

Thermal Degradation and Kinetics of Bituminous Coal-Palm Kernel Shell Blends

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Abstract

Employing a thermogravimetric analyzer, the degradation behaviour and kinetics of blends of Nigerian bituminous coal and palm kernel shell (PKS) were studied at temperatures ranging from 30 to 900 °C and with a blend ratio of 10, 20, 30, 40, and 50% weight of PKS. All fuel blends showed a peak devolatilization temperature that was higher than the bituminous coal's, causing a shift in coal devolatilization in the direction of a higher temperature. The maximal rate of mass loss falls as the blend's PKS content rises. Blends of bituminous coal and PKS with ratios of 10% and 20% yielded the lowest maximum rate of mass losses and the lowest peak devolatilization temperature. Furthermore, a blend containing 10% PKS produced the lowest activation energy. The outcomes demonstrated that PKS had a considerable impact on the coal/PKS blends' response rate. The significant impact of PKS structure on coal/PKS blends during co-pyrolysis further demonstrated the synergy between bituminous coal and palm kernel shell.

Keywords: Thermogravimetric Analysis; Kinetics; Coal-PKS blends; Thermal degradation; Devolatilization.

1. Introduction

Global energy demand is rising quickly due to changes in the world economy and population. In many areas, there is serious worry about the difficulty of satisfying high demand. Despite making up more than 40% of the world's electricity production in 2010 [1], coal—sometimes referred to as the foundation of the energy supply—is not environmentally benign. Thermochemical conversion processes such as coal pyrolysis, combustion, and gasification release harmful volatiles, particulate matter, and gases that cause acid rain and greenhouse effects [2]. However, there is currently a major push for alternative energy sources to replace coal entirely or in part with other carbonaceous fuel sources, which causes less issues.

Since biomass can be renewed, is widely available, and has the advantage of being carbon neutral in terms of lowering greenhouse gas emissions and the global warming effect, it has been acknowledged as an alternative and renewable energy source [3]. However, because of some of its drawbacks, such as reduced calorific value, increased moisture content, and particle density, using biomass has proven difficult [4-5]. Although their benefits and drawbacks will balance each other out, using a combination of biomass and coal will be a more sustainable fuel than using either one alone. Our main supply of carbon will be coal. An increased oxygen content in biomass will make the carbon more reactive. Because of its increased hydrogen concentration, coal will receive more hydrogen from it, improving conversion and producing more energy [6-8].

A crucial phase in thermochemical conversion processes is devolatilization. For this reason, understanding the behavior, reactivity, and kinetics of coal-biomass blends during thermal

decomposition is crucial when building and simulating the safe and effective operation of combustor or boiler units, gasifiers, and pyrolysis reactors. The fuel samples' derivative thermogravimetry (DTG) and thermogravimetric analysis (TGA) provide this information.

In TGA, an isothermal or non-isothermal process is used to continuously measure and record the rate of mass loss as a function of temperature and time in an inert atmosphere. Based on the information gathered, the kinetic parameters of the thermal breakdown reaction are estimated [9].

Numerous studies on the pyrolysis of biomass alone [13-14] and coal alone [9-12,28] have been conducted. Additionally, employing various types of coal and biomass sources, the kinetics of coal-biomass blends have been studied in recent years [2,6,8,15-17]. It has been demonstrated that blending biomass with coals increases coal reactivities and lowers emissions related to coal burning. In order to improve their use in systems for generating heat and power, this study intends to demonstrate the thermal behaviour of blends of palm kernel shell and Nigerian Lafia-Obi bituminous coal. The impact of introducing a local biomass residue on the thermal decomposition pattern and the coal devolatilization kinetics is examined using thermogravimetric analysis techniques.

2. Materials and method

2.1. Sample preparation

The biomass residue used in this study was palm kernel shell (PKS), which was gathered from local sources, while the coal was sourced from the Lafia-obi coal field in the Lafia-obi local government area of Nassarawa state, Nigeria. The samples of biomass and coal were ground into a fine powder using a hammer mill and then sieved independently. For the experimental examination, the fine, powdery particles were collected and kept in storage. Coal and biomass mixtures with varying mass blend ratios (90:10, 80:20, 70:30, 60:40, and 50:50) were made and manually mixed to ensure homogenization. Table 1 displays the coal and PKS's higher heating value (HHV) and proximate analysis.

