THERMOGRAVIMETRIC ANALYSIS OF ENUGU COAL UNDER INERT AND OXIDATIVE ATMOSPHERES

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ABSTRACT

The thermal degradation and kinetics of Enugu coal have been evaluated under inert and air atmospheres using non-isothermal thermogravimetry analysis (TGA). The devolatilization characteristics of coal pyrolysis and combustion (ignition and peak temperature) were evaluated. Coats-Redfern method was applied to determine the apparent activation energy (Eα) of the thermal decomposition of process. The main devolatilization stage of coal pyrolysis takes place in two steps between a temperature of 180-568 ^oC during which volatile matter was released. On the other hand, the devolatilization stage of coal combustion was characterized by only one single step occurring between a temperature of 370-640 ^oC where volatiles were released and burned. The peak pyrolysis temperature was 31 ^oC higher than 420 ^oC obtained for the combustion process. The result of residual weight of coal at the end of completion of combustion was 11.5 wt% of the initial weight. This quantity is appreciably lower than 78.5 wt% of the initial weights of 100 wt% under inert atmosphere. The mean activation energy of the pyrolysis of the coal was 73.71 kJ mol^{-1} as against 97.75 kJ mol^{-1} for coal combustion. The result obtained can be effectively employed in design and optimization of coal combustion furnace.

Key words: Coal, thermal degradation, pyrolysis, combustion, devolatilization, kinetic.

1. INTRODUCTION

Nigeria is blessed with over 4 billion metric tonnes of coal and large reserves of crude oil, natural gas, lignite, tar sand, nuclear elements, hydropower, solar radiation, and wind energy, that have remained untapped. Despite the abundant and diverse energy resources, the country electric energy supply is grossly inadequate [1]. Nigeria has about 8039 MW installed electricity generation capacity, only about 30 % of the installed generation capacity is actually operational [2]. For over four decade the country electricity generation is purely dependent on hydropower, natural gas and coal with hydropower system and gas-fired system taking precedence over coal. Oji River Power Plant, the only coal power plant is in comatose. It is was reported that the nation requires power generating capacity of 140,000 MW to maintain the target of Millennium Development goals [3]. In view of this, the Nigerian Government earlier state that country will increase the diversity in her electricity generation mix by investing in coal power plants. To this effect, Nigeria has started the construction of the 1200 MW Itobe power plant in Kogi State with a proposed operation date of 2018 [4]. The the nations project when completed have the potential to contribute to the energy security. Coal is not subjected to climatic changes when compared to hydropower and bunkering as the case with petroleum products.

Coals are of different types and ranks, and the individual properties of coal play a key role in establishing its suitability for relevant domestic and industrial applications. Large deposits of the Nigerian coal have been neglected over the years as a result of the flourishing petroleum fuel driven economy. These hitherto neglected natural resource is presently been sought after for energy generation. Substantial amount of these coal deposits can be found in Benue trough and Anambra Basin of the country. The Anambra Basin has been singled out as the largest producer of coal with new deposit been discovered in spite of the massive exploration and utilization of these deposits. The present concern for a relative abundant, reliable and accessible energy source has led to a renewed interest in coal utilization for energy and power generation [5].

Thermogravimetric analysis (TGA) is one of the most important techniques used nowadays to rapidly evaluate the thermal degradation and kinetics of the solid fuels (coal and biomass) pyrolysis and combustion [6-8]. It has the ability to measure the weight loss of a sample as a function of temperature and time. The temperatures at which thermal degradation in the sample start and end is closely followed by TGA. Data extracted from TGA curve can be used to obtain kinetic parameters such as activation energy and pre-exponential (frequency) factor. The kinetics of the thermal decomposition can be estimated from the Arrhenius equation which separate slopes of constant weight loss [9, 10]. Information obtained from TGA decomposition profiles of laboratory scale can provide insight into the understanding of combustion behaviour on industrial scale. Combustion remains the single leading source of energy production [11]. Holistic knowledge of the thermal decomposition of coal combustion and kinetics is essential for clear understanding, design, optimization and fabrication of combustion furnaces on industrial scale [12] .

Many studies on the kinetics of coal decomposition are focused on pyrolysis of coal under inert atmospheres [13]. However, recent research studies now focuses on the study of coal under oxidative atmosphere, a subject about which information is still scarce on Nigeria coal. The aim of this work is to investigate a comparative study of TGA of coal under nitrogen and oxidative atmospheres.

