

Co-Pyrolysis of Oil Palm Mesocarp Fiber and Bituminous Coal Blends via Thermogravimetric Analysis

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Abstract

This study investigates the pyrolysis and co-pyrolysis behavior of oil palm mesocarp fiber (MF) bituminous coal fines (CF) from Ankpa in Nigeria in a thermogravimetric analyzer in nitrogen environment (100 mL/min). Pyrolysis of each feedstock and their blends (MF:CF%: 100:0%, 75:25%, 50:50%, 25:75%, 0:100%) was carried out with temperatures ranging from ambient to 900°C. This was done at heating rates of 5, 10, and 15°C/min. Each feedstock showed two distinct behaviors during the active pyrolysis stages and this trend was maintained in their blends. Increasing the proportion of CF reduced the peak mass loss rate and increased the corresponding peak temperature across all blends and heating rates. Blending with $\geq 25\%$ MF lowered the peak devolatilization temperature and raised the maximum mass loss rate, indicating a catalytic effect on coal pyrolysis. Higher heating rates shifted decomposition to higher temperatures while intensifying mass loss rates. Residual mass decreased slightly with increasing heating rate but rose with higher CF content. The activation energy for CF was substantially higher than that of MF for all heating rates. In addition, the activation energy for the second-stage reactions of the blends was higher than that of MF but lower than that of CF for all heating rates. The increase in the values of activation energy as the percentage of MF reduces in the blend suggests a progressive reduction in the reactivity of the solid fuel mix. Also, blending with $\geq 25\%$ MF led to a marked reduction in the activation energy relative to pure CF, affirming the catalytic effect of MF on Ankpa bituminous coal in co-pyrolysis.

Categories: Geothermal and Biomass Energy, Energy Efficiency and Conservation, Thermal and Fluid Systems

Keywords: pyrolysis, thermogravimetric analysis, heating rates, devolatilize, blends, peak temperature

Introduction

Technology is a major element of economic advancement and overall growth of a nation, just as energy is indisputably the facilitator of every technological initiative. The sustainability of both technological and industrial advancement in a nation is driven by its expertise in harnessing of energy from both its renewable and non-renewable sources [1,2]. In view of this fact, the development of renewable sources is no longer an option but a necessity. Recently, research interest in alternative sources has soared owing to the menace of climate change, emission of greenhouse gases, reduction in fossil fuel reserves, agricultural and municipal solid wastes, and other environmental issues that are associated with emissions [3,4].

Biomass is widely tipped as a competing alternative to conventional fuels chiefly due to its availability [5,6]. It is widely regarded as a group comprising essentially carbon with other chemical constituents in varying proportions and are generally renewable in nature [7]. Residues from agricultural-based activities are adjudged to be the largest source of

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biomass with most of these ending up as waste [8]. Also, attention is being drawn toward hybridizing biomass with coal with the aim of reducing the net emission from the combustion of the hybrid solid fuel produced [9,10]. Mesocarp fiber (MF) is a by-product of the processing of oil palm fruits for the extraction of palm oil. Before sorting, it consists of fiber mixed with crushed kernels and shells [11,12].

Coal is a variety of sedimentary rock whose color can either be brownish-black or outrightly black. It consists mainly of carbon, alongside other elements such as oxygen, hydrogen, nitrogen, and sulfur in varying proportions [13]. The combustion of coal leads to the release of greenhouse gases, therefore its major downside is its contribution to climate change [14]. Consequently, there is an ongoing globally-driven energy transition program geared toward reducing and subsequently eliminating the dependence on coal power [15]. Coal has been widely used for energy generation and other applications. Its major setback is its potential to emit greenhouse gases. For this and other reasons, the blending of biomass with coal is a research area that is being explored by researchers all over the world [16].

Pyrolysis is a thermochemical method that is being widely researched due to its capacity to produce carbonaceous fuel materials in all three states. It is commonly employed as the initial step in most thermochemical conversion procedures [17]. The reactivity of a fuel material is determined by its activation energy (E_a) while its pre-exponential factor (A) has more to do with its structure. Therefore, more reactive fuels possess lower activation energy and vice versa [18]. Tarka et al. [19] carried out research into the burning properties of solid fuel produced from maize chaff and MF. The binder used was cassava extract. The properties of the fuel were all found to be affected by both the percentage composition and particle size of the briquettes. It was discovered that the larger the size of the feedstocks, the better the performance based on the properties under consideration. Also, the briquettes with 20% MF gave the optimum heating value (HV) and percentage ash content, while the ones with 60% MF, in addition to being the most durable, also had the highest heating efficiency.

Alias et al. [20] did a study on the decomposition characteristics of oil palm trunk and empty fruit bunch in a thermogravimetric analyzer in a pyrolytic environment. During the decomposition of oil palm trunk, smaller oil palm trunk sizes had 0.04-0.86% more volatile constituents under both heating rates used and empty fruit bunch gave a 3.81-9.81% increase in volatile matter under the two heating rates considered. Nyakuma et al. [21] also explored the thermochemical properties of briquettes fabricated from empty fruit bunch. The decomposition behavior of the fuel was studied in a thermogravimetric analyzer that was operated at the rate of 10°C/min rate while heating from a temperature of 50°C through 900°C. One of the conclusions drawn from the analysis was that drying, heating, devolatilization, and char aggregation are the four distinct stages that thermal decomposition of the fuel underwent. The main pyrolysis stage began at 206°C and reached its peak at 325°C with the total weight loss amounting to 70% of the material. Lin et al. [17] investigated the characteristics of cornstalk, lignite, and bituminous coal during co-pyrolysis. A TG-FTIR approach was used, and it was confirmed that coal influences the thermal characteristics of lignocellulosic biomass. Distinct thermal characteristics were also observed between the two feedstocks which made it possible to study the potential synergy between them without overlap.

Adewole et al. [18] studied the thermal characteristics of coconut shell, bituminous coal, and their blends in a thermogravimetric analyzer. The main pyrolysis stages for the 20-50 wt% coconut blends were characterized by two (2) stages of active pyrolysis. As the coconut shell composition decreased from 50 to 10%, a reduction in the second peak could be observed, while an increase in the third peak was observed as the coal composition increased from 50 to 90% in the blends. The discontinuity in the DTG curve peaks became prominent for 20 to 50% wt% of coconut shell. Nyakuma et al. [22] examined the thermal behavior and kinetic parameters of Akunza, Ome, and Shiga, newly discovered coals in Nigeria based on the Coats-Redfern model. All three samples were found to have high reactivity and, in addition, possessed relatively low activation energy and pre-exponential factor when pyrolysis was done under oxidative and non-oxidative environments.

Biomass materials such as woody biomass and coconut shell have been blended with coal for production of solid fuel. However, MF has not yet been blended with coal, neither have its properties been holistically compared with those of any conventional fuel like coal. There is a dearth of data on a comprehensive study of the pyrolysis behavior of MF,

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bituminous coal, and their blends. A thorough study and reporting of the co-pyrolysis characteristics of blends of MF and bituminous coal in comparison to those of the parent feedstocks would help to establish a much-needed basis for further research into other applicable thermochemical methods and relevant industry-based designs. It is also expected to help develop data for the effective and predictable harnessing of energy from this source.

Materials And Methods

Preparations of feedstocks

The feedstocks employed in this study are MF and bituminous coal fines (CF). Oil palm MF was obtained from a palm fruit-processing factory in Osogbo, Osun State, Nigeria, and bituminous coal was obtained from a coal deposit in Ankpa, Kogi State, Nigeria. The proximate and ultimate analyses of the feedstocks were done in order to ascertain their suitability as solid fuels. The coal was obtained in lump form. After sorting, washing, and drying of the fiber, both feedstocks were pulverized to ≤ 1 mm in particle size, as shown in Figure 1. From these samples, homogeneous MF-coal blends were prepared by thorough manual mixing in order to obtain 100%, 75%, 50%, 25%, and 0% by mass of MF, which corresponds to 0%, 25%, 50%, 75% and 100% by mass of bituminous coal, respectively.

Ultimate and proximate analysis

The ultimate analysis of the feedstocks was done using an EMA 502 Elemental Analyzer for CHNO contents based on the standard ASTM D5373-16 (2016) [23]. For the detection of percentage by mass of CHN, oxygen flow at 400 ml/min was used as the carrier gas, while argon was utilized for determining the percentage of oxygen. The summation of CHNO percentages was removed from 100 to estimate the percentage of sulfur present [24]. The proximate analysis entails the determination of percentage volatile matter, moisture content, fixed carbon content, and ash content, and this was done using the dry-basis approach [15,25]. The IS: 1350-1 (1984) [26] standard was followed for CF analysis, while the standards listed in Table 1 [27-29] were followed for that of MF. The percentage fixed carbon content was obtained by subtraction using Equation (1). The calorific value, also known as the HV, was estimated from the proximate analysis results using Equation (2) [15,19]:

$$FC = 100 - (MC + VC + AC)(1)$$
$$HV = 2.326(147.6FC + 144VM) \text{ kJ/kg}(2)$$

Property	Analytical method
Moisture content	ASTM E871-82 (2013)
Volatile matter	BS EN 15148 (2009)
Ash content	ASTM E1755-01 (2015)
Fixed carbon	By Subtraction

TABLE 1: Approach adopted for the proximate analysis of MF
MF, mesocarp fiber

Thermogravimetric analysis

The thermogravimetric analyzer (Model: TGA 4000 Perkin Elmer) was used to investigate the pyrolysis and co-pyrolysis characteristics of MF, CF, and their blends. About 10 mg of each sample in MF:CF mass ratios of 100:0, 75:25, 50:50, 25:75, and 0:100 was placed into the equipment's crucible. Pyrolysis and co-pyrolysis were carried out on the respective samples from room temperature to 900°C while maintaining an inert atmosphere through a continuous flow of nitrogen at a rate of 100 ml/min [30]. Each sample's behavior was studied under three heating rates of 5, 10, and 15°C/min, respectively. The thermogravimetric analysis (TGA) data were evaluated and recorded by running a temperature scan. Each experiment was repeated to confirm the reproducibility of the generated results. The differential thermogravimetric (DTG) data, which represent the weight loss per unit time, were derived from the TGA results. In addition to this, the activation energy and pre-exponential factor for the feedstocks and their blends were evaluated from the TGA results [21].

Study of kinetic behavior

The Coats-Redfern method was employed to model the decomposition kinetics of MF, CF, and their blends. The advantage of this model is the ease with which it can be used to determine the order of reaction, especially at a single heating rate per time. The rate of decomposition (X) was calculated at a constant temperature using Equation (3) [18].

$$X = \frac{M_i - M_t}{M_i - M_f} \quad (3)$$

Where M_i is the initial mass (mg) of the feedstock sample, M_t is the mass (mg) at time t , and M_f is the final mass (mg) at the end of the thermal conversion reaction. An n -th order model can be used to depict the decomposition of the fuel material with respect to time as shown in Equation 4.

$$\frac{dX}{dt} = A \exp \left[-\frac{E_a}{RT} \right] (1 - X)^n \quad (4)$$

Where the left side of Equation (4) is the rate of conversion (min^{-1}), t is the time (s), A is the pre-exponential factor (min^{-1}), E_a is the activation energy (kJ/mol), R is the universal gas constant, and T is the temperature (K). For a non-isothermal process taking place at a constant heating rate, Equation (4) can be expressed as follows:

$$\frac{dX}{(1 - X)^n} = \frac{A}{\beta} \exp \left(-\frac{E_a}{RT} \right) dT \quad (5)$$

where β is the heating rate.

In a non-isothermal kinetic reaction process, the reaction rate is usually expressed by Equation (5). Integration of Equation (5) results in an exponential integral. Some authors have proposed different approaches to solving the exponential integral. The Coats-Redfern method [18,30] made some approximations and proposed the linear equation presented in Equation (6). This equation is applicable only when the thermal degradation of a solid fuel is of first order ($n = 1$).

$$\ln \left[\frac{-\ln(1 - X)}{T^2} \right] = \ln \frac{AR}{\beta E_a} \left[1 - \frac{2RT}{E} \right] - \frac{E_a}{RT} \quad (6)$$

The value of $2RT/E$ is so small that it can be neglected, therefore Equation (6) can be expressed thus:

$$\ln \left[\frac{-\ln(1 - X)}{T^2} \right] = \ln \frac{AR}{\beta E_a} - \frac{E_a}{RT} \quad (7)$$

Equation (7) has been shown to be constant for the temperature range of combustion under study and for most values of E_a [18]. When the left side of Equation (7) is plotted against $1/T$, the kinetic parameters, for instance, activation energy (E_a) and pre-exponential factor (A) for each reaction, can be obtained from the slope and intercept of the line, respectively

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[30]. If the process is assumed to be first-order, a straight-line graph can be obtained. For the purpose of this study, the value of the left side of Equation (7) was plotted against $1/T$. The activation energy and pre-exponential factor were derived from the slope (m) and intercept (l) of the regression line, respectively.

Results And Discussion

Ultimate and proximate analysis

Table 2 presents the results for the ultimate and proximate analysis of the samples. The results presented for MF's quantitative analysis are essentially in agreement with the ones presented for oil palm fruit fiber (OPFF), in other words, MF, by Abdullah et al. [31]. It is also comparable to the results reported by Nyakuma et al. [21] for empty fruit bunch (EFB), which is the outer part of the palm fruit bunch left after the palm fruits have been harvested. This suggests that MF possesses a comparable solid fuel producing capacity to EFB. Also, the data reported for CF's quantitative analysis exhibits close agreement with the ones reported for coal by Adeleke et al. [24,25]. The results showed that due to the higher amount of carbon in CF, it can potentially provide a higher amount of energy compared to MF when used as solid fuel. Since hydrogen is present in both feedstocks, both can potentially produce water as a by-product of combustion.