Table 1. Properties of coal and biomass used in the study.

Property	Coal	PKS
<i>Proximate analysis (% wt)</i>		
Moisture content (MC)	9.50	10.3
Volatile matter (VM)	27.12	66.5
Ash content (AC)	20.18	9.08
Fixed carbon (FC)	43.20	14.12
HHV(MJ/kg)	36.8	51.1

2.2. Thermogravimetric analysis (TGA)

Employing a Perkin Elmer TGA 4000 thermogravimetric analyzer, the fuel's thermo-gravimetric properties (TG and DTG) were determined in order to define the fuel's decomposition pattern. The coal-biomass blends' ground-up fuel sample, weighing about 10 mg, was heated in the analyzer. Continuous heating was carried out between 30 °C and 900°C at a uniform heating rate of 50°C per minute in an inert nitrogen gas atmosphere that was passing through the analyzer at a rate of 100 mL per minute.

The same configuration was used for all coal samples, and blend ratios of 90:10, 80:20, 70:30, 60:40, and 50:50 were examined for the coal-biomass blend. The device automatically gathered and stored the data on the ongoing weight loss and its derivative with regard to temperature and time. Plotting the thermogravimetric curve (TG) and the derivative thermogravimetric curve (DTG) was done using the data that were acquired.

2.3. Kinetic study of fuel samples

The oxidation mechanism of fuel samples was examined by the application of kinetic parameters, including activation energy (E_a) and pre-exponential factor (A). The Coats and Redfern modified equation (1), as reported by Lu *et al.* 2013 [18], was applied.

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

The plot of $\ln \left[-\frac{\ln(1-X)}{T^2} \right]$ against $\frac{1}{T}$ gave a straight line with high correlation coefficient. For each stage, the activation energy (E_a) was calculated from the line's slope and (A) from the regression equation's intercept. Kinetic parameters were calculated using the work of Gil *et al.* [19], assuming that coal combustion included a single independent process while biomass and coal/biomass mixes involved two or three independent reactions [19]. Thus, kinetic parameters were computed for each step of palm kernel shell and coal/palm kernel shell blends in this work, as well as for the single stage of Lafia-Obi bituminous coal.

3. Results and discussions

3.1. Co-pyrolysis of bituminous Lafia-Obi coal/palm kernel shell blends

Using a Perkin Elmer (TGA 4000) thermogravimetric analyzer, the behaviour and thermal reactivity indicators of bituminous coal/palm kernel shell blends were studied during co-pyrolysis. In contrast to the three-stage thermal reaction seen for pure 100% coal and the four-stage thermal reaction found for 100% palm kernel shells, the pyrolysis of coal/palm kernel shell blends was characterized by a five-stage thermal reaction. For fuel mixtures containing 10, 20, 30, 40, and 50% PKS, pyrolysis of the fuel blends was noted.

The co-pyrolysis of coal and palm kernel shells involved four stages: moisture evolution in the first, hemicellulose and cellulose decomposition in the second, lignin decomposition in the third, and coal pyrolysis in the fourth. The final step resulted from the burning of coal and palm kernel shells, which was not taken into account in this investigation.

Experimental TG and DTG curves for the co-pyrolysis of bituminous coal/palm kernel shell blends at 10, 20, 30, 40, and 50% PKS, respectively, are shown in Figure 1(a-e). A three-stage thermal reaction was observed in the mix with 10% PKS (Figure 1a), whereas a five-stage reaction was seen in the blend with another ratio. Because of the low PKS percentage in the blend, the behavior of the 10% blend ratio was comparable to that of 100% coal. The additional two phases resulted from an increase in the content of cellulose, hemicellulose, and lignin caused by the PKS rise.

