COMPARING THE REACTIVITY IN TWO HIGH RANK COALS: RAW AND DEMINERALIZED FORMS

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Abstract

Transformations from coal to char using a high heating rate have been well-evaluated; however, there is less information on the transition of coal to chars using slow heating rates. In this study, the physical and chemical changes accompany in the coal to char transition were examined by conventional and advanced analytical techniques. Two high rank coals (SA and ANT) of ≤75 μm were demineralized, and subjected to a slow heating rate of 25 ºC/min from 450 to 700 ºC at atmospheric atmosphere. The chars were characterized by physical, chemical and petrographic evaluations. The coals were high rank C semi-anthracite (Rov = 2.48) and high rank B anthracite (Rov = 3.26) respectively. Char properties determined by conventional technique (proximate, ultimate and calorific value) and FTIR revealed correlations of the chemical structural changes during the coal to char transition. The fuel ratio was determined to be in the range of 11.6 – 29.6 for the semi-anthracite coal and 16.5 – 27.8 for anthracite coal.

Keywords: Southern hemisphere coal; char transition; pyrolysis; fuel ratio; rank parameter; FTIR

Introduction

A large portion of energy used worldwide originates from fossil fuel; coal in particular is a major resource for mechanical and electrical power production. Pyrolysis remains a fundamental process for thermo-chemical coal conversion as an individual process for char and tar/oil production or as a starting step of other coal conversion processes such as combustion, gasification and liquefaction. The provision of energy in the form of electricity, heat, or fuels and the production of primary chemicals are often achieved by these thermo-chemical processes, of which combustion gasification and pyrolysis are important. During gasification, the coal passes through four distinct stages: drying, pyrolysis, reduction and combustion [1]. In the pyrolysis stage, volatiles are driven off and the properties of the formed char changes significantly when compared to the original coal. The thermal behaviour of coal under pyrolysis has be linked to many factors like coal rank, particle size, porosity, surface area, mineral content, petrographic composition, process temperature, process pressure, catalyst and heating rate that are basically cantered on the coal properties and process conditions [2 – 13]. In the analysis of coal structure, there is need to understand the composition of both the organic and inorganic component of the coal. The inorganic component of coal, also regarded as coal minerals has been identified to be responsible for poor and unstable performance of coal conversion processes [8, 14 - 15]. With the increase in environmental legislation and the push for a "clean coal" economy, so much concern has been raised on the integrity and performance of coal conversion processes. One critical development in clean coal technologies to address this concern is in coal beneficiation, through solvent extraction, which allows the reduction of ash or inert content of the coal thereby generating an ultraclean coal [16 - 17]. The evaluation of the chemical, petrographic and physical properties of coal and how it impacts on coal conversion processes has been extensively investigated relative to the atomic H/C ratio, which is a good test to measure the rate of coalification [18 – 20]; to aromaticity, which is defined as coal maturity index as a result of the structural re-ordering of coal molecules due to thermal treatment [18]; to petrography using the reflectance of vitrinite as a parameter of coal maturity [19] and fuel ratio defined as the combustibility index, the ratio of the fixed carbon to the volatile matter content of coal, is generally accepted as coal maturity parameter [20]. The characterization of resultant chars from coal conversion

processes based on the factors of atomic H/C, aromaticity, petrography and fuel ratio has equally been given some serious level of evaluation by researchers but only limited information is available at present [17]. However, the transition process that leads to the formation of char from coal has been least investigated and as such there is no or limited information available at present. But it has been realized that tracing the changes in the char structure during coal conversion process is essential for a better understanding of the conversion mechanism. In the course of this investigation, the fuel ratio among the coal maturity indices discussed has not been given due attention but with the developed understanding obtained; it becomes necessary to propose the fuel ratio as a maturity index for coal measurement.

This study aims to investigate the chemical structural changes that results from the thermal treatment of two high rank coals under pyrolysis and also looks at the effects of these changes on char reactivity. The changes in the char structure were traced by establishing some relationship between coal maturity indices and coal/char properties. And to achieve this, the selected coals used for this investigation were de-mineralized believing that inherent minerals are the integral part of coal that could play either catalytic or inhibitory role on coal combustion or gasification and to knock off their effect on coal pyrolysis.

