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Investigation on the interactions among lignocellulosic constituents and minerals of biomass and their influences on co-firing

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Abstract

The influences of biomass constituents, such as lignocellulosic components and minerals, on the combustion of coal/biomass blends are of significant importance in co-firing due to its potential impacts on ignition, flame stability and burnout. In this research, combustion characteristics of pure lignocellulosic elements, Rosewood, Mengxi coal and their blends were studied in detail. The effect of minerals in Rosewood on combustion of biomass/Mengxi coal blends was investigated which revealed reductions in the ignition (≤ 20 °C), peak (≤ 12 °C) and burnout temperatures (≤ 6 °C). The results also demonstrate the existence of interactions between lignocellulosic constituents in the model biomass, which is dominated by the interactions of cellulose-derived products with xylan and lignin respectively which led to ~8% reduction in char oxidation temperature. The minerals in biomass showed different impacts at different stages of the combustion process, such as inhibition effect during the devolatilization stage, and promotive synergy (mainly due to calcium) on ignition and char oxidation.

Keywords: Co-firing; thermogravimetric analysis; biomass; lignocellulosic; catalytic effect

List of Abbreviations 1

1

AAEMs	Alkali & Alkaline earth metals
ADF	Acid detergent fiber

1. Introduction

Biomass is a promising alternative for reducing fossil fuel consumption globally. This is mainly attributed to its renewability a potential to meet a significant portion of global primary energy demand in diverse forms, i.e. a solid, liquid or gaseous fuel [1]. Co-firing of biomass with coal for electricity generation has been widely adopted in western countries for the large scale utilization of biomass as an energy source [2]. This has proved to be an economical and efficient approach for mitigating greenhouse gas emissions [3]. The co-utilization of biomass and coal has therefore increased rapidly worldwide in the past two decades. Currently, there are at least 150 coal-fired power stations that are burning biomass or other carbonaceous wastes with coal to generate heat and/or power [2].

To date, numerous studies have been conducted to understand the co-combustion of biomass/coal blends [1, 3-7]. The need for this is due to the differences in combustion behaviour of biomass samples in comparison to those of coal and the interactions between the samples during thermal reactions. Synergistic effects have been observed from these fuel blends resulting in promotive changes in fuel reactivity and product distribution [8-11], reaction rate and higher volatile yields [12], characteristic temperatures, maximum reaction rates and kinetic parameters [5, 13-15], etc. Contrary to these, other studies have reported contradictory findings of either negligible interactions or inhibitive consequences during co-

ADL	Acid detergent lignin
DTG	Differential thermogravimetric
LTA	Low temperature ash
MC	Mengxi coal
mRW	Model Rosewood
NDF	Neutral detergent fibre
RW	Rosewood
TGA	Thermogravimetric analyzer

firing of such fuels [14-16]. Thus, an exploratory study on how the addition of biomass influences the combustion characteristics of biomass/coal blends is of significant importance due to its influence on the safety of boiler operations.

Consequently, some researchers have adopted different strategies to isolate the different modes of synergy, for instance, the impacts of organic and inorganic components of biomass on combustion can be evaluated by demineralization and the impregnation of samples with alkali metal salts or the addition of high-temperature ash respectively. Improvements in reactivity, combustibility and burnout of the coal particles and fuel blends observed in their experimental results were linked to the non-catalytic and/or catalytic synergy between coal and biomass [17-21]. It was established from these studies that the high content of alkali metals in biomass had a catalytic effect on the decomposition of coal upon heating [22]. However, the extent of this influence remained quite vague as the preparation of the biomass ash sample used in these studies were conducted at a temperature above 500°C [23-25]. The volatility and thermal behaviour of alkali metals are highly temperature-dependent as some portion of alkali metals in biomass have been observed to be released at temperatures as low as 180 °C [26, 27]. This is more significant for sodium, the release of which is around 10% during the torrefaction process at 200-300°C[28]. Therefore, the use of biomass ash prepared at temperatures above 500 °C would result in the loss of some alkali metals, such as Na and K, which might assist in the catalysis of the thermal breakdown of biomass and coal. To fully understand the interactions between biomass and coal during co-processing, it is necessary to reveal how minerals in biomass promote combustion at lower temperatures by using low-temperature ash, as well as to show the interactions among lignocellulosic components in biomass and their interactions with coal.

This study is intended to add to knowledge in the field of coal and biomass blending as a tool

for low-rank coal upgrading by utilisation of the low-grade Mengxi coal. A simple approach was adopted to understand the influence of biomass organic contents and ash on co-firing. Lignocellulosic constituents, such as lignin, hemicellulose and cellulose, were studied to understand their interactions and the influence of organic constituents on co-firing. In addition, model Rosewood was prepared using these pure lignocellulosic components [29] to show the organic constituents' interactions during the combustion of biomass. Furthermore, low-temperature ash was used to investigate the influence of biomass minerals on co-combustion. Lastly, the differences between high-temperature and low-temperature ash samples of biomass and how they affect the behaviour of the fuel blends were also investigated.

