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

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Abstract

The quest for renewable energy due to population explosion and dwindling energy derivation from non-renewable sources, discovery of new coal deposits in Nigeria presents solutions for the nation's energy crises and prospects for socio-economic growth and sustainable development. The transformation of coal to char is considered a critical and important step in coal conversion processes. The knowledge of the physical and chemical properties of this transition plays a major role in the reactivity of the coal char. However, a lack of comprehensive data on physicochemical and thermal properties of Nigerian coals has greatly limited their utilization. Hence, in this study, two Nigerian low rank coals, one lignite (UGW) and a sub-bituminous (ENU) were demineralized and characterized. The thermal analysis under different process condition were also examined to determine the impact of demineralization on the coal's reactivity.

The results indicate that the coals contain high proportions of percent carbon and a sufficiently high heating value (HHV) for energy conversion. The thermal analysis of both the raw and demineralized coal on reactivity were found to confirm to well-established trends. The effect of temperature in the high temperature range was, however, strongly affected by pore and film diffusion during combustion. The coal classification revealed the thermochemical and pyrolytic fuel properties of the coal and indicates that the coal can potentially be utilized for future clean energy applications.

Keywords: Nigerian coal; char, coal transformation; energy efficiency; energy recovery; technical performance

Introduction

A large portion of energy used worldwide, about 84 percent precisely originates from fossil fuel; coal in particular is a major resource for mechanical and electrical power production [1]. The complex and complicated nature and behaviour of coal has made the investigation of this carbonaceous material an on-going and continuous process in order to optimize coal conversion processes [2]. The heterogeneous complex nature of coal makes it to exhibit a wide range of physical and chemical properties when exposed to different heating rates and higher temperatures [3]. A good knowledge of the physical and chemical properties of coal can be used to predict coal behaviour and can also serve as a useful indicator of the quality of coal [4, 5, 6]. Coal is made of organic polymeric material with some inorganic impurities. The organic materials are known as macerals, while the inorganic impurities are considered as the minerals [7, 8, 9]. When exposed to heat-treatment, the physical, chemical, thermal and electrical properties in both the maceral and mineral components of coal undergo transformation [10, 11]. One of the parameters that are used in measuring the technical performance and chemical stability of this transformation is the aromaticity; it gives a good representation of the maceral to char transformation, which stands as a good indicator of coal maturity due to the realignment of the carbon molecules [8, 9, 10, 12]. The change in the carbonaceous structure due to the modification of the organic and inorganic constituents in coal and its subsequent char is stated to be one of the key factors that affect the reactivity of coal/char in coal conversion processes such as combustion, gasification and liquefaction [12, 13, 14, 15]. Results from research have revealed that heat treatment leads to the increase in the carbon content of coal and that demineralization and solvent swelling increases the active nature of carbon [16, 17, 18, 19, 20]. With the renewed interest in research on clean coal technology and for coal to remain relevant as a viable source of secure energy, focus is on chemical treatment of coal (coal demineralization) to limit or reduce the mineral effects during utilization [17, 19, 20, 21, 22].

Corresponding Author: Andrew O.O., Email:Andrew.odeh@uniben.edu, Tel: +2348033188797 Journal of the Nigerian Association of Mathematical Physics Volume 56, (March - May 2020 Issue), 53 –60 Coal and coal products chemical and physical properties have been extensively studied and characterized employing both conventional (proximate, ultimate and calorific value) and advanced analytical techniques (FTIR, SEM, HRTEM, SAN, NMR, XRD and petrographics) over the years [18, 19, 20, 21, 22, 23, 24, 25]. Most previous studies and evaluation of the properties: chemical, petrographic and physical of coal and coal char and how it influence on coal conversion processes has been on northern hemisphere coals and southern hemisphere coals from South Africa [16, 17, 18, 19]. However, detailed evaluation of typical Nigerian coals has been least investigated and as such there is limited information available at present in the open literature on Nigerian coals. The lack of data on the thermo-chemical fuel properties of the coals is an impediment to more accurate assessment of their technological applications and efficient industrial utilization. With the knowledge of coal deposits in nations like Nigeria, its importance as an industrial and commercial commodity will unquestionably increase in the future. However, the studies on the fuel properties and potential applications of coals in Nigeria are limited.

In this communication, the physical and chemical transformation that takes place when two typical low rank Nigerian coals; a lignite and a sub-bituminous is subjected to heat treatment under different process parameter is presented. Therefore, the main objective of this paper is to characterize and examine the physico-chemical and thermal properties of two low rank Nigerian coals. The paper also presents novel data on the reactivity of the two coals and comparison in reactivity between the raw and demineralized coals form under the same process conditions which serves as a fundamental requirement for assessing its future potential utilization in the clean coal technology age. This is vital for the engineering design, modelling and optimization of thermochemical processes, conversion equipment, and environmental impact assessment of coals in Nigeria.

