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Investigation of Thermal Behaviour of Mesocarp Fibre and Bituminous Coal with their Blends

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Abstract: *In this study, an investigation was carried out on the thermal behaviour of mesocarp fibre, bituminous coal and their blends through dynamic thermogravimetric analysis. The analysis was carried out using 100% percentage composition of mesocarp fibre and bituminous coal respectively, and their blends (75, 50, and 25 wt% of mesocarp fibre, which implied 25, 50 and 75 wt% of coal). Two different heating rates were employed and pyrolysis temperature was between 30 through 900 ^oC. Three different thermal stages were identified from the DTG curve, and the mass loss during the first stage was attributed to the release of moisture still contained in the feedstock material. The decomposition intensity of MF was higher than that of CF for 5 ^oC/min while for 10 ^oC/min, the decomposition intensity of CF was substantially higher than that of MF for 100% MF and 100% CF by weight. For 5 ^oC/min, as the percentage by mass of CF increased in the sample, the initial temperature increased and final temperature decreased for stage 2 of the thermal stages, which was accompanied by a gradual decrease in weight loss. Although, the blending of MF with CF was found to have significant effects on the thermal behaviour of both feedstocks, due to a better pattern in the feedstocks' behaviour at 5 ^oC/min heating rate, it can be deduced that this rate helps to have a better insight into the thermal behaviour of the feedstocks studied.*

Keywords: *Bituminous Coal, Thermal Stages, Mesocarp Fiber, Decomposition Intensity, Proximate and Thermogravimetric Analyse*

1. INTRODUCTION

In spite of the vast conventional and renewable energy resources of Nigeria, there is still a vast gap to be filled between supply of and demand for energy [1]. Conventional fuel resources, for instance, natural gas, crude oil and coal, have held a major stake in meeting energy needs both in Nigeria and globally [2]. However, the reasons for growth in interest in alternative sources include amongst others, the depletion in fossil fuel reserves, concerns over greenhouse gases emission and climate change and other environmental issues that comes with these emissions [2, 3]. Hydropower, wind, biomass, solar and geothermal and so on, have the potential to help address over-dependence on conventional sources [4, 5]. Naturally occurring carbon-containing materials with its origin from biological sources are generally referred to as biomass. It is a family of complex renewable materials with its major constituents being carbon, hydrogen, oxygen, nitrogen and other chemical constituents in trace amounts [6]. Based on data from recent research, it was reported that when biomass is blended with coal, the combustion properties of resulting briquettes is enhanced and emission is drastically reduced [7]. These hybrid biomass-coal briquettes are made from densification of pulverized coal and biomass materials using suitable binders. Bituminous and sub-bituminous coals are readily available in Nigeria and altogether, it has been estimated that there are up to 2.5 Gt of coal available within the shores of Nigeria. That notwithstanding, they are largely non-coking coals with deposits mainly in Enugu, Nassarawa, Kogi states and other places in the country [8]. Oil palm mesocarp fibre (OPMF), simply called mesocarp fibre (MF), is obtained as residues from palm oil processing. Rural dwellers have utilized this by-product for domestic cooking and heating by employing the improvised and grossly inefficient briquetting means (hand-moulding), but most part of the residues still end up in the garbage, causing environmental pollution and its attendant hazards [9]. Researchers continue to turn their attention towards addition of biomass to coal for solid fuel production because of its many advantages, one of which is the recovery of energy from waste materials. The decomposition behaviour of feedstocks for solid fuel production has been studied in previous

researches. Nyakuma *et al.* [10] studied the decomposition behaviour of empty fruit bunch in a thermogravimetric analyzer as it was heated from 50 ^{o}C through 900 ^{o}C at the heating rate of 10 ^{o}C/min. The four thermal stages through which the decomposition passed through were identified as drying, heating, devolatization and char aggregation. The highest weight loss (70 %) occurred during the devolatization stage which started at 206 ^{o}C and peaked at 325 ^{o}C. Adewole *et al.* [11] carried out an investigation into the thermal behaviour of bituminous coal, coconut shell and their blends through thermogravimetric analysis. The 10% blend of coconut shell showed thermal behaviour similar to that of coal but with a slightly higher peak intensity. For 20-50% blends, two stages of active pyrolysis were identified which correspond to second and third peak. The second peak is attributed to the pyrolysis of coconut shell while the third to the pyrolysis of coal. Although the thermal degradation behaviour of many biomass materials blended together or blended with coal have been studied, data on the co-pyrolysis of mesocarp fibre and coal are not readily available. The blending of oil palm mesocarp fibre with bituminous coal in the production of composite briquettes can potentially offer a more sustainable and environmentally friendly alternative energy source while also providing economic opportunities for palm oil producing economy. One major step towards achieving this is to carry out a study of the thermal decomposition behaviour of these feedstocks and their blends and this is the knowledge gap that this study aims to fill.

