

Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

ISSN: (Print) (Online) Journal homepage: <https://www.tandfonline.com/loi/ueso20>

CO-pyrolysis of bituminous coal and coconut shell blends via thermogravimetric analysis

Bamiji Zacheous Adewole , Busayo Sunday Adeboye , Babafemi Olamide Malomo , Sirajudeen Olanrewaju Obayopo , Solomon Almanto Mamuru & Abraham Awolola Asere

To cite this article: Bamiji Zacheous Adewole , Busayo Sunday Adeboye , Babafemi Olamide Malomo , Sirajudeen Olanrewaju Obayopo , Solomon Almanto Mamuru & Abraham Awolola Asere (2020): CO-pyrolysis of bituminous coal and coconut shell blends via thermogravimetric analysis, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects

To link to this article: <https://doi.org/10.1080/15567036.2020.1798567>



Published online: 11 Aug 2020.



Submit your article to this journal [↗](#)



View related articles [↗](#)



View Crossmark data [↗](#)



CO-pyrolysis of bituminous coal and coconut shell blends via thermogravimetric analysis

Bamiji Zacheous Adewole ^a, Busayo Sunday Adebayo ^b, Babafemi Olamide Malomo ^a, Sirajudeen Olanrewaju Obayopo^a, Solomon Almanto Mamuru^c, and Abraham Awolola Asere^a

^aDepartment of Mechanical Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria; ^bDepartment of Mechanical Engineering, Osun State University, Osogbo, Nigeria; ^cDepartment of Chemistry, Adamawa State University, Mubi, Nigeria

ABSTRACT

The thermal behavior of bituminous coal, coconut shell, and their blends during pyrolysis process was investigated in this study. The experiments were conducted at different weight percent of coconut shell (10, 20, 30, 40, and 50 wt%) and temperatures ranging from 30°C to 900°C. The DTG data for fuel blends showed additive profiles that reflected behavior of the individual fuel. When coconut shell was mixed with coal under weight percent of 20–50%, the nature of peaks in DTG profiles changed from higher to lower in the third stage reaction, shifting devolatilization temperature from 400°C to 450°C. This led to a decrease in the maximum rate of mass loss from 10.6% to 7.4%/min. However, the 10 wt% blend caused a slight increase in the maximum rate of mass loss from 10.6% to 11%/min. In addition, co-pyrolysis kinetics of fuel blends indicated that the blending of coconut shell with coal at BBR higher than 30% can increase the value of activation energy and induce slow pyrolysis of blends.

ARTICLE HISTORY

Received 29 March 2020
Revised 9 July 2020
Accepted 11 July 2020

KEYWORDS

Thermogravimetric analysis; biomass blend ratio; co-pyrolysis kinetics; devolatilization temperature; maximum rate of mass loss

Introduction

Pyrolysis is a thermal reaction process that occurs in the absence of an oxidizer and carried out with the sole aim of achieving end products that can be classified as gases, solid char residues, and a complex blend of hydrocarbons (Zhou et al. 2016). Specifically, it is a highly significant and effective intermediate operation in the conversion and utilization of coal, and for the production of salient hydrocarbon derivatives such as methanol, dimethyl ether, bio-oil, etc. (Miao et al. 2019).

During the pyrolysis of coal for the production of solid char, its organic structure is modified disadvantageously by a thermal decomposition process that eventually culminates into the release of deleterious volatiles to the environment at high temperatures. The agglomeration of these volatiles and other combustible elements is inherently hazardous and poses serious health risks and potential long-term negative environmental effects. However, in response to the need to circumvent the stringent environmental regulations associated with the use of coal, biomass which is considered as a viable and representative alternative has been gaining research attention over the years (Wang et al. 2020). As a matter of fact, biomass constitutes about 12.83% of the renewable energy stock for the environment and it is expected that its utilization would span decades to come, against the backdrop of the depletion of fossil fuel reserves amidst global warming concerns (Meng et al. 2013). It has been observed that certain properties of the biomass such as high moisture content, low heating value, and low density limit its combustion, pyrolysis, and gasification potentials on a large scale (Haykiri-Acma, Yaman, and Kucukbayrak 2013). Hence, to achieve an effective utilization of biomass, there is an onerous task to

improve its combustion performance and output. In light of this, co-combustion (Alobaid et al. 2020), co-pyrolysis (Wu et al. 2019) or co-gasification (Thengane, Gupta, and Mahajani 2018) has been identified and proposed as a veritable strategy to improve the energy content of biomass and reduce the environmental impact of indiscriminate use of coal, in order to achieve sustainable and efficient systems for clean energy generation.

Consequently, there is significant thrust of research efforts on the co-pyrolysis of coal and biomass. State-of-the art thermochemical biomass conversion investigations were conducted by Wei et al. (2018) with emphasis on the application of the thermogravimetric-mass spectroscopy (TG-MS) analysis to address the chemical composition and gaseous product evolution process in coal and biomass; a comparative study on the pyrolysis reactivity and gas release characteristics of biomass and coal where a definitive relationship was discovered between the gaseous products released during pyrolysis and the presence of different functional groups of the samples investigated. An experimental study on co-pyrolysis of bituminous coal and biomass has also been recently performed through a pressured fluidized bed reactor by Huang et al. (2019) where the authors successfully varied the blend ratio of biomass in the mixture between 0 and 100 wt% and found the composition with the best synergistic effect. Similarly, Ismail et al. (2020), developed a numerical model to validate some experimental data on the synergistic behavior of fluidized bed experiments of coal and biomass conducted under stringent conditions. In the same context with the foregoing, Ma et al. (2020), investigated co-pyrolysis behavior of cow manure and coal, their results elicited an activation energy-dependent distinctive reactivity of the blend formulations underscoring a significant interaction mechanism for improving the compositions.

From the foregoing and in spite of the high volatility and reactivity of biomass, the blend ratio still remains a strategic challenge to achieve the optimal utilization and performance characterization of biomass in coal blends. Some school of thought have argued that co-combustion of coal and biomass is most effective for blend ratio ranging between 10%-30% in order to control CO, CO₂, NO_x and SO₂ (Haykiri-Acma, Yaman, and Kucukbayrak 2013) emissions while in contrast, there is still an extensive variability in the reported blend ratio-performance dynamics spanning over a decade in the range of 5–80 wt% (Gil et al. 2010), 0–100 wt% (Huang et al. 2019; Lu et al. 2013) and coal-biomass ratio in the range of 3:1, 1:1 and 1:3 (Ma et al. 2020).