2. MATERIALS AND METHOD

2.1 Experiment Setup

Thermal degradation of Enugu coals were carried out by a means Setaram TAG24 analyzer under nitrogen and oxidative atmosphere. 20 mg samples of the coal with particle size <150µm are heated up to 1100 ◦C at the rate 10 ◦C/min under nitrogen flow rate of 50 cm^3/min. The system is connected to a compatible personal computer, which records the temperature via a thermocouple placed beneath the alumina crucible. The coal sample is then placed inside the crucible and place in the TGA apparatus. The sample is then heated and weight loss was continuously until the experiment end. At the end of pyrolysis, dry air of about 20 % oxygen was introduced into the TGA alumina crucible region in the same conditions to nitrogen. The experiments were duplicated for each test in order to ascertain it reproducibility of the results.

2.2 Kinetic Method

The degradation of solid fuel can be described as break down of solid substance into char and volatiles [14] .

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E_a}{RT}\right)} f(\alpha) \quad (1)$$

where, A is the pre-exponential factor, Ea is the activation energy, T is absolute temperature, R is the gas constant, α is the conversion factor f(α) is the reaction model. Conversion, α is defined by:

$$\alpha = \frac{mo - mt}{mo - mf} \quad (2)$$

Where mo is the initial weight of sample, mt and mf refer to the initial weight at temperature T and at the final temperature of pyrolysis, respectively. Many researchers based their assumption on first order reaction in describing solid fuel degradation [9, 14]., therefore, the degradation reaction equation of solid fuel transformed into Eq. (3):

$$\frac{d\alpha}{dt} = Ae^{-\left(\frac{E_a}{RT}\right)} (1-\alpha) \quad (3)$$

The coal samples were heated at a constant rate, rearranging and integrating Eq. (3) by using the Coats-Redfern method gives:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right]\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad (4)$$

where β = dT/dt is the heating rate. It has been shown that for most value of E and for the temperature range of pyrolysis, E/RT>> 1, thus the expression ln[(AR/βE) × (1-2 RT/E)] in Eq. (4) is a constant, which gives:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = -\frac{E_a}{RT} \times \frac{1}{T} + \ln\left(\frac{AR}{\beta E_a}\right) \quad (5)$$

The plot of $\ln[-\ln(1-\alpha)/T^2]$ versus 1/T gives a straight line of slope –Ea/R. The Eα and pre-exponential factor A can be determined from the slope.

To describe the change in pyrolysis of coal, Cumming [15] proposed mean activation energy (Em). The Em is defined as follows:

$$E_m = \sum E_i F_i \quad (6)$$

where Ei is the activation energy of various stages, Fi is the mass loss fraction of various stages.

3. RESULTS AND DISCUSSION

3.1 Thermal degradation characteristics

Coal combustion is generally referred as the combination of two main steps. The first step is devolatilization (pyrolysis) of coal into char due to heat application. The second one is the char-oxygen reaction (combustion) due to continuous of heat application [16]. The thermograph has the ability to elucidate the complexities in the thermal decomposition of the solid fuels. Consequently, the kinetic information are extracted from the thermographs for the design and control of combustion boilers and furnaces [9]. Coal pyrolysis and combustion can be evaluated by TGA. TGA is a cost-effective thermochemical method of analysis that measured weight loss as a function of temperature or time). The decomposition of solid sample is express by two thermograms or curves (thermograph; TG and derivative thermograph; DTG).