2. MATERIALS AND METHODS

2.1 Materials and Sample Preparations

Mesocarp fibre and coal from Ankpa coal deposits were used as raw materials. The mesocarp fibre (MF) was obtained as left over from freshly processed palm oil at the palm oil factory of Adeleke University, Ede, Osun State, Nigeria, while the coal lumps, from which the coal fines (CF) was produced, were obtained from coal deposits at Ankpa in Kogi State, Nigeria. Impurities were removed from the MF before it was washed with detergent to further rid it of oil and dirt [9]. After then, it was dried for two (2) days in the sun. As for the coal lumps, it was delivered in its dry form. The mesocarp fibre was pulverized by a bur mill while the coal lumps were first pulverized using hammer mill and further processed using a bur mill. Both feedstocks were screened by a sieve of size 1 mm. Particles of ≤ 1.00 mm is capable of binding very well in accordance with standard [12].

2.2 Proximate and Ultimate Analysis

The proximate analysis of the feedstocks was obtained on the dry basis to ascertain the percentage volatile matter, moisture content, fixed carbon and ash content. The proximate analysis for coal was done based on standard IS: 1350-1 [13] while that of mesocarp fibre was done based on the methods listed in Table 1 [8, 14, 15, 16, 17, 18]. The heating value (HV) also known as calorific value was estimated using Equation 1 [14, 23].

$$HV = 2.326(147.6FC + 144VM)kJ/kg \quad (1)$$

Table 1: The methods employed for proximate analysis

Property	Analytical method
Moisture content (MC)	ASTM E871-82, (2013)
Volatile matter (VM)	BS EN 15148, (2009)
Ash content (AC)	ASTM E1755-01, (2015)
Fixed carbon (FC) $FC = 100 - (MC + VC + AC)$	By subtraction

The EMA 502 Elemental Analyser was used for the quantitative analysis of the feedstocks for carbon, hydrogen, nitrogen and oxygen based on standard ASTM D5373-16 [19]. In order to determine the percentage by mass of oxygen in the sample, the EMA 502 Elemental Analyser was set up with argon as carrier gas and for the percentage by mass of CHN, oxygen flowing at the rate of 400 ml/min was passed through the analyzer. Approximately 2 g of the samples were used for the analysis. Sulphur content was calculated by subtracting the sum of CHNO percentages from 100 [20].

2.3 Thermogravimetric Analysis

The thermal degradation and decomposition behaviour of mesocarp fibre (MF), coal fines (CF) and their blends were studied with the use of a thermogravimetric analyzer (Model: TGA 4000 Perkin Elmer). The thermogravimetric analysis was carried on different mixtures in MF:CF ratio (100:0, 75:25, 50:50, 25:75, 0:100) of the feedstocks and all samples were studied through dynamic TGA at 5 and 10 ^{o}C/min heating rates, respectively. The blends were thoroughly mixed manually in the stated ratios. In order to carry out the procedure, about 10 g of test sample was placed in the crucible of the equipment. An inert atmosphere was maintained in the equipment by maintaining a continuous nitrogen flow at the rate of 100 ml/min. Biomass sample was heated from 30 through 800 ^{o}C and coal was heated through 900 ^{o}C while their blends was heated through 900 ^{o}C [8, 10]. The TGA tests for each sample were replicated twice and the results were found to be consistent.