In regards to co-pyrolysis of coal and coconut shell, there is still dearth of data on the TGA and kinetic study of coconut shell pyrolysis with coal. Coconut shell which is a lignocellulosic agrowaste has been identified as an abundant energy crop residue in Nigeria (Ben-Iwo, Manovic, and Longhurst 2016) and other parts of the world (Gao et al. 2016; Mahir et al. 2015). Coconut shell with a high calorific value of 20.8 MJ/kg (Zafar 2020) is burned indiscriminately and without adherence to any regulation to generate charcoal in the rural areas of the country. This is so worrisome because of the significant contributions of CO₂ and methane to the environment, and in order to address this conundrum, there is a need to explore options to safely harness the energy potential of the coconut shell. This imperatively provides the motivation for this study where the central objective is to investigate the effects of varying coconut shell percentages on the thermal degradation characteristics and pyrolysis kinetics of coal-coconut shell blends in a TGA-based thermochemical framework with a view to establish an optimal biomass blend ratio for co-pyrolysis reactivity and kinetics of coal and coconut shell blends.

Materials and methods

Fuels

Nigeria Lafia–Obi coal and coconut shell were used as the raw materials. Lafia–Obi coal which is bituminous coal, is potentially abundant in Nigeria with an estimated reserve of 156 million tonnes and proven reserve of 21.42 million tonnes (Sambo 2008). It is characterized by low moisture content, volatile matter, high carbon content, and high calorific value in the range of 20,934 – 25,120 kJ/kg

(Popoola and Asere 2010). The combustibility, grindability, and high calorific value of Lafia-Obi coal suggest its optimal suitability for thermochemical processing. Coconut is a multifunctional plant and has a lot of economic, environmental, and technological benefits. As of 2017, Food and Agricultural Organization estimated the annual production of coconut in Nigeria to be 288,615 tons (FAO 2017). Nigeria is rated the fifth largest producer of coconut in Africa and 19th in the world. Coconut shell is mainly composed of cellulose, hemicellulose, and lignin. It has a tough natural structure, low ash content, higher volatile matter, and higher oxygen content compared to coal. Major gas products from coconut shell pyrolysis include CO₂, CO, CH₄, and H₂ (Mahir et al. 2015). The thermal properties of coconut shell make it ideal for any physical processing with low environmental impact. Table 1 shows the ultimate and proximate analysis of Lafia-Obi coal and coconut shell on air dry basis.

Sample preparation

Prior to the experiment, both Lafia-obi coal and coconut shell were pulverized to 250 µm sizes (Figure 1) to provide the basis for the experiment. The blends of Lafia-Obi coal and coconut shells were simply obtained by mixing and manually homogenized grounded 250 µm of Lafia-Obi coal with grounded 250 µm of coconut shells to obtain the predetermined percentage of 10%, 20%, 30%, 40%, and 50% weights of biomass.

Thermogravimetric analysis

The pyrolysis and co-pyrolysis characteristics of coal, coconut shell, and their blends (90:10; 80:20; 70:30; 60:40; 50:50) were investigated in thermogravimetric analyzer (Model: TGA 4000 Perkin Elmer) available at Adamawa State University, Nigeria. Approximately 10 mg of 250 microns each of Lafia-

Table 1. Ultimate and proximate analysis of Lafia-Obi coal and coconut shell on air dry basis.

	Lafia-Obi Coal	Coconut shell
<i>Elemental analysis (%wt)</i>		
Carbon	72.10	59.20
Oxygen	24.20	39.30
Hydrogen	5.49	4.90
Nitrogen	1.45	0.10
Sulfur	1.34	0.26
<i>Proximate analysis (%wt)</i>		
Moisture	9.50	8.50
Ash	20.18	28.82
Volatile matter	27.12	47.80
Fixed carbon	43.20	14.89

Source: Adewole (2017).



Figure 1. Pulverized coconut shell and coal.

Obi coal and coconut shell and their blends were loaded into a quartz pan and mounted in the TGA. Samples were thermally heated at a heating rate of 50°C/min from ambient temperature to 900 °C under nitrogen flow of 100 ml/min to keep the environment inert. Arrhenius and Coats and Redfern equations in which a single step decomposition and first-order kinetic are assumed for processing TGA data were applied for determining the kinetic parameters. Similar approach was used by Lu et al. 2013; Haykiri-Acma, Yaman, and Kucukbayrak 2013 with a single heating rate of 20° C/min and 40°C/min for non-isothermal decomposition of sample respectively. Temperature scan was run to measure and record sample weight loss with increasing temperature or with time. Sample weight, program temperature, and sample temperature were measured and recorded. Experiments were repeated to ascertain the reproducibility of results. TG (wt%) and DTG (wt%/min) data were developed from percentage sample weight loss and percentage weight loss per unit time, respectively. Thermogravimetric (TG) and derivative thermogravimetric (DTG) profiles were obtained by plotting percentage sample weight and percentage sample derivatives against sample temperature.

Kinetic study

The approach used to calculate the kinetic parameters in the study was based on Arrhenius equation. TG data from thermal decomposition reaction of fuel samples and their blends over the entire temperature range were used and so, the kinetics of reaction was described as:

$$\frac{dX}{dt} = kf(X) \quad (1)$$

where $f(X)$ is the differential conversion and X is the fuel conversion.

$$X = \frac{W_i - W}{W_i - W_f} \quad (2)$$

where, W_i , W_f , and W are the initial weight, final weight, and weight change per time, respectively.

The mass loss of a material with respect to time can be represented by Arrhenius equation according to Equation (3):

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where k is the reaction rate constant, E_a (kJ/mol) is the activation energy, A is the pre-exponential factor (min^{-1}), R is gas constant ($8.314 \text{ J/K}^{-1} \text{ mol}^{-1}$) and T is the reaction temperature ($^{\circ}\text{C}$). By writing

$$f(X) = (1 - X)^n \quad (4)$$

and then substitute Equation (4) into Equation (1), gives:

$$\frac{dX}{dt} = k(1 - X)^n \quad (5)$$

Substitute Equation (3) into Equation (5) gives:

$$\frac{dX}{dt} = A \exp\left(\frac{-E_a}{RT}\right) (1 - X)^n \quad (6)$$

where E , A , and $f(X)$ are typical outcomes of the kinetic analysis of the samples and (n) is the reaction order. Equation (6) is required to provide mathematical description of the decomposition process and it can be used to predict the kinetic or the time to reach any extent of conversion outside the experimental temperature ranges. For a constant linear heating rate ($\beta = dT/dt$) during thermal decomposition process, Equation (6) becomes;

$$\frac{dX}{dt} = \beta \frac{dX}{dT} = A \exp\left(\frac{-E_a}{RT}\right) (1 - X)^n \quad (7)$$

where

$$\frac{dX}{dT} = \left(\frac{1}{\beta}\right) A \exp\left(\frac{-E_a}{RT}\right) (1 - X)^n \quad (8)$$

