



Characterization and co-firing potential of a high ash coal with *Bambusa balcooa*



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HIGHLIGHTS

- The potential of *Bambusa Balcooa* (BB) as a co-fired fuel was tested.
- BB was torrefied and carbonized at temperature between 250 °C and 380 °C.
- The raw bamboo has the highest fuel reactivity and lowest ignition temperature.
- Thermogravimetric test was conducted on all samples along with coal/bamboo blends.
- The DTG profiles of CBB 350 and 380 °C showed a DTG curve with a similar burning profile to coal.

ARTICLE INFO

Article history:

Received 2 October 2014

Received in revised form 25 December 2014

Accepted 21 January 2015

Available online 11 February 2015

Keywords:

Bamboo
Blending
Carbonization
Coal
Combustion
Torrefaction

ABSTRACT

Two pre-treatment methods, i.e. torrefaction and low-temperature carbonization, were applied to a bamboo species, "*Bambusa balcooa*" at a temperature between 250 °C and 380 °C. The physicochemical characteristics and thermal behavior of the coal, raw bamboo and thermally treated bamboo sourced from South Africa were investigated using thermogravimetric analysis (TGA). The aim was to enhance the fuel quality and to determine the combustion potential of *B. balcooa* solely, or co-fired with a low rank bituminous coal. The co-firing of the raw and thermally treated bamboo samples with coal of 27.50% ash content was conducted in the absence of oxygen, using a ratio of coal inclusion of 10%, 30%, 50% and 75%.

Results obtained from the proximate and ultimate analyses show a considerable difference in the quality of the raw bamboo from the thermally-treated samples. The ash content and fixed carbon "dry basis" of the raw *B. balcooa* (BB) were found to be 0.49% and 6.01%, respectively, with a calorific value of 18.53 MJ/kg. After the BB was torrefied (TBB) at 280 °C and carbonized (CBB) at 380 °C, a fuel with 3.63% ash content and 38.20% fixed carbon, with calorific values of 24.02 MJ/kg and 28.20 MJ/kg respectively was produced. The nitrogen content of the raw BB was found to be 0.22% while the sulfur was untraceable.

Using the TGA data, activation energy (E_a) of 64.12 kJ/mol was obtained from the coal tested, which was higher than that obtained from the raw BB (11.24–31.60) kJ/mol. Higher E_a values were obtained as the thermal treatment temperature increased. The E_a values for the carbonized samples were within the range of (67.33–71.71) kJ/mol compared to the torrefied samples (43.70–44.70) kJ/mol. The TG curves were fitted using the Coats Redfern model. In summary, the results showed that the most effective mechanisms for controlling the combustion process in all samples under stage 3 "carbon combustion" were the chemical reaction models (O1, O2 and O3).

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1. Introduction

The known reserves of high quality coal in South Africa (SA) are fast depleting, and as long as the country solely depends on coal for generating electricity, the emission of greenhouse gases will continue. More than 22% of the world total energy is generated from coal [1], and about 92.8% of electricity in South Africa also

generated from coal [2]. Coal is known among all fossil fuels as the highest emitter of CO₂, and with SA consistently powered by coal, the CO₂ emissions have increased tremendously with about 85% of the country's total 119 Mt emissions generated from coal [3]. Public outcry has increased globally and within South Africa in the reduction and finding of an alternative source of power generating fuel in lieu of fossil fuel. In addition, the supply of thermal coal for power generation is already in crisis, with finance banks such as the World Bank, European Investment Bank, US export-import Bank pledging to stop funding of Greenfield projects in developing world. This will definitely lead to shortage of coal supply in the near future for power generation. However, with the research into the utilization of renewable “biomass” co-fired with coal, the consumption of coal can be reduced significantly thereby reducing coal fired power plants carbon footprint [4].

Among all biomass available, bamboo was proposed as an alternative source of fuel, and utilized in this investigation because of its growth rate “foot/30.48 cm/day”, strength and high quality fuel physiochemical properties [5,6], along with a better viable production rate than pine [7]. The species utilized is called *Bambusa balcooa* (BB), a clumping bamboo and perhaps the most widely utilized bamboo in South Africa. It has very thick wall culms, height within 15–20 m, and internode of about 20–45 cm, and a raw material for pulp (paper production), construction, scaffolding and energy source. With different techniques, such as combustion and pyrolysis available for converting biomass as a single or co-fired source of fuel, biomass still faced with different limitations. There exist problems of uneven physiochemical properties, high grindability, varied combustion characteristic, low ash melting point, high moisture and volatile components of biomass [7,8]. These problems limit the economic viability and the potential of biomass for energy production.

Nevertheless, some of the aforementioned limitations could be addressed through the pre-heating of raw BB bamboo species to produce biomass with high energy yield and homogenized structure. During the thermal pre-treatment of the raw BB, the three main functional groups, i.e. hemicellulose, cellulose, and lignin of the bamboo undergo structural modification. The modification experienced by these functional groups depends on the extent of the thermal treatment temperature to which the bamboo is subjected. Previous investigation conducted by Rousset et al. [9] and Bada et al. [10] on different species of bamboo using FTIR supported the fact that changes or modification occurred in the chemical structure of a raw bamboo after being subjected to a thermal treatment. In these investigations torrefaction and low temperature carbonization was utilized in converting the raw biomass into a carbon-rich solid (biochar). Torrefaction is a thermal process conducted within 200–300 °C in an inert environment to facilitate the homogenization of biomass through the decomposition of hemicellulose or lignocellulosic constituents of biomass. The carbon rich products produced are seen with an improved physical and chemical characteristic, in terms of higher calorific value, easy to grind, and non-polar unsaturated products [11,12]. With low temperature carbonization, the process is more severe and conducted at a temperature above 300 °C in an inert atmosphere. The biochars produced in this investigation above 300 °C were similar in fuel characteristics to the low rank bituminous coal used in this study. This makes the low-carbonized product to be more acceptable for co-firing compared to torrefied and raw biomass.

An investigation conducted by Li et al. [13] has shown that torrefied products have significant reduction in NO emissions over coal as a result of their lower nitrogen content, and the ability to convert the nitrogen in the biomass to volatile NH₃ [14]. Another investigation also shows that the char produced from torrefied biomass have a higher specific surface area than that produced from the raw biomass, and Jones et al. [15] also showed that torrefied

willow has a longer flame during combustion compared to raw willow. Low temperature carbonization tests conducted by Park and Jang [16] between 400 and 500 °C on different biomasses shows an improved biomass with fuel characteristics moving toward that of coal-band. Pyrolysis test on wood chip and wood pellet under similar conditions by the same authors also shows an enhancement in the calorific value content of the two samples. Wood chip and wood pellet with calorific values of 14.90 and 18.60 MJ/kg were increased to 30.85 and 33.48 MJ/kg, respectively. These values are far higher than the calorific value (26.73) MJ/kg of the coal utilized by the authors.