2. Experimentals

2.1 Sample preparation

Two low rank coals, a lignite coal from the Ugwuasi-uku coal field in Delta state denoted as UGW and a sub-bituminous coal from the Enugu coal field in Enugu state, Nigeria, were used for this study. The coal samples were pulverized to coal particle size of $\leq 75 \,\mu$ m 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 μ m was finally obtained from screening the particles from the rotary mill using a 75 μ m 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 °C/min to the target temperature, and held isothermally for 60 minutes. The target temperature ranged from 450 to 700 °C, 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 °C for the coals and chars respectively. The evacuated sample was analysed at 0 °C 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 $900 - 700 \text{ cm}^{-1}$ region to the aliphatic and aromatic bands in the $3000 - 2815 \text{ cm}^{-1}$ 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 °C. 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 °C/min. Sample masses of approximately 2g, with a particle size distribution of \leq 75 µm, were used to reduce mass transfer effects [26]. 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)

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Where W is the weight of the char (daf basis) at any given time 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 show some considerable differences as a result of demineralization and heat treatment. Samples are referred to as "UGW450, ENU700" to clearly indicate the sample identity and the temperature to which it was heat treated. From the analysis in Table 1, the carbon content of the coals on dry ash free basis (daf) varies from 75.4 to 71.4% for the sub-bituminous (ENU) to the lignite coal (UGW) for the untreated (parent) coal and 75.3 to 72.2% for the demineralized coals The total sulphur content of 2.9 and 3.5% (daf basis) for the lignite coal, which together with the other properties would make this parent coal undesirable for combustion in conventional pulverised boilers because of the generation of especially sulphur dioxide and solids handling problems. On the other hand, the total sulphur content of 0.4 and 0.2% would make the sub-bituminous coal a choice coal 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 4.4% as compared to 32.5% at 450°C from a parent coal with a value of 44.3% (air dried basis) for the lignite coal. Similar significant reduction in the volatiles was also observed for the sub-bituminous with values of 46% at 700°C, 24.3% at 450% and 36.6% (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 lignite coal (UGW) has the higher value of H/C (0.10) compared to the sub-bituminous that has a H/C value of 0.07. 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 0.012 at the charring temperature of 700°C. Similar trend of decrease with increasing charring formation temperature were observed for the atomic O/C (Table 2). There was, however, a convergence to a value of 0.04 at a temperature of 650 °C. This implies that the maximum temperature to get the heat effects of the coals is 650 °C. The calorific value determined for the lignite coal was 23.2 and 29.8MJ/kg for the parent coal and the demineralized version respectively. While for the sub-bituminous, the determined calorific values of 25.3 and 30.1MJ/kg for the parent and demineralized coals respectively. The impact of demineralization is visible as the calorific value increased in value. 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, the sub-bituminous has a higher fuel ratio compared to the lignite and with increase in charring formation temperature. Though slight differences can be observed in the values obtained both the parent coal and the demineralized coals, the impart is more noticed in the heat treated coals and a convergence is noticed around 700 °C (Table 2). 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 0.67 - 0.80 for the lignite coal and 0.77 - 0.88 for the sub-bituminous coal.

The internal structure and morphology of both coal and coal chars demonstrated similar behaviour (Figure 1, 2 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 $174 - 266 \text{ m}^2/\text{g}$ and $162 - 258 \text{ m}^2/\text{g}$ for the lignite and sub-bituminous 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 lignite coal is likely to be more porous than the sub-bituminous 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. Figure 3 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.

One of the approaches to coal optimization is a good fundamental understanding of the kinetics and data treatment of the thermal history of the material. Since coal is a complex and complicated carbonaceous polymer, reactions of practical interest often involves a complex set of consecutive and parallel reactions with overlaps that are often impossible to characterize at any significant level of detail. Many researchers have conducted intensive kinetic studies on carbonaceous materials, both experimentally and by simulation using the pioneer empirical relationship developed by Arrhenius in 1889. However, in thus communication, the data obtained from the thermogravimetric analyser were fitted experimental. The best fit for the data obtained was a fourth order polynomial (Figures 4 and 5). 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 and 4. 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 [25]. Previous research reports has demonstrated some level of inconsistencies with the data obtained for combustion reactivity for the low rank coals. However, in this report, the inconsistencies were limited as reflected in Table 3 and 4. 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 CO₂ adsorption surface area to get the intrinsic reactivity,

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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 (Table 3 and 4). Odeh [19], reported that inherent minerals in the low rank coals do have favourable 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 344 to 178 KJ/mol for UGW from 450 to 700 °C. While for ENU, the activation energy was determined in the range of 298 to 158 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 reploymerization which leads to char formation [26]. The determined average activation energy of 156 KJ/mol for the lignite coal and 166 KJ/mol for the sub-bituminous 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 low rank Nigerian can be considered to possess great energy potentials.