In non-isothermal kinetic reaction process, it is usually accepted that the reaction rate is given by Equation (8). Integration of Equation (8) gives Equation (9) expressed in form of integral law as:

$$g(x) = \frac{A}{\beta_0} \exp\left(\frac{E_a}{RT}\right) dT \quad (9)$$

where $g(x)$ represents the limiting stage of reaction. By replacing $\frac{E_a}{RT}$ by (u) and transform the integration limit (Georgieva, Zvezdovaz, and Vlaev 2012). Equation (9) becomes:

$$g(x) = \frac{AE_a}{\beta R} \int_u^\infty \frac{e^{-u}}{u^2} du = \frac{AE_a}{\beta R} p(u) \quad (10)$$

where $p(u)$ is the exponential integral. Several authors have suggested different ways to solve this exponential integral. Coats and Redfern (Lu et al. (2013) made some approximations and proposed linear equation given in Equation (11). This equation is applied when the thermal degradation of solid fuel is of first order ($n = 1$)

$$\ln\left[\frac{-\ln(1 - X)}{T^2}\right] = \ln\frac{AR}{\beta E_a} \left[1 - \frac{2RT}{E}\right] - \frac{E_a}{RT} \quad n = 1 \quad (11)$$

The value of $2RT/E$ is small and can be neglected. Hence, Equation (11) becomes;

$$\ln\left[\frac{-\ln(1 - X)}{T^2}\right] = \ln\frac{AR}{\beta E_a} - \frac{E_a}{RT} \quad (12)$$

It has been demonstrated by Georgieva, Zvezdovaz, and Vlaev (2012), Lu et al. (2013) and Ma et al. (2020) that Equation (12) is constant for the temperature range of combustion and for most values of E . Also, the plot of $\ln\left[\frac{-\ln(1-X)}{T^2}\right]$ against $1/T$ should give a straight line with high correlation coefficient. The value of the activation energy (E_a) and pre-exponential factor (A) can be calculated from the slope and intercept of the line, respectively. In the present study, the value of $\ln\left[\frac{-\ln(1-X)}{T^2}\right]$ was computed and plotted against $1/T$ to give a straight line. Accordingly, activation energy (E_a) and pre-exponential factor (A) were extracted from the slope (m) and intercept (I) of the regression line respectively, where $m = \frac{E_a}{R}$ and $A = E_a \beta (\text{Exp}(I))/R$.

Results and discussion

Pyrolysis characteristics of Lafia-obi coal and coconut shell

The pyrolysis profiles of Lafia-Obi coal and coconut shell are displayed in Figure 2(a,b). The pyrolysis behavior of the two fuels is characterized by three-stage thermal reaction. The first stage reaction is attributed to the release of moisture. The peak temperature in the first stage is extended beyond 200°C due to the release of bonded water. Similar finding was reported by Shi et al. (2013).

Table 2 presents the observed thermal stages and corresponding temperature ranges for fuel samples. The second stage reaction of Lafia-obi coal occurs between 249°C and 560°C while that of coconut shell occurs between 234°C and 564°C. The pyrolysis reaction of coal occurs at a higher temperature but the weight loss (decomposition intensity) during the process (34.23% °C⁻¹) is lower

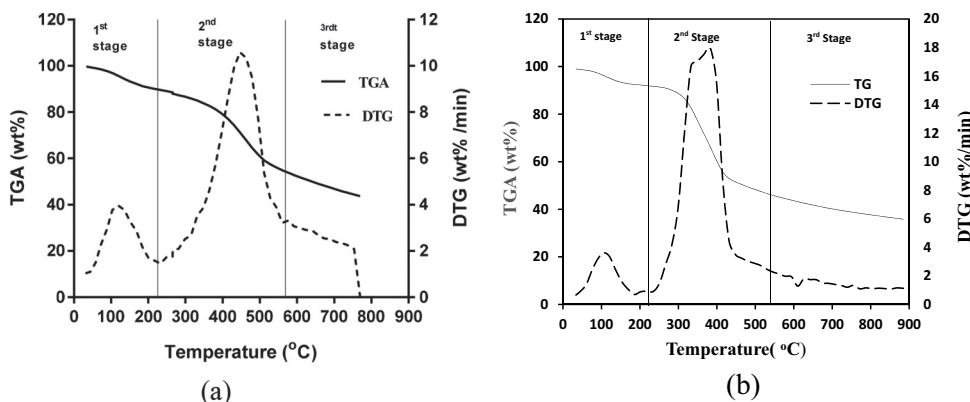


Figure 2. TG and DTG curve of (a) Lafia-obi coal and (b) Coconut shell.

Table 2. Temperature and weight loss for different thermal stages of Lafia-Obi coal and coconut shell.

Parameters	Samples	Stage 2		Stage 3	
		Initial	Final	Initial	Final
Temperature (°C)	LOC	249	560	561	770
	CNS	234	564	513	884
Weight loss (%)	LOC	34.23			
	CNS	40.2			
Peak temperature (°C)	LOC	446.6			
	CNS	382.5			
Max rate of mass loss (%/min ⁻¹)	LOC	10.6			
	CNS	18.0			

than that of coconut shell ($40.2\% \text{ } ^\circ\text{C}^{-1}$). Similar results were observed for Shenhua bituminous coal with sawdust and rice straw (Wei et al. 2018), South African coal and stone pine wood (Ferrara et al. 2014), lignite and waste wood (Sadhukhan et al. 2008), and Australian coal and raw/torrefied wood (Liu et al. 2013).