MF contains a relatively higher oxygen percentage; it is therefore likely to produce solid fuel with lower combustion temperature and higher burning potential. The amount of oxygen present in CF is good for a moderate combustion rate in a good solid fuel, but will give it higher combustion temperature compared to MF. The emission of acidic oxides (SO_x) after combustion is most likely due to the presence of sulfur in MF and CF. Its presence is therefore undesirable [32]. The results presented for MF's qualitative analysis are essentially in agreement with the one presented for OPFF by Abdullah et al. [31] and Nyakuma et al. [21] for EFB. The results reported for CF's qualitative analysis exhibit close agreement with the one reported for coal by Adeleke et al. [24,25].

Due to a higher moisture content, fuel produced from MF is more likely to have a longer ignition time and also to produce more smoke during combustion compared to the fuel produced from CF. MF has a very high volatile matter (80.35%) relative to CF (13.72%) while CF possesses a very high fixed carbon content (66.98%) relative to MF (7.03%). The volatile matter contained in each fuel indicates that both can undergo devolatilization; however, MF devolatilization would proceed at a faster rate than CF due to its very high percentage of volatile matter [30]. With the high percentage of volatile matter in MF, a large part of its mass is likely to be lost as vapor when heated at elevated temperatures. On the other hand, with a high fixed carbon content of CF, more carbon is available to be burnt in fuel produced from CF than the one produced from MF. CF had a relatively high ash content (17.82%) compared to MF (4.2%). The ash content is suggestive of the percentage of fuel that is left after combustion [30]. With its high ash content, fuel produced from CF will have a high amount of non-aqueous residue after combustion, and this contributes to a decrease in its HV. All of these properties suggest their complementarity when used in composite solid fuel applications.

	Proximate				Ultimate					HHV (MJ/kg)
	MC	VM	AC	FC	C	H	N	O	S	
MF	8.42	80.35	4.2	7.03	65.98	6.58	2.92	23.98	0.54	29.04
CF	1.48	13.72	17.82	66.98	73.2	3.43	1.82	20.59	0.96	27.59

TABLE 2: Ultimate and proximate analysis results of MF and CF

MF, mesocarp fiber; CF, coal fines; HHV, higher heating value

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Effect of percentage composition on the decomposition behavior of MF, CF, and their blends

Figures 1-6 display the TGA and DTG profiles of the parent feedstocks and their blends at heating rates of 5, 10, and 15°C/min, respectively. The TG profile of Figure 1 shows that the pyrolysis of 100% MF advanced at a faster rate relative to the blends (75, 50, 25% MF), and 100% CF. It can also be observed that the introduction of CF slowed down the rate and extent of pyrolysis consequently increasing the amount of remnant, majorly ash content, left at the end of the pyrolysis. Generally, there is a steady increase in the maximum temperature of the main pyrolysis stage as CF's percentage was increased in the blends at 5°C/min heating rate. The trend was the same for 10 and 15°C/min heating rates except that the pyrolysis took place at relatively higher temperatures and left slightly smaller amounts of remnants for each mix. The DTG profiles in Figure 2 imply that 100% MF and 100% CF have one peak in their main pyrolysis stage, while two peaks can be observed for the main pyrolysis stages of 75, 50, and 25% MF blends. The second peak decreases with increase in CF composition, which corresponds to decrease in percentage composition of MF. An increase in the third peak can also be observed with increase in CF composition. This is in agreement with similar work reported by Adewole et al. [18].

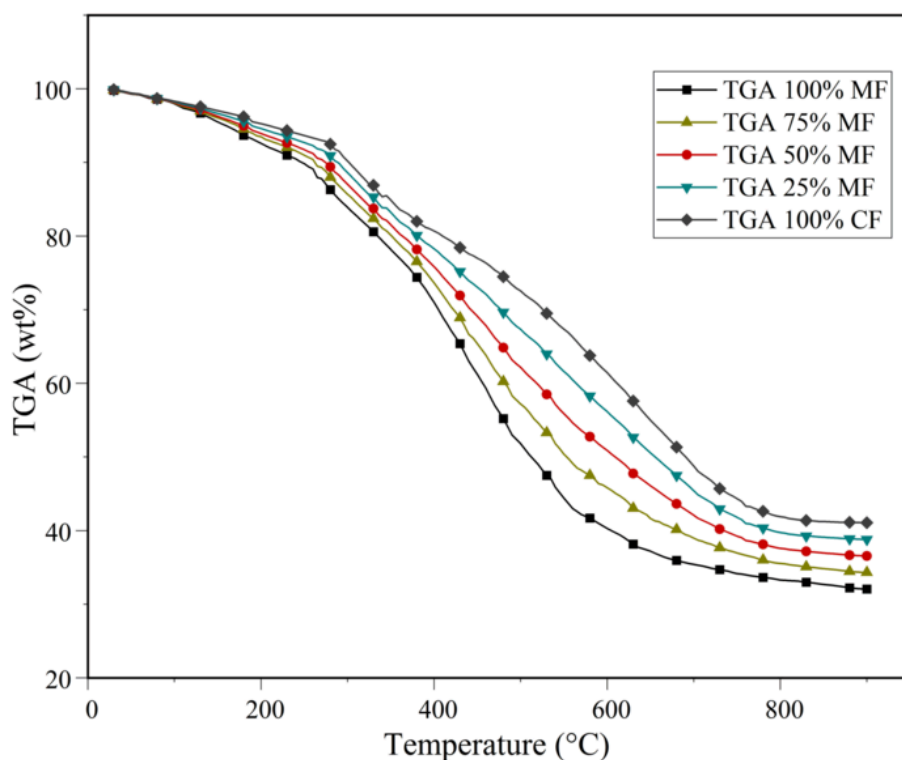


FIGURE 1: Comparative pyrolysis TGA profiles at 5°C/min heating rate

TGA, thermogravimetric analysis

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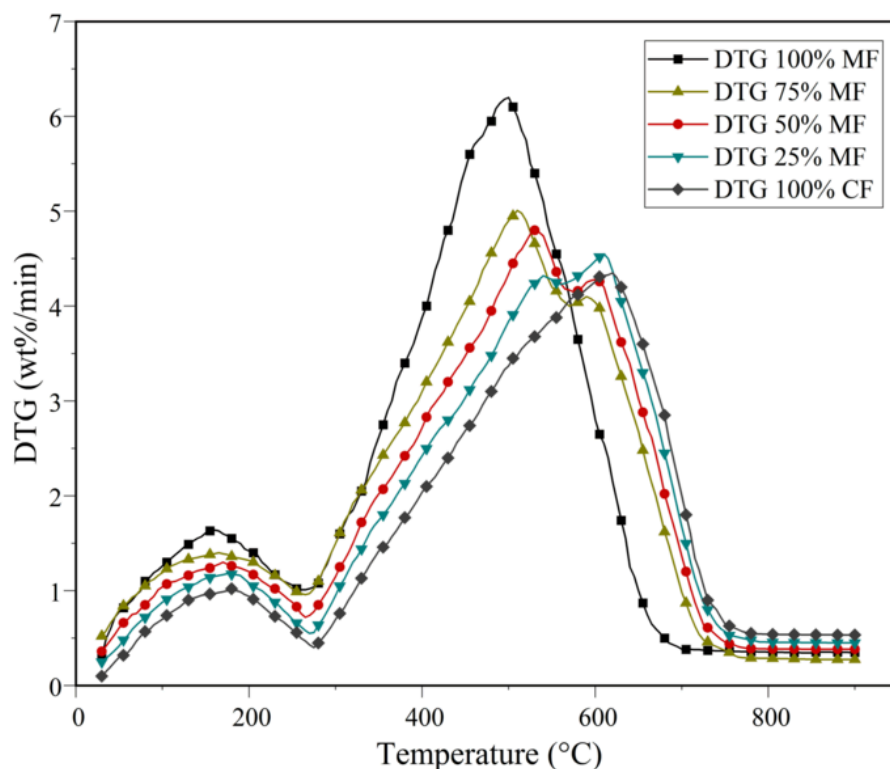


FIGURE 2: Comparative pyrolysis DTG profiles at 5°C/min heating rate

DTG, differential thermogravimetric

At 50:50 percentage composition of MF:CF, the second peak remained higher than the third because although their percentage by mass was the same, the volume of MF was far more than that of CF, hence its effect remained dominant. However, at 25% MF, the higher peak shifted from being the second to the third making the presence of CF more dominant. For 75, 50, and 25% MF between stages 2 and 3, discontinuity and subsequent change in peak can be observed in the DTG curves, which can be attributed to completion of rapid mass loss from MF in stage 2 and the increasing amount of coal in the blends which led to consequent increase in coal devolatilization [18]. The peak DTG curve of 100% MF is higher than that of 75, 50, 25% MF and 100% CF under all heating conditions. MF contains hemicellulose and cellulose, which break down easily. Its main pyrolysis appears to occur in the second-stage reaction, leading to a relatively high decomposition rate. Compared to 100% CF, the peak DTG curve shifted to a lower devolatilization temperature accompanied by an increase in the peak mass loss rate for 25% MF, indicating that the addition of MF at or above 25% by mass could potentially improve the pyrolysis characteristics of coal [18].

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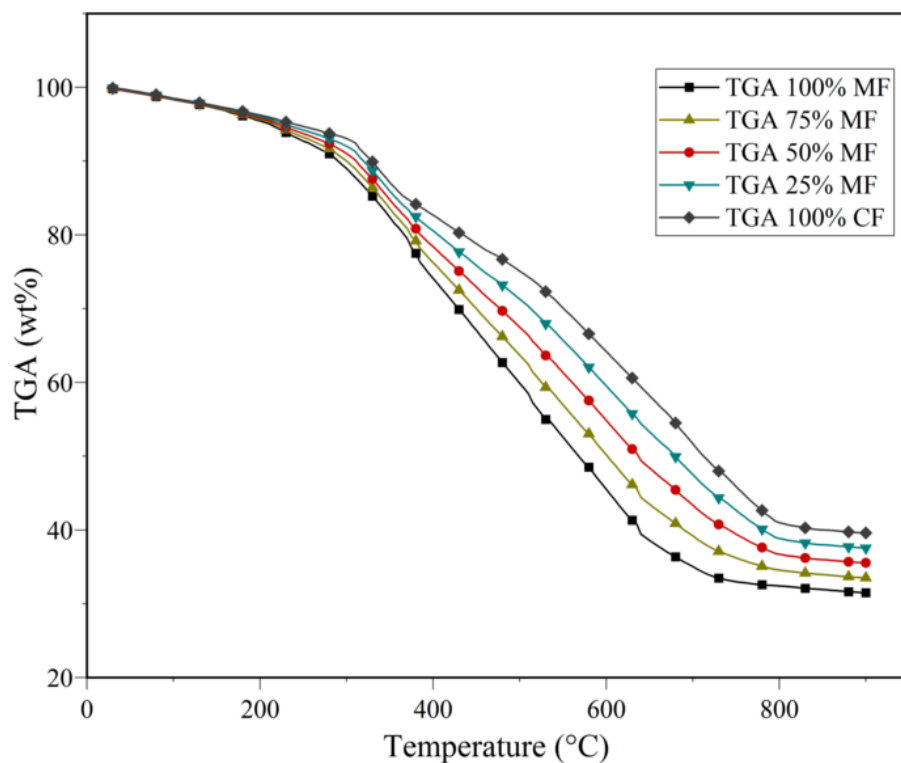


FIGURE 3: Comparative pyrolysis TGA profiles at 10°C/min heating rate

TGA, thermogravimetric analysis

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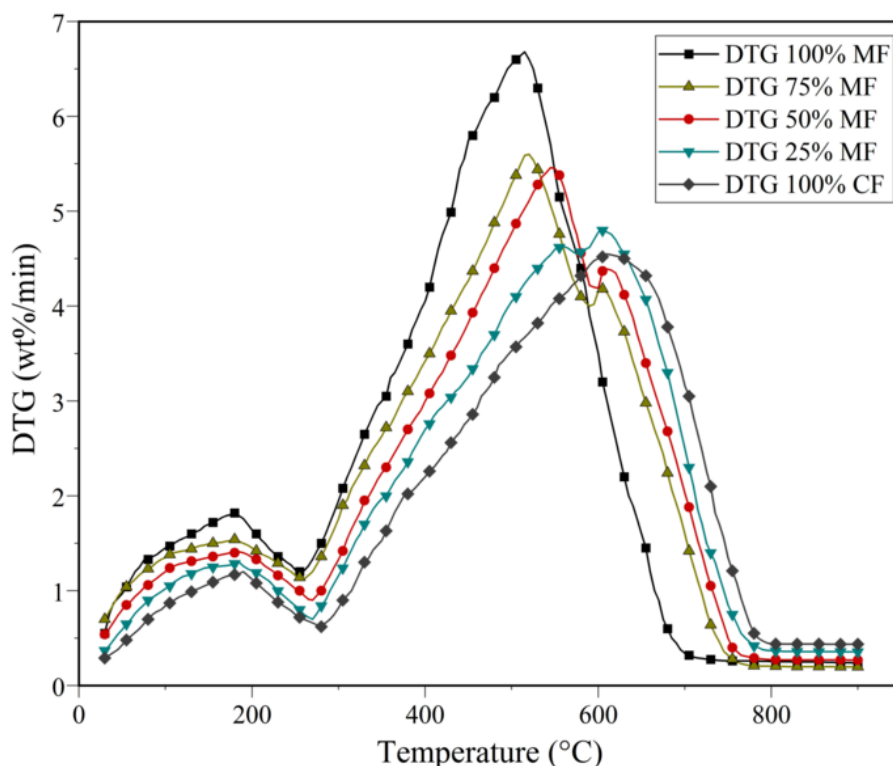


FIGURE 4: Comparative pyrolysis DTG profiles at 10°C/min heating rate

DTG, differential thermogravimetric

For the three blends at the three heating rates, a decrease in the peak mass loss rates in the second stage and an increase in the same in the third stage, all accompanied generally by an increase in peak temperatures reached, made the effects of increasing CF composition in the blends obvious. Coal possesses a complex chemical structure due to the presence of many covalent bonds. These bonds offer resistance to its thermal degradation, thereby inducing slow pyrolysis. Lin et al. [17] reported similar findings for cornstalk with lignite and bituminous coal. Tables 3 and 4 highlight the key properties of the thermal stages undergone by all samples under the three pyrolysis conditions.