4. Conclusion

Nigeria as a country is endowed with so much natural resources. In the 1960's, coal was exploited and used for the generation of electricity. This natural resource, coal, was however abandoned with the discovery of crude oil. With the advent of corona virus (CONVID-19) coupled with dwindling oil wells and price, the GDP of countries such as Nigeria, which is monopolistic in nature would be affected. Therefore the dire need to investigate the properties of Nigerian coal for effective and efficient utilization cannot be over-emphasized in this context. Coal when subjected to chemical and heat treatment undergoes changes as observed in this study. This changes affects the chemical, physical, mechanical, heat and electrical properties of the coal.

It can be concluded that the two low rank Nigerian coals show a similar behaviour in char properties, when subjected to elevated temperatures; the (O/C) and (H/C) ratio, decrease with temperature, while the aromaticity, fuel ratio and BET surface area increase with charring temperature. The order of the determined characteristics is consistent with the rank of the parent coal when compared to what obtains in open literatures. This demonstrates the great potentials embedded in the Nigerian coals waiting to be explored and exploited for energy recovery. Since pyrolysis has been identified potentially as a promising, sustainable conversion process for the utilization of carbonaceous fuels such as coal into clean fuels and power generation. The data and knowledge obtained from this study would be vital for the future implementation of clean coal technologies and applications in Nigeria.



Figure 1: SEM micrograph of the lignite coal

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Figure2: SEM micrograph of the sub-bituminous coal



Figure 3: Petrographic pictures of both coal samples

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Table 1: Properties of both coal

Coal	UGW	UGW-D	ENU	ENU-D
Inherent moisture(air dried) wt.%	18.2	2.1	9.4	1.8
Ash (air-dried) wt.%	11.6	0.8	9.2	2.0
Volatile matter (air-dried) wt.%	44.3	59.7	36.6	42.2
Fixed carbon (air-dried) wt.%	25.9	37.4	44.8	54.0
Carbon (daf) wt.%	71.4	72.2	75.4	75.3
Hydrogen (daf) wt.%	7.1	6.8	5.4	5.2
Nitrogen (daf) wt.%	1.2	0.9	0.9	1.8
Oxygen (daf) wt.%	16.8	17.2	17.9	17.5
Sulphur (daf) wt.%	3.5	2.9	0.4	0.2
Gross calorific value (MJ/kg) (air-dried)	23.2	29.8	25.3	30.1
H/C (daf).	0.10	0.09	0.07	0.07
O/C (daf)	0.24	0.24	0.24	0.23
fa	0.35	0.38	0.54	0.61
Fuel ratio	0.6	0.6	1.2	1.3
CO ₂ BET surface area (m ² /g)	72	71	102	97
Rank (mean random vitrinite reflectance %)	0.28	0.33	0.45	0.49

UGW-D demineralized coal ENU-D demineralized coal

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

CHAR	V	Wt % (daf)				daf daf			m²/g					
UGW	Mois.	Ash	V.M	F.C	С	Н	Ν	0	S	O/C	H/C	fa	FR	BET
450	2.7	1.6	32.5	63.2	82.9	3.0	1.1	10.3	2.6	0.12	0.036	0.67	1.9	174
500	2.6	1.6	29.5	66.3	85.1	2.7	1.1	8.5	2.5	0.10	0.032	0.69	2.3	201
550	2.5	1.7	22.1	73.7	88.9	2.0	1.1	5.7	2.4	0.06	0.022	0.72	3.3	228
600	2.4	1.7	9.7	86.1	90.4	2.0	1.0	4.2	2.4	0.05	0.022	0.73	8.9	247
650	2.4	1.9	6.8	89.1	91.9	1.5	1.0	3.4	2.3	0.04	0.016	0.75	13.1	261
700	3.0	2.3	4.4	90.1	93.2	1.0	1.0	2.6	2.3	0.03	0.011	0.80	20.5	266
ENU														
450	3.1	2.6	24.3	70.0	84.9	3.3	2.3	9.4	0.6	0.11	0.039	0.77	2.9	162
500	3.1	2.3	22.2	72.4	87.4	2.6	2.2	7.3	0.5	0.08	0.030	0.79	3.3	195
550	3.1	1.8	21.6	73.4	89.8	2.5	2.2	5.2	0.5	0.06	0.028	0.81	3.4	197
600	3.3	2.3	13.2	81.2	91.2	2.1	2.2	4.2	0.5	0.05	0.023	0.83	6.2	245
650	3.4	2.6	8.9	85.1	92.1	1.6	2.1	3.8	0.5	0.04	0.017	0.86	9.6	249
700	3.9	2.4	4.6	89.2	93.0	1.1	2.1	3.5	0.5	0.04	0.012	0.88	19.4	258