The recent investigation conducted by Bada et al. [17] on the fuel characteristic and co-firing potential of raw *Bambusa multiplex* (BM) showed that the raw sample of this bamboo had a calorific value of 17.60 MJ/kg. A higher calorific value of 18.53 MJ/kg was achieved from *B. balcooa* (BB) used in this study. When exposed to torrefaction and low-temperature carbonization, *B. multiplex* was found to have lower calorific values compared to the *B. balcooa*, namely, 23 MJ/kg after torrefaction and 28 MJ/kg after low temperature carbonization. It has not been possible to compare the co-firing properties of both “*B. multiplex* and *B. balcooa*” with their relevant coals because, in the previously published paper on the co-firing potential of *B. multiplex*, a low ash coal was used; ash of 8.26% (dry basis (db)) and volatile matter of 45.08% (db) whereas a high ash coal was used in the current study, ash of 27.49% (db) and volatile matter 51.75% (db). As the two co-fired coals as well as the two bamboo species would all behave differently, it is currently not possible to make a direct comparison between the combustion characteristics of the co-fired coals and bamboos. Further work to establish standardized control samples for comparative purposes is currently being planned and results will be published in the near future.

Although, few facts are available in literature on the potential of bamboo as a substitute or co-fired fuel for energy generation, a recent investigation conducted by Kumar and Chandrashekar [18] in India on the combustion characteristics of five different species of bamboo has shown that bamboo can be used for energy generation. With *B. balcooa* occurring as a naturalized species of bamboo in South Africa, it was considered important to study the combustion and co-combustion behavior of that particular species whilst still appreciating that more than 1250 species within 75 genera are available worldwide. In this study, the impact of both torrefaction and low temperature carbonization on *B. balcooa* fuel characteristic were evaluated. In addition, the reaction kinetics of the BB, the combustion profiles obtained under air condition and constant heating rate were analyzed using differential thermogravimetric (DTG) technique. The apparent activation energies for all samples were obtained via Coats Redfern model.

2. Experimental

2.1. Sample selection and thermal preparation

A high ash coal of about 27.49% (dry basis) and *B. balcooa* bamboo samples, (referred to as raw BB) were utilized as co-fired fuel at different weight proportions. The coal sample was milled in a hammer mill and then pulverized down to –212 µm, with the representative fractions prepared for the combustion and co-combustion investigation. The bamboo culm was divided into five different sections representing raw BB, the torrefied BB (TBB at 250 °C and 280 °C) and low temperature carbonized BB (CBB at 350 °C and 380 °C) as shown in Table 1. The thermal treated products (TBB 250 °C and TBB 280 °C), and (CBB 350 °C and CBB 380 °C), along with the raw BB were milled using a Retsch PM 100 cutting mill to –212 µm size fraction.

Table 1
Temperature influence on the characteristic of *Bambusa balcooa*.

	Samples					
	Raw BB	TBB 250 °C	TBB 280 °C	CBB 350 °C	CBB 380 °C	Coal
R_m (%/min/°C)	6.83	6.60	4.61	5.51	5.68	4.17
η_M (%)	–	70.51	56.10	35.61	29.88	–
η_E (%)	–	73.30	72.72	52.67	46.01	–
CV (MJ/kg)	18.53	19.26	24.02	27.41	28.16	19.44

CV: calorific values; R_m : fuel reactivity; η_M : mass yield and η_E : energy yield.

The thermal treatment processes conducted on the raw BB utilized in this investigation were known as torrefaction and low temperature carbonization. Torrefaction is a slight pyrolysis process carried out within the range of 200–300 °C under an inert environment, with the aim to produce a densified and carbon rich solid with improved grindability. The raw BB was torrefied at 250 °C and 280 °C based on the fact that torrefaction of biomass below 250 °C will produce products with poor grindability. The raw BB was also subjected to further treatment at 350 °C and 380 °C using low temperature carbonization process. The process was conducted at a higher temperature compared to torrefaction, and in an oxygen free environment. The thermal processes were carried out in a gas tight muffle furnace at a constant heating rate of 4 °C/min under argon and held for 1 h. The bamboo samples were covered with a container after removing them from the furnace to prevent oxidation, and milled to –212 µm size fraction. Several blends of coal and bamboo were then prepared from raw BB, torrefied BB (TBB 250 °C and TBB 280 °C) and low-carbonized BB (CBB 350 °C and CBB 380 °C), and adding at 10%, 30%, 50% and 75% of coal by weight for the investigation.

2.2. Analytical methods

Ultimate and sulfur analyses of all samples were performed according to ASTM D 5373-02 and ASTM D 4239-05 for CHN and sulfur content, respectively using LECO CHN 628 with add on 628 S module. The proximate analyses for all samples were conducted in accordance with the ASTM D-5142, with approximately 1 g used in determining the inherent moisture, ash content and volatile matter present. The fixed carbon for the samples is expressed as the 100% – (ash content + volatile matter + moisture content). The calorific value known as the measure of the heat content was determined for both coal and bamboos using a Leco AC 500 calorimeter in accordance with ASTM D5865-04. The system uses an electronic thermometer with an accuracy of 0.0001 °C to measure the temperature every 6 s, with the results obtained within 4.5–7.5 min. The particle size of the samples was measured using a laser based particle size analyzer, namely a Mastersizer (2000) of Malvern Instruments Ltd.

2.3. Differential thermogravimetric (DTG) analysis, energy and mass yield

The thermogravimetric analysis (TG) was conducted in a TGA 701 Leco, under air at volume flow of 3.5 l min^{–1} with approximately 80 mg of fuel used for each experiment. The operating procedure involved heating all samples at a constant heating rate of 10 °C/min, from 25 °C to 750 °C and held until there is constancy in weight loss. These step parameters and conditions were applied to coal, raw BB, all thermally treated samples and bamboo/coal blends from different torrefaction and carbonization temperatures. The combustion characteristics of the raw fuels and blends are determined from the DTG curves generated. The influence of thermal treatment on the mass and energy yield of the BB bamboo after torrefaction and low-carbonization at different temperatures

were evaluated using the mass yield and energy yield formula as stated in Eqs. (1) and (2) below. In addition, the calorific values of all samples were determined three times to ascertain the repeatability of the equipment. The mean values were used as the reported calorific values.