The peak temperature and maximum rate of mass loss for Lafia-obi coal and coconut shell are determined from their DTG curves. The peak temperature in the second stage reaction for Lafia-obi coal (446.6°C) is higher than that of coconut shell (382.5°C) with a maximum rate of mass loss of $10.6 \text{ wt } \%/ \text{min}$ and $18.0 \text{ wt } \%/ \text{min}$ for coal and coconut shell, respectively. The peak DTG curve exhibited for coal in Figure 2(a) is attributed to the release of volatile matter during the pyrolysis process while the decomposition of hemicellulose and cellulose content; and devolatilization of coconut shell lignin lead to the peak exhibited in Figure 2(b). Akinriola et al. (2014) explained that the devolatilization and char combustion peak temperature as well as the highest maximum rate of mass loss are often used as indicators for fuel reactivity. The lower the peak devolatilization temperature, the more reactive the fuel. Further, the fuel with the highest rate of mass loss indicates the most reactive fuel. Coconut shell decomposed earlier and faster than Lafia-obi coal due to its higher oxygen and volatile matter contents.

Pyrolysis characteristics of coal and coconut shell blends

Figure 3(a,b) presents the pyrolysis TG and DTG profiles of blends and the individual fuel at biomass blend ratio of 10–50 wt% in steps of 10 wt%. In Figure 3(a), it is seen that the TG curves for all blends almost overlap that of coal, though with little difference. The contributions of coal and coconut shell to these curves are obvious. In Figure 3(b), the blends show four stages of thermal decomposition in

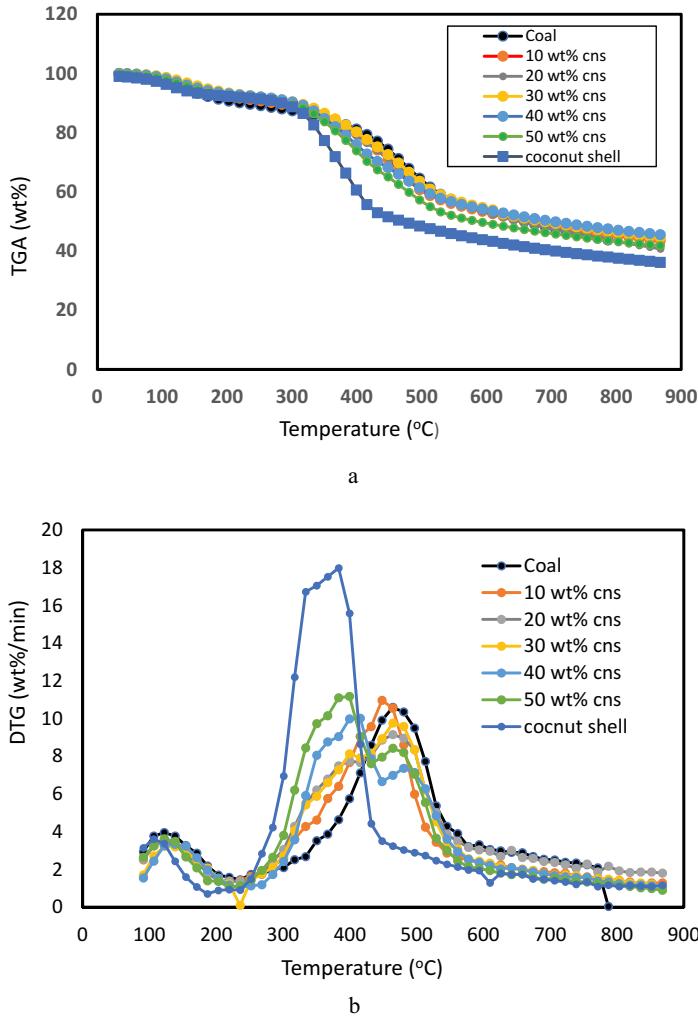


Figure 3. (a) Pyrolysis TG profiles of the blends. (b) Pyrolysis DTG profiles of the blends.

contrast to the three stages observed for the parent fuel. The DTG curve for 20–50 wt% blends show three peaks in contrast to two peaks display for the parent fuels. The 10 wt% blend behave similar to coal though with slightly higher peak intensity. The 20–50 wt% blends exhibit two stages of active pyrolysis corresponding to the second peak and the third peak, respectively. The second peak is attributed to the pyrolysis of coconut shell while the third peak is attributed to the pyrolysis of coal. The second peak decreases with the decrease in coconut shell contents from 50 to 10 wt% while the third peak increases with an increase in coal contents from 50 to 90 wt% in the blends. The pyrolytic behavior of the blends shows additive profiles that reflected the behavior of the individual fuel. This may be attributed to the difference in volatile matter content and chemical structure of coal and biomass (Lin et al. 2019).

The peak decomposition intensity of coconut shell is higher than those of the blends and coal in the temperature range between 234°C–431°C and 249°C–560°C, respectively. Degradation of hemicellulose and cellulose composed in coconut shell which easily breakdown appears to take place in the second stage reaction leading to higher rate of mass loss. For the blends, the corresponding discontinuity in peak in DTG curves is prominent for 50, 40, 30, and 20 wt% and the trend is increasing with decreasing BBR due to the reduction in volatile matter content of biomass (Gil et al.

2010). For higher percentage blends (40 and 50 wt%), effect of higher amount of coconut shell becomes predominant, inducing higher mass loss. At 450°C, the peak in DTG curve for 40 and 50 wt% blends shifts from higher in the second stage reaction to lower in the third stage reaction. For 20–30 wt% blends, the nature of the peaks also changes from lower in the second stage reaction to higher in the third stage reaction and the trend is increasing with the decreasing coconut shell percentage. The peak DTG curve for these blends is however lower to that of coal. The change in peak in DTG curves in stage 3 may be attributed to the completion of mass loss from biomass in stage 2 and subsequent increase in coal devolatilization due to higher amount of coal in the blend. Gil et al. (2010) reported that the mass loss from biomass was over at approximately 480°C for the blends of high volatile bituminous coal and pine sawdust.

Comparing the pyrolysis rate of coal with those of coal-coconut shell blends in stage 3, pyrolysis rate of blends for 50, 40, 30, and 20 coconut wt% has much lower mass loss (DTG peak). As the weight percentage of coconut shell increases, the mass loss rate of the blends decreases. Lignin which is more resistant to degrade due to its strong lignocellulosic structure appears to be predominant. In addition, complex coal structure with many covalent bonds offers resistant to thermal degradation of coal thereby, inducing slow pyrolysis. Similar finding was reported by Lin et al. (2019) for cotton stalk with lignite and bituminous coal. For 10 wt% blend, the DTG curve shifts slightly to a lower devolatilization temperature with little increase in the rate of mass loss. This indicates that the addition of coconut shell at or below 10 wt% could enhance the pyrolysis rate of coal.