For each bituminous Lafia-Obi coal/palm kernel shell blend, Table 2 displays the weight loss for the various thermal phases of the blend, whereas Table 3 displays the maximum mass loss rate and peak temperature. The addition of biomass and the rise in oxygen and volatile matter in the blends are demonstrated by the fact that the overall weight loss increased as PKS increased. According to Lin *et al.* [20], the compositional and volatile matter differences between biomass and coal account for the additive pyrolytic behaviour of biomass blends.

As shown in Table 3.2, the maximum rate of mass loss for all fuel mixes at stages 2, 3, and 4 decreased as a result of a shift in the devolatilization temperatures of PKS and Lafia-Obi bituminous coal from lower to higher temperatures. During the second stage of hemicellulose decomposition, the fuel mix containing 30% PKS has the lowest peak devolatilization temperature (334 °C). This is followed by the blends containing 20% PKS (334 °C), 40% PKS (333.8 °C), and 50% PKS (334 °C).

The blend containing 20% PKS has the lowest peak devolatilization temperature (339.4 °C) at the third stage (during cellulose decomposition), followed by the blends containing 30, 40%, and 50% PKS, in that order. A blend containing 20% PKS has the lowest peak devolatilization temperature during the fourth stage (coal devolatilization), and the peak temperature rises as the blend's coal percentage increases.

Due to PKS lignin decomposition in the fourth stage, all of the blends' peak temperatures in stage 4 were higher than the peak temperatures of Lafia-Obi bituminous coal. This indicates a shift in coal devolatilization towards higher temperatures. In stages 2 and 3, the mixes with a greater proportion of PKS had an increase in the maximum rate of mass loss. Nevertheless, in stage 4, the maximal rate of mass loss falls as the blend's PKS level rises. The lowest peak

devolatilization temperature and the highest maximum rate of mass losses are obtained when using a coal/PKS blend at blend ratios of 10% and 20%.

The highest maximum rate of mass loss and the peak temperature of char burning and devolatilization are indices of fuel reactivity, according to research by Akinriola *et al.* [21], Peak height and fuel reactivity are directly correlated, but peak temperature and reactivity are inversely correlated.