From Figures 2, 4, and 6, it can be deduced that at all heating rates considered, 100% MF's mass loss rate was highest, but its peak devolatilization temperature was lowest, while 100% CF's mass loss rate was lowest with its peak devolatilization temperature being the highest. The TGA curves shown in Figures 1, 3, and 6 suggest that as CF composition increases in the blends, the percentage of fuel left as residue increased. This agrees with similar work reported by Lu et al. [33]. Also, as CF composition increased in the blends, the peak DTG temperatures increased steadily and the peak mass loss rate reduced significantly in the stage 2 reactions. In stage 3 reactions, both peak DTG temperatures and the peak mass loss rate increased as the percentage of CF increased in the blends.

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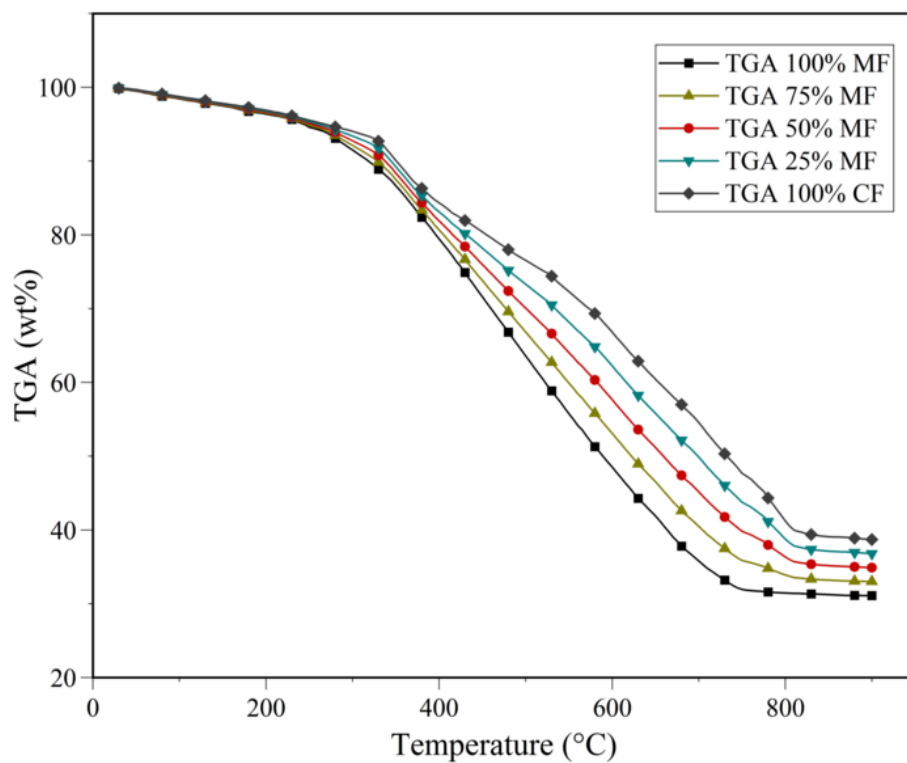


FIGURE 5: Comparative pyrolysis TGA profiles at 15°C/min heating rate

TGA, thermogravimetric analysis

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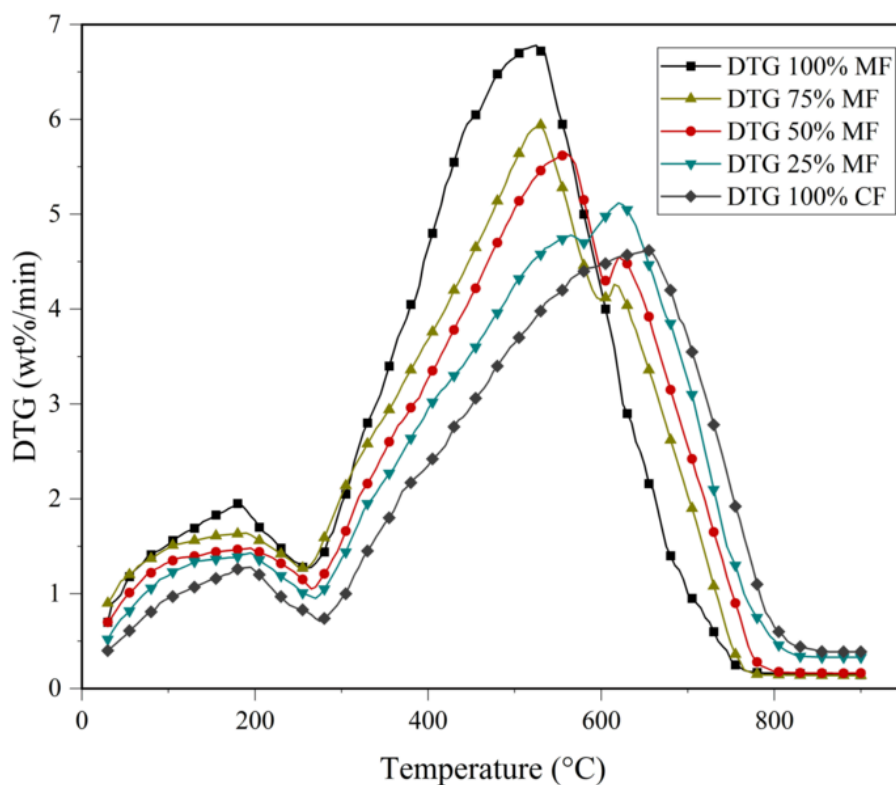


FIGURE 6: Comparative pyrolysis DTG profiles at 15°C/min heating rate

DTG, differential thermogravimetric

TG results generally showed that co-pyrolysis of MF with CF will potentially produce solid fuels whose properties are determined by the combined attributes of both parent feedstocks, which agrees largely with previous works carried out by Lin et al. [17] and Adewole et al. [18] for lignocellulosic biomass and bituminous coal.

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	Heating rate of 5°C/min					Heating rate of 10°C/min			
Parameters	Samples	Stage 2		Stage 3		Stage 2		Stage 3	
		Initial	Final	Initial	Final	Initial	Final	Initial	Final
Temperature (°C)	100% MF	265	615			260	635		
	75% MF	270	570	575	685	265	590	595	700
	50% MF	275	575	580	690	270	595	600	705
	25% MF	280	565	570	695	275	580	585	710
	100% CF	280	710			285	735		
Weight loss (%)	100% MF	48.58				51.39			
	75% MF	41.14		8		40.89		11.68	
	50% MF	36.79		9.88		37.33		12.01	
	25% MF	31.06		13.33		31.16		15.11	
	100% CF	44.9				45.98			
Peak Temp. (°C)	100% MF	500				515			
	75% MF	510		590		520		605	
	50% MF	530		600		545		610	
	25% MF	540		610		560		605	
	100% CF	615				615			
Max rate of mass loss (%wt/min)	100% MF	6.2				6.68			
	75% MF	5.01		4.1		5.6		4.18	
	50% MF	4.8		4.28		5.46		4.39	

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	25% MF	4.32	4.55	4.63	4.8
	100% CF	4.33		4.54	

TABLE 3: Properties of key thermal stages of MF, CF, and their blends at 5°C/min and 10°C/min heating rates

MF, mesocarp fiber, CF, coal fines

		Heating rate of 15°C/min			
Parameters	Samples	Stage 2		Stage 3	
		Initial	Final	Initial	Final
Temperature (°C)	100% MF	265	655		
	75% MF	260	600	605	715
	50% MF	270	605	610	720
	25% MF	275	580	585	725
	100% CF	285	755		
Weight loss (%)	100% MF	52.9			
	75% MF	41.46		13.49	
	50% MF	37.45		13.45	
	25% MF	31.18		17.6	
	100% CF	47.2			
Peak Temp. (°C)	100% MF	520			
	75% MF	530		615	
	50% MF	560		620	
	25% MF	565		620	
	100% CF	655			
Max rate of mass loss (%wt/min)	100% MF	6.77			
	75% MF	5.94		4.26	
	50% MF	5.64		4.55	
	25% MF	4.78		5.12	
	100% CF	4.62			

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TABLE 4: Properties of key thermal stages of MF, CF, and their blends at 15°C/min

MF, mesocarp fiber, CF, coal fines

Effects of heating rates on the decomposition behavior of MF, CF, and their blends

Figures 7-11 present comparative TGA and DTG curves for CF, MF, and their blends at three different heating rates. From the TGA curve of 100% MF (Figure 7), if an imaginary line is drawn parallel to the 80 wt% mark, the same decomposition intensity can be seen to have occurred at elevated temperature with increasing heating rate. From the DTG curve of Figure 7, the stage 2 reactions of 100% MF occurred over a wider temperature range as the heating rates increased, consequently, giving rise to relatively higher decomposition intensities. This is in close agreement with similar work carried out by Nyakuma et al. [34]. From Tables 3 and 4, the decomposition intensities were 48.58%, 51.39%, and 52.9% for stage 2 of 100% MF for the three heating rates, respectively. The peak devolatilization temperature shifted progressively to the right as the heating rate increased, implying an increase in its value and this was accompanied by increasing peak rate of mass loss. Therefore, a change in the heating rates typically affects the temperature profiles and decomposition behavior of the fuel materials [34]. The peak devolatilization temperatures reached were 500, 515 and 520°C with corresponding peak mass loss rate being 6.2, 6.68, and 6.77 wt%/min for main pyrolysis stage of 100% MF.

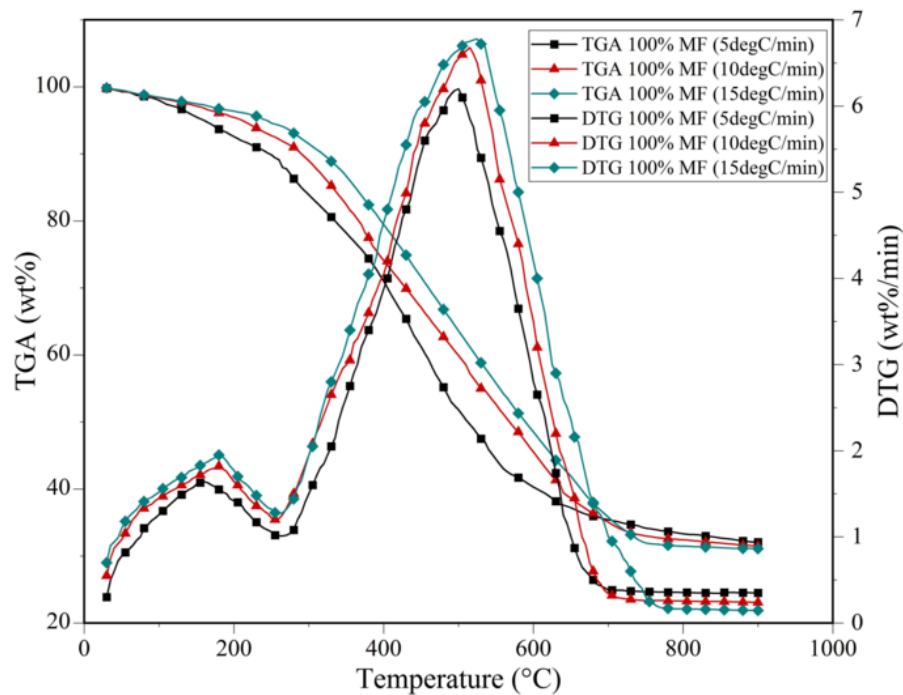


FIGURE 7: Comparative TGA and DTG curves at different heating rates for 100% MF

DTG, differential thermogravimetric; TGA, thermogravimetric analysis; MF, mesocarp fiber

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From the TGA curve of 75% MF (Figure 8), an increase in heating rate also caused the same decomposition intensity to occur at elevated temperatures. From the DTG curves (Figure 9), it can be observed that stages 2 and 3 reactions occurred over a wider temperature range as the heating rate increased. This was also accompanied by higher decomposition intensities as reported in Tables 3 and 4. The DTG curves show a gradual increase in the peak devolatilization temperatures with increasing heating rate. The peak mass loss rate also increased significantly with increase in the heating rates [18]. In its stage 2 reaction, the peak mass loss rates were 5.01, 5.6, and 5.94 wt%/min with corresponding peak temperatures of 510, 520, and 530°C, respectively, while for its stage 3, the peak mass loss rates were 4.1, 4.18, and 4.26 wt%/min with corresponding peak temperatures of 590, 605, and 615°C, respectively.