2. Experimentals
2.1 Sample preparation
Two high rank coals, a semi-anthracite coal from the middle belt trough coal field in Kogi state denoted as SA and an anthracite coal from the Afuze coal field in Edo state denoted as ANT, Nigeria, were used for this study. The coal samples were pulverized to coal particle size of $\leq$ 75 μm by employing a mechanical size reduction jaw crusher (Samuel Osborne (SA) LTD, model: 66YROLL) and a Fritsch P-14 rotary mill containing ceramic balls (Model number: 46 – 126). The required particle size of -75 μm was finally obtained from screening the particles from the rotary mill using a 75 μm screen. The prepared samples were stored under argon prior to analysis in sealed bags. The prepared coal samples were acid washed by sequential leaching with hydrofluoric acid (HF) and hydrochloric acid (HCl) as detailed in Strydom et al. [17].The HF (48%) and HCl (32%) were obtained from Turraco Industrials Ltd, Nigeria.

2.2 Apparatus and procedure
The coal samples (20g) were placed in a ceramic boat in a horizontal tube furnace at atmospheric conditions initially. The samples were flushed with nitrogen (AFROX, ultra high purity grade) at atmospheric conditions, to remove oxygen from the oven for 15 min. at a flow rate of 1 litre/min. The furnace was then heated at 20 ºC/min to the target temperature, and held isothermally for 60 minutes. The target temperature ranged from 450 to 700 ºC, while keeping the samples under a nitrogen atmosphere. The char samples were stored in sealed bags.

The calorific value and conventional chemical analyses (proximate and ultimate analyses) of the raw coal, acid treated and heat treated samples were performed according to the ISO 1928, ASTM 3172 and ASTM 3176 standards respectively at Eunandy laboratories, Warri, Nigeria. The surface areas of the various samples were determined using the carbon dioxide adsorption BET method on a Micromeritics ASAP2020 surface area analyser as detailed in [19]. Prior to CO_2 adsorption, the samples (about 0.20 g) were degassed under vacuum (10.0 μmHg), for 48 hours at 25 and 380 ºC for the coals and chars respectively. The evacuated sample was analysed at 0 ºC in an ice bath. The results were processed using the Accelerated Surface Area and Porosimetry System (ASAP) 2020 software linked to the Surface Area Analyzer. The coal morphology and that of the resultant char obtained in the transition of coal to char was observed using scanning electron microscope (SEM) model FEI Quanta 250 with FEG emitter, equipped with an EDS detector that does the elemental composition analysis The spectra used in obtaining the structural properties of both the coal and char were obtained from the Fourier-transform infrared spectrometer equipped with an attenuated total reflectance (FTIR-ATR), model Perkin-Elmer Spectrum 400. The procedure of FTIR-ATR as detailed by Odeh, 2015, was used [20]. Aromaticity (f_a) was obtained from the ratio of aromatic bands in the 900 – 700 cm^{-1} region to the aliphatic and aromatic bands in the 3000 – 2815 cm^{-1} region [18]. The vitrinite reflectance of the parent coals were obtained following the procedure and equipment at the advanced coal technology, Coal and coal products laboratory, South Africa as detailed in and reported in Odeh, 2015b [19].

Thermogravimetric analyses of the chars were carried in a Leco TGA701 thermogravimetric analyzer with pneumatic carousel assembly with capacity of being loaded with 19 samples per run. The analyses were performed at Coal and Carbon laboratory, University of Pretoria, South Africa. The char combustion experiments were carried out isothermally at four different temperature ranging from 365 to 410 ºC. The samples were heated under nitrogen from ambient temperature to the target temperature for an hour, after weight stabilization the nitrogen was replaced by oxygen atmosphere (10 volume %) [18], and held isothermal for six hours at a heating rate of 10 ºC/min. Sample masses of approximately 2g, with a particle size distribution of $\leq$ 75 μm, were used to reduce mass transfer effects [15]. The selection of these experimental conditions

were based on recommendations from researchers on the need for the samples to be distributed uniformly on the bed of the analyzer and not having a bed thickness > 1 mm [5]. The specific reactivity of the char was calculated by:

$$R = \frac{1}{W}\frac{dW}{dt}$$ (1)

Where W is the weight of the char (daf basis) at any given time t. The intrinsic reactivity was obtained by normalizing the specific reactivity of the char by the DR micro-pore surface area obtained from the ASAP 2020 surface area analyzer [12].