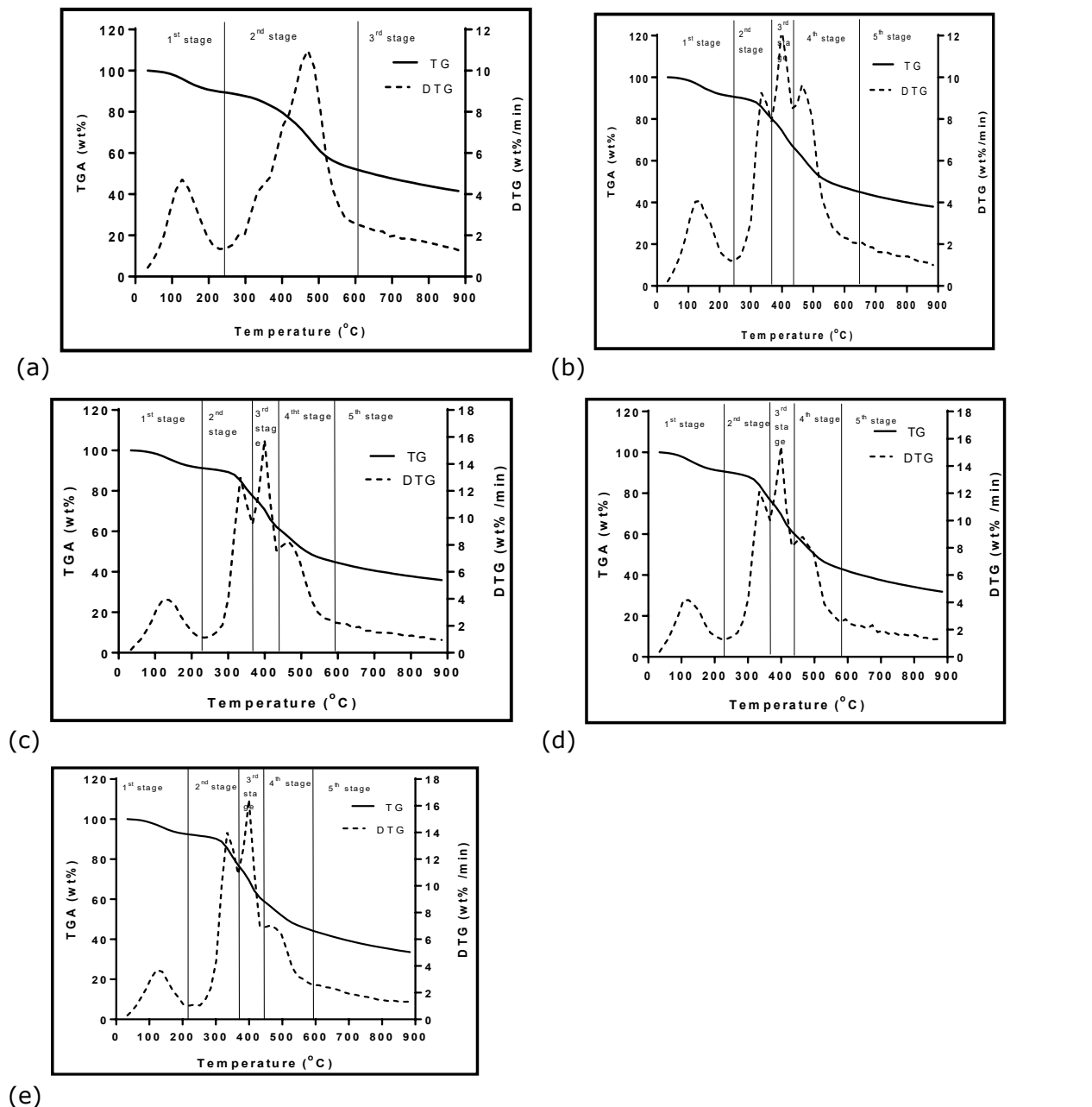


Figure 1. TG and DTG curves for bituminous coal/palm kernel shell blends at (a) 10 % BBR (b) 20 % BBR (c) 30 % BBR and (d) 40 % BBR and (e) 50% BBR.

Table 2. Weight loss for different thermal stages of bituminous coal/palm kernel shells blends after loss of moisture.

Sample	BBR (%)	Stage 2	Stage 3	Stage 4	W _t (%)
BC/PKS	10	-	-	36.59	36.59
	20	10.36	12.82	19.88	43.06
	30	13.26	18.66	13.35	45.27
	40	13.33	15.37	18.14	46.84
	50	14.33	18.81	14.38	47.52

Table 3. Peak temperature and maximum rate of mass loss for bituminous coal/palm kernel shell blends.

Sample	BBR (%)	Peak temperature (°C)			Max rate of mass loss(%/min)		
		Stage 2	Stage 3	Stage 4	Stage 2	Stage 3	Stage 4
100BC	-	-	-	446.6	-	-	10.6
100PKS	-	332.2	398.5	-	26.4	26.0	
BC/PKS							
10%	10	-	-	470.7	-	-	11.0
20%	20	333.7	339.4	464.2	9.3	12.4	9.6
30%	30	333.5	399.3`	464.3	13.0	15.8	8.3
40%	40	333.8	399.4	464.5	12.1	15.4	8.8
50%	50	334.0	399.5	480.6	14.0	16.5	6.8

3.2. Pyrolysis kinetics of bituminous coal and palm kernel shells

A linear regression model for determining the kinetic parameters—activation energy (E_a) and pre-exponential factor (A)—for 100% bituminous coal and palm kernel shell, respectively, are shown in Figures 2(a) and (b). The TGA data of the two samples through various reaction phases was used to create the figures.

For both samples, the plot of $\ln(-\ln(1-x)/T^2)$ against $1/T$ that had the highest correlation coefficients was shown. The second stage of the Lafia-Obi bituminous coal reaction and the second and third stage reactions of the palm kernel shell reaction showed strong correlation coefficient values, indicating that all samples' reaction models satisfactorily fit the experimental data.