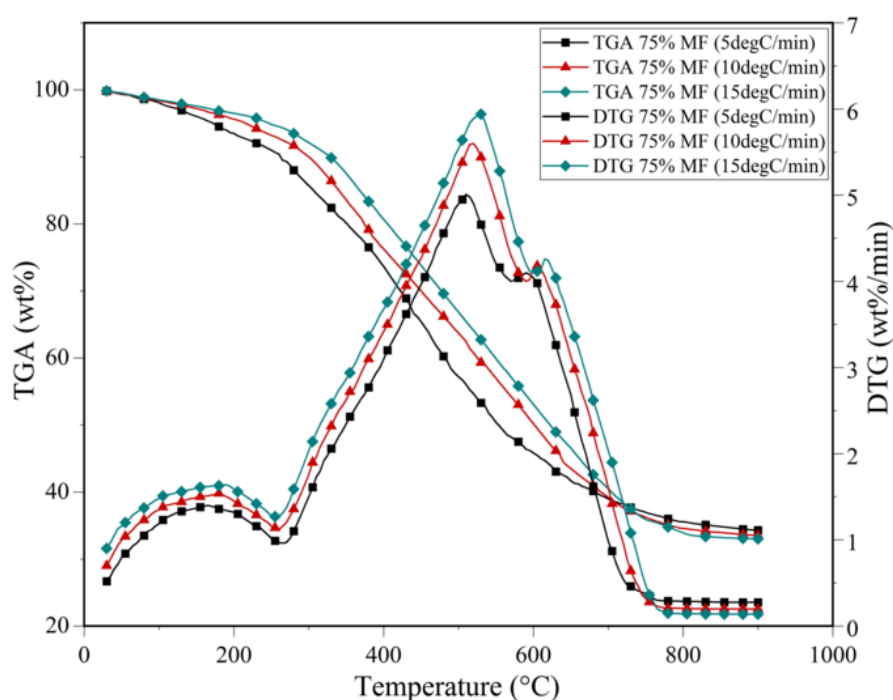


FIGURE 8: Comparative TGA and DTG curves at different heating rates for 75% MF

DTG, differential thermogravimetric; TGA, thermogravimetric analysis; MF, mesocarp fiber

For 50% MF (Figure 9), an obvious increase can be observed in both peak temperatures and mass loss rate with increasing heating rates. In its stage 2 reaction, the peak mass loss rates were 4.8, 5.46, and 5.64 wt%/min with corresponding peak temperatures of 530, 545, and 560°C, respectively, while for its stage 3, the peak mass loss rates were 4.28, 4.39, and 4.55 wt%/min with corresponding peak temperatures of 600, 610, and 620°C, respectively.

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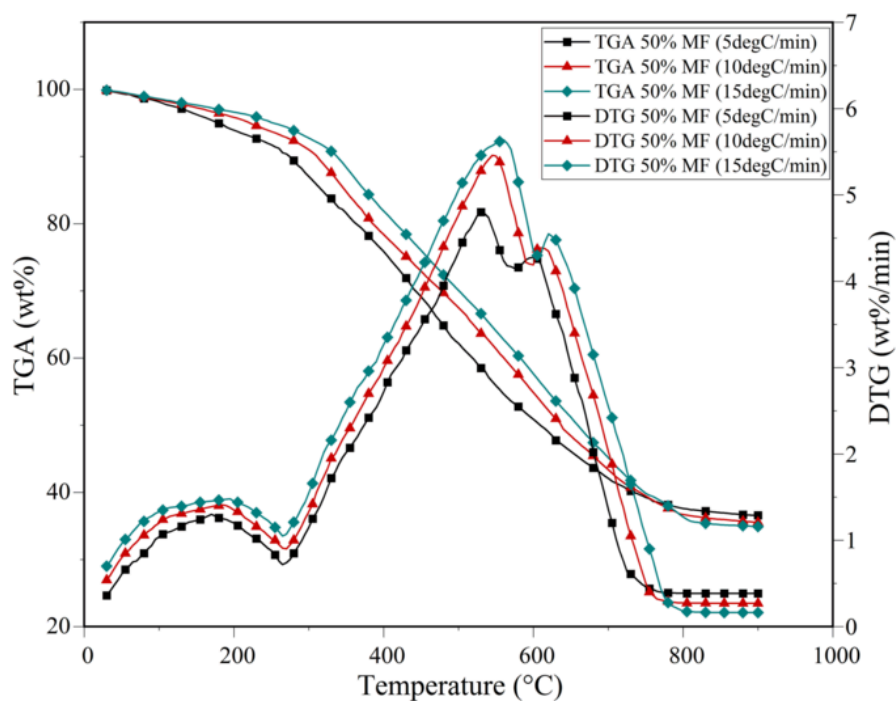


FIGURE 9: Comparative TGA and DTG curves at different heating rates for 50% MF

DTG, differential thermogravimetric; TGA, thermogravimetric analysis; MF, mesocarp fiber

From the TGA curve of 25% MF (Figure 10), an increase in heating rate also gave rise to slightly higher decomposition intensity in the stage 2 reaction, but the increase became more obvious in the stage 3 reactions. The intensities were 31.06, 31.16, and 31.18% for stage 2, and 13.33, 15.11, and 17.6% for stage 3. This is probably due to the dominance of coal devolatilization in the stage 3 of this 25% MF mix. The peak temperatures and mass loss rates followed the same pattern as in the 75% and 50% MF blends.

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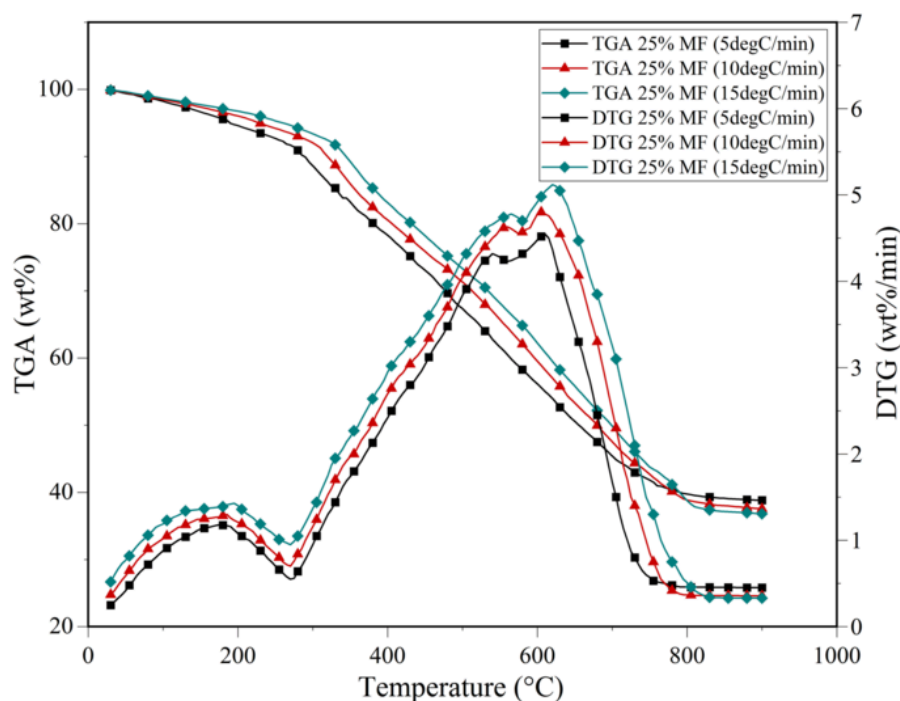


FIGURE 10: Comparative TGA and DTG curves at different heating rates for 25% MF

DTG, differential thermogravimetric; TGA, thermogravimetric analysis; MF, mesocarp fiber

For 100% CF (Figure 17), an increase in heating rates also increased the range within which active pyrolysis occurred while increasing the decomposition intensities in the process. The peak temperatures and mass loss rates also increased as the heating rate increased. With only one stage of active pyrolysis, which is its second stage, the peak mass loss rates were 4.33, 4.54, and 4.62 wt%/min with corresponding peak temperatures of 615, 615, and 655°C, respectively. For all five samples and at all heating rates, the remnant left at the end of pyrolysis slightly reduced with increasing heating rates as shown in all TGA curves. This is in line with similar work reported by Adeleke et al. [16].

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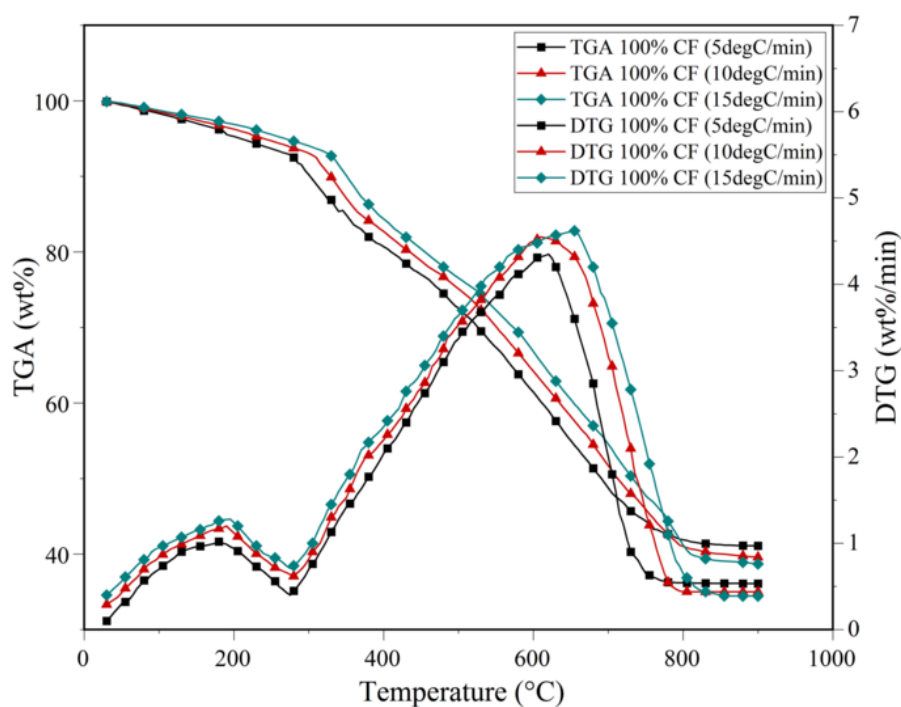


FIGURE 11: Comparative TGA and DTG curves at different heating rates for 100% CF

DTG, differential thermogravimetric; TGA, thermogravimetric analysis; CF, coal fines

Pyrolysis kinetics of MF and CF

Figures 12–17 depict the linear regression model for deriving activation energy (E_a) and pre-exponential factor (A) for MF and CF at 5, 10 and 15°C/min heating rates, respectively. For these parent fuels, the active pyrolysis stage was taken to be the second-stage reactions in line with previous work [18]. The activation energy and pre-exponential factor for MF, CF and their blends are presented in Tables 5–7. The activation energy gotten for MF and CF were 25.4 and 43.24 kJ/mol, 27.08 and 45.44 kJ/mol, and 28.35 and 46.31 kJ/mol for the three heating rates, respectively. These values were compared with data from previous works. Adewole et al. [18] obtained an activation energy of 41.7 kJ/mol for Lafia-obi bituminous coal in its second stage pyrolysis reaction based on Arrhenius equation and Coats and Redfern approximation. Nyakuma et al. [22] employed the Coats-Redfern Model to obtain activation energies of 23.81, 28.74, and 36.96 kJ/mol for Akunza, Ome, and Shiga coal under pyrolysis conditions in their second-stage reactions.

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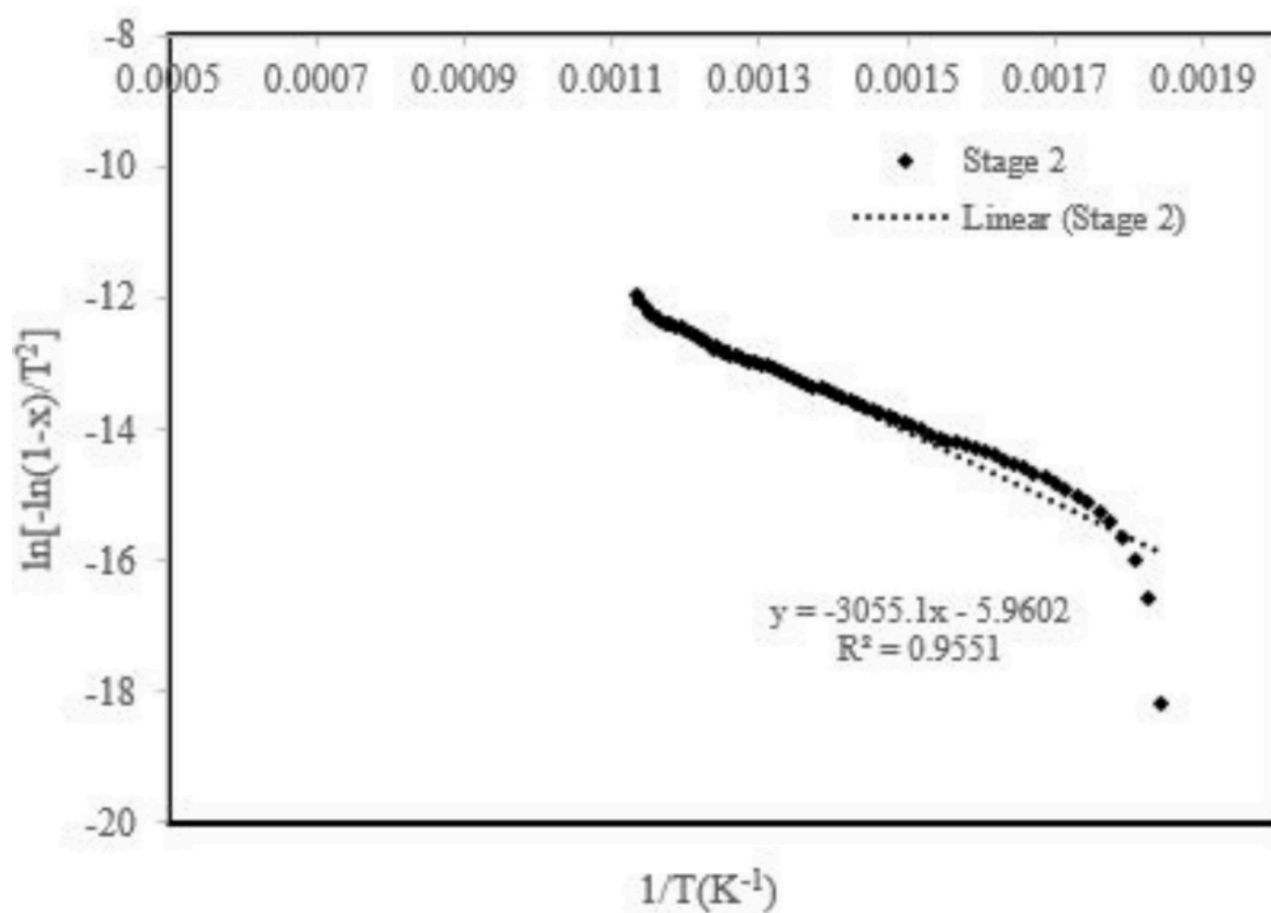