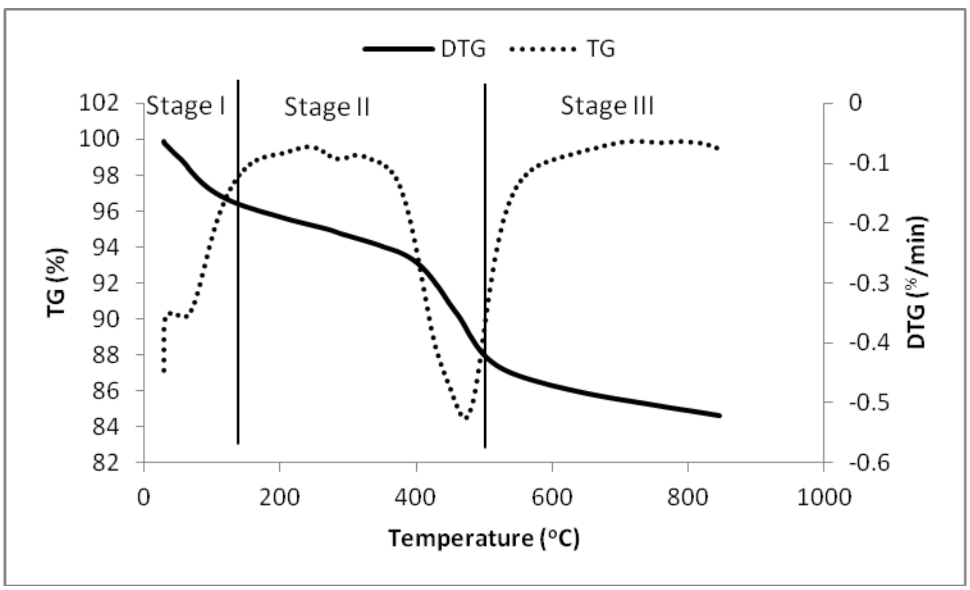

Figure 1: Thermal profile of the coal samples under inert atmosphere.

Figure 1 show TG/DTG curves for the thermal decomposition of coal under inert atmosphere. The first fall in the TG curve corresponding to the first stage (stage I) is attributed to drying occurring between 30-180 ^{o}C where water is removed. The further decrease in TG curve corresponding to the second peak is usually to be due to the main devolatilisation process (stage II) in which compounds containing carbon, hydrogen and oxygen are ultimately released. The third stage (stage III) indicates the secondary devolatilisation that is associated with methane and hydrogen released [9].

It is evident from the TGA/DTG curves in Figure 2 that the coal demonstrated three weight loss stages; the first account for water removal and volatilization of light molecules, the second is due to oxidative degradation and the third stage relates to the char combustion. The first stage (stage I) in the curved started from room temperature to 398 °C. This stage was similar to the first stage in the pyrolysis curve. The second stage (stage II) of weight loss which occurs at temperatures ranged of 398 - 560 °C differs significantly with pyrolysis curve. This result indicates that the process is exothermic in nature and is always accompanied by heat loss. According to Haykırı-Açma [17] the second stage of combustion curve is associated with burning and subsequent release of volatiles matter. The third stage (stage III) is the burn out stage where coal burn continusly to burn until 100 % conversion is achieved. The result of solid residual (Sr) generated at the end of combustion (weight of coal after combustion) was about 11.5 wt% of the initial mass. This quantity is appreciably lower than 78.5 wt% of the initial weight under inert atmosphere as shown in Table 1.

Table 1: Pyrolysis and combustion characteristics of Enugu coal.

Type of degradation	Temperature range (^{o}C)	Ti (^{o}C)	Tp (^{o}C)	Sr (%)
Pyrolysis	180-568	-	451	78.5
Combustion	380-620	393	420	11.5

Sr – solid residual generated at the end of thermal decomposition.

The TG/DTG curves of coal combustion shows the important combustion characteristics (ignition, burnout, and peak temperature). Table 1 depicted the characteristic parameters of coal combustion deduced from the TG/DTG curves, where Ti is the ignition temperature and Tp refers to the peak temperature. The DTG trend under inert atmosphere was different from oxidizing condition. The combustion curve show higher weight loss than pyrolysis. The observed weight losses were: 89 wt% and 16 wt% for combustion and pyrolysis curves respectively. Comparing the pyrolysis and combustion DTG curves (Figure 1 and 2), it can be observed that combustion curves have more intense peak in the DTG curve. The temperature at this peak is often considered a measure of the reactivity of the coal [17]. In this region the weight loss fall untill that it reaches its maximum value at low temperature in combustion curve than in pyrolysis. The peak temperatures were 31 ^{o}C lower for combustion when compared to pyrolysis degradation. However, the difference in the rates of weight loss was significantly higher under combustion.

