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An Investigation into the Thermal Decomposition of Nigerian Coal

[1]O.O. Sonibare, [2]O.A. Ehinola, [3]R. Egashira and [3]Lim KeanGiap
[1]Chemistry Department, Petroleum and Environmental Geochemistry Research Group,
University of Ibadan, Nigeria, [2]Geology Department , University of Ibadan, Nigeria
[3]Department of International Development Engineering,
Tokyo Institute of Technology, Tokyo 152-8550, Japan

Abstract: Five coal samples from Nigeria were characterized by thermogravimetry (TG) analysis. Thermal decomposition in air (combustion) and inert (pyrolysis) environment at temperature up to 1000°C classified the coals as belonging to the low-rank class, within the Lignite and sub-bituminous group. The coals are not cokable alone but could serve as suitable blends with coking coal of higher ranks. The apparent activation energies of the combustion and pyrolysis processes ranged from 68.5 to 90.0 kJ mol^{-1} and 34.1 to 57.2 kJ mol^{-1}, respectively.

Key words: Nigerian coal, thermal analysis, burning profile, volatile profile, burn-out temperature, peak temperature

INTRODUCTION

Much attention has been focused in recent years on coal as an alternative source of energy. In assessing the quality of coal, it is always essential to study the thermal decomposition processes involved during its conversion to liquid and gaseous fuel. Thermo-analytical methods such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have proved to play important role in the study of thermal decomposition of solid fuels[1-6].

Thermogravimetric analysis is a rapid and cost effective technique for monitoring coal burning and volatile profiles. Differential thermal analysis has been used to differentiate between ranks of coal[1]. Five distinct thermal curve types are recognized, based upon physical, chemical and structural changes in coals of different ranks. Podder *et al.*[7] have used differential thermal analysis (DTA) and thermogravimetry (TG) analysis in investigating the thermal behavior of Bangladeshi coals. On heat-treatment in an inert atmosphere up to 600°C, 20-27% weight loss occurs due to removal of various volatile materials. The DTA results indicated that primary and secondary devolitilization peaks occur within the temperature range of 410-550°C. Kok *et al.*[8] have studied the effect of particle size on coal pyrolysis by thermogarvimetry (TG/DTG). Different fractions of the coal showed differences in TG/DTG curves, peak temperatures and residue values. The kinetic parameters of the pyrolysis were determined from the TG/DTG data. TG-DTA has been described as an excellent method for accurate determination of the ignition of coal particles[9]. The burning profile of coals has been studied by thermogravimetric analysis[10]. It was reported that burning profile could provide a valuable, rapid laboratory method of ranking coals in terms of their burnout performance.

In southern Nigeria, coal-bearing Formation occurs within the geological units known as the coal measures which belong to the Campanian-Maastrichtian age. Both the lignite and coal have an estimated reserve of about 1.8 billion tons[11]. Presently, exploration and exploitation of coal deposits in Nigeria have been intensified with a view of diversifying the economy which has been solely dependent on oil and gas. In the present study, the burning and volatile profiles of Nigerian coals with a view of assessing their suitability as future source of energy, was reported.

MATERIALS AND METHODS

The coal samples used in this study were collected from five different locations in Nigeria (Fig. 1). The samples were ground into fine powder of particle size < 150 μm. The TG and DTA measurement were carried out in a TG/DTA 320 Seiko thermal analyzer. 10-15 mg of the samples were placed in a platinum crucible and heated at a linear heating rate of 10°C min^{-1} over a temperature range of 25 to 1000°C. The experiments were performed

Corresponding Author: O.O. Sonibare, Chemistry Department, Petroleum and Environmental Geochemistry Research Group, University of Ibadan, Nigeria E-mail: sonibaredayo@yahoo.com

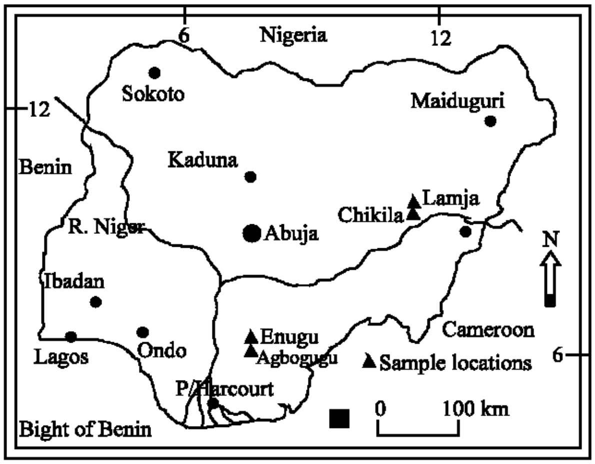

Fig. 1: Sample locations

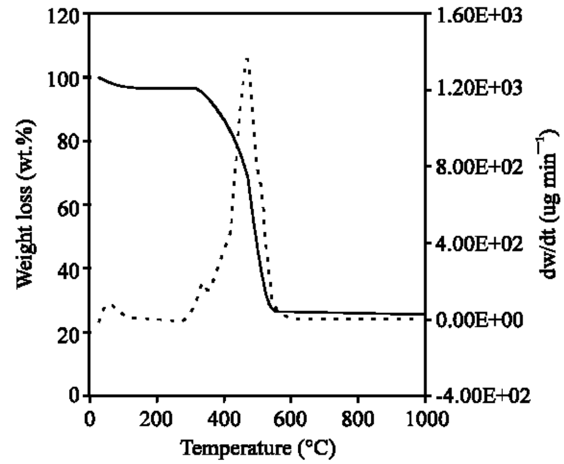

Fig. 2: TG/DTG curve of Lamja coal (combustion)

separately in air and nitrogen gas at a flow rate of 50 mL min^{-1}. The TG/DTA equipment was calibrated for temperature reading using indium as reference material before the commencement of the experiment.