The mass yield (η_M) and energy yield (η_E) of the thermally treated bamboo were calculated using the equations reported by Park et al. [12], and Park and Jang [16]. The mass yield η_M is obtained from the ratio of sample's mass left after torrefaction and carbonization (M_t), and sample's mass before torrefaction and carbonization (M_0) using Eq. (1) below:

$$\eta_M = \left[\frac{M_t}{M_0} \right] \text{ dry basis} \quad (1)$$

The gross calorific value for untreated or raw bamboo is GCV_u and GCV_t is the gross calorific value of torrefied or low-carbonized bamboo, and η_E is the energy yield obtained at different temperatures as stated below:

$$\eta_E = \eta_M \left(\frac{GCV_t}{GCV_u} \right) \text{ dry basis} \quad (2)$$

The weight loss per temperature or an average of the fuel reactivity was determined from the expression provided below:

$$R_m = 100 \times DTG_{\max} PT^{-1} \quad (3)$$

where R_m is the fuel reactivity (%/min/°C), DTG_{\max} is the weight loss rate (%/min), and PT is the peak temperature °C.

2.4. Kinetic analysis

The combustion and co-combustion of biomass is a complex multiple step reaction, which makes it difficult to determine the overall reaction mechanism and formulate the reaction kinetics [19]. The kinetic approach used in this investigation to determine the kinetic parameters controlling the combustion and co-combustion of bamboo biomass and coal was based on the Arrhenius equation. Coats–Redfern model has been used by many researchers to determine the kinetic and mechanism of thermal decomposition of biomass and co-combustion with coal under an oxidative environment [20,21]. This model is based on the premises that during two stage reaction kinetics of a thermal decomposition of biomass in an oxidative environment (DTG curves), two independent reactions occur. Thus, these two separate reactions are known to be governed by the first-order Arrhenius law, and the following equations stated below were used in deriving their reaction kinetics:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (4)$$

$$k = A \exp(-E/RT) \quad (5)$$

$$\alpha = \left(\frac{W_0 - W_t}{W_0 - W_f} \right) \quad (6)$$

where W_0 represent the initial mass of the sample, W_t is the mass of the sample at time t , and W_f is the final mass of the sample. Since the model is based on a constant heating rate β (°C min^{–1}) during combustion of the raw fuels and blended fuels. Then ($\beta = \frac{dT}{dt}$), is substituted into Arrhenius (Eq. (4)) and then integrated to obtain Coats–Redfern model below;

$$\frac{d\alpha}{f(\alpha)} = \left(\frac{k}{\beta} \right) dT \quad (7)$$

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (8)$$

Based on the assumption that for most values of E and for the range of combustion temperature obtained, the expression $\ln \left[\frac{AR}{E} \left(1 - \frac{2RT}{E} \right) \right]$ in Eq. (8) above is fundamentally constant [22]. Therefore, a plot of $\ln \left[\frac{g(\alpha)}{T^2} \right]$ versus $\frac{1}{T}$ is expected to provide a straight line with a high correlation coefficient. The activation energy E (kJ mol⁻¹) can be calculated from the slope of the line $\frac{E}{R}$, while the pre-exponential factor A (S⁻¹) also be determined from the temperature at which $W_t = \left(\frac{W_0 + W_f}{2} \right)$.

The W_0 represent the initial mass of the sample, W_t is the mass of the sample at time t , and W_f is the final mass of the sample. The function $g(\alpha)$ or $f(\alpha)$ that give a straight line with the highest correlation coefficient will be considered from the function of the model that best represents the kinetics of mass loss for each separate reaction and describe the mechanism controlling the combustion reactions of raw fuels and blended fuels.

The following functions of $g(\alpha)$ listed below are used in determining the actual reaction mechanism controlling the thermal oxidation of all samples used in this investigation:

$$-\ln(1-\alpha), (1-\alpha)^{-1}, (1-\alpha)^{-2}, 1-(1-\alpha)^{\frac{1}{2}}, 1-(1-\alpha)^{\frac{1}{3}}, (\alpha)^2, (1-\alpha)\ln(1-\alpha) + \alpha, [1-(1-\alpha)^{1/3}]^2$$

3. Result and discussion

3.1. Energy characteristic of raw and thermally treated Bamboo

The effect of torrefaction and low temperature carbonization on the weight loss of raw BB is depicted in the degradation profile plotted in Fig. 1. The initial heating and drying of all samples started at the same time and ends under 40 min, but the torrefied sample (250 °C) reached the torrefaction stage before the other three samples. The loss in sample's weight seen as the temperature increases from 25 °C could be attributed to the loss of moisture, depolymerization of the functional group of the *B. balcooa* and the release of chemical energy in the form of gases, water and solid residue. Thus, the solid residue left is known as bio-char, and with the torrefied sample (250 °C) possessing the lowest weight loss <30% and highest mass yield of 70.51%. Increasing torrefaction temperature to 280 °C further lead to additional removal in the hemicellulose content of the raw BB with a significant decreased in weight loss and mass yield. The lowest mass yield solid product of 29.88% was obtained at a low carbonization temperature of 380 °C. The higher mass lost attained between the thermal temperature of 350 °C and 380 °C could be as a result of the devolatilization of compounds associated with high oxygen content, cellulose

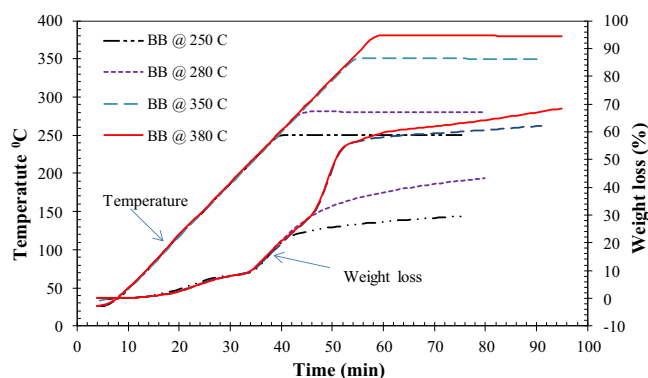


Fig. 1. Degradation profile of raw BB and mass loss (%) during different thermal temperatures.

and fractions of lignin. Table 1 shows a tremendous decrease in the oxygen content of the raw BB as the temperature increases with an improved fuel quality. Also, the highest mass decomposition (wt.%) seen within this thermal temperature range was in agreement with thermal treatment on Switchgrass conducted by Sadaka et al. [23].