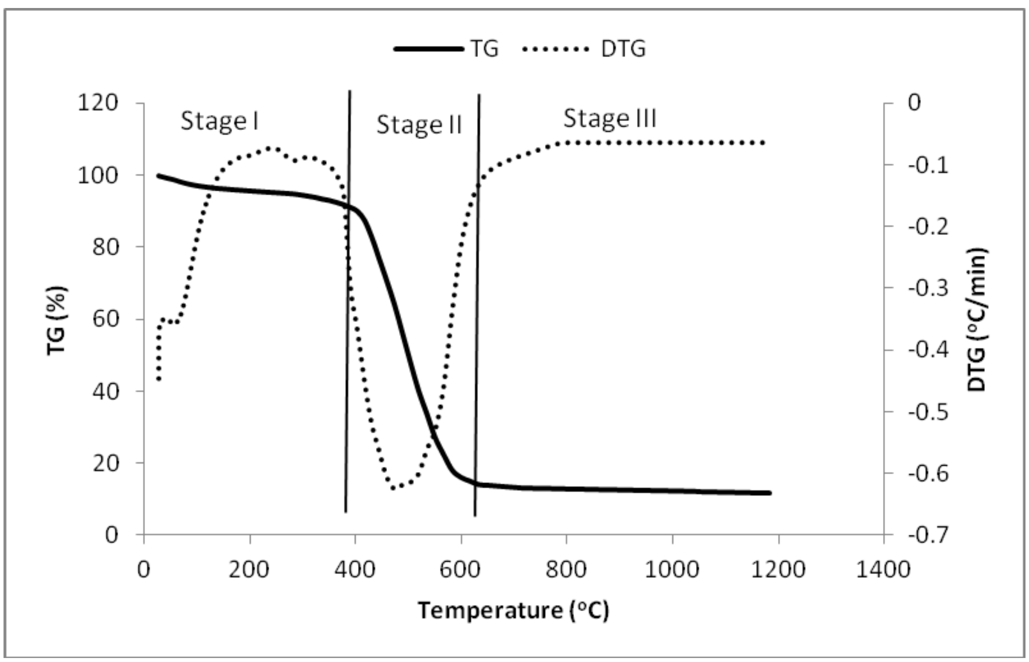

Figure 2: Thermal profile of the coal samples under air atmosphere.

The Ti is the temperature at which the mass loss curves in the combustion and pyrolysis experiments deviate. In the present study, TG curves of pyrolysis and combustion were compared and Ti was deduced from the curves as shown in Figure 3. Coals with lower peak temperatures generally can be ignited and burned easier. In this study, the Ti of coal sample was 398 ^{o}C. Prior to ignition temperature, slight increase in weight loss may occur due to the chemisorption of oxygen [7]. This is obvious from the negative values in the DTG curves of the sample. In second stage, combustion curve exhibit higher maximum weight loss rate than pyrolysis curve which suggests faster rate of weight loss.

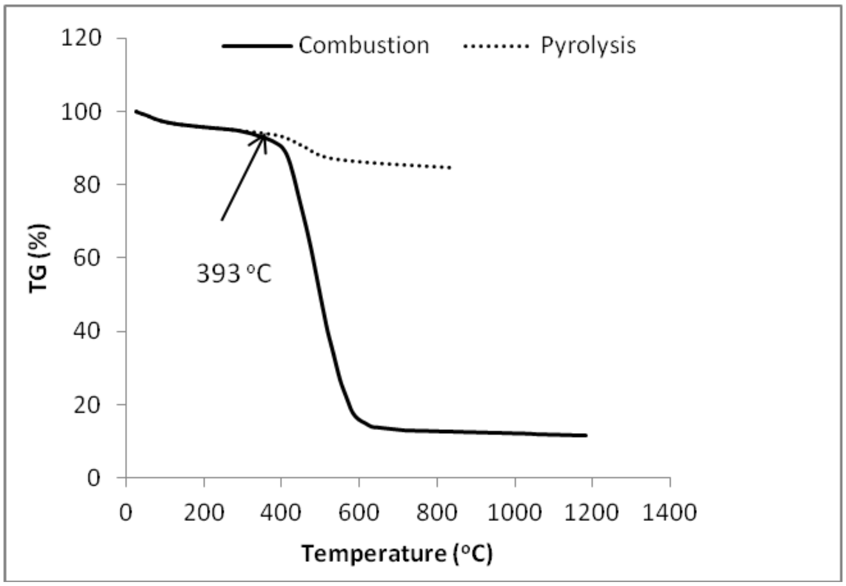

Figure 3: TG curves under oxygen and nitrogen atmospheres for coal ignition temperature determination.

3.2 Kinetic analysis

Thermal degradation of coal under inert and oxidative atmospheres is complex and involves different chemical and physical mechanisms. In TGA, these mechanisms contribute to the total mass loss. Therefore, the kinetic parameters cannot be considered as a true representative of any one mechanism but rather as apparent values [18].