3. RESULTS AND DISCUSSION

3.1 Proximate and Ultimate Analysis

The quantitative analysis of the feedstocks was carried out to determine the percentage composition of carbon, hydrogen, nitrogen and oxygen based on ASTM standards. The results for the analysis for both feedstocks (MF and CF) are as shown in Table 2. This ultimate analysis results for MF agree largely with the one reported by Abdullah *et al.* [21] for oil palm fruit fibre (OPFF), simply referred to as mesocarp fibre (MF). In line with that, the results presented for CF is in agreement with those reported by Adeleke *et al.* [15, 20] for coal. Both feedstocks are capable of producing water after combustion due to the presence of hydrogen. With the higher amount of oxygen, MF will produce solid fuel with higher burning potential. This fuel will also burn at lower temperature relative to solid fuel made from CF. However, with the amount of oxygen present in CF, it will still possess a good combustion rate. The presence of sulphur in both feedstocks can cause emission of acidic oxides (SOx) as by-products of its combustion making its presence undesirable [22]. Likewise, the qualitative analysis of feedstocks was carried out for raw biomass and coal to determine the percentage VM, MC, FC and AC. This proximate analysis results for MF agree largely with the one reported by Abdullah *et al*. [21] for mesocarp fibre. In line with that, the results presented for CF is in agreement with those reported by Adeleke *et al.* [15, 20] for coal.

3.2 Thermogravimetric analysis of CF and MF

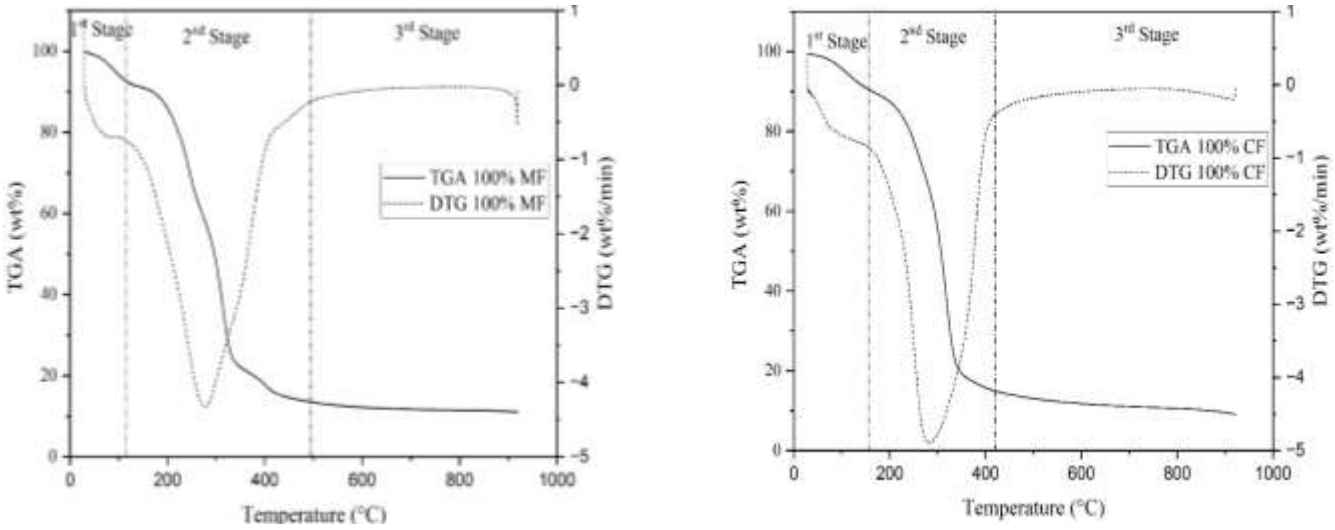
The thermogravimetric analysis (TGA) and derived thermogravimetric (DTG) curves of CF and MF are as shown in Figures 1 (a, b) and 2 (a, b) for 5 ^{o}C/min and 10 ^{o}C/min heating rates respectively. Three different stages were identified from the TGA and DTG curves for the two feedstocks. The mass loss during the first stage of pyrolysis is attributed to the release of the moisture still contained in the feedstocks [11]. Tables 3 and 4 show the obvious thermal stages and their corresponding temperature ranges for MF and CF (A1, A5) at 5 ^{o}C/min heating rate and (B1, B5) at 10 ^{o}C/min heating rate. The second stage reaction of MF took place between 116 and 495 ^{o}C for 5 ^{o}C/min heating rate as shown in Table 3, and 157 and 557 ^{o}C for 10 ^{o}C/min heating rate respectively as shown in Table 4. For CF, the second stage reaction occurred between 156 and 419 ^{o}C for 5 ^{o}C/min heating rate, and 231 and 605 ^{o}C for 10 ^{o}C/min heating rate respectively. For both feedstocks, the second stage started and ended at higher temperature for heating rate of 10 ^{o}C/min compared to 5 ^{o}C/min heating rate. Also, the weight loss was higher for the higher heating rate (88.43% $^{o}C^{-1}$) compared to the lower (78.98% $^{o}C^{-1}$) for MF. The trend can be observed also for CF (94.74 % $^{o}C^{-1}$ and 75.59% $^{o}C^{-1}$ respectively). The pyrolysis reaction for CF occurred at higher temperature compared to MF. However, the decomposition intensity of MF was higher than that of CF for 5 ^{o}C/min. This agrees with the trend reported by Adewole *et al.* [11] for coconut shell and coal. Wei *et al.* [24] also attributed higher pyrolysis rates of biomass materials relative to coal to the chemical composition of the materials and evolution of gaseous products. At 10 ^{o}C/min heating rate however, the rate of decomposition of CF was substantially higher than that of MF. At higher heating rates, both feedstocks decomposed at a higher rate. From the DTG curves presented in Figure 1 (a, b), the maximum rate of mass loss was 4.31%wt/min for MF and 4.89%wt/min both occurring at the peak temperature of 272.54 ^{o}C and 282.18 ^{o}C respectively. The peak temperature shown for MF is lower than that of CF, but on the other hand, CF exhibited a higher maximum rate of mass loss relative to MF. From the DTG curves of the second heating rate as shown in Figure 2 (a, b), the maximum rate of mass loss was 4.81%wt/min for MF and 6.05%wt/min for CF, both occurring at the peak temperatures of 326.95 ^{o}C and 356.14 ^{o}C respectively. Here also, the peak temperature shown by MF is lower than that of CF, but CF exhibited a much higher maximum rate of mass loss relative to MF. The peak of the DTG curve shown in Figure 1a and 2a is due to the decomposition of hemicellulose and cellulose content and the devolatization of lignin content contained in MF while the peak DTG as shown in Figure 1b and 2b can be attributed to the release of volatile matter content during the pyrolysis procedure [11].