3. Results and discussion

The coal samples used for the investigation are of the same rank but of different grades and as such it is expected that the chemical composition and physical properties will demonstrate considerable differences as a result of demineralization and heat treatment. Samples are referred to as "SA450, ANT700" to clearly indicate the sample identity and the temperature to which it was heat treated. From Table 1, the carbon content of the coals on dry ash free basis (daf) varies from 90.4 to 89.0% for the semi-anthracite coal (SA) between the parent coal (untreated coal) and the demineralized version. For the ANT, the variation is from 90.2 to 85.6 for both the parent coal and the demineralized coal. In contrast to the increased trend in both the low and medium rank coals, the trend in the percentage of carbon after demineralization is decreasing. The total sulphur content of 0.9 and 2.3% (daf basis) for the SA and ANT coals is considered to be on high side, and as such, will make these parent coals undesirable for combustion in conventional pulverised boilers, thus, making both coals, undesirable choice for combustion processes. The effect of charring temperature is as given in Table 2 and it can be seen that there is a significant reduction of the volatiles at 700°C to 3.2% as compared to 7.8% at 450°C from a parent coal with a value of 9.6% (air dried basis) for the SA coal. Similar significant reduction in the volatiles was also observed for the ANT coal with values of 3.4% at 700°C, 5.6% at 450% and 6.8% (air dried basis) respectively. Observation of the atomic H/C ratio in this study is generally consistent with previous reports on coal systems in that the semi-anthracite coal (SA) has the higher value of H/C (0.46) compared to the anthracite coal (ANT) that has a H/C value of 0.36. The same trend was obtained for the demineralized coal and the heat treated coal samples. The trend of decrease of H/C ratio with increasing charring formation temperature for the acid treated (demineralized) coals was the same which converged to almost the same value of 0.10 at the charring temperature of 700°C. The calorific value determined for the SA coal was 28.7 and 33.3 MJ/kg for the parent coal and the demineralized version respectively. While for the ANT coal, the determined calorific values of 29.6 and 32.7 MJ/kg for the parent and demineralized coals respectively. The impact of demineralization is visible as the calorific value increased in value. Though slight differences can be observed in the values obtained both the parent coal and the demineralized coals, the impact is more noticed in the heat treated coals and there is a convergence to a value of 33 MJ/kg around 700 °C (Table 2. From the proximate analysis, the fuel ratio, which is the ratio of the fixed carbon to volatile matter content, was calculated (Table 1 and 2). It can be seen that the fuel ratio increases with increase in coal rank, SA coal has a higher fuel ratio compared to the ANT coal and with increase in charring formation temperature.). The spectra obtained from the FTIR were used to determine the aromaticity, which is a technical performance index for measuring the maturity and usefulness of coal in coal conversion processes was calculated (Table 1 and 2). The aromaticity was determined to be in the range of 0.94 - 1.00 for the SA coal and 0.97 - 1.00 for the ANT coal. The aromaticity shows similar trend that converged to the same value at the charring temperature of 700 °C (Table 2).

The internal structure and morphology of both coal and coal chars demonstrated similar behaviour (Figures 1- 4 and Table 2). The BET surface area determined is consistent with the rank of the coal [17]. The surface area for the heat treated coals were determined to be in the range of 138 – 197 m²/g and 114 – 164 m²/g for the SA and ANT coals respectively. Since the pathway for the formation of char is affected by the heating rate, the results of the surface area obtained from the slow heating rate used in this study corroborates results reported by Odeh [18]. This gives an indication that the SA is likely to be more porous than the AFZ coal. It can be depicted from both Figures 1 and 2 that the pores in the coals opens up at elevated temperature most especially at 550 °C. Figures 3 and 4 also illustrates the impact of heat on coal during utilization processes when viewed under petrographic microscope. It can be seen that there is a colour change from grey to white when the lowest charring temperature of 450 °C is compared to the highest charring temperature of 700 °C. This colour change can be attributed to the spontaneous reaction of the reactive components (vitinite + liptinite) of the macerals in the coals when subjected to elevated temperatures.