2. Experimental

2.1 Materials

Mengxi coal (MC) and Rosewood (RW) were used as the coal and biomass in this research. Standard procedures were followed in the preparation of samples [30], which involved the division of sample into rations of uniform mass and representative fractions. Individual samples were milled to a size smaller than 212 μm after being air-dried for 24 h.

Alkali lignin (Sigma, CAS 8068-05-1), hemicellulose (Sigma, CAS 9014-63-5), and cellulose (microgranular, Sigma, CAS 9004-34-6) were also used as pure lignocellulosic constituents of biomass. According to the lignocellulosic composition of RW, cellulose, hemicellulose and alkali lignin were mixed to produce model RW (mRW), a simulated biomass sample without the presence of minerals.

2.2 Characterisation of coal, biomass and ash samples

Proximate analysis was conducted using a Thermogravimetric analyser (TGA) (NETZSCH STA449F3, Germany) following standard procedures described elsewhere [5, 31, 32]. In each test, the amount of sample used was approximately 5.0 mg. Prior to each test, to eliminate diffusion effects, samples were further ground manually. The CHNS of those samples was determined by analysing ~ 2.0 mg of the sample using an elemental analyser (Perkin Elmer 2400, USA), while oxygen content was determined by difference based on dry and ash free basis.

Lignocellulosic content of biomass was determined by ADL, ADF and NDF methods [33].

Results of ultimate, proximate and lignocellulosic analyses are illustrated in Table 1.

Table 1 Characteristics of Mengxi Coal and Rosewood

	Mengxi Coal /wt%	Rosewood /wt%
Moisture	5.9	5.6
Proximate analysis ^a		
Fixed carbon	52.1	15.4
Volatiles	34.9	77.0
Ash	13.0	7.6
Ultimate analysis ^b		
C	76.8	54.9
H	4.8	6.6
O (by difference)	15.8	37.4
N	1.6	0.5
S	1.0	0.6
Lignocellulosic components ^a		
Hemicellulose	-	15.5
Cellulose	-	48.0
Lignin	-	24.3

^a dry basis

^b dry and ash free basis

The results revealed that RW contains 87.8 wt% of lignocellulosic components, 7.6wt% ash,

and other organic constituents, for example, tannin and ester [34, 35].

High-temperature ash (HTA) of the biomass was prepared following the procedure specified by the Chinese Standard (GB/T 212-2008). Biomass sample was heated in a muffle furnace (5E-MF 6000, Kaiyuan Instruments Co. Ltd., China) to 500 °C. It was kept isothermal for 30 mins and then heated up and kept isothermal at 550 °C for 60 mins to obtain the high-temperature ash sample. Similarly, the low-temperature ash (LTA) of the biomass was prepared by using a plasma ashing device (PR300, Yamato, Japan). The whole ashing process was carried out below 150 °C to avoid the release of AAEMs in biomass during ashing, which followed the process described elsewhere [36].

Mineral content was determined by using an XRF (ThermoFisher Scientific, USA). XRD (D8 Advanced A25, Bruker, Germany) was also applied to analyse both HTA and LTA samples. The goniometer radius was 280 mm. The generator power and current were 40kV and 40mA respectively. The scan type selected was coupled Two Theta/Theta with Two Theta ranging from 10° to 100° at an interval of 0.01°. The twin primary and secondary slits were 0.6 mm and 5.5 mm.

2.3 Combustion characteristics

Combustion characteristics of RW, mRW, MC, lignin, xylan, cellulose, MC/RW blends, MC/mRW blends and MC/RW LTA blends were investigated using a TGA. In each test, the sample (approximately 5.0 mg) was heated to and kept isothermal at 105 °C for 30 min to remove moisture. The temperature was then raised to and maintained at 900 °C for 30 min. The heating rate was 20 °C min⁻¹, with an air flow rate of 200 mL min⁻¹. Combustion characteristics, such as devolatilization temperature, ignition temperature, peak and burnout temperatures were extracted from the TGA profiles. The combustion kinetics under similar

combustion condition was studied, during which Arrhenius equation was adopted. The activation energy is the minimum energy required for reaction while the pre-exponential factor is a measure of collision frequency between the fuel molecules during thermal reaction [38]. With the assumption of a first-order reaction kinetics, the reaction rate constant method was used to derive the kinetic parameters obtained from equations (1) and (2):

$$k = Ae^{(-E/RT)} \quad (1)$$

$$\frac{dD}{dt} = k(1 - D)^n \quad (2)$$

Where k is rate constant; R is the gas constant; T is the temperature (K); A is the pre-exponential factor (min^{-1}); E is the activation energy (kJ mol^{-1}); α is the degree of thermal conversion; n is the reaction order ($= 1$) and t is time.