3.3 Thermogravimetric Analysis of CF and MF Blends

The graphs for the blends are presented in Figures 3 (a, b, c) and 4 (a, b, c) for 5 ^{o}C/min and 10 ^{o}C/min heating rates respectively. The key thermal stages under the two heating rates are as presented in Tables 3 and 4. As presented in Table 3, the blending of 25% by weight of CF led to a drop in the initial and final temperatures of the second stage reaction, making the effect of CF obvious. Afterwards, a gradual increase in the initial temperature and decrease in the final temperature was observed for 50, 75 and 100% by weight of CF. Therefore, as the percentage by mass of CF increased in the sample, the initial temperature increased and final temperature decreased for stage 2 of the thermal stages. Also, an initial increase in weight loss was observed for the blend of 25% CF before a gradual decrease in the weight loss through the blend of 50, 75 and 100% CF. From the DTG curves of 5 ^{o}C/min heating rate as shown in Figure 3, the maximum rate of mass loss increased for 25% by mass of CF in the blend, and decreased for 50 and 75% blends of CF before a sharp increase was observed for 100% percentage by mass of CF. As presented in Table 4, the blending of 25% by mass of CF led to an increase in initial and decrease in final temperature of second stage reaction, making the effect of CF obvious. Therefore, an irregular pattern was established with the trend of initial and final temperature of stage 2 reaction. From the DTG curves of 10 ^{o}C/min heating rate as shown in Figure 4, an initial drop can be observed in the maximum rate of mass loss making the 25% blend of CF obvious. This was followed by a slight decrease for 50% and substantial increase for 75% and 100% CF composition. Considering the peak temperatures, 25% by weight of CF led to decrease followed by a massive increase in peak temperatures for 50% CF and a decrease for 75% CF composition.