RESULTS AND DISCUSSION

Burning profile: In selecting coal for combustion, it is very important to compare their combustibility characteristic or burning profile. This is necessary to assess the reactivity of the coal. A burning profile is obtained when coal is heated in an oxidizing environment. The TG/DTG curves of all the coal samples in air show the same trend in behavior, having two peaks. The TG /DTG curve of a representative coal is shown in Fig. 2. The first small peak that occurs at temperature below 120°C is due to elimination of moisture content of the coal. The estimated moisture content calculated ranged from 3.11 to 12.43% (Table 1). The amount of water evolved is an indication of the coal rank. The lower-rank coal with the greatest porosity usually have the highest moisture[12]. The second peak appearing at 300-620°C corresponds to devolatilization of the organic matter of the coal. The main characteristic point on the DTG curve is the peak temperature (PT) and Burnout temperature (BT). The peak temperature represent where the rate of weight loss is at a maximum. This parameter is used chiefly in the assessment of combustibility. Lower temperature indicates more easily burned coal. The burnout temperature represents the temperature where sample oxidation is complete. The characteristic temperatures of the coal samples derived from the combustion profile are listed in Table 1. The low values of peak temperature recorded (445-500°C) classified the coal as belonging to low-rank class, within the lignite and sub-bituminous group[13].

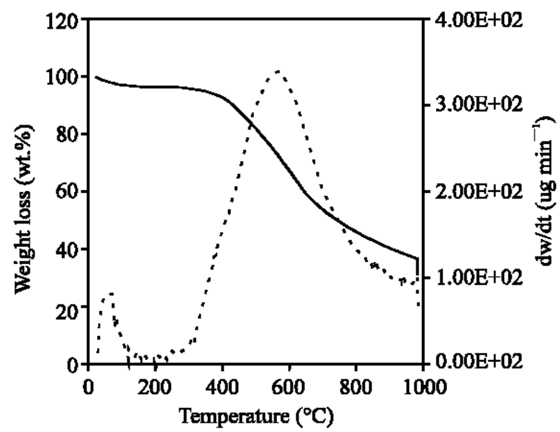

Fig. 3: TG/DTG curve of Lamja coal (pyrolysis)

Volatile profile: Volatile profile is applicable in gasification and coking studies. It is used mainly in identifying and comparing coal samples. A volatile release profile is produced when coal is heated in an inert atmosphere. The derivative weight changes indicate the progressive thermal breakdown of the organic matter present in the coal and loss of gaseous products. The coals studied show similar trend in behavior when heated in nitrogen atmosphere. A representative TG/DTG curve is shown in Fig. 3. Two peaks were observed on the plot. The first temperature range of 25-130°C represent the region where water loss occurs. Lost of volatile materials due to primary and secondary devolatization occurs within the range of 300-780°C. The amount of volatile matter, which represents the weight after the evolution of moisture minus the weight of residue left after the coal pyrolysis is completed range from 31.6 to 57.0% (Table 1). With the exception of Chikila coal, all the samples have volatile matter values greater than 40%. These values classified the coals as low-rank. The coals classified as

Table 1: Termogravimetric characteristics of Nigerian coals

Samples	Peak temperature (C°)	Burn-out temperature (C°)	Estimated moisture content (wt %)	Volatile matter (wt %)
Combustion				
Lamja	475	585	3.3	-
Chikila	500	620	10.2	-
Enugu (Akwuka)	445	610	5.1	-
Enugu (Okpara)	450	560	5.4	-
Agbogugu	455	620	5.0	-
Pyrolysis				
Lamja	580	750	3.1	57.0
Chikila	515	775	10.1	31.6
Enugu (Akwuka)	470	730	4.8	44.6
Enugu (Okpara)	515	780	5.4	51.5
Agbogugu	560	752	5.0	47.6

Table 2: Kinetic parameters for the non-isothermal decomposition of Nigerian coals

Samples	E (KJ mol^{-1})	A(min^{-1})	cc
Combustion			
Lamja	88.2	2.3×10^{2}	0.992
Chikila	82.6	5.8×10^{1}	0.994
Enugu (Akwuka)	68.5	1.1×10^{1}	0.991
Enugu (Okpara)	90.9	6.7×10^{2}	0.980
Agbogugu	78.3	4.3×10^{1}	0.992
Pyrolysis			
Lamja	45.7	2.4×10^{-2}	0.976
Chikila	57.2	3.0×10^{-1}	0.996
Enugu (Akwuka)	41.2	1.1×10^{-2}	0.976
Enugu (Okpara)	46.1	3.2×10^{-2}	0.971
Agbogugu	34.1	4.6×10^{-3}	0.995

cc: correlation co-efficient

Flammkohle type coal (i.e. coal with volatile matter content greater than 40%) on Standard German classification of rank and coking property[1]. This type of coal is not cokable alone. The characteristic temperatures (peak and burn-out) of the volatile profile of the coal are shown in Table 1.