2.4 Summary of experimental methods

Table 2 shows a summary of all the experimental methods adopted in this study.

Table 2 Experimental methods

	Experimental Methods	Equipment / Method	Sample Size	Process / Reference
Fuel properties	Proximate analysis	TGA	~5.0mg	[10, 33, 34]
	Ultimate analysis	CHNS/O Elemental Analyser	~2.0mg	Pre-set equipment at 800°C
	Lignocellulosic analysis	ADF, NDF and ADL methods	~3g	[35]
Sample preparation	Model Biomass	Mixing pure cellulose, semicellulose and lignin based on the lignocellulosic composition of RW		mRW was prepared based on the result of the lignocellulosic analysis
	High temperature ashing	Muffle Furnace	~20g	Heated up to and kept isothermal at 500 °C for 30 min, and further heated up to and kept isothermal at 815 °C for 60 min.

	Low temperature ashing	Plasma asher	~20g	Heated up to 150 °C, held for ≥12 hours [36]
Combustion characteristics and kinetic study	Thermal analysis	TGA	5 ~ 10 mg	Heated up to 105 °C, kept isothermal for 30 mins, and heated up and kept isothermal at 900 °C for 30 mins. Air flowrate: 200mL min ⁻¹ . Heating rate: 20 °C min ⁻¹
Mineral analysis	Mineral phase analysis	X-ray diffraction	~3 g	Generator power and current (40kV and 40mA). Coupled Two Theta/Theta scan for 10° to 100° range at 0.01° interval
	Mineral Elemental analysis	X-ray Fluorescence	~3 g	[37]

3. Results and Discussion

3.1 Combustion characteristics of Rosewood and lignocellulosic components

DTG curves of the RW and lignocellulosic components are shown in Figure 1. For cellulose, xylan (hemicellulose) and lignin, their weight loss reached peak values of 71.9, 12.6 and 8.9 wt.% min⁻¹ at 286, 350 and 506 °C respectively. Similar to this observation, a shoulder peak at 300°C and 2 main peaks at 322 and 419°C were found in the DTG profile of actual RW, which is associated with the decomposition of its lignocellulose constituents [14, 39]. The two main peak temperatures of RW are less than those of cellulose and lignin, which suggests possible interactions between these constituents leading to a lower temperature of decomposition. The interactions of the volatile species from the cellulose and lignin boosts low molecular weight products from cellulose by constraining their thermal polymerization [42]. Subsequently, this leads to the formation of lower molecular weight and aliphatic products from the cellulose and lignin. Therefore, the reductions in temperatures can be associated to these variations.

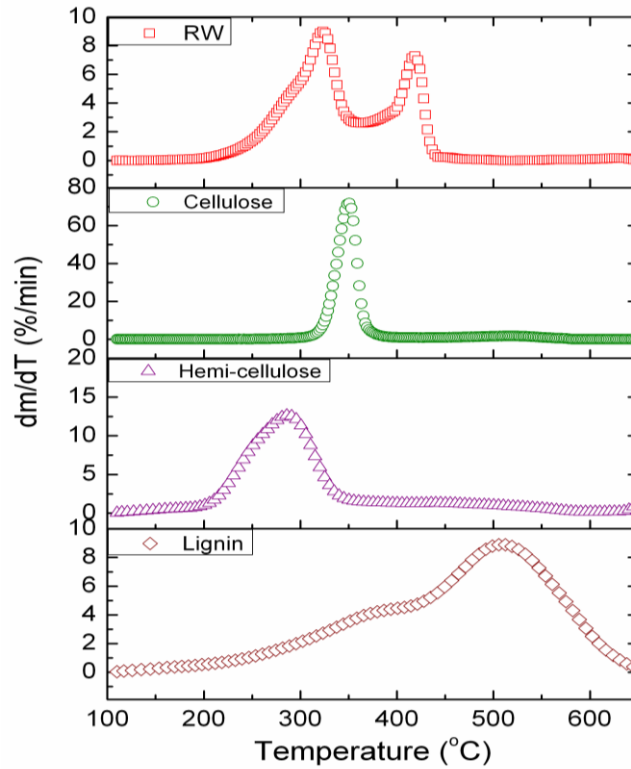


Figure 1 DTG curves of RW and lignocelluloses

3.2 Combustion characteristics of Rosewood, model Rosewood and Mengxi coal

The combustion profile of the unblended fuel samples in Figure 2 shows that the devolatilization of the model biomass mRW commenced at the lowest temperature (131°C) while the actual RW started devolatilization at about 181°C, which is higher than that of the mRW. Regardless of this, the first peak temperature of RW (322°C) was lower than that of the mRW (364°C). Likewise, the char oxidation zone has a peak temperature of 479°C for the mRW and 418°C for the RW. This disparity is indicative of the catalytic influence of minerals in Rosewood, which led to the shift in the first and second peak temperatures to lower values. From Figure 2, it is obvious that mRW has the highest weight loss rate at the devolatilization stage and char oxidation stage, suggesting high volatility which indicates high reactivity with high volatile release. This is attributed to the decomposition of lignocellulose components without any mineral constituents [38]. Normally, peak temperature is an indicator of combustibility and reactivity of the fuel [39].