In this communication, the data obtained from the thermogravimetric analyser were fitted experimentally. The best fit for the data obtained was a fourth order polynomial (Figures 5 and 6). Both the parent and the demineralized version of the two coals subjected to heat treatment were fitted to the fourth order from where the kinetic parameters were calculated to define the coals reactivity. (It should be noted that the coals were demineralized to reduce the amount of mineral matter present in them as well as to minimise their influence during quantitative analysis and the reactivity of the coals). This initiative of demineralization is a drive towards clean coal technology for efficient and effective uses of coal and coal products

resources. From the specific and intrinsic reactivity data generated from the thermogravimetric analysis in Table 3, It can be seen that both the specific and intrinsic reactivity decreases with increasing charring for the four combustion programme employed for this investigation. The decrease of reactivity with increasing charring temperature has been reported to be due to the reduction of the hydrogen content in chars which is related to the reduction of active sites giving room for more desorption reaction with oxygen [18]. Previous research reports has demonstrated some level of inconsistencies with the data obtained for combustion reactivity for the medium rank coals. However, in this report, the inconsistencies were limited as reflected in Table 3. The inconsistency can be attributed to the irregular and random distribution of the specific reactivity with increasing char formation temperature. To correct the irregular phenomenon of the specific reactivity, the specific reaction rate data were normalized to the measured CO_2 adsorption surface area to get the intrinsic reactivity, which gives better representation and interpretation of the reactivity of a coal sample. On comparing the reactivity between the parent and the demineralized coal, the parent coal seems to be more reactive than the demineralized coals. Odeh [19], reported that inherent minerals in the high rank coals do have an unfavourable catalytic effects during coal processing. These inherent minerals would have been removed or reduced in content in the course of the demineralization in this study. These minerals are mostly found in clay minerals (calcite and dolomite) consisting of aluminium oxides and oxides of calcium and potassium which plays active role in the de-alkylation and dehydrogenation reaction at high charring temperatures and in the cracking (decarboxylation/decarbonylation reactions) of oxygen functional groups at charring temperatures [6]. For a better and greater insights of this investigation, the activation energy for the demineralized coals, which is a temperature predominant parameter of the intrinsic reaction rate was determined. The activation energy was determined to be in the range of 239 to 130 KJ/mol for SA from 450 to 700 °C. While for ANT, the activation energy was determined in the range of 79 to 218 KJ/mol. The activation energy is found to vary dramatically over the course of the combustion analysis, exhibiting a sharp maximum in the early stages of char combustion. This dramatic behaviour can be attributed to the fact that when coal is heated, two processes occur competitively: one is the depolymerization process through which gas, water vapour and tar are formed and the other is the condensation or replymerization which leads to char formation [20]. The determined average activation energy of 113 KJ/mol for the SA and 152 KJ/mol for the ANT coal obtained in this work falls within the range of values previously reported in the open literatures. From the detailed characterization and energy content evaluation, the two high rank coals can be considered to possess great energy potentials.