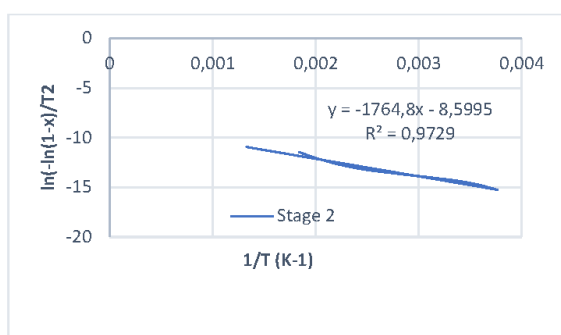


Figure 2a. Linear regression for the extraction of kinetic parameters of Lafia-Obi bituminous coal.

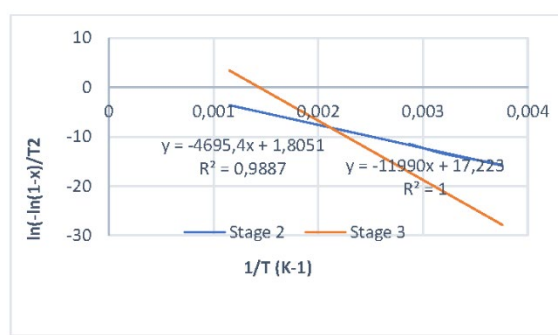


Figure 2b Linear regression for the extraction of kinetic parameters palm kernel shell

Table 4 indicates that the bituminous coal rapid decomposition zone is in the second stage, whereas the PKS pyrolysis zone is in the second and third stages. Bituminous coal and palm kernel shell have activation energy (E_a) values at the second stage of 14.7 kJ/mol and 39.04 kJ/mol, respectively, but PKS has an activation energy of 99.69 kJ/mol at the third stage. We compared these results with some data from the literature: For thermogravimetric data of Nigerian Owukpa sub-bituminous coal breakdown, Nyakuma *et al.* derived activation energy

between 28.86 to 57.29 kJ/mol [22]. The following activation energies were measured during the pyrolysis of several Nigerian coals by Sonibare et al. (2005): 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) [23].

Activation energy (E_a) determines a sample's reactivity, while pre-exponential factor (A) is more closely related to the material structures, according to Yorulmaz and Atimtay [24]. More reactive fuels are generally linked to lower activation energies. The greater carbon-carbon bond in the palm kernel shell, which was linked to its lignin content and may have indicated a sluggish reaction during co-pyrolysis, was the cause of the higher activation energy value. The values of E_a and A in the palm kernel shell pyrolysis reaction were higher in the third stage than in the second. For a certain biomass, Shen et al. [25] and Wang et al. [26] obtained similar results.

Table 4. Kinetic parameters of bituminous coal and palm kernel shell in the second and the third stage.

Samples	Temperature (°C)	E_a (kJ/mol)	A (min ⁻¹)	R^2
<i>Second stage reaction</i>				
100% BC	249-560	14.67	4.79×10^8	0.9729
100% PKS	249-365	39.04	1.43×10^6	0.9887
<i>Third stage reaction</i>				
100 PKS	382-431	99.69	$1.8 \text{ E}+14$	1

3.3. Pyrolysis kinetics of bituminous Lafia-Obi coal-palm kernel shell blends

The linear regression model for extracting kinetic parameters for blends of bituminous coal and palm kernel shells at 10, 20, 30, 40, and 50% PKS concentrations is shown in Figure 3.(a) to (e). The fuel blends demonstrated a five-step thermal breakdown, with stage 2 marking the beginning of devolatilization and stage 4 marking its conclusion. The correlation coefficients for 10, 20, 30, 40, and 50% PKS content in the stage 2-reaction model are 0.9875, 0.9852, 0.98, 0.972, and 0.7766, respectively. The blended sample reaction models satisfactorily suited the experimental data, as demonstrated by the high correlation coefficient values.