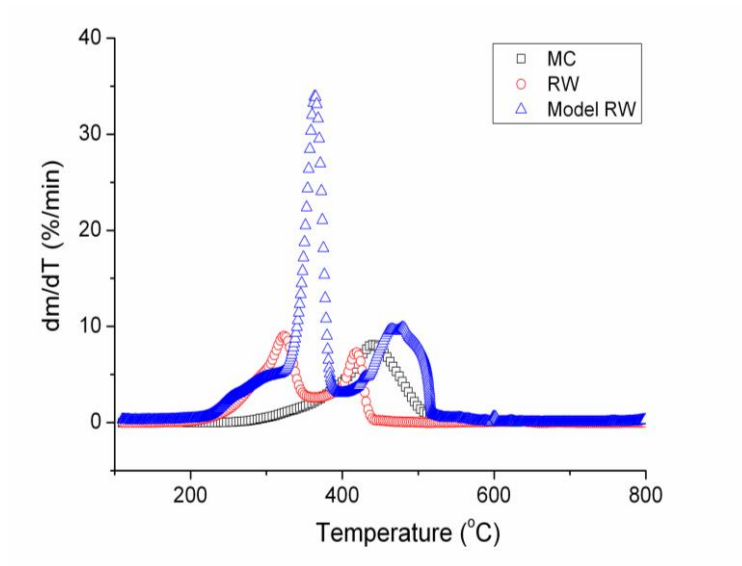


Figure 2 DTG profiles of coal, biomass and model biomass

Table 3 Combustion characteristics of MC, RW and mRW

	Devolatilization temperature (°C)	Ignition temperature (°C)	Peak temperature (°C)		Burnout temperature (°C)
			Peak 1	Peak 2	
MC	268	379	-	440	560
RW	181	281	323	418	435
mRW	131	326	364	479	518

Hence, the higher peak temperatures of mRW specify a longer time for complete combustion[40]. These results suggest that cellulose is the main reactive constituent during the devolatilization stage which has a significant influence on ignition and fuel reactivity, whereas burnout temperature is dependent on the decomposition of lignin. The 2nd peak temperature of mRW is the highest at 479°C, but lower than the peak temperature of lignin (506 °C). The high decomposition rate observed in the first peak devolatilisation stage (from cellulose and hemicellulose decomposition) leads to the increase in particle temperature which increases the fuel’s reactivity and contributes to a faster char burnout. This might be the cause of the reduction in 2nd peak temperature, and hence faster burnout of mRW in comparison to the additive expectations. This corroborates the presence of interactions

among lignin, hemicellulose and cellulose in the model biomass, particularly in the second reaction zone, which is consistent with previously observation by others [41]. Furthermore, the second peak temperature of mRW and RW are 479 and 418°C respectively, suggesting the catalytic effects of RW ash in reducing the peak temperature of RW. Therefore, the results indicate that the ash matter in RW leads to the reduction in the decomposition rate of cellulose and hemicellulose, and also decreases the peak and burnout temperatures during combustion.

3.3 Non-additive interactions in model Rosewood (mRW)

In the previous section, the heating profile of mRW illustrates the non-additive interaction of the lignocellulosic constituents used in the model biomass. Hence, this is further examined in Figure 3, which shows the experimental heating profile of mRW and the theoretical curve assuming additive property applies. Figure 3a reveals the close fit of the DTG curves at temperatures below 250°C for both the experimental and predicted curve, which suggest negligible interaction of the solid particles. However, with further increase in temperature, the experimental weight loss rate of mRW reduces. This reduction can be described as a decrease in devolatilization rate of the hemicellulose and cellulose, which is attributed to the interaction of xylan and lignin with the levoglucosan released from the thermal decomposition of cellulose [42].