4. Conclusion

The study of the transformations undergone by two high rank coals during pyrolysis indicates an enhancement of the total reflectance with increasing temperature. This enhancement is influenced by the maceral composition of the parent coal. The SA coal with higher vitrinite component compared to the other coal tends to devolatilized more. On the other hand, the ANT coal, because of its high inertinite component tends to take longer to begin combusting than the reactive vitrinite coal (SA). This equally impacts on the coal reactivity. The data obtained in this work was able to demonstrate that the fuel ratio is an important parameter that could be used in evaluating coal samples needed in coal conversion processes. Since studies have revealed that coals containing less substituted chains attached to the aromatic ring appear to be more suitable for producing larger quantities of char during pyrolysis, the fuel ratio data generated from this study will serve as a database for energy experts to develop new technologies to rehabilitate low-quality coals in coal-fired utility plants and other coal conversion processes.
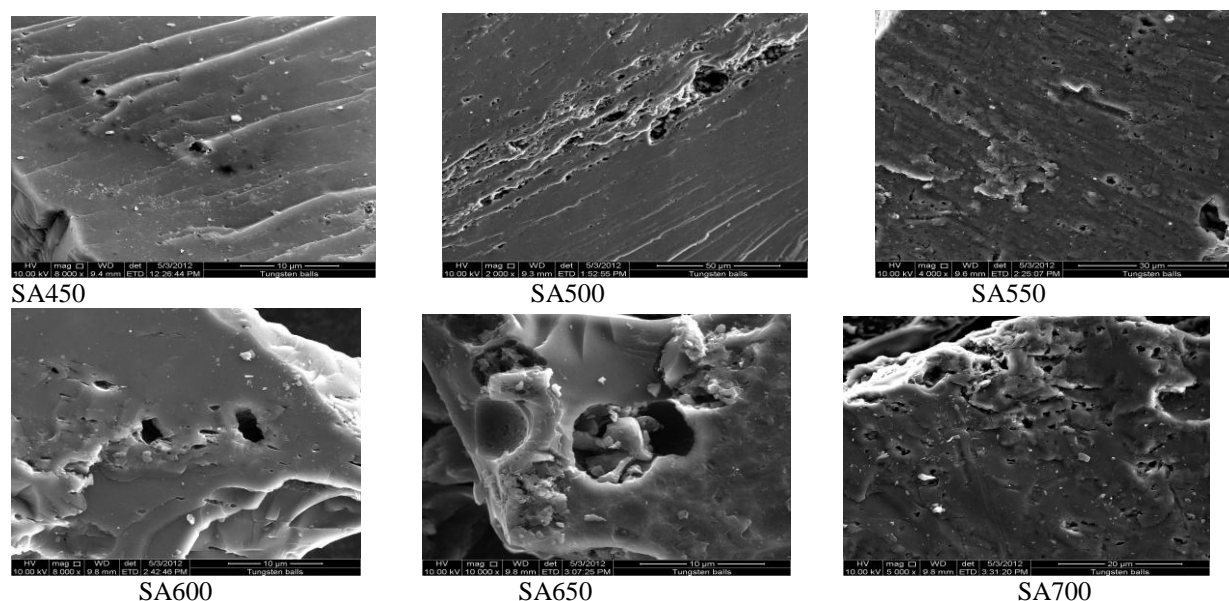

SA450	SA500	SA550
SA600	SA650	SA700

Figure 1: SEM micrographs of the transition of coal to char (450 – 700 °C) for SA samples

ANT450   ANT500   ANT550
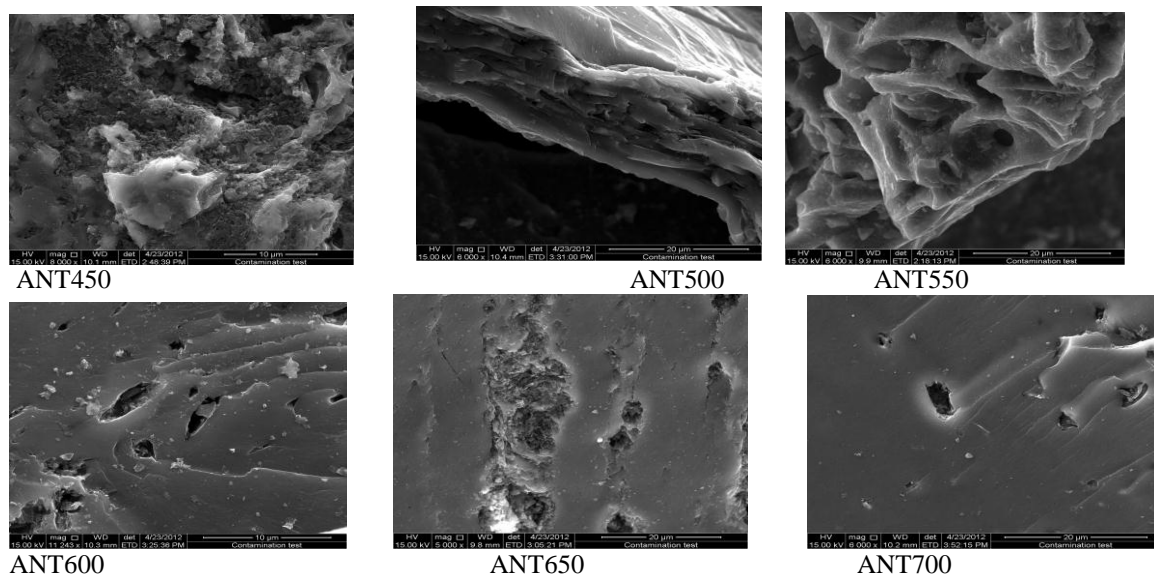
ANT600   ANT650   ANT700

