Journal of NAMP 67, 2 (2024) 159-166

The Nigerian Association of Mathematical Physics

Journal homepage: https://nampjournals.org.ng

Conventional and Advanced Analysis of Char Formation of Coals.

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ARTICLE INFO

Article history:
Received xxxxx
Revised xxxxx
Accepted xxxxx
Available online xxxx

Keywords:
Coal,
Char,
Pyrolysis,
Coal Conversion
Energy content.

ABSTRACT

The knowledge of the physical and chemical properties of the transition of coal to char plays a major role in the reactivity of the coal char. Though previous research findings have reported the characterization of coal and the subsequent chars from such coals, analysis on the transition stage have not been critically considered. This study entails the characterization of coal and chars of different ranks using both conventional and advanced analytical techniques.

Six coal samples of different ranks were used in this study. From the ultimate analysis, the carbon content of the coals (daf) varies from 92.3 to 70.5% for anthracite to lignite respectively for the parent coal and from 89.0 to 69.2% for the demineralized coals. The atomic ratio O/C decreases (0.20 for lignite to 0.02 for anthracite); and the H/C ratio equally decreases with increase in coal rank (1.16 for lignite to 0.36 for anthracite).

1. Introduction

The complex and complicated nature and behavior of coal has made the investigation of this carbonaceous material an on-going and continuous process in order to optimize coal conversion processes. The heterogeneous complex nature of coal makes it to exhibit a wide range of physical and chemical properties. Coal conversion and utilization processes such as combustion, gasification and liquefaction are centralized around proper and reliable understanding of the composition and internal structure of carbon [1]. A good knowledge of the physical and chemical properties of coal can be used to predict coal behavior and can also serve as a useful indicator of the quality of coal [2-3]. 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, SAXS, SAN, NMR, XRD and Petrographics) over the years [1-6].

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https://doi.org/10.60787/jnamp.v67i2.365
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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 [4-8]. 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 [9-18]. 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 [13]. When exposed to heat-treatment; the physical, chemical, thermal, mechanical and electrical properties of coal undergo transformation [19]. One of the parameters that are used in measuring the 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 [20-23]. The change in 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 [17; 22; 24-26]. Though previous research findings has reported the characterization of coal and the subsequent chars from such coals, analysis on the transition stage (coal to char) have not been critically considered by researchers. In this communication, we report the physical and chemical transformation that takes place when coal of different rank (lignite to anthracite) is subjected to heat treatment by pyrolysis. However, our discussion in this paper will be limited to conventional analysis, and FTIR analysis.

2. Experimentals

2.1 Coal samples

Six coals of varying rank: a lignite coal from Germany, coded in this study as GER; a sub-bituminous coal from Nigeria, coded in this study as NGR; two bituminous coal from South Africa (In the case of the bituminous coals; one is low volatile bituminous, coded in this study as BCH and the other high volatile bituminous coal, coded in this study as SSL); a semi-anthracite from South Africa, coded in this study as SM; an anthracite from South Africa, coded in this study as SPL. The coal samples were subjected to coal preparation and pulverized to coal particle size of -75µm. All the samples were stored under argon prior to analysis.
The prepared coal samples were demineralized to reduce the amount of mineral matter present in them as well as to minimize their influence during quantitative analysis. The procedure used for the chemical cleaning of the coal followed the sequential leaching with hydrofluoric acid (HF) and hydrochloric acid (HCI); a more detailed procedure is reported in [27].

2.2 Apparatus and procedure

The char production sequence from the parent coal samples are as follows: The measured coal samples (40g) were placed in a boat and put in a horizontal tube furnace at 60^{o}C and for 10 minutes. The sample temperature was equilibrated to ambient temperature and pressure in a flow of nitrogen at a flow rate of 1L/min. The furnace was then heated at 20^{o}C.min^{-}1 to the target temperature, and held isothermally at this temperature for 60 minutes. The target temperature varies from 450^{o}C to 700^{o}C.
The conventional chemical analysis (both proximate and ultimate analyses) of the untreated coal, acid treated and heat treated samples were done according to the international ASTM 3172 and ASTM 3176 method respectively. 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 using (FTIR-ATR), model Perkin-Elmer Spectrum 400. More

information on the procedure and advantages of using FTIR-ATR technique has been reported by [24].
The results of the proximate, ultimate and calorific values of the heat treated coal along with the aromaticity obtained from the FTIR spectra are presented in Table 3.

3. Results and discussion

The coal samples used for the investigation are of different rank and as such it is expected that the chemical composition and physical properties will show some considerable differences as a result of chemical and heat treatment. Samples are referred to as "GER 500, NGR 700" to clearly indicate the sample identity and the temperature to which it was heat treated. From the ultimate analysis in Table 1 and 2, the carbon content of the coals on dry ash free basis (daf) varies from 92.3 to 70.5% for anthracite to lignite respectively for the parent coal and from 89.0 to 69.2% for the demineralized coals. The atomic ratio O/C decreases with increase in coal rank (0.20 for lignite to 0.02 for anthracite); the ratio H/C equally decreases with increase in coal rank (1.16 for lignite to 0.36 for anthracite).

