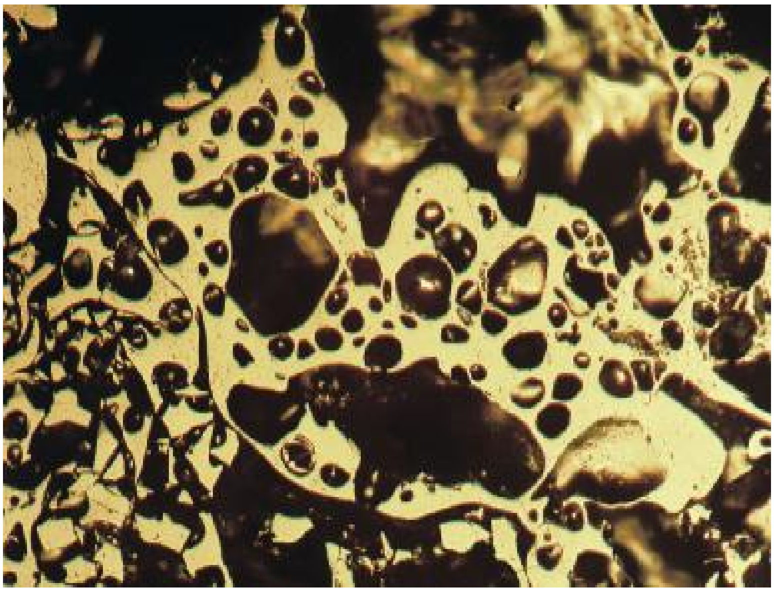


Figure 5: Thick-walled Isotropic coke

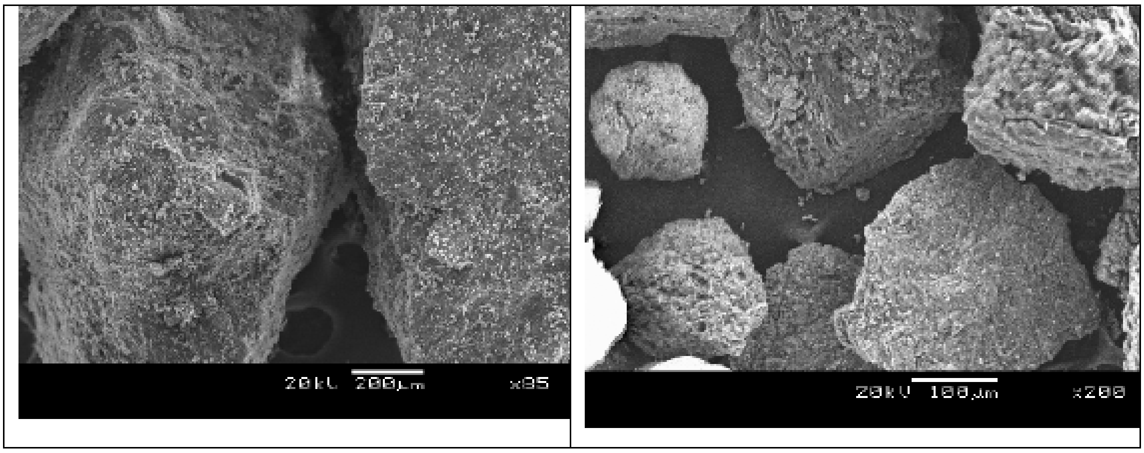
- **VISIBLE MINERALS**

Highly varying relative proportions carbon/inorganic matter were present in these chars. The total carbon accounted for 64% in the Grootegeluk char, for only 6% in the Matla, and 16% in the Duhva sample. Some coal minerals remained, usually closely associated with the organic material in carbominerite. Greatly varying quantities of mineral “slag” bodies were encountered (from approximately 20% by volume in the Grootegeluk sample up to around 75% in the other two chars. Sometimes this “slag” had formed borders against the organic char or melted around carbon fragments. Occasionally, “slag” had penetrated into the carbon matrix.