Table 3 shows the peak temperature and maximum rate of mass loss for 100% Lafia-obi coal, coconut shell, and their blends. The maximum rate of mass loss is considered directly proportional to the reactivity of fuel and the faster the rate of mass loss, the higher the reactivity of fuel (Gil et al. 2010). The pyrolysis peak temperature exhibited by 100% Lafia-obi coal in stage 3 is lower than the peak temperature exhibited by all blends. As explained above, lignin and coal become very difficult to decompose thereby offer greater resistance to thermal degradation of the blend thus, explaining the increase in peak devolatilization temperature. The maximum rate of mass loss of the blends is lower than what is observed for the individual fuels except for 10 wt% blend in stage 3. This implies that the interaction between the components of the blend is significantly affected by the presence of coal or coconut shell respectively.

Pyrolysis kinetics of coal and coconut shell

Figure 4(a,b) presents linear regression model for the extraction of activation energy (E_a) and pre-exponential factor (A) for Lafia-obi coal and coconut shell. The second stage or rapid decomposition zone is considered as the active pyrolysis stage. Similar approach was used by Lu et al. (2013) for Australian coal and Mahir et al. (2015) for coconut shell pyrolysis. The activation energy obtained for coal and coconut shell was 41.7 and 24.8 kJ/mol respectively. These values are compared with some literature data. For thermogravimetric data of Nigerian Owukpa sub-bituminous coal decomposition over the temperature range of 30°C–900°C, Bemgba et al. (2019) obtained activation energy between 28.86 and 57.29 kJ/mol by Kissinger method. Sonibare et al. (2005) applied a first-order single reaction model for pyrolysis of some Nigerian coals over the temperature range of 25°C–1000°C and obtained the following

Table 3. Peak temperature and maximum rate of mass loss for the individual fuel and the blends.

Sample	BBR (%)	Peak Temperature (°C)		Max Rate of Mass loss (%/min)		
		Stage 2	Stage 3	Stage 2	Stage 3	Total
LOC	100	-	446.6	-	10.6	10.6
CNS	100	382.5	-	16.7	18.0	34.7
LOC/CNS	10	419.6	470.9	8.3	11.0	19.3
	20	399.6	464.7	7.8	9.2	17.4
	30	398.6	480.0	8.1	9.6	17.7
	40	415.5	480.7	10.0	7.4	17.4
	50	398.24	479.8	11.2	8.1	19.3

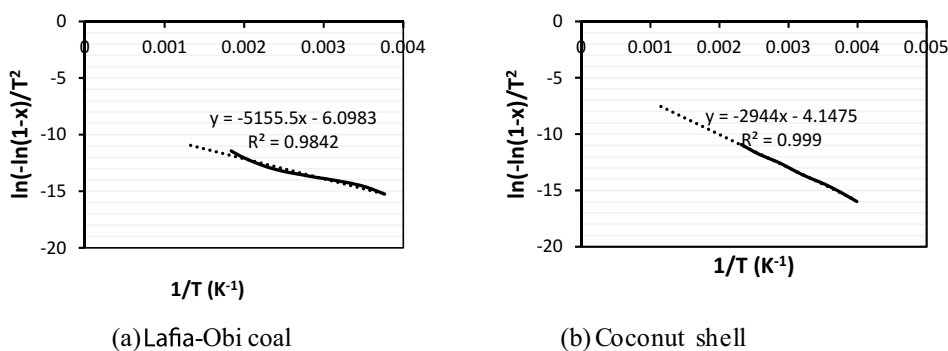


Figure 4. Linear regression for the extraction of kinetic parameters for Lafia-Obi coal and coconut shell.

activation energy: Lamja (45.7 kJ/mol), Chikila (57.2 kJ/mol), Akwuka (41.2 kJ/mol), Okpara (46.1 kJ/mol) and Agbogugu coal (34.1 kJ/mol). Rout (2013) studied pyrolysis of coconut shell and obtained activation energy of 19.40 kJ/mol for the second stage reaction and 47.68 kJ/mol for the third stage reaction.

According to Yorulmaz and Atimtay (2009), the reactivity of samples is determined by the activation energy (E_a) while pre-exponential factor (A) is more related to the material structure. Generally, lower activation energy is associated with more reactive fuels. Higher value of activation energy for coal may indicate slow reaction during co-pyrolysis. Pre-exponential factor (A) of 4.79×10^8 and 9.31×10^6 was obtained for Lafia-obi coal and coconut shell respectively.

Kinetics of blends

Figure 5(a-e) displays the linear regression model for the extraction of kinetic parameters for the blends of Lafia-Obi coal and coconut shell at 10%, 20%, 30%, 40%, and 50% BBR respectively. In both stages 2 and 3 reactions, the values of R^2 are not less than 0.94 indicating that the pyrolysis process of fuel blends in these two stages are well correlated with the experimental data. Similar correlation was observed by many authors including Gil et al. (2010) and Liu et al. (2013). Activation energy (E_a) and pre-exponential factors (A) values for Lafia-obi coal, coconut shell, and their blends are presented in Table 4. In stage 2, activation energy of 39.78, 33.06, 31.60, 26.96 and 22.69 kJ/mol is obtained for 10, 20, 30, 40, and 50 wt% coconut shell respectively whereas, the values in stage 3 are 41.21, 40.78, 40.65, 45.78 and 44.20 kJ/mol. The activation energy for the blends in stage 2 and stage 3 is close to those of the individual fuel.

In the second stage reaction, the blends with 40 and 50 wt% present values closer to that of coconut shell. In these cases, the presence of coconut shell is dominant. The calculated values of E_a for coconut shell are lower than the value for the blends below 50%. These results agree with those obtained in a study conducted to evaluate the co-pyrolysis of pine sawdust and coal (Gil et al. 2010), raw/torrefied wood with coal (Lu et al. 2013) and cotton stalk with lignite and bituminous coal (Lin et al. 2019). For the third stage reaction, the estimated activation energies for 10, 20, and 30 wt% blend are slightly lower than that of coal. However, for the blends with 40 and 50 wt%, the values of E_a are higher than the value for coal and increase by about 20% and 37% for 40% and 50% coconut shell blends, respectively. As shown in Table 4, the blending of coconut shell with coal at BBR higher than 30% can increase the value of E_a and thus, induce slow pyrolysis of blends. Similar observation was reported by Ma et al. (2020) for cow manure and Meihuajing bituminous coal blends. The pre-exponential factor shows a decreasing trend as the percentage of coconut shell increases in the blend in both stage 2 and 3 reaction. This further indicates the influence of coconut shell structure on the pyrolysis process of coal.