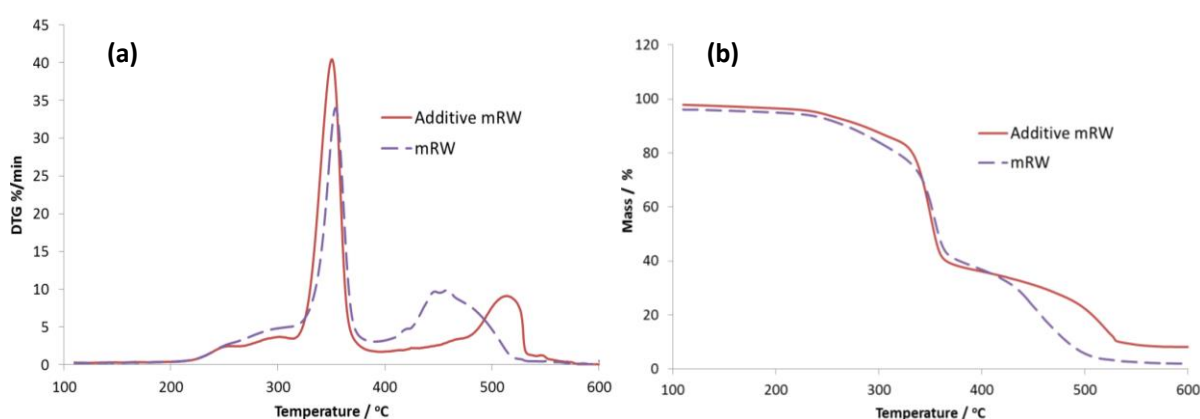


Figure 3 DTG (a) and TG (b) curves of the model Rosewood and the additive expectations from mRW's constituents

After devolatilization, mRW generated a highly reactive char which decomposes at lower temperature range with a higher degree of burnout in comparison to the additive expectation. All these are indications of increase in reactivity of lignin fraction of the model Rosewood, which can only be attributed to the effect of interactions between lignin and cellulose[43]. Therefore, observed improvement in the char degradation is associated with either the secondary reactions of cellulose-derived intermediates with lignin during char oxidation or the interactions occurring between lignin and cellulose during the devolatilisation stage [41, 42]. This indicates that the reaction pathway of lignocellulose components is complicated due to the physical and chemical interactions that occur between xylan, cellulose and hemicellulose, which affects product distribution, morphology and thermal reactivity of the char.

3.4 Impacts of lignocellulosic constituents on co-combustion

The influence of biomass organic components and minerals on the combustion of the blends was investigated by comparing combustion profiles of MC/RW and MC/mRW. The results are shown in Figure 4. The decomposition of cellulose and hemicellulose, and the release of volatiles in coal occurred in the first stage, while char derived from both coal and lignin in biomass starts to burn in the second stage. For the MC/mRW blends, both peak and burnout temperatures reduced noticeably with the increase in the percentage of biomass in comparison to that of MC. In this work, any disparity in the MC/RW and MC/mRW profiles is attributed to the catalytic effect of minerals in Rosewood with the assumption that minerals in biomass are the only difference of MC/RW and MC/mRW. These results showed that the

minerals of biomass catalysed the combustion of the blend.