Char Morphology

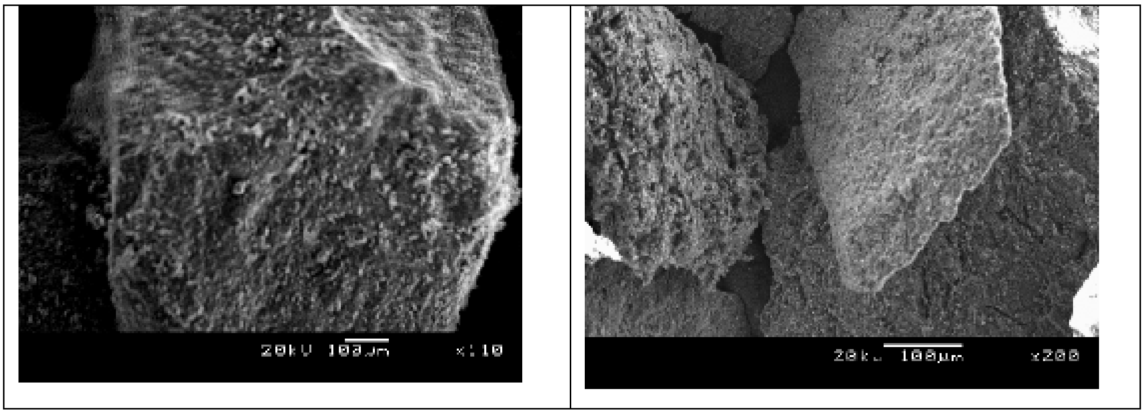
Scanning electron microscopy (SEM) SEM is also a good technique that can be used to study the microfeatures of residual char such as unreacted coal and unswelled particles (Valentim *et al*. 2006). SEM images for the different types of coals are presented in Figure 9-11. The surface morphology of Duhva and Matla char were characterised with small open pores and with some cracks on the surfaces. This indicates that there was a little change in the morphology of the parent coal. Similar result was reported by Yu *et al*. (2003) for high ash and high inertinite coal. They suggested that the high inertinite content and high ash level had a negative effect on amount the volatiles generation and release. It is more difficult for released volatiles to escape from these types of coal. This leads in the enhanced cracking and generation of small pores from the reactive macerals. This suggestion has recently been collaborated by Cousins *et al.* (2006) and Everson *et al.* (2008). In this study, the inertinite content for Matla and Duhva coal were 3-4 times higher than Grootegeluk coal, further analysis of the char also showed that Matla and Duhva had higher level of ash and inertinite content.

However, there was a significant change in the morphology of the Grootegeluk char; this was evident with the larger pore on the surface of the char. The significance difference in the physical structure of the residual char of could be attributed to the rank, maceral composition (Alvarez *et al*. 1997) and mineral content (Yu *et al* (2003). In general, particles containing liptinite or vitrinite generate porous char structure, while those containing inertinite generate relatively dense char structures. The question how much vitrinite content or inertinite content is required to form a particular type of char structure. From the different coal considered in our study, 52% of vitrinite and above is required for the formation of porous char while 57% of inertinite and above is required for the formation of solid/dense structure.