Figure2: SEM micrographs of the transition of coal to char (450 – 700 ºC.) for ANT samples

SA450   SA500   SA600
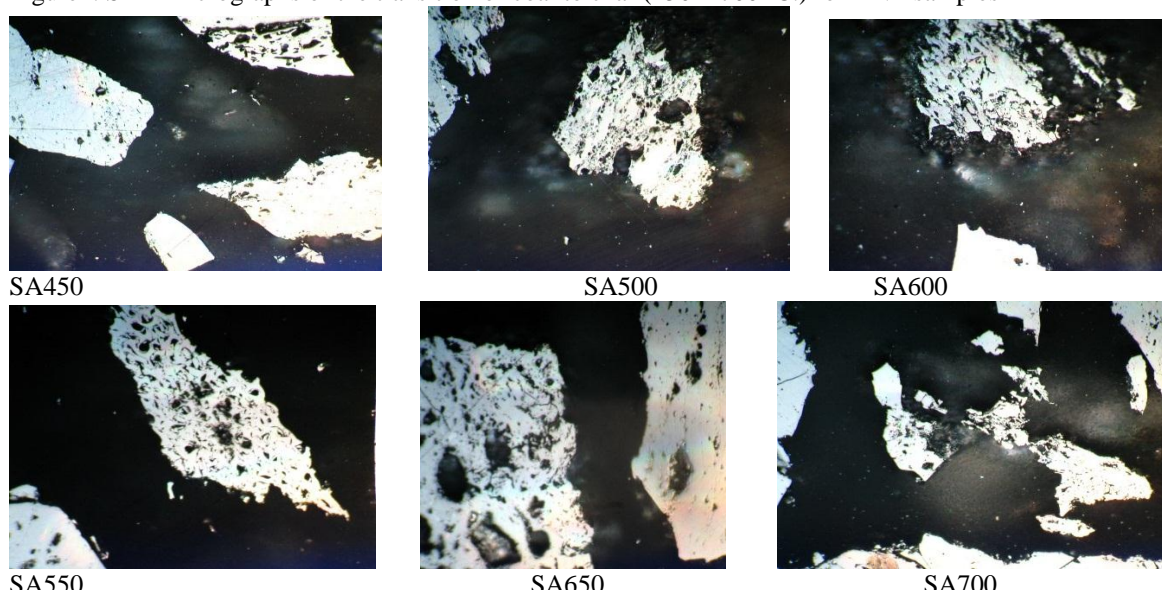
SA550   SA650   SA700

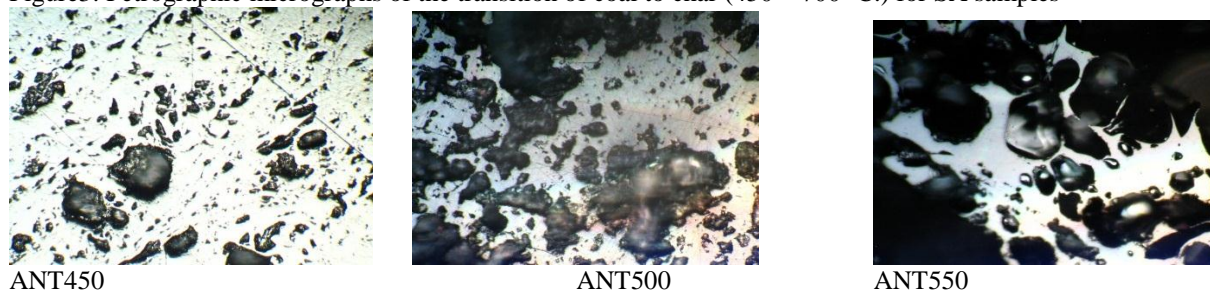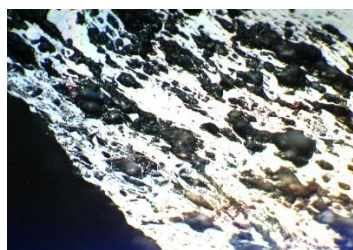Figure3: Petrographic micrographs of the transition of coal to char (450 – 700 ºC.) for SA samples