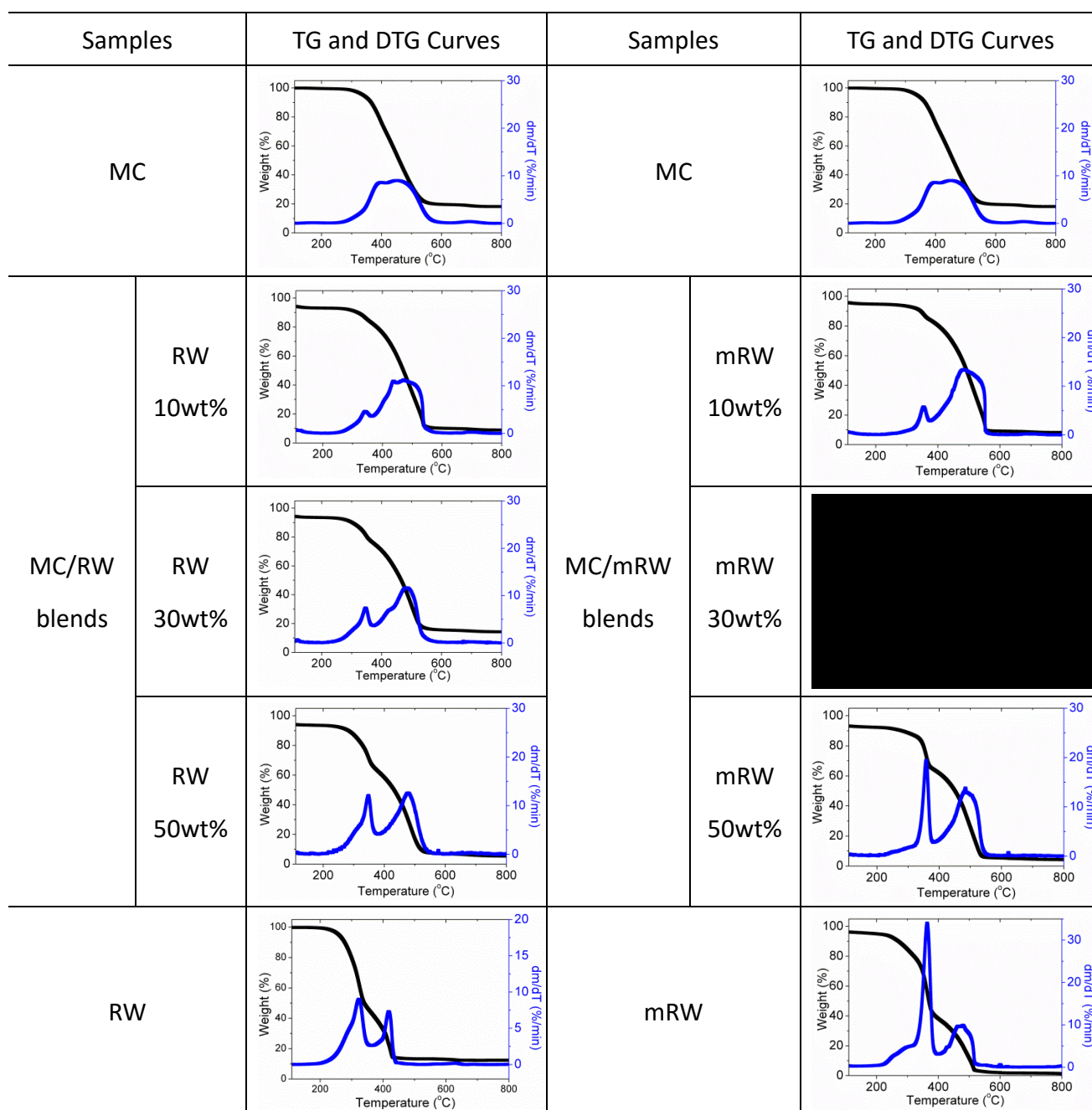
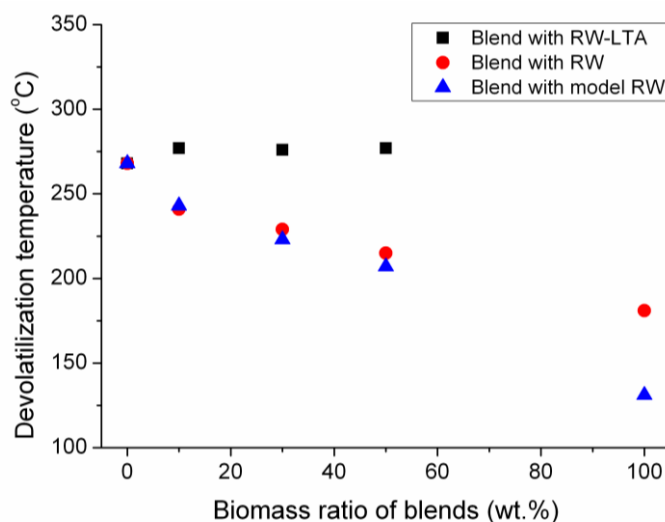


Figure 4 TG and DTG curves of coal, biomass, model biomass and their blends

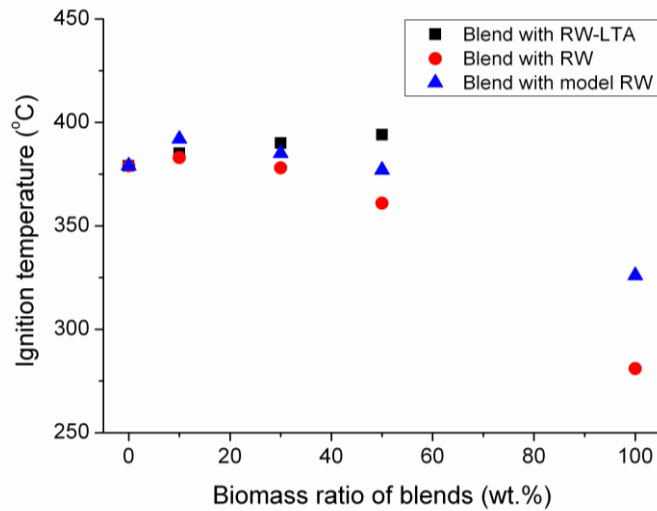
Based on the comparison of the DTG profiles between MC/RW blends and MC/mRW blends, it is clear that the maximum decomposition rate of MC/RW is lower than that of MC/mRW. This difference implies the higher reactivity of the MC/mRW, which is due to the absence of catalytic influence of biomass ash during the devolatilization and char oxidation stage as previously observed by others [44].