FIGURE 12: Linear regression for the extraction of kinetic parameters for MF at heating rate of 5°C/min

MF, mesocarp fiber

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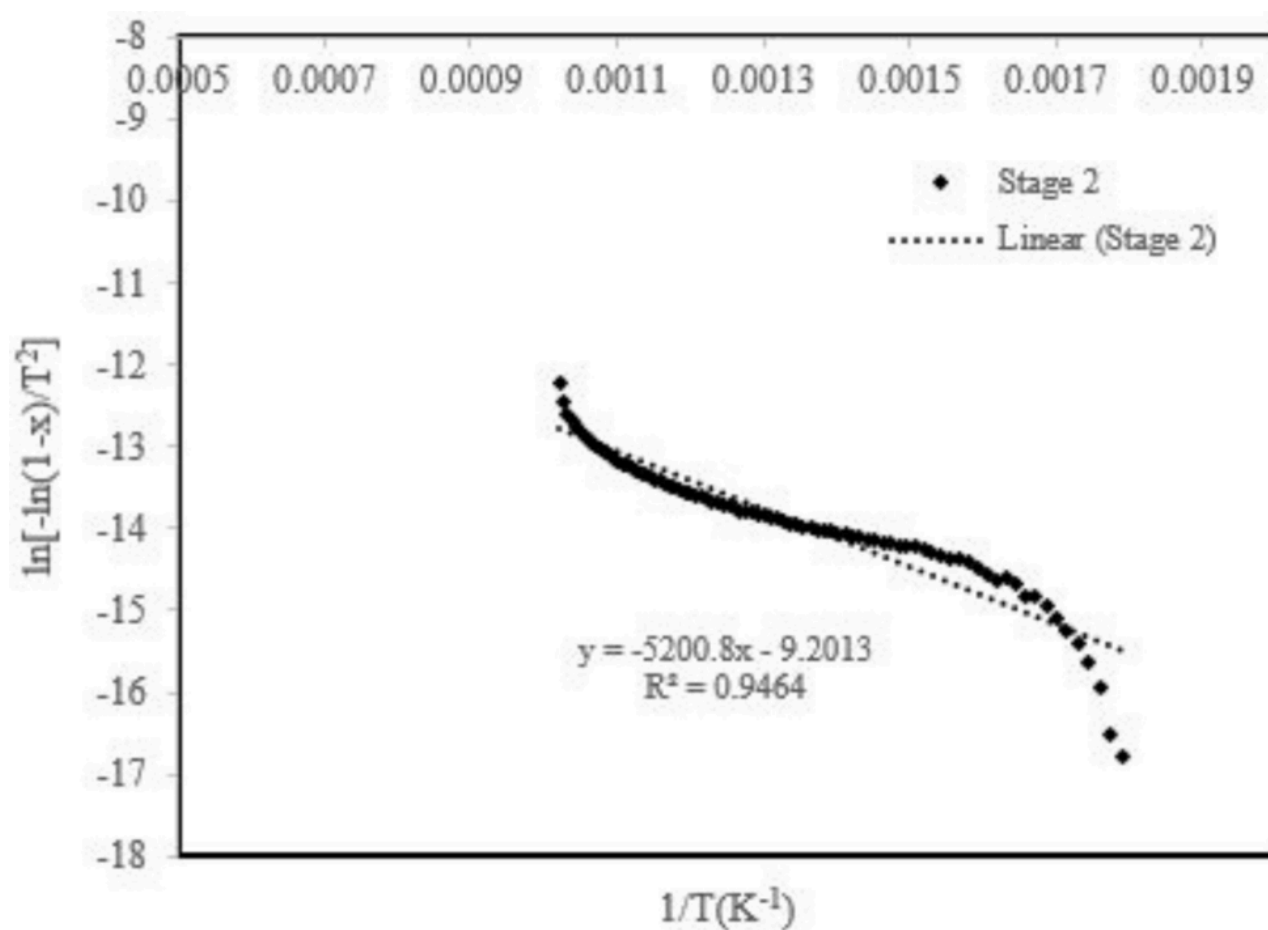


FIGURE 13: Linear regression for the extraction of kinetic parameters for CF at heating rate of 5°C/min

CF, coal fines

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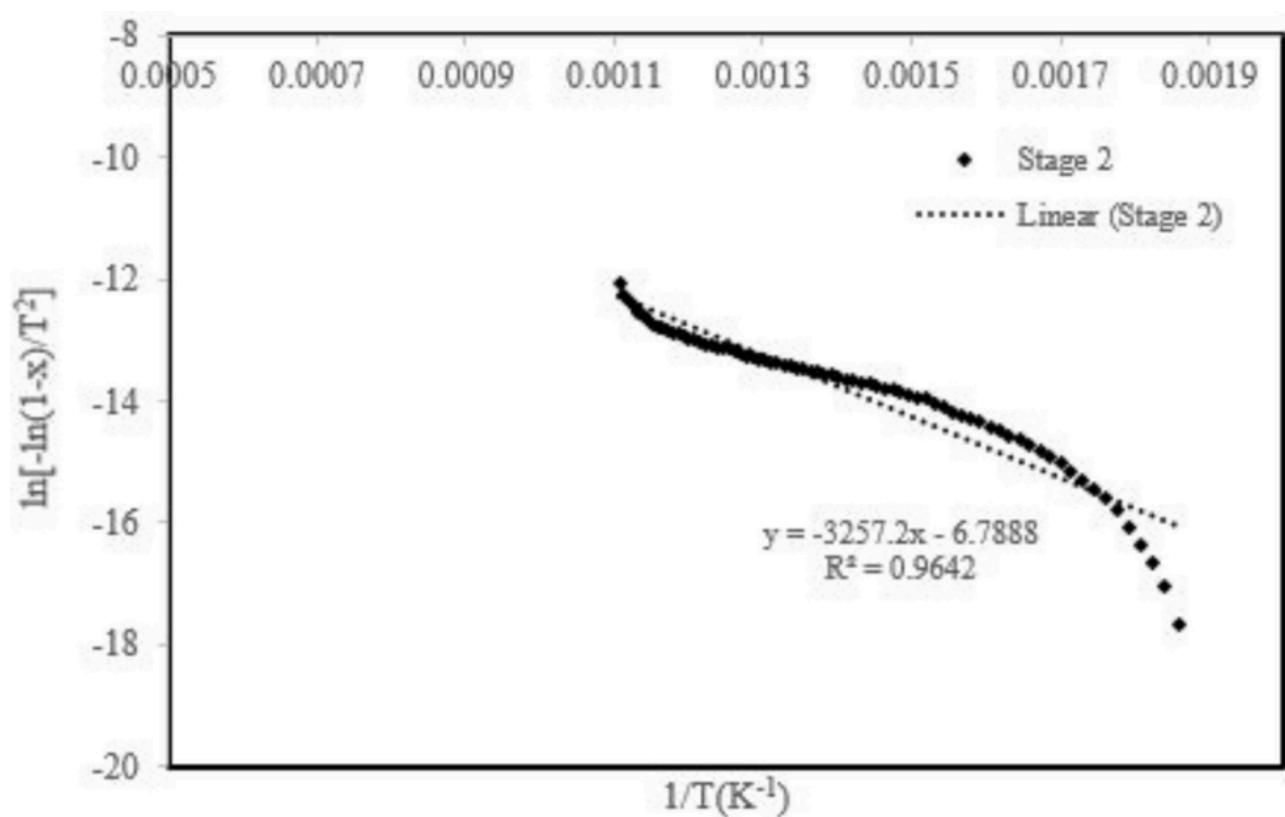


FIGURE 14: Linear regression for the extraction of kinetic parameters for MF at heating rate of 10°C/min

MF, mesocarp fiber

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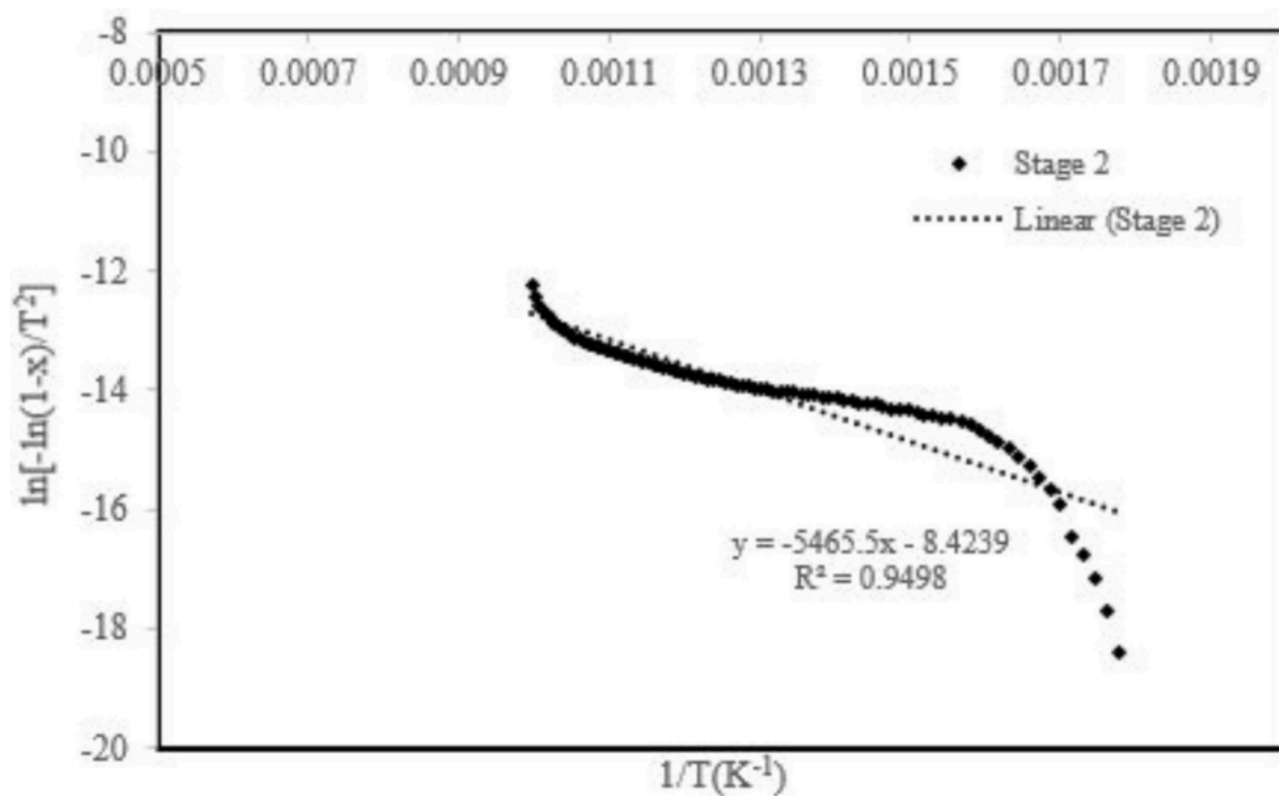


FIGURE 15: Linear regression for the extraction of kinetic parameters for CF at heating rate of 10°C/min

CF, coal fines

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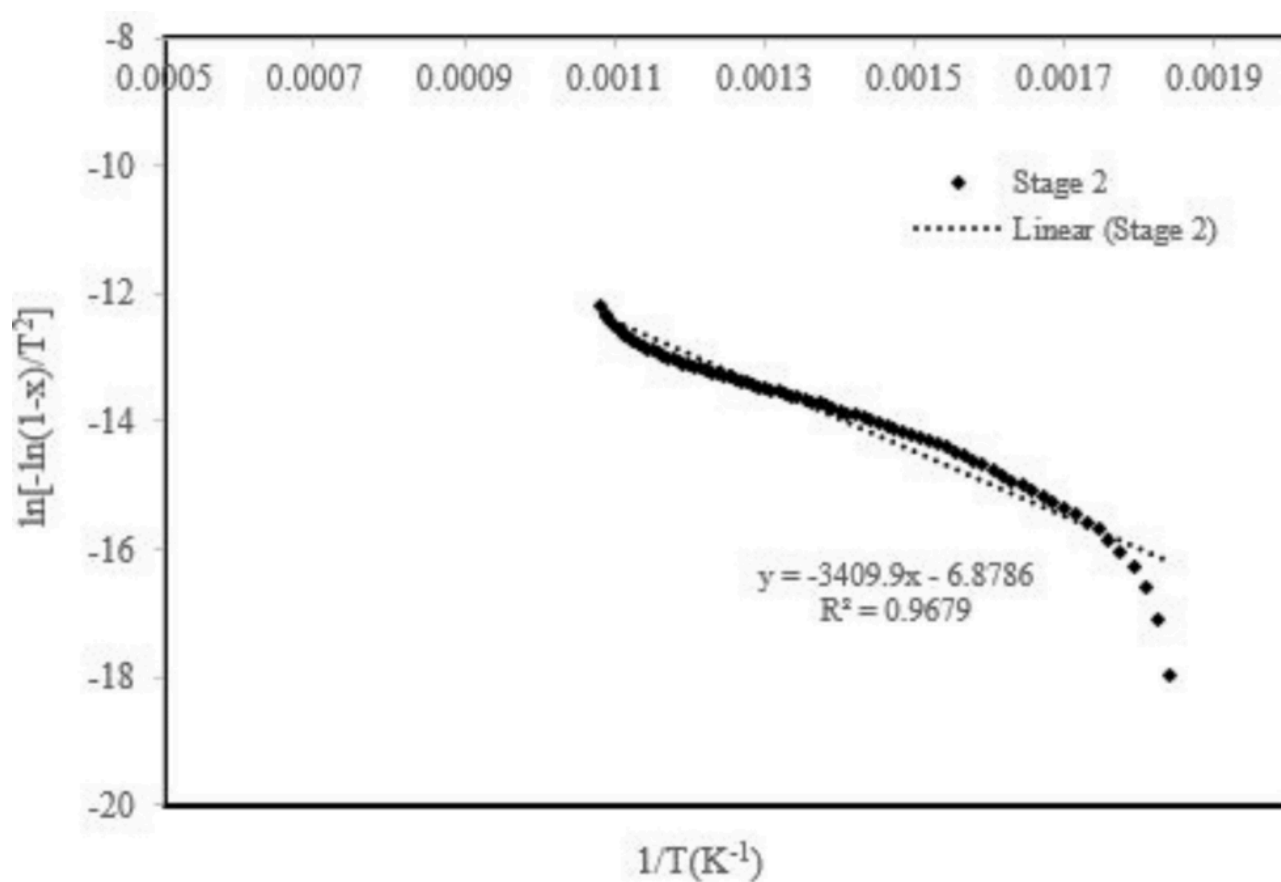