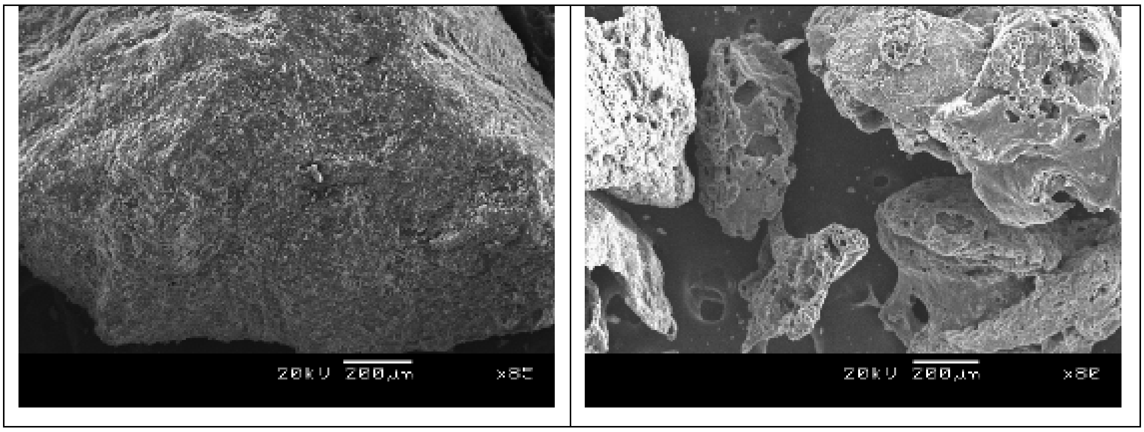
(a) **(b)**

Figure 9: SEM images of Duhva coal and its derived char at 918^{O}c. (a) Parent coal, (b) Char obtained



(a) **(b)**

Figure 10: SEM images of Matla coal and its derived char at 935^{O}c. (a) Parent coal, (b) Char obtained



(a) (b)

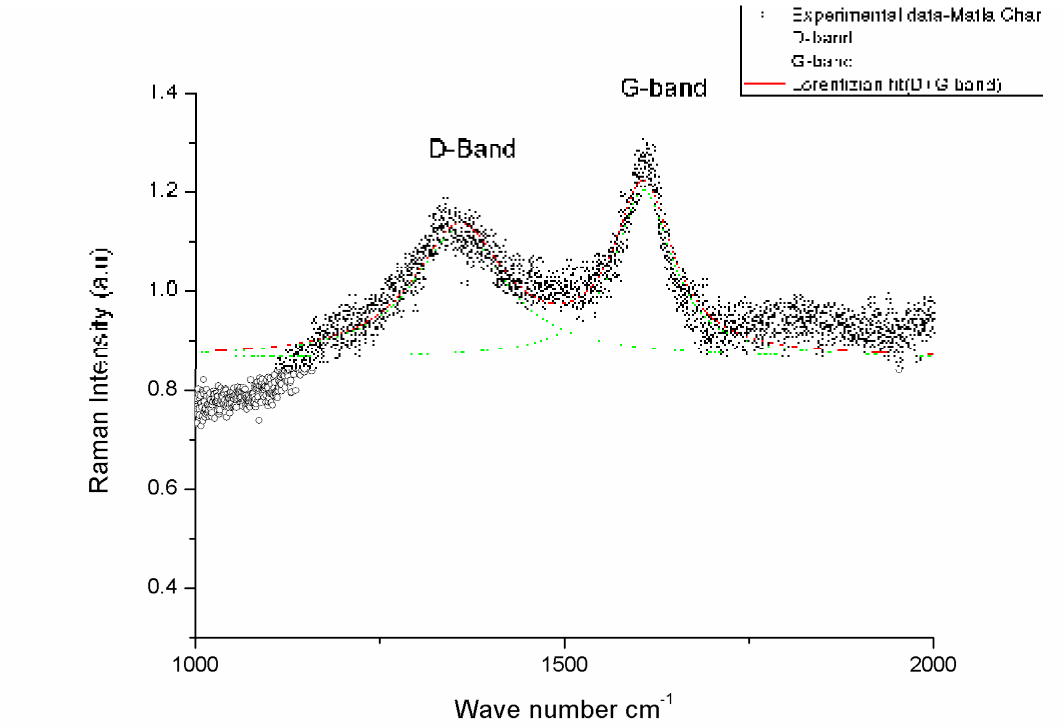
Figure 11. SEM images of Grootegeluk coal and its derived char at 903^{O}c. (a) Parent coal, (b) Char obtained