Figure 5(a) shows the initiation temperature of devolatilization. The biomass constituents,

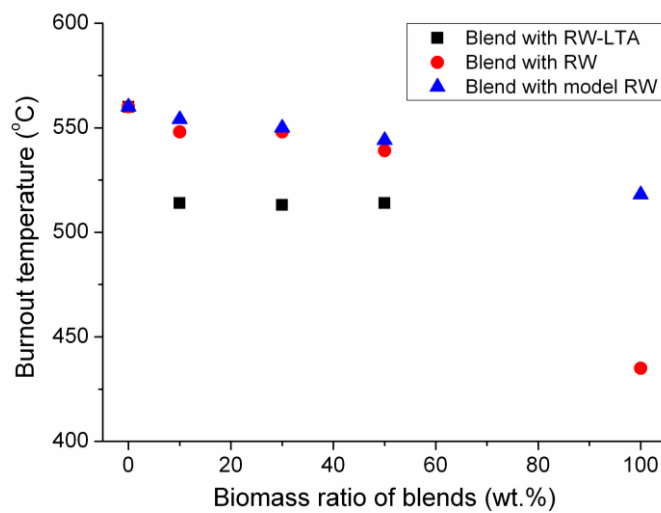
such as cellulose and hemicelluloses, are easy to decompose at low temperatures as observed in RW and mRW and this reduces the initiation temperature of the fuel blends [3]. In contrast, MC blended with low-temperature ash of RW revealed similar devolatilization initiation temperature as that of MC regardless of percentage of biomass ash in the blends. This is an indication that the minerals in RW do not have any catalytic influence on the initiation of devolatilization of the coal in the blend. For the MC/RW blends, the devolatilization temperature decreases with the increase in the biomass blending level. Interestingly, MC/RW and MC/mRW have similar devolatilization temperatures when the biomass blend ratio is less than 30wt%. However, once the percentage of biomass is higher than 30wt%, the devolatilization temperature of MC/mRW is lower than that of the MC/RW blends. This difference implies that the mineral content in RW has some inhibition effects on the devolatilization process, which exerts resistance on both heat and mass transfer processes and results in a delay in the initiation of devolatilization. This inhibition leads to a more significant temperature gradient which subsequently results in a higher devolatilization temperature. Additionally, this could induce further resistance to gas diffusion during the reaction, which would subsequently cause a delay in ignition. This explains the higher ignition temperature in RW-LTA blends in comparison to RW and mRW blend.



(a)



(b)



(c)

Figure 5 Influence of blending ratio on devolatilization (a), ignition (b) and burnout (c) temperatures

The combustion profile of the MC/RW, MC/mRW and MC/RW-LTA blends also revealed changes in the ignition characteristics of the fuels. This is represented in Figure 5b, which shows that MC/mRW has higher ignition temperature than MC/RW. This suggests that the minerals in RW have catalytic effects on ignition temperature, particularly at higher biomass blend ratios. The blends with mRW revealed negligible reduction ($\pm 5^\circ\text{C}$) in ignition temperatures, which indicates that the lignocellulosic constituents of biomass do not contribute independently to the improvement in ignition characteristics. Similarly, the combustion of MC/RW-LTA blends shows no noticeable improvement of ignition temperature

with the blending ratio. This suggests that the organic and mineral contents in biomass cannot improve ignition of the coal independently. Also, at low RW blending ratio, both ash and organic content have limited impacts on co-combustion. When the percentage of biomass is greater than 30 wt%, the ignition temperature of the blends decreases significantly ($\sim 20^{\circ}\text{C}$), while the reduction was only 2°C reduction for MC/mRW blends. This indicates that at high blending ratio, the interaction of both lignocellulosic and minerals in biomass with the coal sample results in lower ignition temperature. This signifies the synergy of biomass/coal blends on the ignition process during co-combustion.

Table 4 illustrates the Peak temperatures of different blends, which were found to be in the range of $342 - 358^{\circ}\text{C}$ and 471 and 484°C for the first and the second reaction zone respectively. These reaction zones are associated with the decomposition of hemicellulose and cellulose during devolatilization and oxidation of lignin and coal-derived chars in the second zone.

Table 4 Peak temperature of MC/RW and MC/mRW

		RW in MC/RW, wt%			mRW in MC/mRW, wt%		
		10	30	50	10	30	50
The 1st Reaction Zone	Peak temperature ($^{\circ}\text{C}$)	342	346	348	354	357	358
	Weight loss rate ($\text{wt}\% \text{ min}^{-1}$)	4.6	7.4	12.1	5.8	10.8	19.4
The 2nd Reaction Zone	Peak temperature ($^{\circ}\text{C}$)	471	484	479	484	484	484
	Weight loss rate ($\text{wt}\% \text{ min}^{-1}$)	11.3	11.6	12.6	13.4	13.4	13.8

As shown in Figure 5c, the burnout temperature of the MC/RW-LTA blends were lower than those of MC/RW and MC/mRW blends at the same blending level. It is evident that biomass ash can effectively reduce the burnout temperature of biomass and coal blends. The burnout temperatures of MC/RW blends ($548 - 539^{\circ}\text{C}$) are lower than those of MC/mRW blends (554