Table 4: Reactivity properties of demineralized coal

CHAR	Rs	RI	Rs	RI	Rs	RI	Rs	RI	KJ/m	ol
	(g/g.s) x 10 ⁻⁵	(g/m ² .s) x 10 ⁻⁷	(g/g.s) x 10 ⁻⁵	(g/m ² .s) x 10 ⁻⁷	(g/g.s) x 10 ⁻⁵	(g/m ² .s) x 10 ⁻⁷	(g/g.s) x 10 ⁻⁵	(g/m ² .s) x 10 ⁻⁷		
C/TEMP	410 °C		395 °C		380 °C		365 °C		Ea	
UGW450	6.31	2.30	6.55	2.35	5.91	2.12	7.75	2.75	344	167
UGW500	6.86	2.17	6.34	1.76	6.63	2.07	8.60	2.65	143	
UGW550	6.55	1.78	6.23	1.67	5.54	1.48	6.81	1.80	132	
UGW600	5.23	1.30	5.37	1.32	5.69	1.41	5.13	1.25	87	
UGW650	4.74	1.09	5.07	1.15	5.39	1.36	4.79	1.74	119	
UGW700	3.76	0.82	3.49	0.75	3.59	0.78	3.34	0.71	178	
ENU450	6.67	2.81	6.32	2.66	6.28	2.60	8.72	3.56	298	154
ENU500	6.13	2.18	6.01	2.14	5.72	2.06	7.05	2.45	157	
ENU550	6.06	2.15	5.88	2.08	5.88	2.00	8.00	2.77	141	
ENU600	5.80	1.55	5.67	1.59	5.76	1.61	7.81	2.04	66	
ENU650	5.62	1.43	5.03	1.28	5.21	1.31	6.18	1.54	104	
ENU700	5.31	1.33	4.31	1.07	4.86	1.20	7.60	1.86	158	

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CHAR	$\mathbf{R}_{\mathbf{S}}\left(\mathbf{g/g.s}\right)\mathbf{x}$	R_{I} (g/m ² .s) x	$R_{S}(g/g.s) x$	R_{I} (g/m ² .s) x	$R_{S}(g/g.s) x$	R_{I} (g/m ² .s) x	$R_{S}(g/g.s) x$	R_{I} (g/m ² .s) x	
	10-5	10-7	10-5	10-7	10-5	10-7	10-5	10-7	
C/TEMP	410 °C		39	5 °C	38	0 °C	365 °C		
LIG450	9.65	3.26	8.64	3.08	7.34	2.52	8.70	2.92	
LIG500	8.90	3.09	7.40	2.30	8.24	2.45	9.65	2.81	
LIG550	8.50	2.53	8.22	2.20	6.88	1.76	7.65	1.91	
LIG600	7.99	1.85	7.08	1.73	7.07	1.67	5.75	1.32	
LIG650	7.25	1.55	6.68	1.51	6.45	1.61	4.75	1.05	
LIG700	5.75	1.16	4.61	0.98	4.46	0.92	3.75	0.76	
SUB450	9.82	3.99	8.62	3.56	7.97	3.15	9.89	3.83	
SUB500	9.37	3.10	8.20	2.89	7.26	2.50	8.00	2.63	
SUB550	9.27	3.05	8.02	2.79	7.46	2.42	9.06	2.97	
SUB600	8.89	2.20	8.14	2.14	7.72	1.94	8.86	2.18	
SUB650	8.59	2.04	6.86	1.72	6.61	1.59	7.01	1.65	
SUB700	8.13	1.89	5.88	1.44	6.16	1.45	6.62	1.49	

Table 3: Reactivity properties of parent coal





Figure 4: Curve fitting of experimental data for the demineralized lignite coal



Figure 5: Curve fitting of experimental data for the demineralized sub-bituminous coal

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