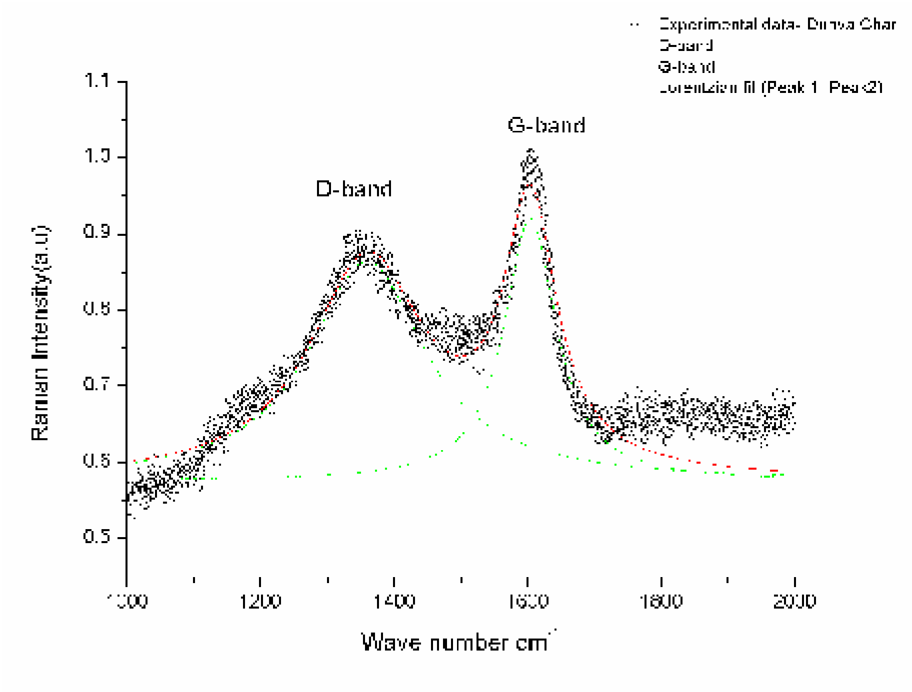
Microstructure of Coal Chars

While the physical structure of the coal and char depends on the char morphology, the chemical structure of the coal/char is related to the amorphous proportions and carbon crystallite form. Microstructural changes occur as a result of the transformation of the organic and inorganic matter in coal during gasification. This change has been linked to the evolution of char reactivity (Senneca ***et al***. 1998; Sheng, 2007). In this study, Raman spectroscopy and X-ray diffraction were used to characterise the microstructure of the selected coal and its different char generated from gasification.

Raman spectroscopy .

The Raman spectra were recorded between 1000-2000cm^{-1}, which corresponds to the spectral region that provides the most valuable data on the microstructure of coal. For perfect graphite, there is only one band at about 1580 cm-1 called the G band in the first-order region. For highly disordered carbons, additional bands induced by the defects in the microcrystalline lattices appear in the first-order region 1150, 1350 and 1530 cm^{-1}. The 1350 cm^{-1} band is commonly called the defect band, D. Since the Raman measurements only yield relative spectra, the spectra were normalised with respect to the G band at 1590. Each spectrum was fitted to a three-band Lorentzian function. The parameters including peak position, full width at half maximum (FWHM), intensity and integrated area of each band were derived from the decomposition. The Raman spectra of the chars produced from the three different coal samples are presented in Fig 12-14. In all the Raman measurements the G and D bands were dominant and a weak 1124 cm^{-1} band was apparent. Qualitavely, the spectra for Duvha and Grootegeluk char are similar while spectra of the Matla char was different. The G band for both Duvha and Grootegeluk char is weaker than D band however it was the opposite for the Matla char. This indicates that the degree of ordering in Grooteleguk and Duhva char is higher than that of Matla. A comparative study of the peak position, intensity, bandwith of the three bands obtained after curve fitting is presented in Table 7. The parameters were used to evaluate the changes in the microstructure of the coal during gasification. The band area ratio, I_D/I_G, is often used as a probe to the extent order of graphitic (Tuinstra and Koenig, 1970). Band area ratio I_D/I_G is inverse proportional to the microcrystalline planar. The decrease of I_D/I_G implies the increase of the average planar size of the graphitic miro-crystallites. Alternatively, as the disorder increases, the band area ratio increases. From the comparison of the evolutions of the band area ratios for the three chars, it was observed that extent of structural transformation was different. For Duvha chars, a decrease in band area ratio was observed after gasification implies an increase in the extent of graphitic ordering. There was relatively no change in the I_D/I_G ratio of Grooteleguk and Matla chars after gasification implying low structural transformation.