FIGURE 16: Linear regression for the extraction of kinetic parameters for MF at heating rate of 15°C/min

MF, mesocarp fiber

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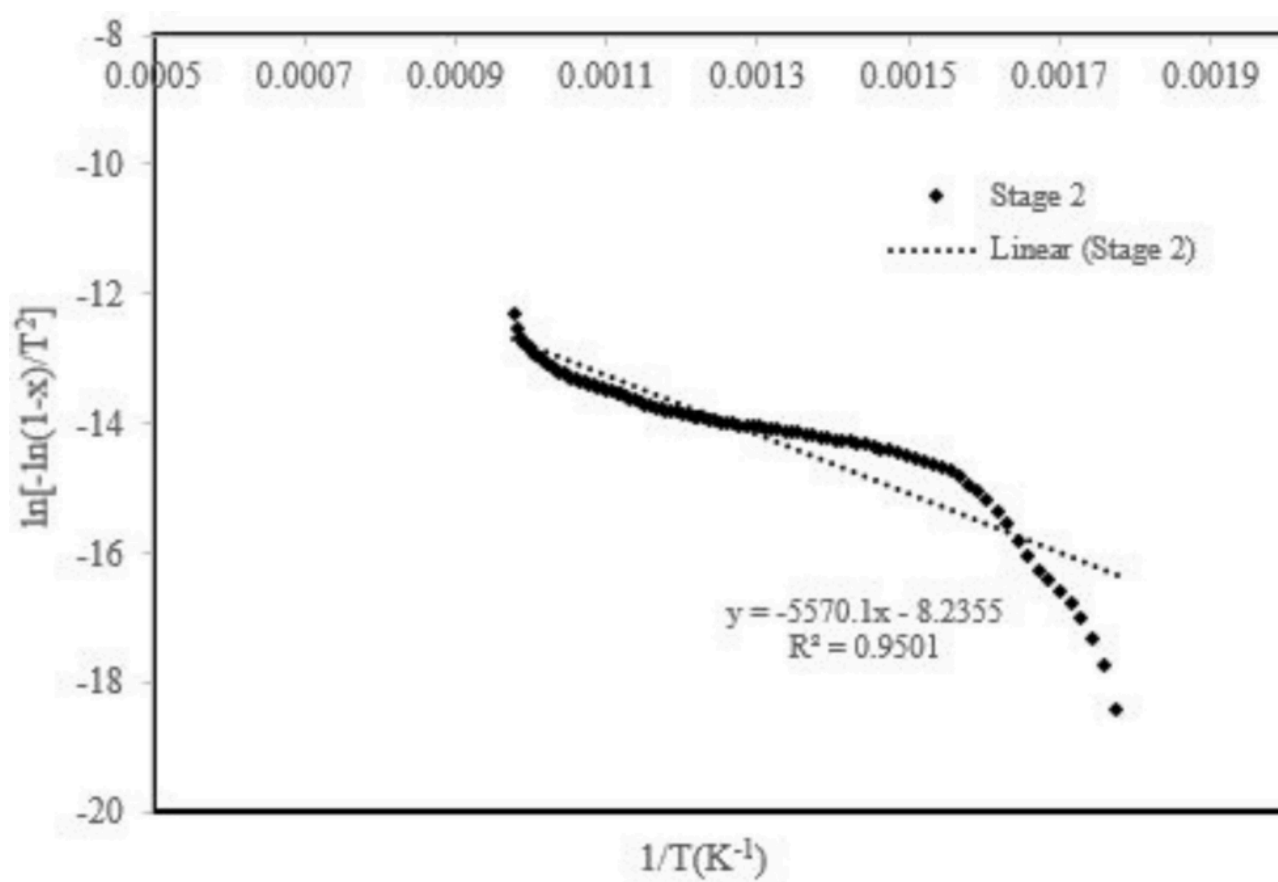


FIGURE 17: Linear regression for the extraction of kinetic parameters for CF at heating rate of 15°C/min

CF, coal fines

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Sample	Temperature (°C)	E _a (KJ/mol)		A (min ⁻¹)	R ²
MF	265 – 615	25.4	4.49 × 10 ⁶		0.9551
CF	280 – 710	43.24	1.23 × 10 ⁸		0.9464
Second-stage reaction					
75% MF	270 – 570	28.68	3.54 × 10 ⁶		0.9617
50% MF	275 – 575	32.72	1.02 × 10 ⁷		0.9501
25% MF	280 – 565	38.84	2.14 × 10 ⁷		0.9484
Third-stage reaction					
75% MF	575 – 685	90.61	1.26 × 10 ⁷		0.9496
50% MF	580 – 690	113.2	2.34 × 10 ⁷		0.9421
25% MF	570 – 695	124.51	5.64 × 10 ⁷		0.9402

TABLE 5: Kinetic parameters for MF, CF, and their blends at 5°C/min heating rate

MF, mesocarp fiber; CF, coal fines

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Sample	Temperature (°C)	E _a (KJ/mol)		A (min ⁻¹)	R ²
MF	260 – 635	27.08	6.04×10^6		0.9642
CF	285 – 735	45.44	1.86×10^8		0.9498
Second-stage reaction					
75% MF	265 – 590	29.02	3.63×10^6		0.9676
50% MF	270 – 595	32.93	1.42×10^7		0.9527
25% MF	275 – 580	39.04	2.43×10^7		0.9492
Third-stage reaction					
75% MF	595 – 700	91.55	1.28×10^7		0.9532
50% MF	600 – 705	115.35	2.76×10^7		0.9493
25% MF	585 – 710	127.97	6.67×10^7		0.9431

TABLE 6: Kinetic parameters for MF, CF, and their blends at 10°C/min heating rate

MF, mesocarp fiber; CF, coal fines

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Sample	Temperature (°C)	E _a (KJ/mol)	A (min ⁻¹)		R ²
MF	265 - 655	28.35	6.07×10^6		0.9679
CF	285 - 755	46.31	1.91×10^8		0.9501
Second-stage reaction					
75% MF	260 - 600	29.92	3.67×10^6		0.9669
50% MF	270 - 605	33.25	1.54×10^7		0.9523
25% MF	275 - 580	39.87	2.61×10^7		0.9475
Third-stage reaction					
75% MF	605 - 715	92.25	1.31×10^7		0.9502
50% MF	610 - 720	116.56	2.68×10^7		0.9539
25% MF	585 - 725	128.85	6.76×10^7		0.9442

TABLE 7: Kinetic parameters for MF, CF, and their blends at 15°C/min heating rate

MF, mesocarp fiber; CF, coal fines

The activation energy determines the reactivity of fuel materials while the pre-exponential factor is more associated with their structure. The fuel with lower activation energy is generally termed the more reactive fuel. The activation energy of MF is lower than that of CF, making it the more reactive fuel. This also implies a faster pyrolysis rate compared to that of CF. The substantially higher value of activation energy for CF may indicate a slower rate of reaction during co-pyrolysis. This is in agreement with the data presented and discussed in the thermogravimetric analysis of the feedstocks. For both feedstocks, a slight increase in activation energy was observed with an increase in the heating rates. The pre-exponential factor of MF and CF was 4.49×10^6 and 1.23×10^8 , 6.04×10^6 and 1.86×10^8 , and 6.07×10^6 and 1.91×10^8 for 5, 10 and 15°C/min heating rates, respectively. All R^2 values evaluated were greater than 0.9.

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Pyrolysis kinetics of MF and CF blends

Figures 18–26 depict the linear regression model for deriving activation energy (E_a) and pre-exponential factor (A) for blends of MF and Ankpa bituminous CF at 5, 10 and 15°C/min heating rates, respectively. For the fuel blends, the second and third stages are regarded as the active pyrolysis stages, the first stage being the drying stage while the fourth is regarded as the char aggregation stage [18,30]. The activation energy and pre-exponential factors for MF, CF, and their blends were presented in Tables 5–7.

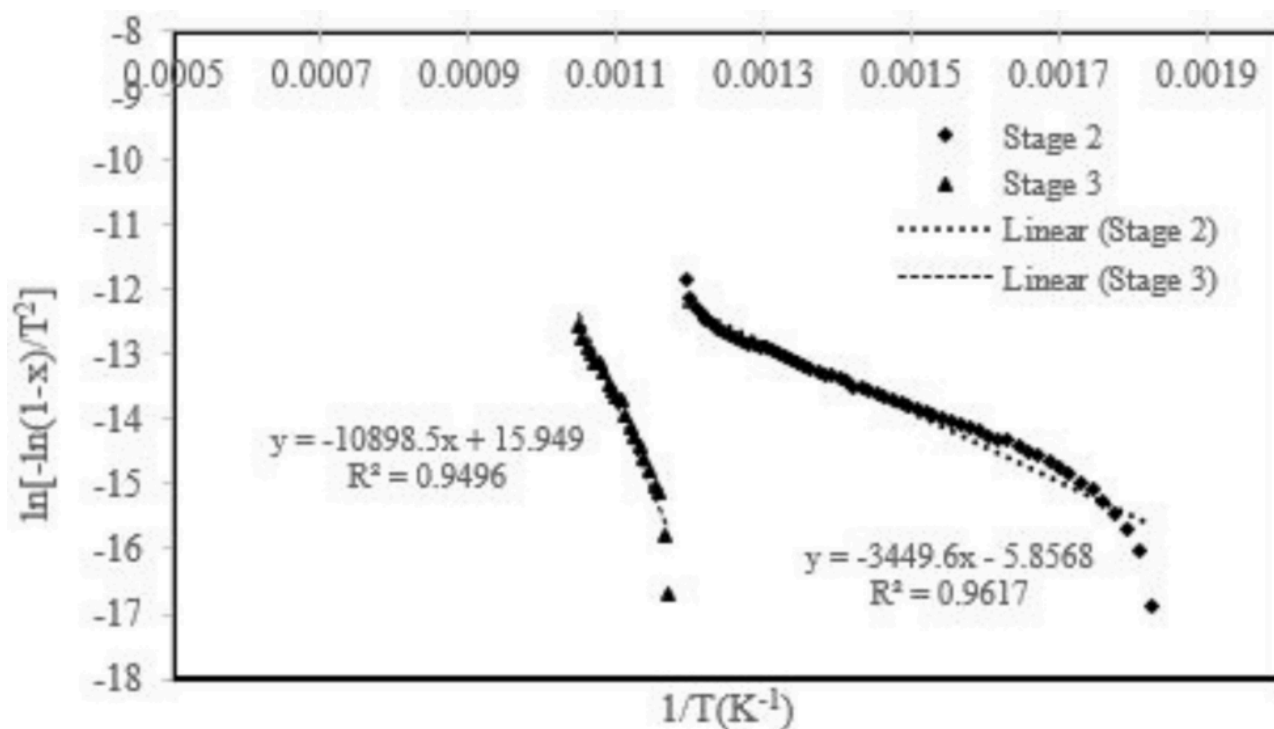


FIGURE 18: Linear regression for the extraction of kinetic parameters for 75% MF at heating rate of 5°C/min

MF, mesocarp fiber

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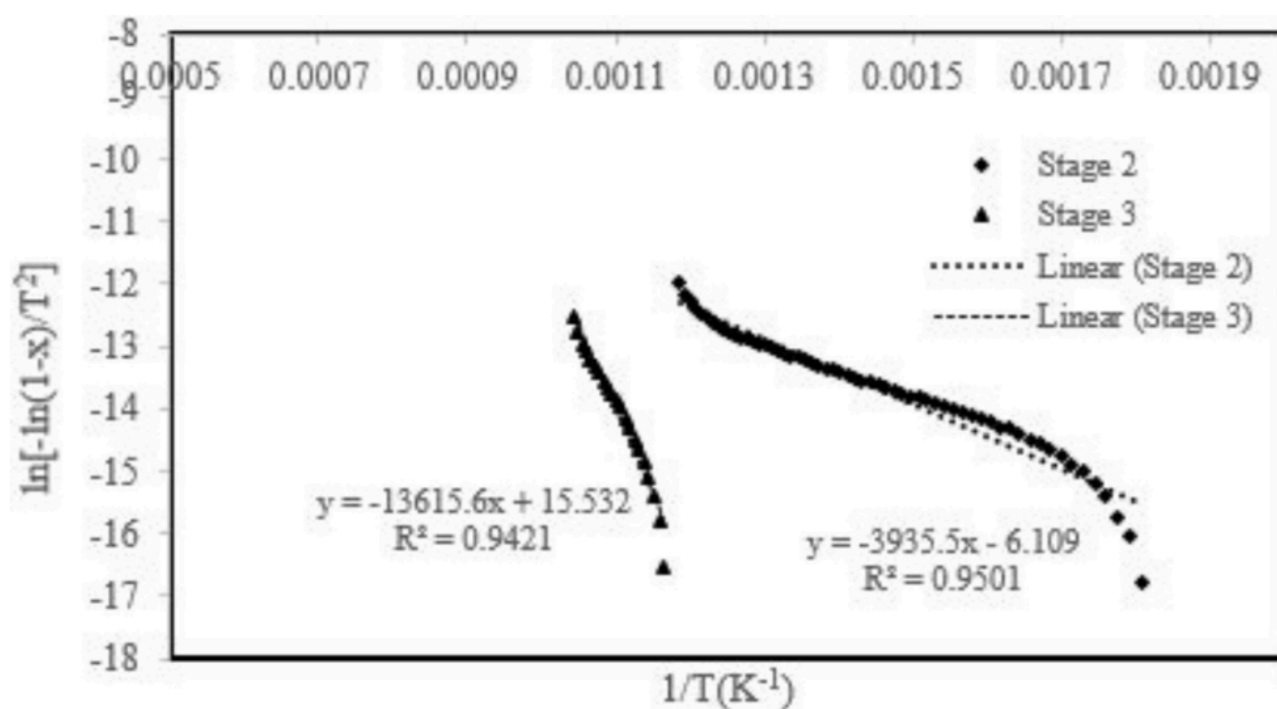