The energy and mass yield attained according to Table 1 depicted an energy yield greater than the mass yield for all samples. The difference in the energy yield and mass yield seen in Table 1 as the thermal treatment temperature increases, was as a result of the decrease in volatile matters, increased element of carbon and increased energy content from TBB 250 °C to CBB 380 °C. It was observed for all torrefied and carbonized products, energy yield was found to be greater than mass yield and more pronounced as pre-treatment temperature equal and above 280 °C. The calorific value for the raw BB used was increased as the thermal treatment temperature increases, and this was found to be parallel to the drop in oxygen content seen in Table 2. An investigation conducted by Rousset et al. [9] on torrefied bamboo at 280 °C shows an increase in calorific value from 18.21 MJ/kg to 23.1 MJ/kg. This was similar to the calorific value of 24.02 MJ/kg obtained after raw BB was torrefied at 280 °C. Under a low carbonization temperature of 375 °C, Park et al. [12] obtained a product with higher calorific value, fixed carbon, and lower volatile matter compared to torrefied products. At a low temperature carbonization of 380 °C, a carbon rich bamboo BB product of 28.16 MJ/kg was obtained and far higher than 19.44 MJ/kg from the coal utilized.

The reactivities of the raw BB and all the thermally treated samples, along with the high ash bituminous coal are all depicted in Table 1. Raw BB has the highest fuel reactivity and is expected to ignite at the lowest temperature compared to torrefied and carbonized bamboos due to its large amount of volatile matter. In conclusion, the high volatile matter of bamboo may aid in its co-firing with coal by increasing the combustion efficiency through faster ignition temperature at the lowest temperature.

3.2. Physico-chemical properties of the coal and bamboo samples

Table 2 shows the results obtained from the proximate analysis conducted on the raw BB, TBB 250 °C & TBB 280 °C, and CBB 350 °C & CBB 380 °C bamboos. Under thermal treatment of raw BB bamboo from 250 °C to 380 °C, an increase in ash content (dry) from 0.49% to 3.63% was observed in Table 2. Compared with other non-woody and woody biomasses such as Bermuda grasses and corn straws, oil palm and polar wood [24–26], the ash content for the raw BB was found to be much lower. The increase noted in ash content as the thermal temperature increases could be as a result of the formation of inorganic carbonates and oxides, known as ash, from the minerals within the biomass. The co-firing of coal with the thermally treated BB at an appropriate ratio might reduce the fouling propensity of this biomass due to its coal like characteristic. The increase in the thermal temperature also caused a decline in the moisture content, which ranged from 4.55% to 7.33%, with the raw BB possessing the highest moisture content. The volatile matter in the raw BB sample decreases from 93.50% to 58.17% after being carbonized at 380 °C, with a parallel relationship found existing between the volatile matter content in the raw BB and the products treated from 250 °C to 380 °C. This reduction in the volatile matter observed could be attributed to the thermal decomposition of the organic functional components of the bamboo.

Chemical changes took place in the structure of the bamboo as the thermal decomposition of the raw BB occurs at higher treatment temperatures. There was an increase in the fixed carbon content of the raw BB from 6.01% to 38.20% (CBB 380 °C) as the thermal temperature intensified. The decomposition of the

Table 2

Physicochemical properties of raw BB, thermally treated BB and coal.

		Samples					
		Raw BB	TBB 250 °C	TBB 280 °C	CBB 350 °C	CBB 380 °C	Coal
Proximate analysis (wt.%, db)	Ash	0.49	1.40	3.15	3.02	3.63	27.49
	FC	6.01	5.76	27.02	36.34	38.20	20.76
	VM	93.50	92.84	69.83	60.64	58.17	51.75
	M	7.33	5.21	4.55	5.67	5.99	6.49
Ultimate analysis (wt.%, db)	C	46.50	49.96	62.33	72.31	71.30	52.70
	H	6.43	6.34	5.59	4.81	4.44	3.53
	O	46.90	43.22	31.81	22.44	23.70	42.43
	N	0.22	0.49	0.27	0.44	0.56	1.36
	S	UT	UT	UT	0.015	UT	0.71

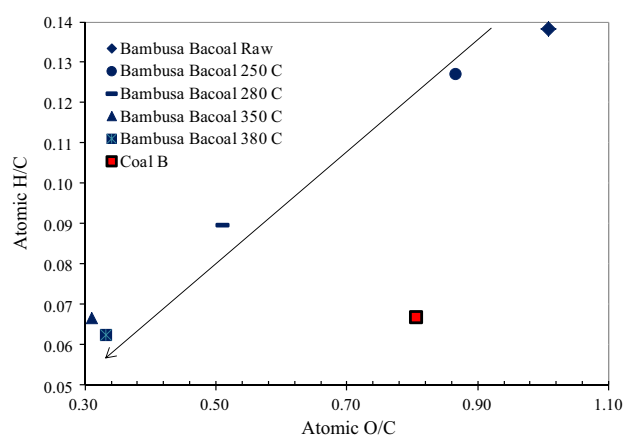
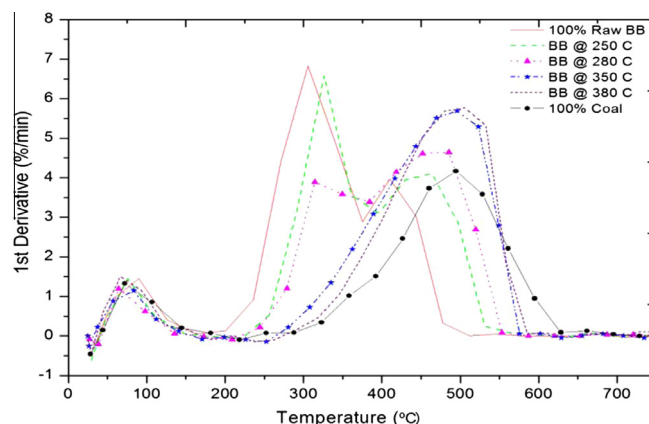
db: on dry basis; VM: volatile matter; FC: fixed carbon; M: moisture; fuel reactivity and UT: untraceable.

hydroxyl group along with the hemicellulose of the bamboo might be responsible for the increase noted. The TBB 280 °C, CBB 350 °C and CBB 380 °C products are noted to have higher fixed carbon than the high ash coal utilized in this study. With the coal like characteristic of these thermally treated bamboos, these products are likely to be a suitable co-fired fuel. As seen from Table 2 below, the elemental concentration of nitrogen and carbon increased as the thermal temperature increases, while the elemental oxygen and the hydrogen content of the raw BB also declined from 250 °C to 380 °C. In addition, raw BB also shows an upgrade in its carbon content from 46.50% to 62.33% after torrefaction at 280 °C. The carbon value obtained was higher compared to the carbon from the high ash coal used in this study and other woody biomass torrefied between 280 °C and 300 °C, and held for 1 h [27–30]. It was also observed that the percentage sulfur in the thermally treated BB is untraceable and nitrogen content increases are minimal as the pre-treatment temperature increases. The firing of this biomass is expected to generate low NO_x emission compared to coal with nitrogen content of 1.36%.