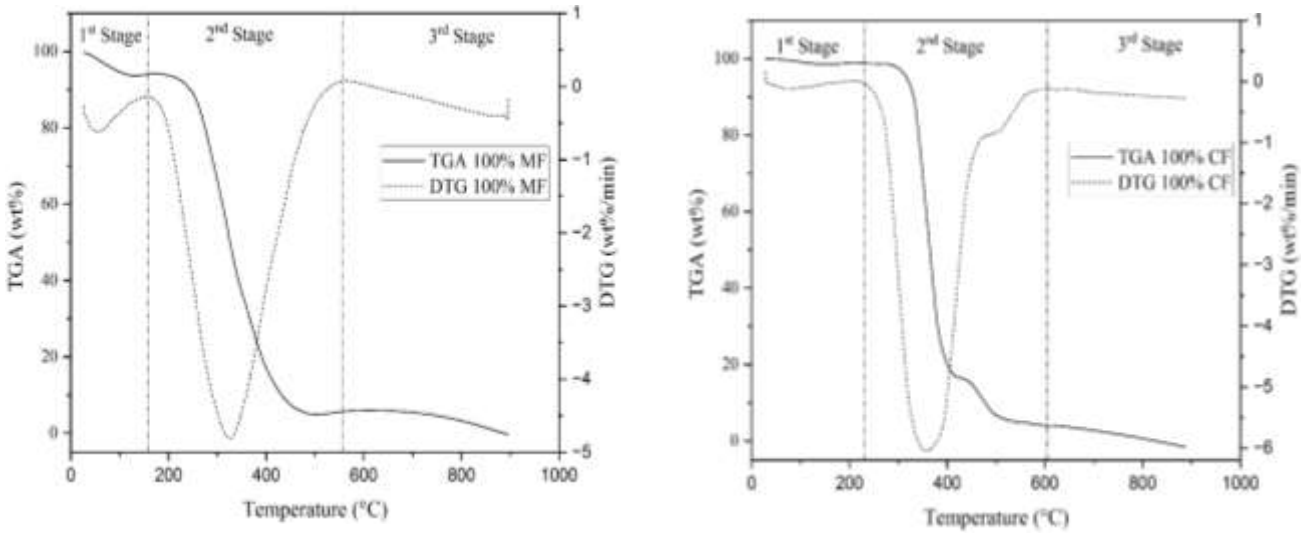
Table 2: Physicochemical properties of MF and CF

	Proximate				Ultimate					HHV (MJ/kg)
	MC	VM	AC	FC	C	H	N	O	S	
MF	8.42	80.35	4.20	7.03	65.98	6.58	2.92	23.98	0.54	29.04
CF	1.48	13.72	17.82	66.98	73.20	3.43	1.82	20.59	0.96	27.59



(a) (b)

Figure 1: TGA and DTG curves of (a) MF and (b) CF at heating rate of 5°C/min



(a) (b)

Figure 2: TGA and DTG curves of (a) MF and (b) CF at heating rate of 10°C/min

Table 3: Properties of Key Thermal stages of MF, CF and their blends at 5 ^{o}C/min rate

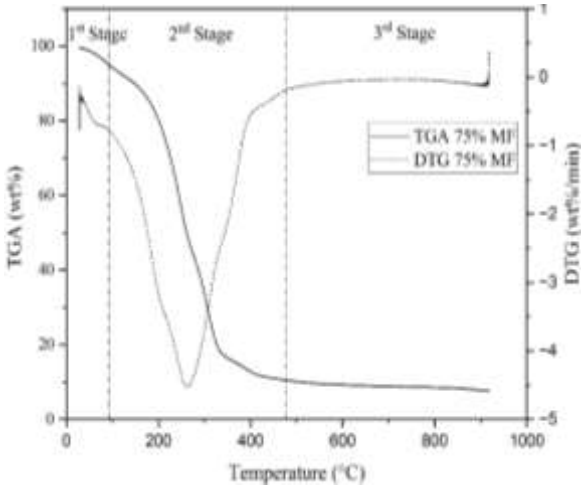
Parameters	**Samples**	**Stage 2**		**Stage 3**	
		Initial	**Final**	**Initial**	**Final**
Temperature (^{o}C)	A1	116	495	496	744
	A2	93	478	479	749
	A3	97	471	472	766
	A4	117	438	439	772
	A5	156	419	420	876
Weight loss (%)	A1	78.98			
	A2	85.37			
	A3	80.55			
	A4	78.94			
	A5	75.59			
Peak Temp. (^{o}C)	A1	272.54			
	A2	263.06			
	A3	285.44			
	A4	287.58			
	A5	282.18			
Max rate of mass (%wt/min)	A1	4.31			
	A2	4.52			
	A3	4.37			
	A4	4.03			
	A5	4.89			