FIGURE 19: Linear regression for the extraction of kinetic parameters for 50% MF at heating rate of 5°C/min

MF, mesocarp fiber

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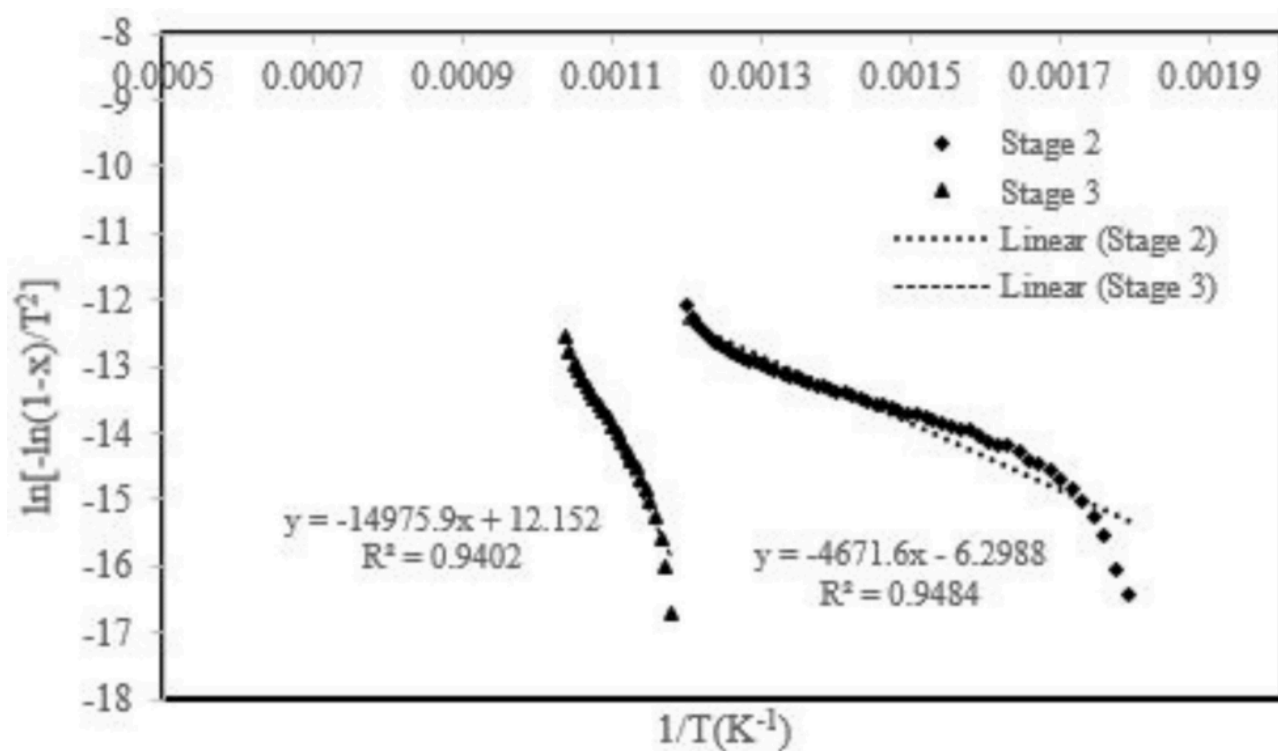


FIGURE 20: Linear regression for the extraction of kinetic parameters for 25% MF at heating rate of 5°C/min

MF, mesocarp fiber

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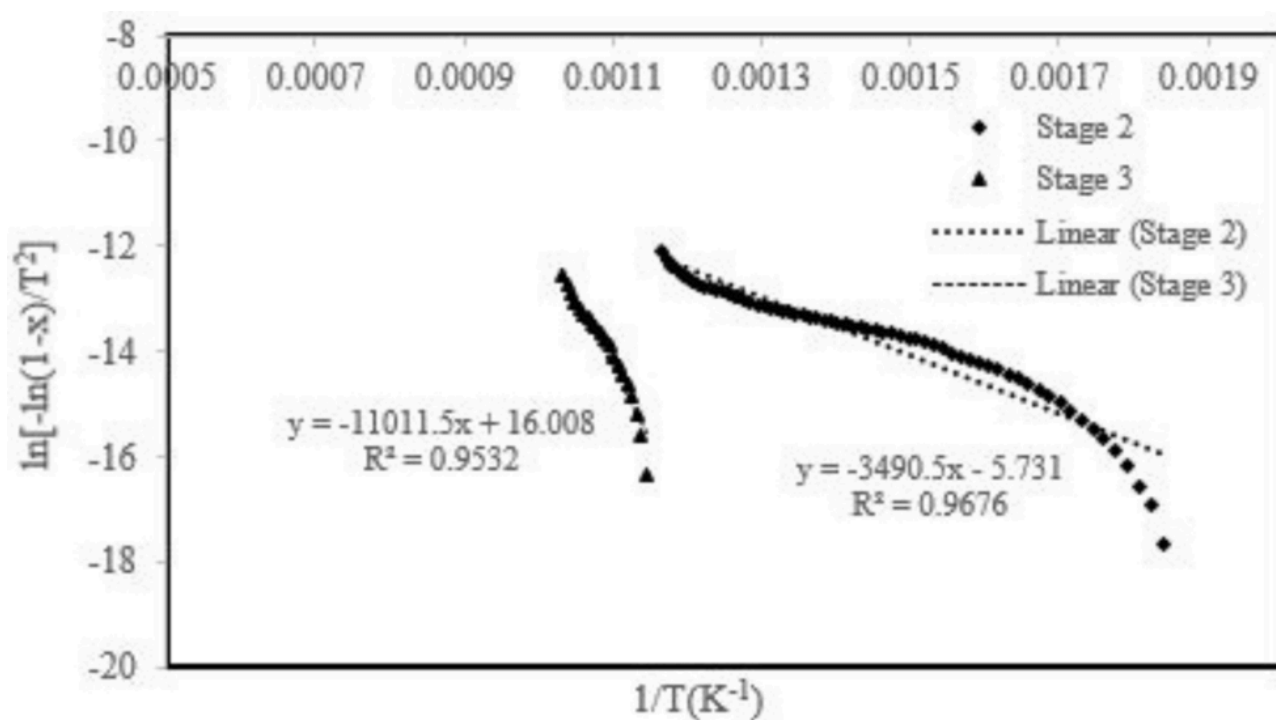


FIGURE 21: Linear regression for the extraction of kinetic parameters for 75% MF at heating rate of 10°C/min

MF, mesocarp fiber

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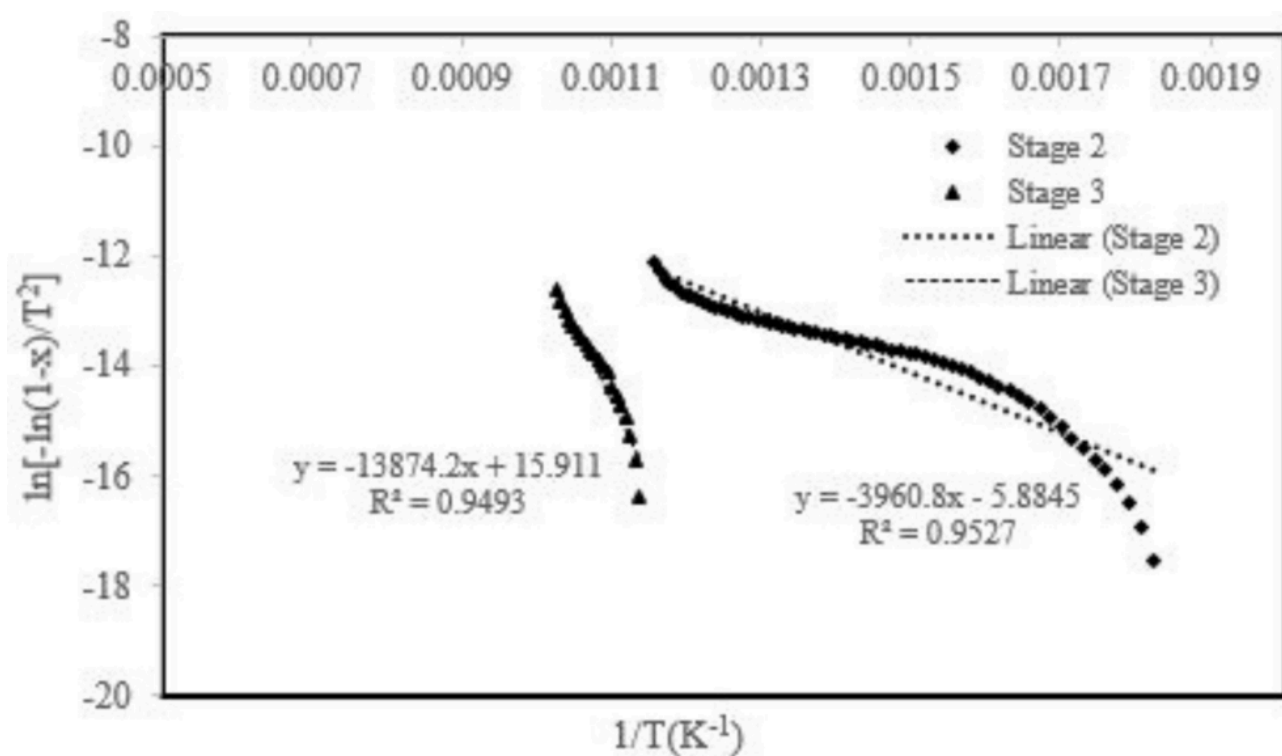


FIGURE 22: Linear regression for the extraction of kinetic parameters for 50% MF at heating rate of 10°C/min

MF, mesocarp fiber

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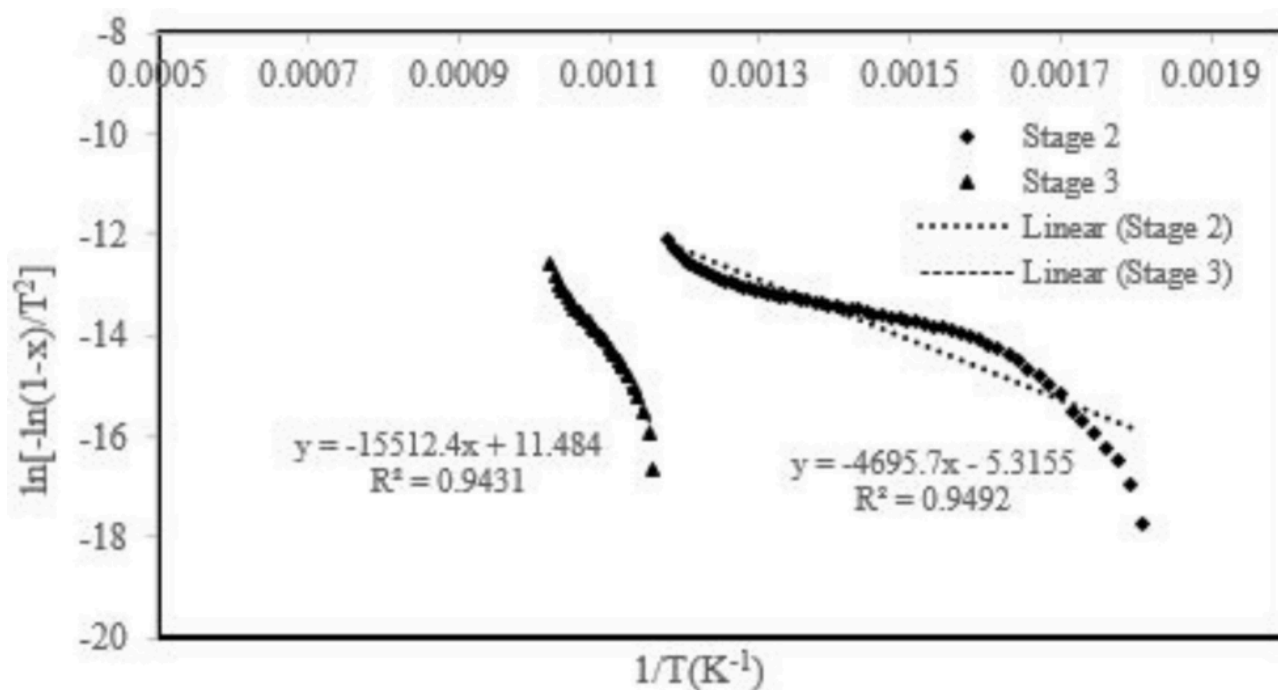


FIGURE 23: Linear regression for the extraction of kinetic parameters for 20% MF at heating rate of 10°C/min