ANT450   ANT500   ANT550

ANT650   ANT600   ANT700

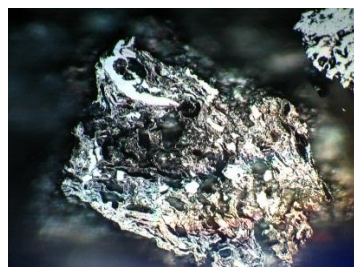Figure4: Petrographic micrographs of the transition of coal to char (450 – 700 ºC.) for ANT samples

Table 1: Properties of both coal

Coal	SA	SA-D	ANT	ANT-D
Inherent moisture(air dried) wt.%	1.0	2.3	1.5	2.5
Ash (air-dried) wt.%	17.3	1.8	11.2	1.5
Volatile matter (air-dried) wt.%	7.6	9.6	5.3	6.8
Fixed carbon (air-dried) wt.%	74.1	86.3	82	89.2
Carbon (daf) wt.%	90.4	89.0	90.2	85.6
Hydrogen (daf) wt.%	3.5	3.3	2.7	2.4
Nitrogen (daf) wt.%	2.0	1.8	2.2	2.0
Oxygen (daf) wt.%	3.3	5.0	2.7	7.7
Sulphur (daf) wt.%	0.9	0.7	2.3	2.1
Gross calorific value (MJ/kg) (air-dried)	28.7	33.3	29.6	32.7
H/C (daf).	0.46	0.4	0.36	0.3
f_a	0.91	0.94	0.97	0.98
Fuel ratio	10	9	16	13
CO_2 BET surface area (m^2/g)	107.78	125.28	122.10	137.56
Rank (mean random vitrinite reflectance %)	2.48	3.26	2.52	3.28

SA-D   demineralized coal   ANT-D   demineralized coal

Table 2: Derived properties of heat treated coals (chars)

CHAR	Wt % (air dried)				Wt % (daf)					MJ/k daf				m^2/g
SA	Mois.	Ash	V.M	F.C	C	H	N	O	S	GCV	H/C	f_a	FR	BET
450	0.6	1.5	7.8	90.1	89.5	3.0	1.9	4.8	0.8	34.7	0.4	0.94	11.6	137.94
500	0.7	1.6	6.6	91.1	90.8	3.0	1.8	7.9	0.8	35.1	0.4	0.95	13.8	148.17
550	0.5	1.2	5.7	92.6	91.4	2.6	2.0	3.2	0.8	34.6	0.3	0.98	16.2	170.35
600	0.5	1.0	4.8	93.7	91.4	2.1	1.9	3.8	0.8	34.7	0.3	1.00	19.5	186.54
650	1.2	1.3	3.7	93.8	92.5	1.6	1.9	3.1	0.8	33.8	0.2	1.00	25.4	194.60
700	0.9	1.3	3.2	94.6	92.9	1.0	1.9	3.4	0.8	33.3	0.1	1.00	29.6	196.99
ANT														
450	0.9	1.3	5.6	92.2	90.0	2.3	2.1	3.6	2.0	33.8	0.3	0.97	16.5	113.93
500	0.8	4.9	5.3	89.0	89.9	2.1	2.1	3.8	2.0	32.8	0.3	0.98	16.8	135.18
550	0.7	8.1	4.4	86.8	90.6	2.1	2.1	3.0	2.1	31.3	0.3	1.00	19.7	136.74
600	0.7	3.4	4.5	91.4	90.4	1.9	2.1	3.6	2.0	33.3	0.3	1.00	20.3	150.98
650	0.8	1.4	6.3	91.5	91.3	1.7	2.1	3.0	2.0	33.8	0.2	1.00	24.5	162.47
700	0.7	1.4	3.4	94.5	91.4	1.0	2.1	3.5	2.0	33.1	0.1	1.00	27.8	164.40