Fig. 2 below depicts the Van Krevelen diagram, which shows a clear correlation between the ratio of the atomic O/C and H/C content of the raw BB, thermally treated BB and coal. This provides insight into their energy density and changes in their elemental composition. As the thermal treatment temperature increases from 250 °C to 280 °C for the torrefied samples, the energy density of the *B. balcooa* followed a pathway similar to that of carbonized samples. Further increase in low carbonization temperature to 350 °C and 380 °C for *B. balcooa* produces products with the lowest H/C and O/C ratios, and higher energy density than coal. This was as a result of intense devolatilization and decarboxylation of the bamboo samples. The coal could be seen with a high ratio of O/C compared to the low temperature carbonized products, and the obtained are supported by the ultimate analysis results presented in Table 2. In summary, the results show a clear trend, namely, increasing temperatures leads to an increase energy density as indicated by the direction of the arrow in Fig. 2.

3.3. Combustion profile of coal, raw and thermal treated *B. balcooa* samples

The DTG curves obtained from the thermal analysis of high ash bituminous coal, raw BB and thermally treated BB bamboo are depicted in Fig. 3 below. The thermograph provided information on the reactivities and firing potential of the individual solid fuel, and also shows the different decomposition stages and a breakdown in the structures of individual fuels as the applied thermal temperature increases. The DTG profiles for the raw BB and torrefied samples (TBB 250 °C and TBB 280 °C) are very similar. Two DTG peaks were observed in these samples, with the highest rate of devolatilization of the volatile matter (hemicellulose and partial

**Fig. 2.** Van Krevelen profiles of high ash coal, raw BB and thermally treated BB samples.**Fig. 3.** DTG curves for the decomposition of raw BB, TBB and CBB bamboo samples.

cellulose) occurring between 150 and 400 °C. This was similar to results obtained by Park and Jang [16], Gil et al. [21] and Varol et al. [31] on different biomasses where two peaks were observed after moisture peak. It can be seen that the raw BB degrades first out of all the fuels utilized and achieved the highest fuel reactivity of 6.83%/min/°C as seen in Table 1, and ignite at the lowest temperature as seen in Table 3. The low temperature carbonized samples (CBB 350 °C and CBB 380 °C) are seen with single DTG peak. The increase in carbon content and intense devolatilization during thermal treatment is responsible for the coal like nature of the low carbonized BB (350 °C and 380 °C), and their single peak burning characteristic. The peaks observed in both samples were seen

Table 3

Ignition, peak and burnout temperature for coal, raw BB and thermal-treated BB.

Sample	IT (VM) (°C)	IT (FC) (°C)	Peak temp. (°C)		Weight loss (%)		Final weight loss (%)
			1st Peak	2nd Peak	1st Peak	2nd Peak	
Raw BB	162.93	236.26	305.61	410.03	48.33	49.97	98.30
TBB 250 °C	221.80	256.22	326.60	463.84	38.80	59.52	97.52
TBB 280 °C	244.56	278.94	314.66	485.60	21.62	75.91	97.53
CBB 350 °C	252.62	335.10	–	496.00	–	76.60	97.50
CBB 380 °C	291.02	345.37	–	506.01	–	77.10	95.60
100% Coal	322.00	392.38	–	494.40	–	49.60	72.33

IT: initiation temperature; IT (VM): ignition volatiles; IT (FC): ignition of FC.

with higher DTG_{max} compared to coal, this represents higher char combustion, basically the remaining cellulose and lignin content of the bamboo.

The decrease in the fuel peak height and weight loss seen in Fig. 3 and Table 3 as the bamboo thermal treatment temperature increases was as a result of changes in the fuel volatile matter and fixed carbon content. This also has an influence on the sample's ignition temperature. In summary, both raw and thermal treated samples are found to be more reactive and ignite at much lower temperatures than the bituminous high ash coal used.

3.4. Thermal decomposition for blends of raw BB and coal at different wt.% ratios

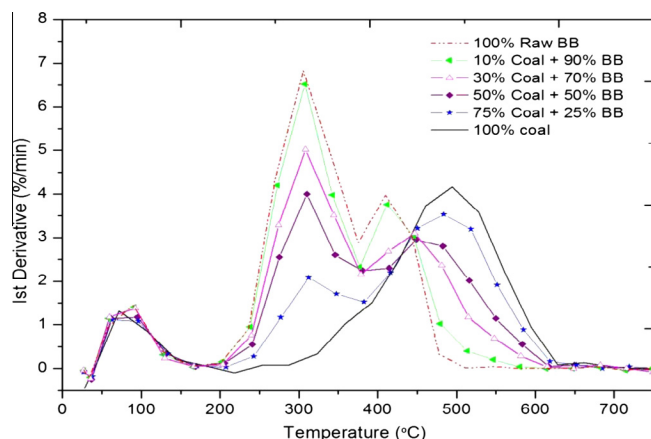
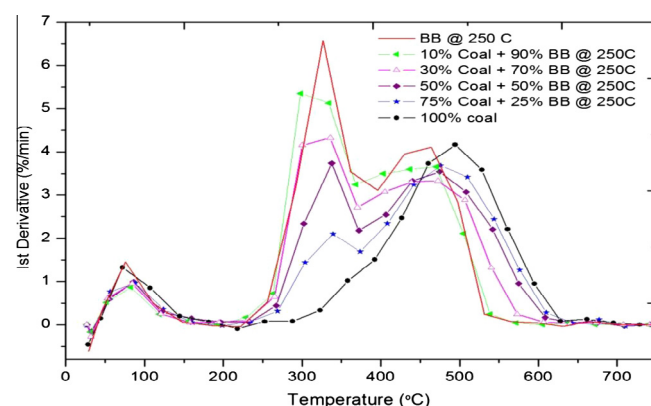
The thermographs in Fig. 4 below depict the DTG combustion profiles of raw BB, and coal blends at different weight ratio. The burning profiles providing insight into the combustion characteristic of replacing raw BB with coal at different weight%. It can be seen that an initial weight loss occurred between the temperature of 25 °C and 107 °C for all samples, due to moisture evaporation, and this stage was denoted as stage 1. The DTG curves for the raw BB and BB/coal blends were seen to separate into two reaction stages after the moisture removal as a result of the modification made to the bamboo through thermal treatment, compared to that of coal. Two different peaks were seen in all biomass samples compared to only one peak obtained from coal. The peaks seen within the temperature range of 163 °C to 484 °C for the curves of raw BB and BB/coal blends were due to the ignition and total decomposition of the hemicellulose, and fraction decomposition of the cellulose and lignin of the bamboo, respectively. This step weight loss was denoted as stage 2, and is in agreement with the findings from [32,33]. The release of the volatile matter from the high ash coal used in this investigation occurs under this stage (stage 2), due to its high reactivity. The raw BB has the highest volatile matter