Table 1: Proximate analysis, ultimate analysis, calorific values, aromaticity and calculated H/C and fuel ratio values for untreated coal

Coal	SPL	SM	BCH	SSL	NGR	GER
wt% Inherent moisture(air dried)	1.5	1.0	2.1	4.2	9.6	15.4
wt% Ash (air-dried)	11.2	17.3	16.2	29.1	9.0	12.4
wt% Volatile matter (air-dried)	5.3	7.6	26.7	21.4	37.6	45.7
wt% Fixed carbon (air-dried)	82	74.1	55.0	45.3	43.8	26.4
wt% Carbon (daf)	90.2	90.4	81.6	77.5	75.6	70.5
wt% Hydrogen (daf)	2.7	3.5	4.6	4.5	5.2	6.6
wt% Nitrogen (daf)	2.2	2.0	2.0	2.2	1.7	0.6
wt% Oxygen (daf)	2.7	3.3	10.7	15.4	16.9	18.5
wt% Sulphur (daf)	2.3	0.9	1.2	0.4	0.7	3.7
Gross calorific value (MJ/kg)	29.6	28.7	26.8	20.0	24.6	21.2
H/C	0.4	0.5	0.7	0.7	0.8	1.1
O/C	0.02	0.03	0.10	0.15	0.17	0.20
f_a (FTIR)	0.97	0.91	0.71	0.70	0.57	0.38
Fuel ratio	16	10	2	2	1.2	0.6

Table 3 gives a comprehensive summary of detailed proximate, ultimate, calorific value and FTIR analyses of the study. Observation of the atomic H/C ratio in this study is generally consistent with previous reports on coal systems that in the lignite coal (GER) has the highest H/C ratio while the high rank coal, anthracite has the lowest H/C ratio. The same trend was obtained for the acid-treated coal and heat treated coal samples. The trend of decrease of H/C ratio with increasing coalification for the acid treated coal was only pronounced in the medium rank to high rank coals while for the low rank coals (lignite and sub-bituminous), the impart of demineralization was absent. For the heat treated coals, the trend was the same with the low temperature treated coals having the highest atomic H/C ratio compare to the high temperature treated coal: The H/C ratio for lignite (GER) was determined to be in the range of 0.5 to 1 from 450°C to 700°C; 0.5 to 0.1 for NGR; 0.5 to 0.1 for BCH, 0.4 to 0.1 SSL; 0.4 to 0.1 for SM and 0.3 to 0.1 for SPL. There was a convergence of the atomic H/C ratio at the temperature of 700°C (char forming temperature) for all heat-treated coal samples. The calorific value increases with increase in coal rank from 21.2

MJ/kg for the lignite to 29.6 MJ/kg for anthracite. The impact of demineralization is visible as the calorific values increases from 21.2 MJ/kg to 28.9 for lignite and from 29.6 to 32.7 MJ/kg for anthracite respectively (Table 1 and 2). The same story of increasing calorific value with increasing temperature can be told until the temperature of 650ºC, thereafter there was a drop in the calorific value. This implies that the maximum temperature to get the heat effects of coal is 650ºC.

Table 2: Proximate analysis, ultimate analysis, calorific values, aromaticity and calculated H/C and fuel ratio values for acid – treated coal

Coal	SPL	SM	BCH	SSL	NGR	GER
wt% Inherent moisture(air dried)	2.5	2.3	2.7	1.3	1.9	1.7
wt% Ash (air-dried)	1.5	1.8	1.2	3.3	2.0	0.8
wt% Volatile matter (air-dried)	6.8	9.6	27.2	25.0	43.2	60.3
wt% Fixed carbon (air-dried)	89.2	86.3	68.9	70.4	53.0	37.3
wt% Carbon (daf)	85.6	89.0	83.4	80.9	75.1	69.2
wt% Hydrogen (daf)	2.4	3.3	4.6	4.2	5.2	6.2
wt% Nitrogen (daf)	2.0	1.8	2.0	2.3	1.8	0.6
wt% Oxygen (daf)	7.7	5.0	9.1	12.3	17.4	20.3
wt% Sulphur (daf)	2.1	0.7	1.0	0.3	0.1	2.7
Gross calorific value (MJ/kg)	32.7	33.3	32.0	30.0	29.3	28.9
H/C	0.3	0.4	0.7	0.6	0.8	1.1
O/C	0.07	0.04	0.08	0.11	0.17	0.22
f_a	0.98	0.84	0.72	0.74	0.58	0.40
Fuel ratio	13	9	2.5	2.8	1.2	0.6