(Note: A1 – 100% MF, A2 – 75% MF, A3 – 50% MF, A4 – 25% MF and A5 – 100% CF)

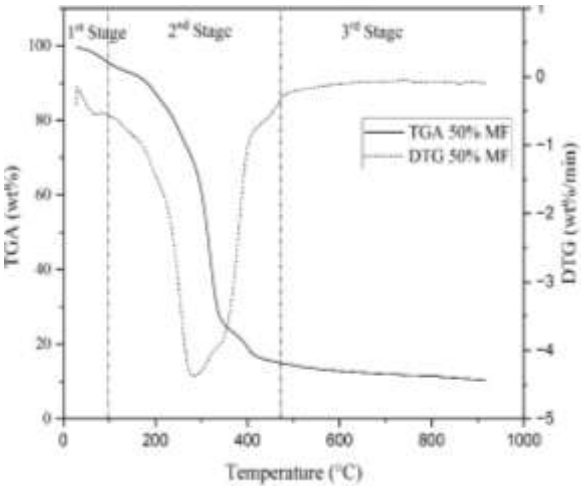
Table Error! No text of specified style in document.: Properties of Key Thermal stages of MF, CF and their blends at 10 ^{o}C/min rate

Parameters	**Samples**	**Stage 2**		**Stage 3**	
		Initial	**Final**	**Initial**	**Final**
Temperature (^{o}C)	B1	157	557	558	893
	B2	175	532	533	843
	B3	174	651	652	883
	B4	222	626	627	849
	B5	231	605	606	879
Weight loss (%)	B1	88.43			
	B2	83.17			
	B3	94.17			
	B4	88.51			
	B5	94.75			
Peak Temp. (^{o}C)	B1	326.95			
	B2	302.11			
	B3	365.44			
	B4	354.05			
	B5	356.14			
Max rate of mass (%wt/min)	B1	4.81			
	B2	4.76			
	B3	3.65			
	B4	4.98			
	B5	6.05			

(Note: B1 – 100% MF, B2 – 75% MF, B3 – 50 % MF, B4 – 25% MF and B5 – 100% CF)



(a)



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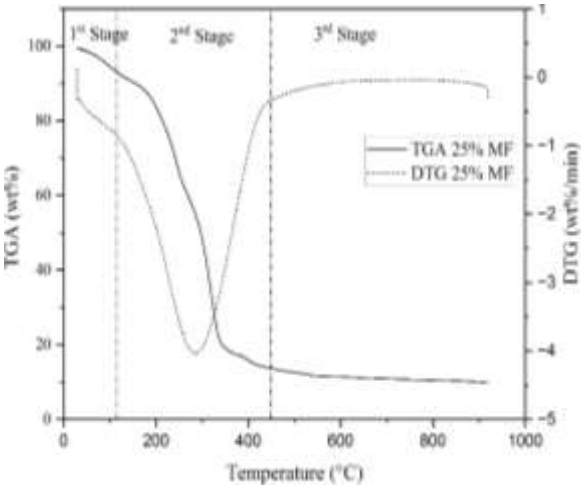
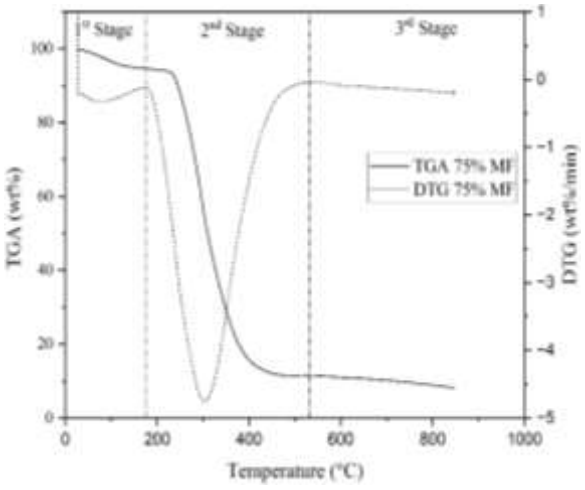
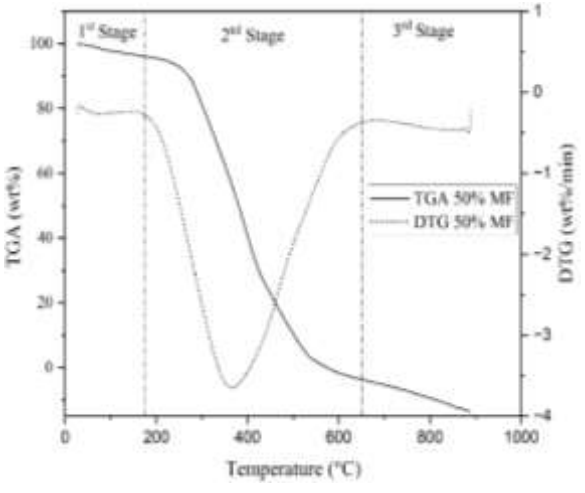