content of 93.50% (dry) and was seen with the highest peak at the lowest temperature of 305.61 °C compared to all samples. In addition, it also devolatilize at 162.9 °C compared to coal at higher temperature of 287.9 °C. As the percentage coal in the mix increases, the peak height decreases, and this corresponds to decrease in the combustion rate as seen in Fig. 3 below.

The coal utilized shows a single peak after combustion and burning of the char, and this reaction was denoted as stage 3. The decomposition of the lignin of the biomass occurs under this 3rd reaction stage, and was seen as the underlying peaks under the coal DTG curve. The 75% coal + 25% raw BB sample was seen with the highest underlying peaks after coal, indicating that the quantity of individual fuel within the blend does affect the combustion behavior and burnout temperature. In conclusion, it will be noted that the combustion efficiency of a low rank bituminous coal can be improved by blending biomass, and with the raw BB as the most efficient of the bamboo samples to ignite.

3.5. DTG profile for blends of torrefied BB and coal at different wt.% ratios

The experimental DTG curves for co-combustion attributes of the TBB 250 °C, 280 °C and their blends are shown in Figs. 5 and 6 below, respectively. The TBB 250 °C and 280 °C are seen ignited at the lowest temperatures with the highest combustion rate for the TBB 250 °C sample achieved under the 2nd reaction stage compared to other fuels. Hence, the coal was still seen exhibiting a burning profile with one peak totally different from the rest of the fuels utilized. As the coal percentage increases in the blends for TBB 250 °C and 280 °C fuels, the combustion rate reduces, and delay in ignition was more pronounced. The underlying peaks seen from the raw BB/coal blends (Fig. 4), under the coal DTG curve during the 3rd reaction stage was less pronounced in the case of TBB 250 °C and 280 °C fuels. The changes in the molecular structure of the bamboo samples after torrefaction, with an increase

**Fig. 4.** DTG curves for raw BB, coal and BB/coal at different wt.% ratios.**Fig. 5.** DTG curves for BB @ 250 °C, coal and BB/coal at different wt.% ratios.

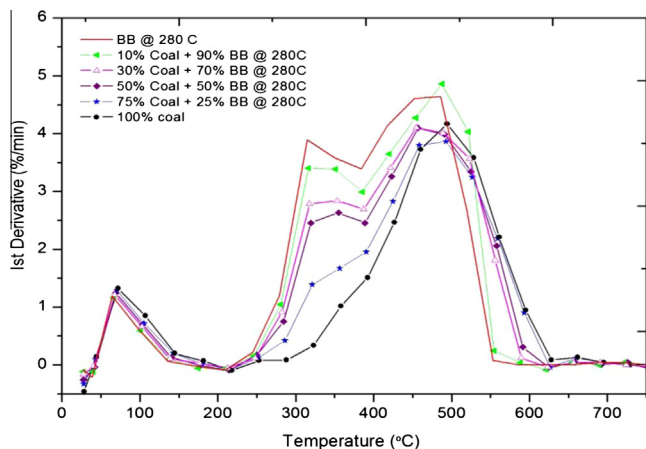


Fig. 6. DTG curves for BB @ 280 °C, coal and BB/coal at different wt.% ratios.

in fixed carbon from 5.76% to 27.02% for TBB 250 °C and 280 °C respectively, and a parallel reduction in the volatile matter content was responsible. That is, the thermal and chemical characteristic of the bamboo samples was improved on significantly after torrefication. The burning profiles of TBB 280 °C blends in Fig. 6 also show a similar burning profile to coal compared to TBB 250 °C blends in Fig. 5. The 75% coal + 25% TBB 280 °C sample was seen to have almost the same DTG profile and peak height with coal. This suggests that the blending of this bituminous high ash coal with a thermally treated BB at 280 °C or higher indicates close compatibility in the co-combustion attributes of the blend.

3.6. Effect of low-carbonization temperature and coal blending on co-combustion characteristic of bamboo and coal

The DTG curves for the low-temperature carbonized samples (CBM at 350 °C and CBM 380 °C), and their coal blends at different weight percentages are shown in Figs. 7 and 8, respectively. As can be seen from both figures, the combustion profiles of all samples show single DTG peaks, which are in contrast to the burning profiles of samples torrefied at 250 °C and 280 °C. The ignition temperature (T_{ig}) for the CBM 350 °C sample was at 335.10 °C, while that of CBM 380 °C and coal is at the temperature of 345.37 °C and 408.41 °C, respectively. Highest DTG_{max} or reactivity was observed for both the CBM 350 °C and CBM 380 °C samples. With an increase in weight percentage of coal mixed with the bamboo, the DTG_{max} for all blended products decreases and moves toward that of coal. At 10%, 30%, 50% and 75% weight percentage coal blended with CBM 350 °C and CBM 380 °C samples, the ignition and peak temperatures were found to be at the lower temperature zone

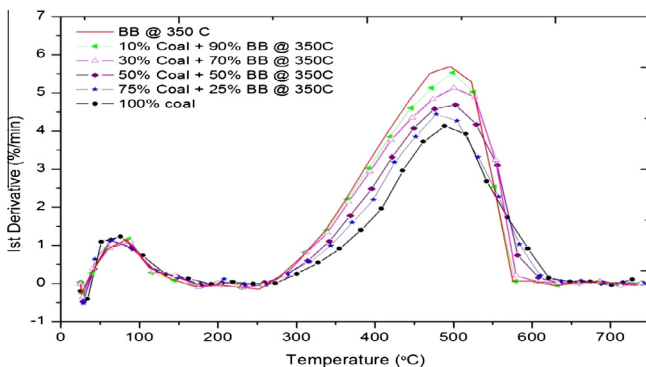


Fig. 7. DTG curves for BB @ 350 °C, coal and BB/coal at different wt.% ratios.