MF, mesocarp fiber

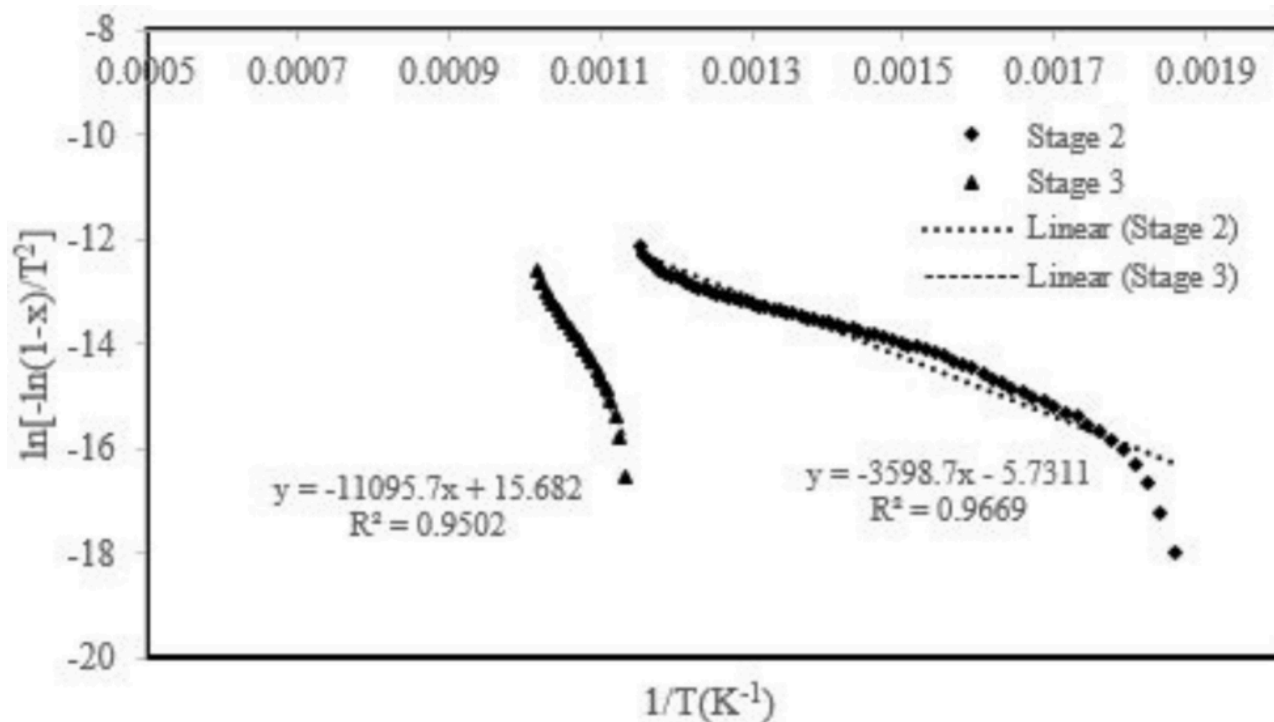


FIGURE 24: Linear regression for the extraction of kinetic parameters for 75% MF at heating rate of 15°C/min

MF, mesocarp fiber

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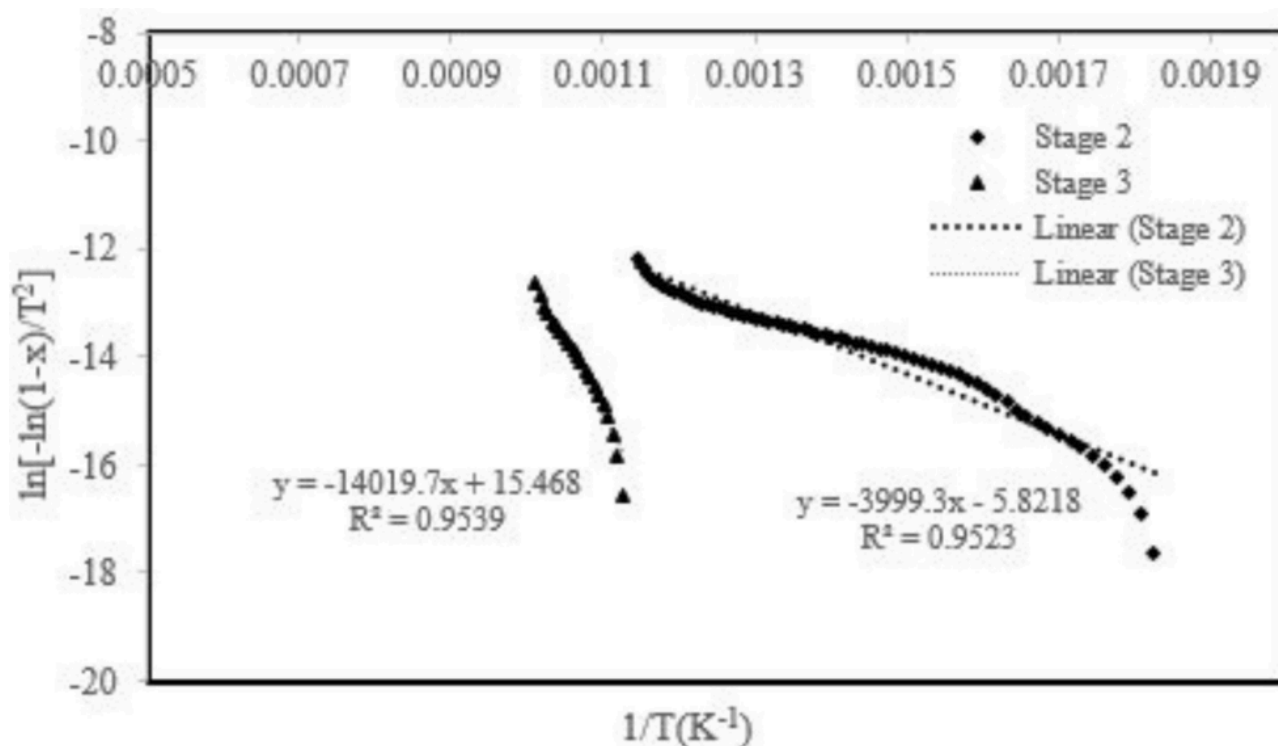


FIGURE 25: Linear regression for the extraction of kinetic parameters for 50% MF at heating rate of 15°C/min

MF, mesocarp fiber

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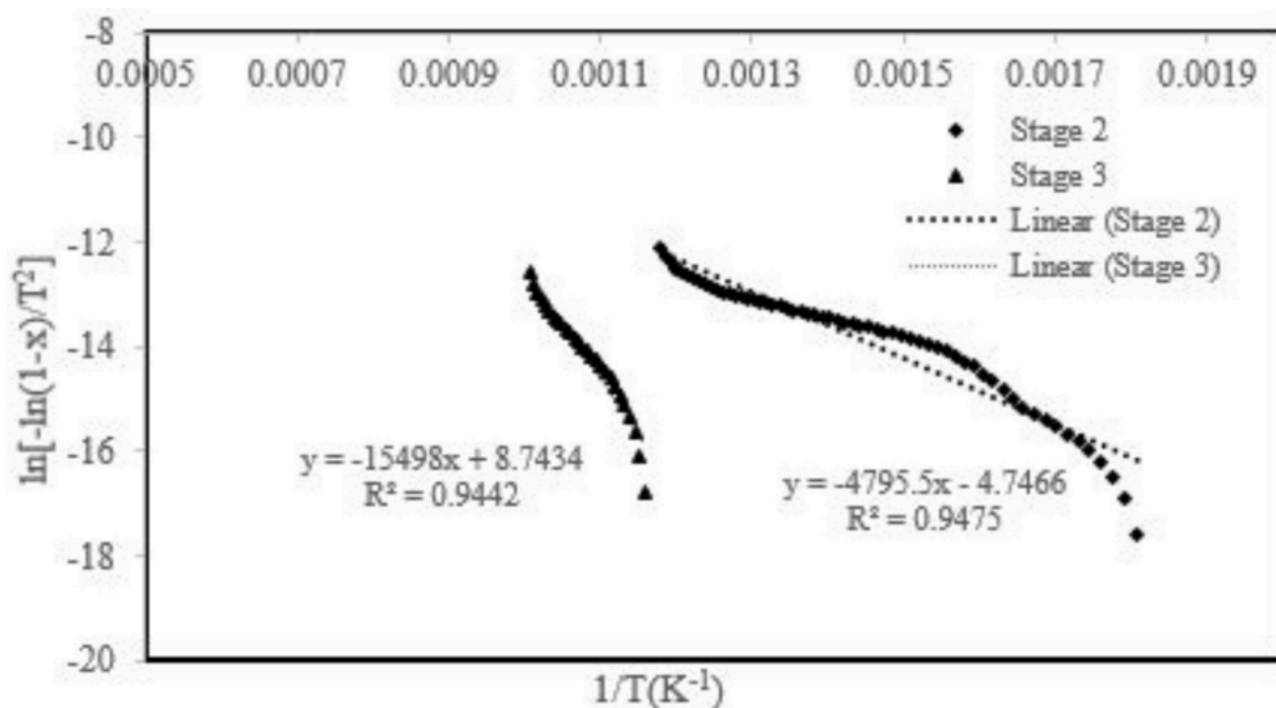


FIGURE 26: Linear regression for the extraction of kinetic parameters for 25% MF at heating rate of 15°C/min

MF, mesocarp fiber

For the second-stage reactions, activation energy of 28.68, 32.72, and 38.84 kJ/mol were evaluated for 75, 50, and 25% MF, respectively at 5°C/min rate. For heating rate of 10°C/min, it was evaluated to be 29.02, 32.93, and 39.04 kJ/mol for 75, 50, and 25% MF, respectively, while for 15°C/min rate, it was 29.92, 33.25, and 39.87 kJ/mol, respectively. In stage 3, the activation energy was 90.61, 113.2, and 124.51 kJ/mol at 5°C/min rate; 91.55, 115.35, and 127.97 at 10°C/min rate; and 92.25, 116.56, and 128.85 for 15°C/min rate; all at 75, 50, and 25% MF, respectively.

In the second-stage reaction, the 75% MF blend has values very close to the values of MF at all heating rates, making the effect of MF dominant at this mix ratio. The 25% MF blend presents values closer to those of CF at all heating rates indicating the dominance of CF in this blend. Generally, for the second stage reaction, the blends have values higher than that of MF but lower than that of CF for all heating rates [18]. In the third-stage reactions, the activation energy also increased with a reduction in percentage of MF (an increase in the percentage of CF) in the blends; however, the values are much higher than those for the second-stage reactions.

As the percentage of MF reduces in the blends (and the percentage of CF increases), there is an increase in the values of activation energy, implying a progressive reduction in the reactivity of the solid fuel mix. On the other hand, the addition of at least 25% MF led to a marked reduction in the activation energy of CF, confirming the catalytic effect of MF on Ankpa bituminous coal in co-pyrolysis. This agrees with the TGA and DTG data presented and discussed in previous sections.

Stages 2 and 3 reactions for all blends at all heating rates have values of R^2 that are not less than 0.94, suggesting that the pyrolysis processes of the blends in these two stages are comparable with data from experimental procedures. Similar correlation was reported in previous study [18].

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Conclusions

This study entails the investigation of the thermal behavior of MF, Ankpa bituminous coal, and their blends. Pyrolysis and co-pyrolysis were carried out on MF, CF, and their blends in a thermogravimetric analyzer from room temperature through 900°C under three heating conditions of 5, 10, and 15°C/min. Five different blend ratios (MF:CF) were examined namely 100:0%, 75:25%, 50:50%, 25:75%, and 0:100%. The pyrolysis of the parent fuel consists of three thermal stages with the second stage reaction being the active pyrolysis stage while the co-pyrolysis of blends had four thermal stages with the second and third reactions being the active pyrolysis stages. The kinetic parameters for the feedstocks and their blends were evaluated from the TGA results. For the three blends at all heating rates, the effects of increasing CF composition became progressively dominant as observed from the decrease in the peak mass loss rate and increase in the peak temperatures for stage 2 reactions, accompanied by a corresponding increase in the peak mass loss rate and peak temperatures for stage 3 reactions. The pyrolysis characteristics of coal can be improved by the addition of MF at a percentage of 25% upward. An increase in heating rates was found to give rise to the same decomposition intensity occurring at elevated temperatures while also giving rise to higher peak mass losses for all compositions. The remnant left at the end of pyrolysis was found to increase as percentage of CF increased in the blends, while reducing slightly as heating rate increased. The activation energy of CF was found to be substantially higher than that of MF. For the second-stage reaction, the blends have activation energy values higher than that of MF but lower than that of CF for all heating rates. As the percentage of MF reduces in the blends, there is an increase in the values of activation energy, implying a progressive reduction in the reactivity of the solid fuel mix. On the other hand, addition of at least 25% MF to CF led to a marked reduction in its activation energy, confirming the catalytic effect of MF on Ankpa bituminous coal in co-pyrolysis. For all blends, a slight increase in activation energy was observed with increase in the heating rates.

Additional Information

Author Contributions

All authors have reviewed the final version to be published and agreed to be accountable for all aspects of the work.

Concept and design: James T. Bamigboye, Busayo S. Adeboye, Seun Oyelami, Oguntola J. Alamu

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Disclosures

Human subjects: All authors have confirmed that this study did not involve human participants or tissue. **Animal subjects:** All authors have confirmed that this study did not involve animal subjects or tissue. **Conflicts of interest:** In compliance with the ICMJE uniform disclosure form, all authors declare the following: **Payment/services info:** All authors have declared that no financial support was received from any organization for the submitted work. **Financial relationships:** All authors have declared that they have no financial relationships at present or within the previous three years with any organizations that might have an interest in the submitted work. **Other relationships:** All authors have declared that there are no other relationships or activities that could appear to have influenced the submitted work.

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Data Availability Statements

Data will not be made available through any means due to the fact that this is an ongoing research project with co-authors having an interest in further analysis of other characteristic behaviors of the feedstocks and their mixtures. It is therefore not wise to make such data available at this point in time.

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