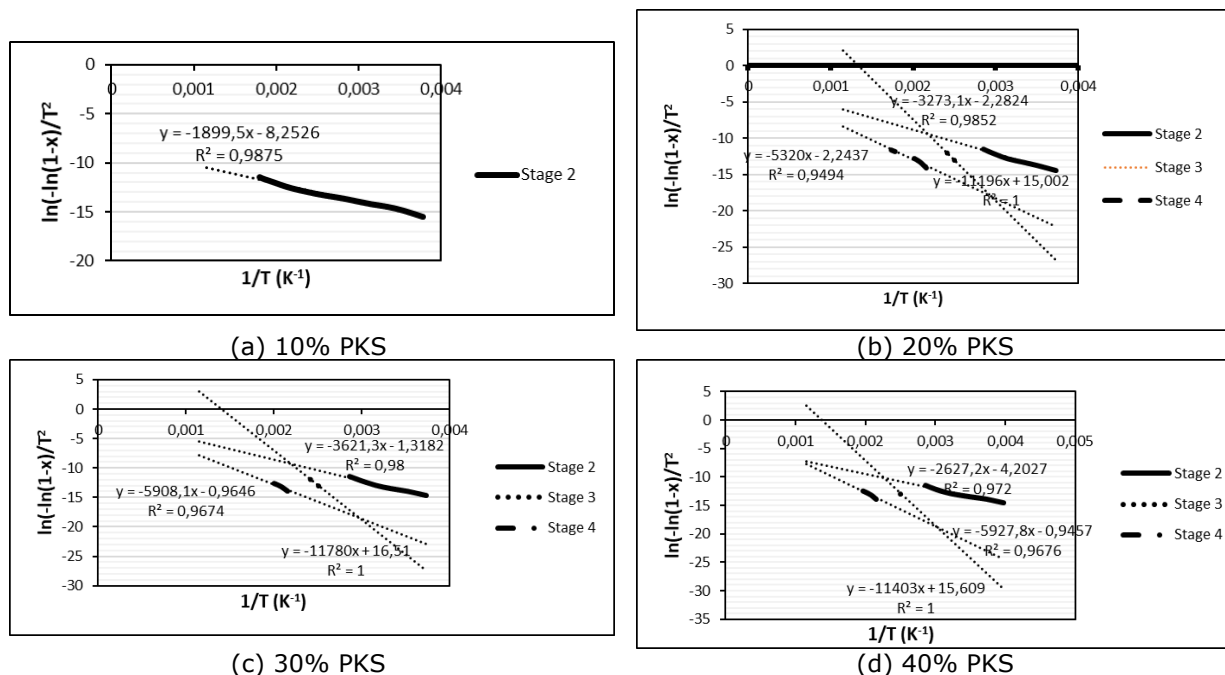
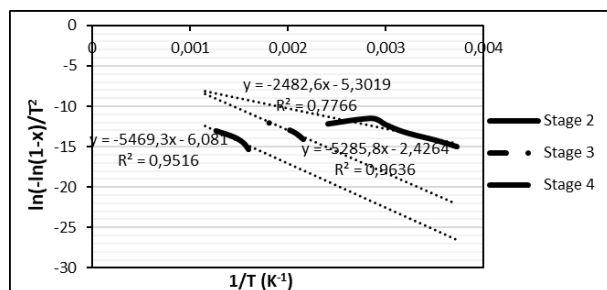


Figure 3. Linear regression for the extraction of kinetic parameters of bituminous Lafia-Obi coal/palm kernel shell blends at (a) 10% (b) 20% (c) 30% (d) 40%.



(e) 50% PKS

Figure 3. Linear regression for the extraction of kinetic parameters of bituminous Lafia-Obi coal/palm kernel shell blends at (e) 50% BBRs.

In Table 5, the pre-exponential factor (A) values were 3.64×10^8 , 1.6×10^6 , 6.76×10^5 , 8.78×10^6 , and 2.49×10^7 , respectively, whereas the activation energy (Ea) values for 10, 20, 30, 40, and 50% PKS in the blends at stage 2 were 15.79, 27.21, 30.10, 21.84, and 20.64 kJ/mol. The activation energy values for all mixes of coal and palm kernel shells were higher than that of bituminous Lafia-obi coal (14.67) and lower than that of pure PKS (39.04). As seen above, a higher carbon-carbon bond linked to a higher lignin content was the cause of the palm kernel shell's higher activation energy.