FR   Fuel ratio   fa   Aromaticity

Table 3: Specific and Intrinsic reactivity of chars

CHAR	R_S (g/g.s) x 10^{-5}	R_I (g/m².s) x 10^{-7}	R_S (g/g.s) x 10^{-5}	R_I (g/m².s) x 10^{-7}	R_S (g/g.s) x 10^{-5}	R_I (g/m².s) x 10^{-7}	R_S (g/g.s) x 10^{-5}	R_I (g/m².s) x 10^{-7}	E_a	E_a
C/TEMP	415 ºC		400 ºC		385 ºC		370 ºC		KJ/mol	KJ/mol
SA450	6.16	2.78	4.38	1.98	4.25	1.92	4.24	1.91	239	113
SA500	5.66	2.38	4.37	1.84	3.81	1.60	3.88	1.63	62	
SA550	4.48	1.64	3.62	1.33	2.99	1.56	4.44	1.62	104	
SA600	4.79	1.60	3.70	1.23	4.27	1.00	2.06	0.69	59	
SA650	4.76	1.52	3.52	1.12	2.22	0.71	2.94	0.94	84	
SA700	3.15	0.86	2.61	0.71	0.90	0.25	1.85	0.50	130	
ANT450	4.31	1.95	2.87	1.49	2.63	1.30	1.23	0.56	79	152
ANT500	3.62	1.73	2.21	1.05	2.05	0.98	0.87	0.42	198	
ANT550	3.01	1.38	1.70	0.78	1.75	0.80	0.43	0.20	208	
ANT600	2.59	1.08	1.53	0.64	1.06	0.44	0.29	0.12	95	
ANT650	2.40	0.92	1.51	0.58	0.35	0.13	0.49	0.19	111	
ANT700	2.04	0.77	1.13	0.43	0.32	0.12	0.49	0.19	218	

R_S Specific reactivity R_I Intrinsic reactivity E_a Activation energy
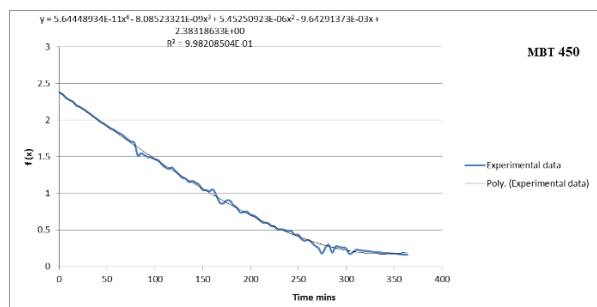

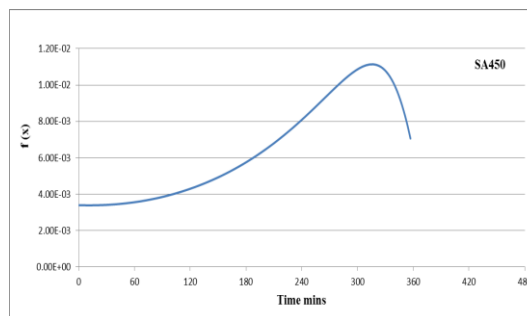Figure 5a: Curve fitting of experimental data for the demineralized SA coal   Figure 5b: Curve fitting of experimental data for the demineralized SA coal
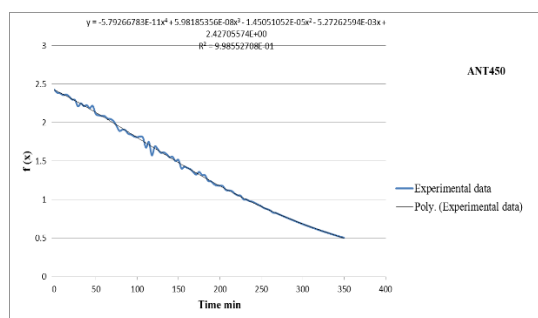

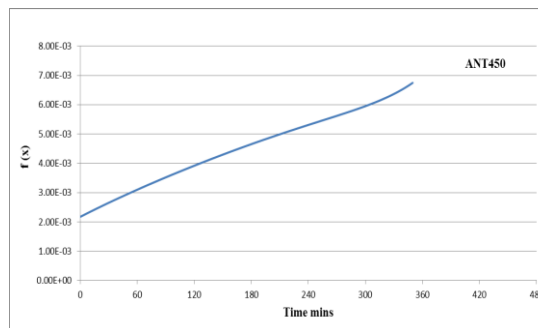Figure 6a: Curve fitting of experimental data for the demineralized ANT coal   Figure 6b: Curve fitting of experimental data for the demineralized ANT coal

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