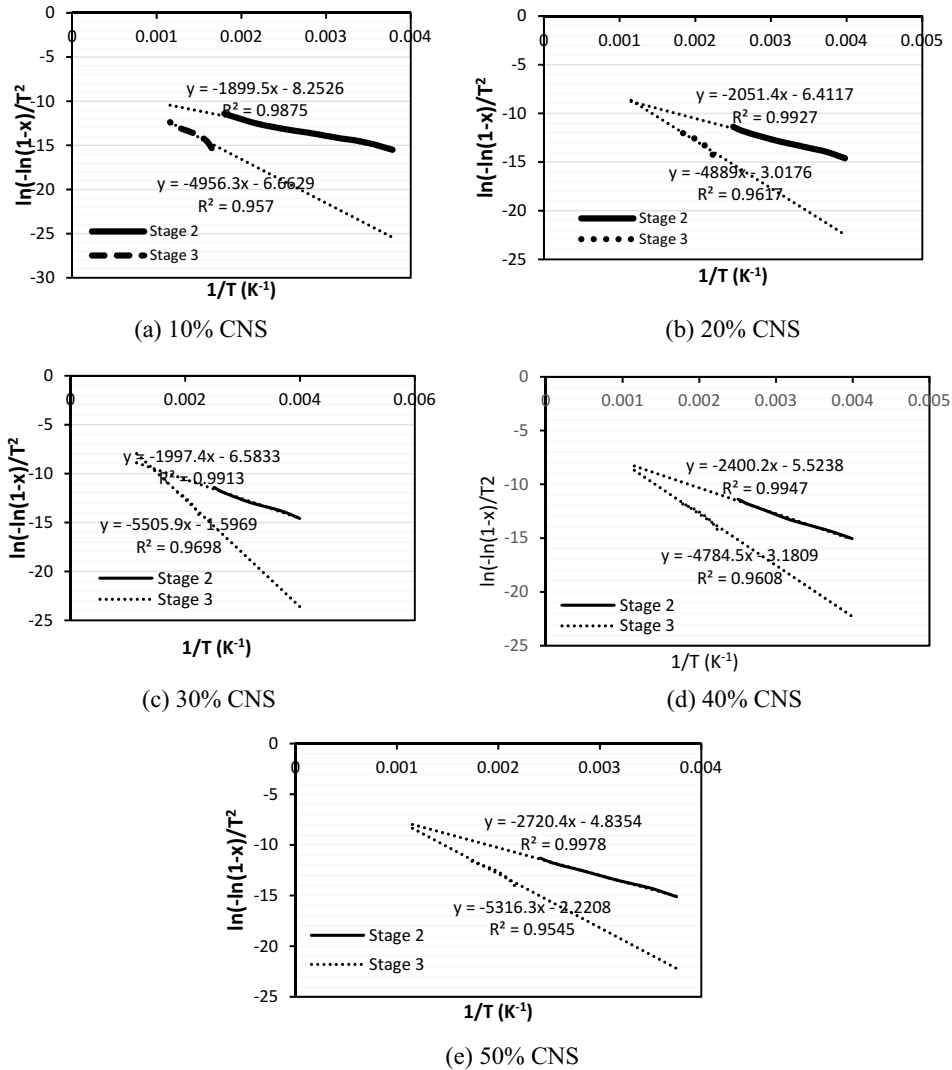


Figure 5. Linear regression model for the extraction of kinetic parameters of coal and coconut shell blends. (a) 10% CNS. (b) 20% CNS. (c) 30% CNS. (d) 40% CNS. (e) 50% CNS.

Conclusion

Coconut shell and Lafia-Obi bituminous coal as well as their blends were subjected to thermogravimetric analysis at temperatures ranging from 30°C to 900°C. Effect of varying coconut shell percentages at five different blend ratios of 10, 20, 30, 40, and 50 wt% was also examined to establish an optimal blend ratio. The pyrolysis process of coal and coconut shell consists of three-stage thermal reaction whereas, for coal-coconut shell blends, the process consists of four-stage thermal reaction. When coconut shell was mixed with coal under weight percentage of 20–50% BBR, pyrolysis rate of blends was lower to that of coal and decreased with increasing coconut shell percentage. The nature of peaks in DTG profiles for these blends changed from higher in the second stage reaction to lower in the third stage reaction, shifting devolatilization temperature from 400°C to 450°C. This led to a decrease in the maximum rate of mass loss from 10.6% to 7.4%/min, whereas the 10 wt% blend caused a slight increase in the maximum rate of mass loss from 10.6 to 11%/min. This result indicated

Table 4. Kinetic parameters for coal, coconut shell, and their blends in the second and third stages. reactions.

Samples	Temperature (°C)	E_a (kJ/mol)	A (min^{-1})	R^2
LOC	249–560	41.70	1.11×10^8	0.9842
CNS	234–564	24.80	9.31×10^6	0.999
<i>Second stage reaction</i>				
10% CNS	247–487	39.78	9.62×10^7	0.9929
20% CNS	235–416	33.06	1.39×10^7	0.9927
30% CNS	234–414	31.60	1.17×10^7	0.9913
40% CNS	234–415	26.96	4.38×10^6	0.9947
50% CNS	249–430	22.69	1.65×10^6	0.9978
<i>Third stage reaction</i>				
10% CNS	470–641	41.21	1.93×10^8	0.9570
20% CNS	432–594	40.78	4.15×10^7	0.9617
30% CNS	431–577	40.65	1.18×10^6	0.9698
40% CNS	432–594	45.78	6.62×10^6	0.9608
50% CNS	448–593	44.20	2.45×10^6	0.9545

that the thermal reactivity of coal and coconut shell blend may be enhanced at or below 10 wt% coconut shell. Co-pyrolysis kinetics analysis of fuel blends however, indicated that the blending of coconut shell with coal at BBR higher than 30% can increase the value of E_a and induce slow pyrolysis of fuel blends.

Nomenclature

A	Pre-exponential factor (min^{-1})
BBR	Biomass blend ratio (wt%)
E_a	Activation energy (kJmol^{-1})
k	Reaction rate constant (s^{-1})
n	Order of reaction
R	Universal gas constant ($=8.314 \text{ J/k}^{-1}\text{mol}^{-1}$)
t	Heating time (min)
T	Temperature (°C)
W	Weight (mg)
X	Fuel conversion

Symbols

β	Heating rate ($^{\circ}\text{C min}^{-1}$)
---------	--

Functions

$f(x)$	Differential function of conversion
$g(x)$	Integral function of conversion

Acknowledgments

Authors are thankful to the Department of Pure and Applied Chemistry, Adamawa State University, Nigeria, for granting us permission to use Perkin Elmer (TGA 4000) Thermogravimetric analyzer. Authors also wish to express their gratitude to the very competent reviewers and editors for their suggestions which have led to the improvement of the content of this paper. BZA will also like to thank NNPC/Addax petroleum for grant aid.