(c)

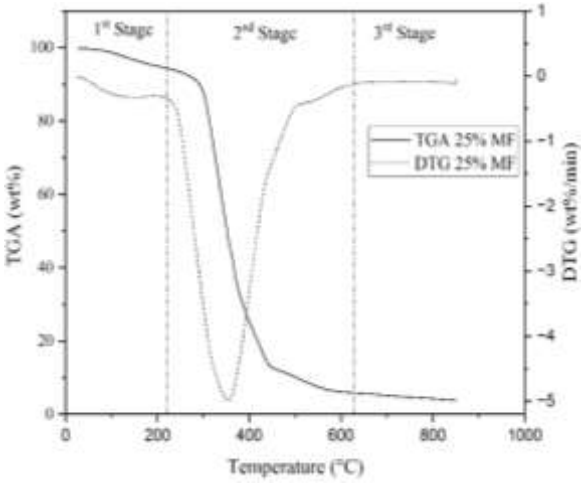
Figure 3: TGA and DTG curves of blends of MF and CF at (a) 75% MF, (b) 50% MF and (c) 25% MF at heating rate of 5^{o}C/min



(a)



(b)



(c)

Figure **Error! No text of specified style in document.**: TGA and DTG curves of blends of MF and CF at (a) 75% MF, (b) 50% MF and (c)

4. CONCLUSION

Thermogravimetric analysis was carried out on mesocarp fibre (MF) and bituminous coal (CF) and their blends for temperature ranging from 30 ^{o}C through 900 ^{o}C at 5 ^{o}C/min and 10 ^{o}C/min heating rates respectively. Three different blend ratios considered were 75, 50, and 25% by mass of MF, equivalent to 25, 50, and 75% by mass of CF respectively, in addition to 100% by mass both of MF and CF separately. The thermogravimetric cycle of both feedstock materials consisted of three (3) thermal reaction stages. The weight loss during the first stage of pyrolysis was attributed to the release of moisture still contained in the materials. For both feedstocks at their 100% composition, the second stage started and ended at higher temperatures for 10 ^{o}C/min heating rate compared to 5 ^{o}C/min. The decomposition intensity and peak temperatures were higher for 10 ^{o}C/min heating rate for both MF and CF. Also, as percentage by mass of CF increased in the samples, the initial temperature increased and final temperature decreased for stage 2 at 5 ^{o}C/min heating rate. This was accompanied by a gradual decrease in the weight loss. Although, the blending of MF with CF has significant effects on the thermal behaviours of both feedstocks, due to a better pattern in its behaviour at 5 ^{o}C/min heating rate, it can be deduced that this rate presents a better insight into the thermal behaviour of the feedstocks studied. Further research efforts can be directed towards the study of kinetic parameters such as the pre-exponential factor and activation energy of feedstocks and also the production of solid fuels from the feedstock materials and their blends and necessary tests can be carried out in order to ascertain their suitability for sustainable energy production.

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