Kinetic analysis: Weight loss kinetics of the thermal decomposition of coal is extremely complicated because of the numerous components that are simultaneously being pyrolysed and oxidized. The overall decomposition processes can be assumed to follow the following equation:

$$d\alpha/dt = k\ (1-\alpha)^n \qquad (1)$$

Where, α is the extent of conversion, k the specific rate constant and n the order of reaction. The temperature dependence of k is expressed by the Arrhenius equation. The extent of conversion, or fraction of material decomposed, α, can be defined by the expression

$$\alpha = w_o - w_t / w_o - w_\alpha \qquad (2)$$

Where, w_o is the initial weight loss, w_t the weight after time t and w_α is the weight left after complete decomposition.

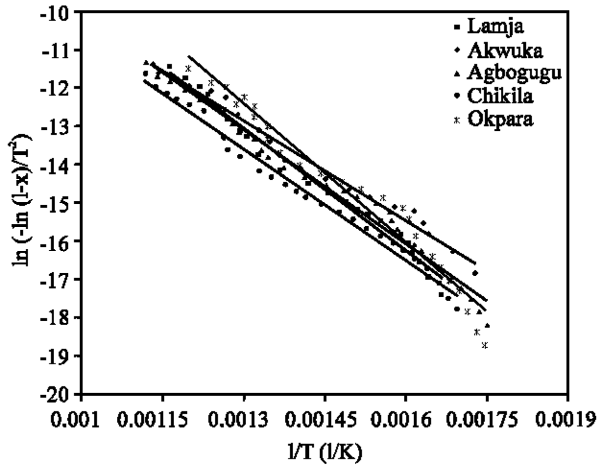

Fig. 4: Arrhenius plots of Nigerian coals (combustion)

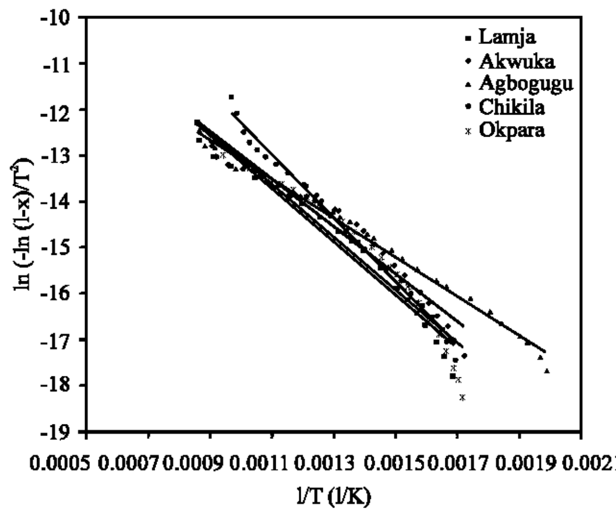

Fig. 5: Arrhenius plots of Nigerian coals (pyrolysis)

$$K = A\exp\ (-E/RT) \qquad (3)$$

Where, A is the Arrhenius constant, E the activation energy, R is the gas constant and T the absolute temperature. Assuming that the reaction order is close to unity, it would be advantageous to simplify the kinetics to first-order. Thus, the rate of coal decomposition is given by combining eq. 1 and 3:

$$d\alpha/dt = A.\exp(-E/RT)(1-\alpha) \qquad (4)$$

For the non-isothermal decomposition of coal, eq., 4 can be modified by introducing the heating rate as:

$$d\alpha/dt.dT/dt = A.\exp(-E/RT).(1-\alpha) \qquad (5)$$

or

$$d\alpha/dt = (A/\beta).\exp(-E/RT).\ (1-\alpha) \qquad (6)$$

Where, β is the heating rate. By integrating equation (6) and taking logarithm we obtain:

$$\ln[-\ln(1-\alpha)/T^2] = \ln AR/ \beta E - E/RT \qquad (7)$$

By using the α and temperature values from the TGA data, a plot of the left side of eq. (7) versus 1/T will give a straight line. Arrhenius constant, A and activation energy, E can be obtained from the intercept and slope of the line. Kinetic parameters were derived for the region where the devolatilization of the organic matter contents of the coal occurs. The Arrhenius plots are shown in Fig. 4 and 5. A regression analysis with the least square method was used in drawing the best straight line. The linear square correlation varied between 0.971 and 0.996. The apparent activation energies and Arrhenius constants were calculated from the slope and intercept of the straight line, respectively (Table 2). The apparent activation energies of the combustion and pyrolysis reactions of the coals varied from and 68.5 to 90.9 kJ mol^{-1} and 34.1 to 57.2, respectively (Table 2).

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