Funding

This work was supported by the NNPC/Addax Petroleum Scholarship.

Notes on contributors

Bamiji Z. Adewole is a lecturer in the Department of Mechanical Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria. He completed his PhD from the same University on the studies on fluidized bed combustion of some coal and biomass for sustainable energy generation. His specific research interests include solid fuel combustion, pyrolysis and gasification, gas combustion and dynamics, sustainable energy systems, heat transfer in fluidized beds, emission control, solar thermal conversion and waste recycling. Over the years, he has made extensive contribution in the area of gas, coal and biomass combustion. He is serving as a reviewer to Nigerian Journal of Technology and he is a member of Nigeria Institution of Mechanical Engineers, Nigeria Society of Engineers and Council for the Regulation of Engineering in Nigeria.

Busayo S. Adeboye completed his M.Sc and Ph.D degree in Mechanical Engineering. He is currently a Lecturer in the Department of Mechanical Engineering, Osun State University, Osogbo, Nigeria. His areas of research interest include conventional and renewable energy, energy conversion and management and waste recycling. He has several publications in reputable journals.

Babafemi O. Malomo is a Senior Lecturer and Researcher at the Obafemi Awolowo University, Ile-Ife, Nigeria. He holds a doctoral degree in Mechanical Engineering and his area of specialization is Materials Design and Structural Mechanics. He is devoted to the teaching, administration and mentoring of undergraduate students in Mechanical Engineering. He is a reviewer at Hindawi scientific publishing and a member of corporate and professional engineering regulatory organizations in Nigeria.

Obayopo Surajudeen Olanrewaju is presently a Senior Lecturer in the Department of Mechanical Engineering, Obafemi Awolowo University Ile-Ife Osun State, Nigeria. He completed his PhD research work at the University of Pretoria, on performance enhancement in proton exchange membrane (PEM) fuel cell using numerical modelling approach coupled with an optimization tool. He further trained in teaching pedagogy at the Massachusetts Institute of Technology (MIT) in USA during his fellowship program in the University. His research interest is in the field of renewable and clean conventional energy systems. He has over the years researched and presented courses in Fluid Mechanics, Fluid Power Engineering and Energy Technology. He is a member of American Society of Mechanical Engineers (ASME), Council for the Regulations of Engineering in Nigeria (COREN) and Nigerian Society of Engineers (NSE). He is also presently serving as a reviewer for Hydrogen Energy (*Elsevier*), Heat and Mass Transfer (*Elsevier*), Agricultural International (CIGR Journal) and other reputable International Journals.

Solomon Almanto Mamuru had his PhD in Chemistry from the University of Pretoria, South Africa and currently an Associate Professor at the Adamawa State University where he lectures chemistry as well as carry out research in Electrochemical Nanotechnology.

Abraham A. Asere is a Professor of Thermofluid and Energy Engineering in the Department of Mechanical Engineering, Faculty of Technology, Obafemi Awolowo University, Ile-Ife, Nigeria. His areas of research interest are in fluidized bed combustion of coal, solar thermal conversion, biodiesel, biogas and gas turbine combustor wall. He has mentored many undergraduate and graduate students in Mechanical Engineering. He has several articles in reputable journals and he is a fellow of Nigeria Society of Engineers, Life member of Renewable Energy Society of Nigeria and a Fellow of the Council for the Regulation of Engineering in Nigeria.

ORCID

Bamiji Zacheous Adewole  <http://orcid.org/0000-0002-6286-036X>

Busayo Sunday Adeboye  <http://orcid.org/0000-0002-6320-3425>

Babafemi Olamide Malomo  <http://orcid.org/0000-0002-3219-7237>

References

- Adewole, B. Z. 2017. Studies on fluidized bed combustion of some blends of coal and biomass for sustainable energy generation. Unpublished Ph.D. Dissertation, Obafemi Awolowo University, Ile-Ife, Nigeria.
- Akinriola, F. S., L. I. Davell, J. M. Jones, A. Williams, and J. A. Fuwape. 2014. Characterization of selected Nigeria biomass for combustion and pyrolysis applications. *Energy and Fuels* 28 (6):3821–32. doi:10.1021/ef500278e.
- Alobaid, F., J. P. Busch, A. Stroh, J. Strohle, and B. Eppler. 2020. Experimental measurements for torrefied biomass Co-combustion in a 1 MWth pulverized coal-fired furnace. *Journal of the Energy Institute* 93 (3):833–46. doi:10.1016/j.joei.2019.07.008.