Table 5. Kinetic parameters of bituminous Lafia-Obi coal /Palm kernel shell blends in the Second, third and the fourth stage reaction.

Samples	Temperature (°C)	Ea (kJ/mol)	A (min ⁻¹)	R ²
<i>Second stage reaction</i>				
10% PKS	247 – 556	15.79	3.64×10^8	0.9875
20% PKS	251 – 366	27.21	1.60×10^6	0.9852
30% PKS	267 – 350	30.10	6.76×10^5	0.9800
40% PKS	251 – 350	21.84	8.78×10^6	0.9720
50% PKS	252 – 366	20.64	2.49×10^7	0.7766
<i>Third stage reaction</i>				
10% PKS	–	–	–	–
20% PKS	383 – 415	93.08	1.83×10^{12}	1.0000
30% PKS	382 – 431	97.94	8.72×10^{12}	1.0000
40% PKS	383 – 431	94.80	3.43×10^{12}	1.0000
50% PKS	399 – 432	43.95	2.99×10^6	0.9636
<i>Fourth stage reaction</i>				
10% PKS	–	–	–	–
20% PKS	448 – 577	44.23	2.50×10^6	0.9494
30% PKS	464 – 561	49.12	7.75×10^5	1.0000
40% PKS	448 – 577	49.28	7.63×10^5	0.9676
50% PKS	448 – 594	45.47	1.19×10^8	0.9516

These findings are consistent with research done by Gil *et al.* [19] to assess the co-pyrolysis of coal and pine sawdust, and by Lu *et al.* [18] to assess the co-pyrolysis of raw/torrefied wood and coal. The activation energy of PKS was reduced by the addition of Lafia-Obi bituminous coal, and the lowest activation energy was achieved with a 10% PKS blend. In the three stages of active pyrolysis, the blending ratio of PKS and coal at 30% BBR has the maximum activation energy, indicating that this blend has the highest level of synergy and reactivity.

The previously stated findings demonstrated bituminous coal's considerable impact on the coal/PKS blends' response rate. All of the stage 2 and stage 4 blends' pre-exponential factor (A) values were less than the bituminous Lafia-obi coal's pre-exponential value. This implies that bituminous coal and palm kernel shell work well together. The third stage of the reaction revealed that the pre-exponential factor for each blend was greater than the value recorded for bituminous Lafia-obi coal. This suggests that the PKS structure has a notable impact on

the co-pyrolysis of bituminous coal and PKS blends. The highest activation energy is found in the third stage, which is comparable to the highest activation energy found in the third stage of the pyrolysis of PKS blends and Malaysian coal [27].

4. Conclusion

In a thermogravimetric analyzer operating at temperatures between 30 and 900 °C, the thermal degradation of blends of palm kernel shell (PKS) and Lafia-Obi bituminous coal was studied. We varied the blend ratio at 10, 20, 30, 40, and 50% weight percentage of PKS to investigate the impact of PKS in the mix. As opposed to the three-stage and four-stage thermal reactions used for the pyrolysis of 100% coal and 100% PKS, the co-pyrolysis of coal-PKS blends is a five-stage thermal process.

There has been a shift in coal devolatilization towards a higher temperature as a result of PKS addition, with all fuel blends exhibiting peak devolatilization temperatures greater than those of Lafia-Obi bituminous coal. The maximal rate of mass loss falls as the blend's PKS content rises. Blends of coal and PKS with blend ratios of 10% and 20% yielded the lowest maximum rate of mass losses and the lowest peak devolatilization temperature. Furthermore, the 10% PKS blend yielded the lowest activation energy.

The results obtained here demonstrated that PKS had a considerable impact on the coal/PKS blends' reaction rate. Because PKS structure has a major impact on coal/PKS blends during co-pyrolysis, there is a clear synergy between bituminous Lafia-obi coal and palm kernel shell. In order to build and simulate safe and effective solid fuel combustors, gasifiers, and pyrolyzers that burn coal and biomass blends for the production of sustainable energy, the study's findings are crucial.

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