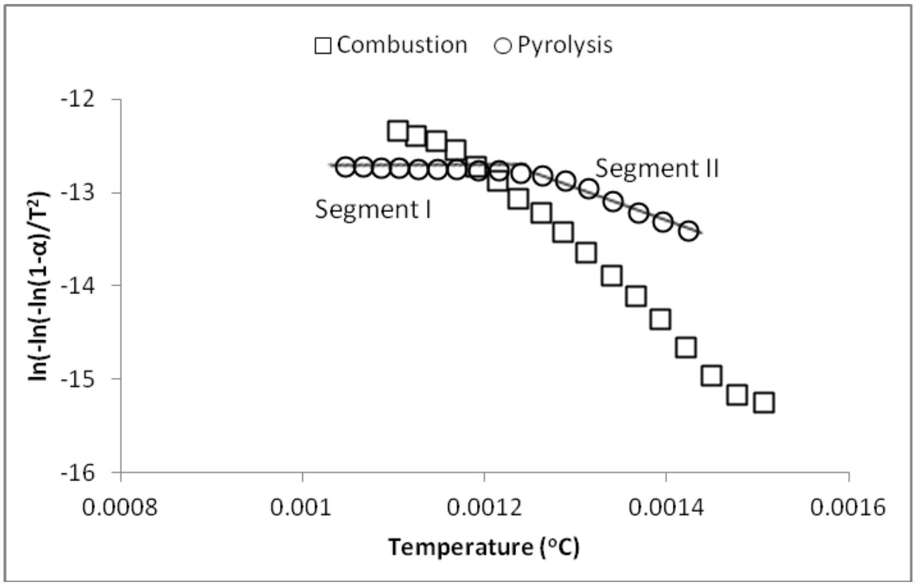

Figure 5. Pyrolysis and combustion analysis curves.

From Figure 5, it can be observed that the kinetic curve of coal pyrolysis exhibit two clear segments (segment I and II) while the kinetic curve of coal combustion shows only one segment. In order to obtain the kinetic parameter for coal pyrolysis, it is therefore necessary to determine the kinetic parameters for each of the segment separately to avoid significant deviations. For each segment, Coats-Redfern method is applied to obtain apparent activation energy (Eα) and pre-exponential factor (A), respectively.

Table 2: Kinetic parameters of coal.

Sample	Temperature	Eα ($kJmol^{-1}$)	R^2
Pyrolysis	180-568	73.71	0.9456
Combustion	370-640	132.11	0.9743

From Table 2, it can be observed that the Eα of segment II is greater thanthat of segment I. the results obtained exhibit quantitative similarity with results obtained by Liu *et al*., [14] and

Vamvuka *et al*.,[19]. According to Vamvuka *et al*. [19] the low value of Eα in segment I is attributed to the fracture of active group and side chain which are associated with poor thermal stability. The authors further added that high value of Eα in segment II is associated with energy required for the formation of char. The mean activation energy (Em) of the pyrolysis of coal was 73.71 KJ mol^{-1}. This value is relatively high when compared to the Em value of 44-48 $kJmol^{-1}$ and 18-27 $kJmol^{-1}$ reported for three Australian and Chinese coals by Ma *et al*., [20] and Wang *et al*., [10], respectively. The difference in the Em value in the present study can be attributed to differences in coal composition, coal rank and experimental conditions. From Table 2, it can be noticed that Eα during combustion of Enugu coal was 101.75 kJ mol^{-1}. This result differs significantly from the Eα value of 27.2-76.2 kJ mol^{-1} reported by Wang *et al*. [10].

4. CONCLUSION

Thermal degradation and kinetic of Enugu coal was evaluated under inert and air atmospheres using non-isothermal thermogravimetry analysis. The devolatilization characteristics of coal pyrolysis and combustion decomposition such as ignition and peak temperature were evaluated. Coats-Redfern method was applied to determine the apparent activation energy of the thermal decomposition of Enugu coal. The main devolatilization stage of coal pyrolysis takes place in two steps while the devolatilization stage in coal combustion is characterized by only one combustion step. The result obtained for the peak temperature of pyrolysis was higher than that of the combustion. The mean activation energy of the pyrolysis of the coal was 73.71 kJ mol^{-1} as against 97.75 kJ mol^{-1} for coal combustion. The knowledge of kinetics is important for design and optimization of combustion furnace.

ACKNOWLEDGEMENT

The authors would like to thank the SPEME of University of Leeds for Setaram TAG24 for analysis of Enugu coal.

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