- Bemgba, B. N., O. Olagoke, A. A. Segun, O. O. Edo, A. J. Gowon, T. A. Tuan-Amran, A. Habib, and H. A. Ali. 2019. Comprehensive evaluation of the combustion kinetic characteristics of Owukpa coal. *Coke and Chemistry* 62 (8):371–78. doi:10.3103/S1068364x19080027.
- Ben-Iwo, J., V. Manovic, and P. Longhurst. 2016. Biomass resources and biofuels potential for the production of transportation fuels in Nigeria. *Renewable and Sustainable Energy Reviews* 63:172–92. doi:10.1016/j.rser.2016.05.050.
- Ferrara, F., A. Orsini, A. Plaisant, and A. Pettinau. 2014. Pyrolysis of coal, biomass and their blends: Performance assessment by thermogravimetric analysis. *Bio Resources Technology* 171:433–41. doi:10.1016/j.biortech.2014.08.104.
- Food and Agriculture Organization. 2017. List of countries by coconut production. FAO statistics, FAO statistics division. Food and Agriculture Organization. Accessed November 12, 2019. <http://www.faostat.fao.org>.
- Gao, O., Y. Yang, Z. Qin, and Y. Sun. 2016. Factors affecting the yield of bio-oil from the pyrolysis of coconut shell. *SpringerPlus* 5 (333):2–8. doi:10.1186/s40064-016-1974-2.
- Georgieva, V., D. Zvezdovaz, and L. Vlaev. 2012. Non-isothermal kinetics of thermal degradation of chitosan. *Chemistry Central Journal* 6 (81):2–10. doi:10.1186/1752-153X-6-81.
- Gil, M. V., D. Casal, C. Pevida, J. J. Pis, and F. Rubiera. 2010. Thermal behaviour and kinetics of coal/biomass blends during co-combustion. *Bioresource Technology* 101:5601–08. doi:10.1016/j.biortech.2010.02.008.
- Haykiri-Acma, H., S. Yaman, and S. Kucukbayrak. 2013. Interaction between biomass and different rank coals during co-pyrolysis. *Applied Thermal Engineering* 50:251–59. doi:10.1016/j.applthermaleng.2012.06.028.
- Huang, Y., N. Wang, Q. Liu, W. Wan, and X. Ma. 2019. Co-pyrolysis of bituminous coal and biomass in a pressurized fluidized bed. *Chinese Journal of Chemical Engineering* 27 (7):1666–73. doi:10.1016/j.cjche.2019.03.012.
- Ismail, T., S. Banks, Y. Yang, H. Yang, Y. Chen, A. Bridgwater, K. Ramzy, and M. El-Salaam. 2020. Coal and biomass co-pyrolysis in a fluidized-bed reactor: Numerical assessment of fuel type and blending conditions. *Fuel* 275:118004. doi:10.1016/j.fuel.2020.118004.
- Lin, B., J. Zhou, Q. Qin, X. Song, and Z. Luo. 2019. Thermal behaviour and gas evolution characteristics during co-pyrolysis of lignocellulosic biomass and coal: A TG-FTIR investigation. *Journal of Analytical and Applied Pyrolysis* 144:104718. doi:10.1016/j.jaap.2019.104718.
- Liu, Q., H. Cheng, M. Huang, S. Zhang, and R. L. Frost. 2013. Application of TG-FTIR to study SO₂ evolved during the thermal decomposition of coal-derived pyrite. *Thermochimica acta* 555:1–6. doi:10.1016/j.tca.2012.12.025.
- Lu, K. M., W. J. Lee, W. H. Chen, and T. Lin. 2013. Thermogravimetric analysis and kinetics of co-pyrolysis of raw/ torrefied wood and coal blends. *Applied Energy* 105:57–65. doi:10.1016/j.apenergy.2012.12.050.
- Ma, M., Y. Bai, X. Song, J. Wang, W. Su, M. Yao, and G. Yu. 2020. Investigation into the co-pyrolysis behavior of cow manure and coal blending by TG-MS. *Science of Total Environment* 728 (1):138828. doi:10.1016/j.scitotenv.2020.138828.
- Mahir, S., J. Geoffrey, M. Cuthbert, and M. Samwel. 2015. The study of kinetic properties and analytical pyrolysis of coconut shells. *Journal of Renewable Energy* 1–8. doi:10.1155/2015/307329.
- Meng, A. H., H. Zhou, L. Qin, Y. G. Zhang, and Q. H. Li. 2013. Quantitative and kinetic TG-FTIR investigation on three kinds of biomass pyrolysis. *Journal of Analytical and Applied Pyrolysis* 104:28–37. doi:10.1016/j.jaap.2013.09.013.
- Miao, Z., Y. Wan, Q. He, Z. Pei, and X. Zhu. 2019. Pyrolysis behaviors and product distribution of Shengli Lignite at different heating rate and final temperature by TG-FTIR and Py-GC-MS. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 1–13. doi:10.1080/15567036.2019.1638994.
- Popoola, O. T., and A. A. Asere. 2010. Emission and combustion characteristics of Lafia-Obi coal in fluidized bed combustor. *Advanced Materials Research* 824:318–26. www.Scientific.net/AMR.824.318.
- Rout, T. K. 2013. Pyrolysis of coconut shell. Master thesis, National Institute of Technology Rourkela, India.
- Sadhukhan, A. K., P. Gupta, T. Goyal, and R. K. Saha. 2008. Modelling of pyrolysis of coal-biomass blends using thermogravimetric analysis. *Bioresources Technology* 99:8022–26. doi:1016/j.biotech.2008.03.047.
- Sambo, A. S. 2008. The place of coal in the Nigerian electricity generation scheme. A keynote address presented at the inauguration of the new president of the Nigeria Society of Engineers, International Conference Centre, Abuja, Nigeria. Accessed February 5, 2020. www.africanpowerplatform.org.
- Shi, L., Q. Liu, X. Guo, W. Wu, and Z. Liu. 2013. Pyrolysis behaviour and bonding information of coal-A TGA study. *Fuel Processing Technology* 108:125–32. doi:10.1016/j.fuproc.2012.06.023.
- Sonibare, O. O., O. A. Ehinola, R. Egashirs, and KeanGiap. 2005. An investigation into the thermal decomposition of Nigeria coal. *Journal of Applied Science* 5 (1):104–07. doi:10.3923/jas.2005.104.107.
- Thengane, S. K., A. Gupta, and S. M. Mahajani. 2018. Co-gasification of high ash biomass and high ash coal in downdraft gasifier. *Bioresource Technology*. doi:10.1016/j.biortech.2018.11.007.
- Wang, J., M. Ma, Y. Bai, W. Su, X. Song, and G. Yu. 2020. Effect of CaO additive on co-pyrolysis behavior of bituminous coal and cow dung. *Fuel* 265 (1):116911. doi:10.1016/j.fuel.2019.116911.

- Wei, J., X. Liu, Q. Guo, X. Chen, and G. Yu. 2018. A comparative study on pyrolysis reactivity and gas release characteristics of biomass and coal using TG-MS analysis. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 40 (17):2063–69. doi:10.1080/15567036.2018.1487483.
- Wu, Z., Y. Li, B. Zhang, W. Yang, and B. Yang. 2019. Co-pyrolysis behavior of microalgae biomass and low-rank coal: Kinetic analysis of the main volatile products. *Bioresource Technology* 271:202–09. doi:10.1016/j.biortech.2018.09.076.
- Yorulmaz, S. W., and A. T. Atimtay. 2009. Investigation of combustion kinetics of treated and untreated waste wood samples with thermogravimetric analysis. *Fuel Processing Technology* 90:939–46. doi:10.1016/j.fuproc.2009.02.010.
- Zafar, S. 2020. Energy potential of coconut biomass. Accessed April 6, 2020. <http://www.bioenergyconsult.com>.
- Zhou, C., G. Liu, X. Wang, and C. Qi. 2016. Co-combustion of bituminous coal and biomass fuel blends: Thermochemical characterization, potential utilization and environmental advantage. *Bioresource Technology* 218:418–27. doi:10.1016/j.biortech.2016.06.134.