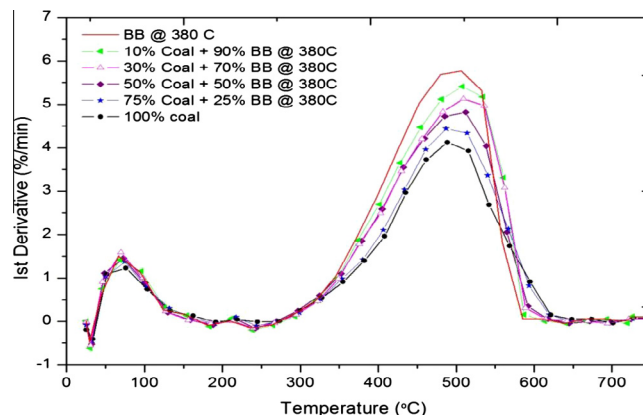


Fig. 8. DTG curves for BB @ 380 °C, coal and BB/coal at different wt.% ratios.

compared to that of coal. With increasing carbonization temperature from 350 °C to 380 °C, the variation in the peak temperature of the blends, seen as the percentage coal increases, reduces the volatile matter and increase the carbon content of the blend, respectively. This reflects the decreasing peak height seen in Fig. 8. It can also be assumed that the increase in thermal treatment temperature for CBM 380 °C promoted the delay in ignition seen in all samples. In conclusion, Figs. 7 and 8 illustrate that the CBB 350 °C, CBB 380 °C samples and all the fuel blends are more reactive than coal.

3.7. Evaluation of the kinetic parameters for all samples

The mechanism controlling the kinetic reaction of the combustion and co-combustion of coal, raw BB, thermally treated BB and their blends are determined using Coats–Redfern methods. The kinetic parameter for coal was determined under a single stage reaction, while other samples were determined by assuming a two stage reaction under a selected temperature range. Table 4 provided data obtained from the plot of $\ln \left[\frac{g(\alpha)}{T^2} \right]$ versus $\frac{1}{T}$ in the form of $g(\alpha)$ for each reaction stage. In addition, the values of the activation energy (E_a) and pre-exponential factor (A) depicted in Table 4 is based on the reaction model that suitably fitted the experimental profiles of the coal, raw BB, thermally treated BB samples, and their blends with the highest correlation factor (R^2).

The result of the DTG plot of 100% coal confirmed that the one way transport diffusion (D1) was the controlling solid-state mechanism for the second step of coal oxidation (stage 2), i.e. the micro-structural changes in this solid reaction take place through diffusion of gas molecules from the solid phase. This is in agreement with the finding from Yorulmaz and Atimtay [34] on the influence of gas diffusion through a solid phase. The 3rd order chemical reaction mechanism (O3) was found to be responsible for the third step of coal and char combustion (stage 3). The raw BB was seen controlled by the phase boundary reaction mechanism (R2) under stage 2; whereas the first order chemical reaction (O1) was found responsible for the combustion of raw BB at stage 3. The general observation drawn from Table 3 are that the kinetic models (R2, R3, D1 and D2) are the controlling models for all samples under stage 2, while chemical reaction models (O1, O2 and O3) control the combustion of all samples at stage 3. The high ash bituminous coal utilized in this study was seen under stage 2 with an activation energy value (E_a) of 64.12 kJ/mol, which was higher than 31.60 kJ/mol obtained from the raw BB. This means coal would require higher temperature and longer reaction time to oxidize compared to raw BB. The activation energy obtained from the combustion of this coal, was similar to the values reported by Cheng-lin

Table 4

Thermal kinetic for coal B, raw BB and their respective blends at different wt.%.

Sample	Stage 2					Stage 3				
	Temp. range (°C)	M	R ²	E _a (kJ/mol)	A (min) ⁻¹	Temp. range (°C)	M	R ²	E _a (kJ/mol)	A (min) ⁻¹
100% coal	288–494	D1	0.9618	64.12	1.46E–02	494–696	O3	0.9915	11.02	8.06E+01
Raw BB	163–410	R2	0.9408	31.60	1.70E+02	410–512	O1	0.8959	11.24	1.13E+02
10C + 90BB	202–412	R2	0.9747	35.47	3.48E+02	412–614	O1	0.9868	8.31	6.43E+01
30C + 70BB	204–447	R2	0.9741	31.50	1.28E+02	447–649	O1	0.9753	8.13	5.81E+01
50C + 50BB	205–449	R2	0.9725	35.10	1.95E+02	449–617	O1	0.9796	8.55	5.97E+01
75C + 25BB	207–484	R2	0.9824	26.80	3.03E+01	484–619	O1	0.988	10.60	7.76E+01
BB250 °C	222–464	R2	0.9692	43.75	1.00E+03	464–599	O1	0.9297	9.70	7.71E+01
10C + 90BB	229–471	D3	0.9823	9.51	4.34E+00	471–605	O1	0.8987	9.71	7.80E+01
30C + 70BB	231–473	D3	0.9811	8.52	3.55E+00	473–640	O1	0.9731	9.89	7.50E+01
50C + 50BB	233–474	R2	0.9838	35.68	1.65E+02	474–642	O1	0.9828	10.00	7.28E+01
75C + 25BB	235–476	R2	0.9862	32.76	7.79E+01	476–643	O1	0.9812	10.32	7.46E+01
BB280 °C	245–486	R2	0.9877	44.70	8.97E+02	486–587	O1	0.800	12.50	1.19E+02
10C + 90BB	246–488	R2	0.988	44.12	7.13E+02	488–588	O2	–	–	–
30C + 70BB	248–455	R2	0.9922	41.55	4.18E+02	455–623	O1	0.9254	11.31	9.11E+01
50C + 50BB	250–457	R2	0.993	41.18	3.63E+02	457–625	O1	0.9231	12.11	1.02E+02
75C + 25BB	286–493	R2	0.9783	32.31	4.97E+01	493–626	O1	0.9332	11.73	9.14E+01
BB350 °C	253–496	D1	0.9689	67.33	3.33E–02	496–629	O1	0.8261	12.66	1.11E+02
10C + 90BB	256–499	D1	0.9711	64.77	2.22E–02	499–632	O1	0.8239	15.33	1.67E+02
30C + 70BB	285–501	D2	0.9949	72.89	8.42E–02	501–713	O1	0.8281	10.71	8.22E+01
50C + 50BB	287–503	D1	0.9861	67.33	3.03E–02	503–715	O1	0.8648	8.62	5.87E+01
75C + 25BB	289–478	D1	0.9753	62.96	1.43E–02	478–716	O1	0.9348	7.44	4.82E+01
BB380 °C	291–506	D1	0.9744	71.71	6.11E–02	506–639	O1	0.8231	11.45	9.11E+01
10C + 90BB	293–508	D1	0.977	70.47	4.43E–02	508–640				
30C + 70BB	297–512	D1	0.9825	67.43	2.95E–02	512–645	O1	0.8885	10.80	8.00E+01
50C + 50BB	295–510	D1	0.9763	67.41	2.63E–02	510–642	O1	0.9197	13.70	1.23E+02
75C + 25BB	299–487	D1	0.9668	60.07	8.55E–03	487–699	O1	0.9261	10.85	6.63E+01