From the proximate analysis, the fuel ratio, which is the ratio of the fixed carbon to volatile matter content, was calculated (Table 1, 2 and 3). It can be seen that the fuel ratio increases with increase in coal rank and the coalification process. Though slight differences can be observed in the values obtained for both the parent coal and the acid treated coals, the impart is more noticed in the heat treated coal and a convergence is noticed around 700ºC most especially for the low rank to medium rank coals (Table 3). The fuel ratio was determined to be in the range of 1.19-21.0 for lignite from 450-700ºC respectively; 3.4-20.3 for sub-bituminous; 5.5-24.0 for bituminous; 11.6-29.6 for semi-anthracite and 16.5-27.8 for anthracite. The spectra obtained from the FTIR were used to determine the aromaticity. The aromaticity was determined to be in the range of 0.66-0.79 for GER from 450-700ºC respectively; 0.75-0.90 for NGR; 0.83-1.00 for BCH; 0.84-1.00 for SSL; 0.94-1.00 for SM and 0.97-1.00 for SPL respectively. From the calculated parameters in Table 3, it can be observed that as the atomic H/C ratio decreases with increase in coal rank and with increasing pyrolysis temperature, there is a corresponding increase in both the aromaticity and fuel ratio.

4. Conclusion

It can be concluded that all different rank of coals show a similar behavior in char properties, when subjected to elevated temperatures, the (H/C) and (O/C) ratio, decrease with temperature, while the aromaticity, as determined by both XRD and FTIR increase with charring temperature. The order of the determined characteristics is consistent with the rank of raw coal.

Table 3: Proximate analysis, ultimate analysis, calorific values, aromaticity and calculated H/C and fuel ratio values for heat – treated coal

COAL	Wt % (air dried)	Wt % (daf)	MJ/kg

GER	Mois.	Ash	V.M	F.C	C	H	N	O	S	GCV	H/C	f_a(FTIR)	FR
450	2.8	1.5	32.6	63.0	82.9	3.1	1.0	10.4	2.5	29.6	0.5	0.66	1.9
500	2.5	1.7	29.8	66.0	85.1	2.8	1.0	8.4	2.6	31.1	0.4	0.69	2.2
550	2.4	1.7	22.3	73.6	88.9	2.1	1.0	5.8	2.3	32.1	0.3	0.73	2.3
600	2.1	1.8	9.8	86.2	90.4	2.1	1.1	4.1	2.3	32.6	0.3	0.74	8.8
650	2.5	1.8	6.7	89.0	91.8	1.6	1.1	3.3	2.3	32.8	0.2	0.76	13.3
700	3.1	2.4	4.3	90.1	93.1	1.0	1.0	2.6	2.3	32.0	0.1	0.79	21.0
NGR													
450	3.0	1.9	21.7	73.3	84.9	3.2	2.2	9.2	0.5	31.0	0.5	0.75	3.4
500	3.2	2.7	24.2	69.9	87.3	2.7	2.3	7.2	0.5	31.4	0.4	0.78	2.9
550	3.1	2.3	22.5	72.1	89.7	2.4	2.3	5.1	0.5	31.8	0.3	0.81	3.2
600	3.2	2.4	13.3	81.1	91.3	2.0	2.3	4.1	0.5	32.3	0.3	0.84	6.1
650	3.6	2.5	8.8	85.1	92.0	1.5	2.2	3.9	0.5	31.9	0.2	0.87	9.7
700	4.0	2.5	4.4	89.1	93.1	1.0	2.0	3.4	0.5	31.4	0.1	0.90	20.3
SSL													
450	1.5	3.6	14.6	80.3	88.1	3.1	2.1	6.4	0.4	31.3	0.4	0.84	5.5
500	1.3	3.7	12.5	82.5	89.7	2.7	2.2	5.1	0.3	32.2	0.4	0.88	6.6
550	1.0	3.6	9.5	85.9	89.7	2.3	2.1	5.5	0.3	32.4	0.3	0.90	9.0
600	0.8	3.6	7.7	87.9	89.6	2.0	2.1	5.5	0.3	32.8	0.3	0.93	11.4
650	0.8	4.1	5.5	89.6	91.7	1.5	2.1	4.3	0.3	32.8	0.2	0.97	16.3
700	1.0	4.2	3.8	91.0	92.6	0.7	2.3	4.1	0.3	32.3	0.1	1.00	24.0
BCH													
450	0.9	1.3	13.9	84.0	88.1	3.3	2.1	5.7	0.8	33.2	0.5	0.83	6.0
500	1.1	1.1	11.4	86.4	89.0	2.9	2.1	5.4	0.7	33.5	0.4	0.86	7.6
550	0.9	0.9	8.6	89.6	91.3	2.6	2.2	3.4	0.5	33.8	0.3	0.89	10.2

600	0.9	1.1	7.3	90.7	92.1	2.2	2.1	3.1	0.5	33.9	0.3	0.92	12.4
650	0.9	1.2	5.0	92.9	93.1	1.7	2.1	2.5	0.6	33.7	0.2	0.95	18.6
700	0.9	1.1	3.9	94.1	95.5	1.1	2.0	0.9	0.6	33.4	0.1	1.00	24.1
SM													
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
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
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
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
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
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
SPL													
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
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
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
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
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
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

F.C fixed carbon; V.M. volatile matter; GCV gross calorific value in MJ/kg; f_a aromaticity; FR fuel ratio.

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