G-band
D-band
1.1
1.0
0.9
0.8
0.7
0.6
0.5
Raman Intensity(a.u)
1000
1200
1400
1600
1800
2000
Wave number cm

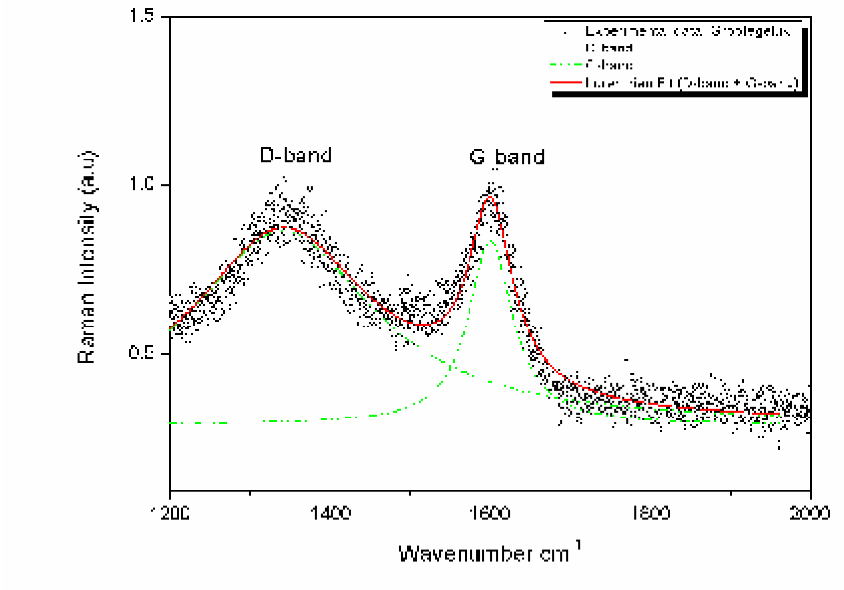

1.5
1.0
0.5
D-band
G band
Raman Intensity (a.u)
1200
1400
1600
1800
2000
Wavenumber cm

Table 7: 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)	Intensity (peak area)	Peak Intensity ratio
Matla				
Coal				
D	1363	153.71	66.88	
G	1604	92.39	60.17	1.11
Char				
D	1357	149.09	61.17	
G	1606	94.57	50.34	1.21
Grootegeluk				
Coal				
D	1370	260.56	100.42	1.98
G	1597	87.10	50.80	
Char				
D	1349	188.32	125.44	2.13
G	1600	69.54	58.88	
Duhva				
Coal				
D	1348	279.36	120.93	3.08
G	1598	58.03	39.28	
Char				
D	1359	211.24	95.76	1.85
G	1603	95.35	51.63	

Structural analysis (BET results)

The surface area and pore volume of the different coal samples and the chars generated from it during gasification was analysed using N2 adsorption. The results are presented in Table 8. The surface areas and pore volumes of Duhva and Matla char can been seen to be very low, this can be attributed to the high inertinite content, however, the surface area and pore volume for the Grootegeluk char. The values were close to those reported for vitrinite-rich coals (Liu *et al.* 2000).

Table 8: Surface area and pore volume of the different coal and char samples

Coal	**Malta coal**	**Matla Bed Char**	**Duhva Coal**	**Duhva Char**	**Grootegeluk Coal**	**Grootegeluk Char**
Surface area (m2/g)	12.12	10.71	7.46	15.04	5.93	141.28
Pore volume (cm3/g)	0.022	0.0311	0.014	0.0007	0.0079	0.038

Conclusion

- There was no direct relationship between carbon content of coal /chars and the carbon burnout values for the different coal.

- Higher proportions of porous chars are found in coals that have higher reactive macerals(vitrinite) such as Grootegeluk coal whereas much higher proportions of inertinitic chars are found in Matla and Duhva

- Higher proportions of melted minerals were found in chars with higher proportions of inertinite macerals. This may reflect the production of higher temperatures during the burning of these higher order carbon-rich relatively inert macerals.

- The degree of graphitic ordering in Grooteleguk and Duhva char is higher than that of Matla

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