C: coal; BB: *Bambusa balcooa*; E_a: activation energy; A: pre-exponential factor; R²: correlation coefficient; M: optimum kinetic mechanism; 10, 25, 30, 50, 75 and 90 are in %.

et al. [35] ranging between 53.30–81.81 kJ/mol after fitting the TG curves using the Coats Redfern model. This coal also shows similar activation energy to 30.73–37.83 kJ/mol, 65 ± 27 kJ/mol and 67 kJ/mol obtained by Tahmasebi et al. [1], Idris et al. [25] and Otero et al. [36], respectively. The low activation energy value obtained from this coal could be as a result of its high volatile matter and reactivity.

Activation energies in the range of 11.02–31.60 kJ/mol obtained for the raw BB was similar to 9.04–30.95 kJ/mol reported by Sait et al. [37] on the combustion of date palm biomass in air. The activation energy for the torrefied BB samples at 250 °C and 280 °C, was in the range of 43.75–44.70 kJ/mol under stage 2, and with a difference of about +13 kJ/mol from that of the raw BB. The low carbonization samples (CBB 350 °C and CBB 380 °C) were seen with increased activation energy in the range of 67.33–71.71 kJ/mol in the 2nd stage, which was higher than the activation energy for coal. For all samples under stage 3, the activation energies achieved were seen smaller compared to activation energy in stage 2, because more energy is required in the devolatilization stage compared to char combustion stage. In regard to the mixed samples, it was found that the blends with 75% coal were seen with a lower activation energy compared to all the main fuels (raw BB and thermally treated BB). In addition, the raw BB and torrefied BB at 250 °C and 280 °C were seen with similar activation energy with fuel blends with 75% coal under 2nd stage, this shows that the presence of coal do not have any significant impact on combustion at this stage. The higher activation energy values achieved for the low carbonized samples at 350 °C and 380 °C, along with their blends compared to the E_a for the high ash coal, could be as a result of the modification made to the structure of these samples during thermal treatment, with reduced oxygen and increased carbon content. Therefore, as the coal within the blends increases, the activation energy reduces as more oxygen is being added to these blends. In this study, most of the kinetic values obtained are found to be different to those reported in some literatures. In addition, a different activation energy range of 134.03–242.33 kJ/mol and 43.61–66.7 kJ/mol had also been reported for same biomass specie

by Chen et al. [38], and Agrawal and Chakraborty [39], respectively. This disagreement could be as a result of various operating conditions (sample weight, heating rate, gas flow rate and atmosphere) set out for different investigations. With higher activation energy which are seen in stage 2 and clearly similar in most samples and their blends, compared to stage 3, it could be concluded that more energy is required in the de-volatilization stage than the char combustion stage using these samples.

4. Conclusions

The chemical analyses and DTG test curves provide detailed combustion and co-combustion characteristics of the raw, torrefied and low carbonized bamboo samples and the coal used in this research with both individual blends. The following conclusions have been drawn from that data:

1. It was observed that the combustion conversion of the raw, torrefied and low temperature carbonized BB were in the range of 95.60–98.30% compared to 72.33% obtained from coal at burnout. With an increase in pre-treatment temperature, the torrefied BB achieved a higher energy yield and higher reactivity compared to low temperature carbonized BB samples, but the low carbonized samples appear to provide higher calorific values.
2. The low temperature carbonized samples (CBB 350 and CBB 380 °C) were seen to have better fuel characteristics relative to coal in the Van Krevelen diagram, i.e. higher carbon in the C/H versus C/O ratios. The raw BB was found to be the most reactive, igniting and burning out at the lowest temperature compared to all other fuels tested.
3. The DTG curve for all the individual raw fuels (raw BB, TBB 250 and 280 °C and CBB 350 and 380 °C) indicated that distinct stages occur during the combustion of these samples with the removal of water noted as stage 1. Further peak steps indicated the decomposition of hemicellulose, cellulose and lignin were observed in the torrefied bamboo samples, but with both low

carbonized samples and coal showed only one peak. The mass loss rate (%/min) of the raw BB was found to be higher than the torrefied and carbonized bamboo samples.

4. The DTG curve showed that as the coal percentage content in the blends increased for both TBB 250 and 280 °C samples the peak indicating the decomposition of the hemicellulose gradually disappeared. The 75% coal + 25% CBB 380 °C sample was seen to have the closest burning profile to coal.
5. The E_a values of the raw BB samples were in the range of 11.24–31.60 kJ/mol while the E_a for the torrefied (TBB) and carbonized (CBB) samples increased as the thermal treatment temperature increased. Higher activation energy values were also noted for the carbonized bamboo samples at 350 °C and 380 °C (and with their blends with coal) compared to the E_a for the coal sample used.

Acknowledgements

The authors gratefully acknowledge with thanks, the financial support of the NRF SARChI Clean Coal Technology and the University of the Witwatersrand. Thanks to the Hortus Capensis (Pty) Ltd., Western Cape for providing the bamboos utilized and the Mineral Processing Department, Mintek for granting permission and access to some of their research facilities.

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