- 544°C). It is therefore clear that the burnout temperature is slightly affected by the minerals in biomass, which is similar to what was reported by Biagini and co-workers [45]. The presence of AAEMs in biomass has been reported to aid faster decomposition of volatile species and improve char combustion and burnout properties. The role of such metals in increasing reactivity and altering reaction mechanisms during fuel combustion greatly alters thermal decomposition of char due to catalysis. The reactions of atomic AAEMs, generated during devolatilization, with phenol groups in char fosters char-bonded AAEMs which readily react with oxidants and other products of combustion at temperatures >400°C to stimulate complete burnout of char [45-46]. This corroborates the burnout temperatures obtained in the coal and RW-LTA blends in Figure 5b. Interestingly, the promoting influence of biomass minerals on the burnout of the fuel blends is lower than that observed in the ash blends, which could be an indication of the presence of competition on synergy between the organic and inorganic constituents of biomass on the coal during co-combustion and hence inhibition as previously explained by other researchers [37].

Table 5 lists the pre-exponential factor and activation energy of the 2 main decomposition regions, i.e., 280 - 380 °C and 380 - 560 °C, respectively.

Table 5 Kinetic parameters of the combustion of coal and biomass blends

Blends		Region One		Region Two	
% biomass	%MC	Activation Energy (kJ mol ⁻¹)	Pre-exponential Factor (min ⁻¹)	Activation Energy (kJ mol ⁻¹)	Pre-exponential Factor (min ⁻¹)
0	100%	-	-	74.0	2.68×10 ⁶
RW 10%	90%	125.5	5.52×10 ¹²	70.2	2.37×10 ⁶

RW 30%	70%	99.5	1.49×10^{10}	80.2	8.29×10^6
RW 50%	50%	87.9	1.63×10^9	92.1	5.71×10^7
RW 100%	0	89.8	2.65×10^9	133.0	2.11×10^{11}
mRW 10%	90%	98.6	1.01×10^{10}	87.9	2.66×10^7
mRW 30%	70%	89.4	1.81×10^9	100.2	1.80×10^8
mRW 50%	50%	86.6	8.51×10^8	108.8	6.69×10^8
mRW 100%	0	75.3	9.79×10^7	88.1	1.81×10^7

In the first region, the values of E and A decreased with the increase blending ratio of RW or mRW. Normally, more biomass in the blend facilitates decomposition and allows easier burning of the fuel blends. Here, the kinetic parameters of MC/RW blends are greater than those of the MC/mRW blends at the same blending ratio, which suggests that the biomass minerals demonstrate inhibition influence and reduce the reactivity of the blends during devolatilization [46]. However, in the char oxidation zone in Region 2, MC/RW blends showed lower activation energy than the MC/mRW blends at the same blending level. This suggests that co-combustion of the MC/RW is easier than the MC/mRW blends. Therefore, it is believed that the catalytic influence of minerals in RW resulted in lower activation energy for the combustion of coal and actual biomass blends.

3.5 Impacts of minerals on co-combustion

The mineralogy analysis of the high and low-temperature ash of RW were carried out by using XRD. The phase-mineral compositions are shown in Table 6, which illustrates the differences in minerals between LTA and HTA. It is evident that the main constituents of HTA are Ca, Si and Mg in the form of CaCO_3 , CaO, MgO and SiO_2 while in the LTA remained amorphous with Ca (Weddelite), Ca- Mg- carbonate (dolomite), K- chlorides and Si-based opal. This result is similar

to the observations of other researchers [47] on biomass and ash composition. It is also clear that high temperature resulted in the release of potassium, from 13.8wt% of K₂O to 5.3wt%.

Table 6 Mineral composition of different biomass ash samples

Minerals in LTA	Content wt. %	Form (mostly amorphous)	Minerals in HTA	Content wt. %	Form (crystalline)
CaO	68.9	Weddelite	CaO	60.5	Lime, calcite, Ankerite, whitlockite & sulphate
MgO	6.1	dolomite	MgO	11.6	Periclase, Ankerite
K ₂ O	13.8	chlorides	K ₂ O	5.3	Arcanite, Sylvite
SiO ₂	4.8	Opal	SiO ₂	14.3	Quartz
Al ₂ O ₃	1.9		Al ₂ O ₃	3.4	Mullite
Fe ₂ O ₃	1.2		Fe ₂ O ₃	2.0	Hematite, Ankerite
SO ₃	1.4	sulphate	SO ₃	0.9	
P ₂ O ₅	0.4	phosphate	P ₂ O ₅	0.8	Hydroxylapatite
Cl	1.5		Cl	0.2	

This suggests that from reaction commencement till 815°C, the reactive organic minerals in Rosewood such as weddelite (CaC₂O₄.2H₂O), other oxalates, chlorides or phosphates of Ca and K would react thermally to form more stable compounds while also influencing the reactivity of the fuel [39, 48]. For example, the CaC₂O₄.2H₂O in RW may convert into CaCO₃ and CaO at higher temperatures. This is similar to the deductions made by other researchers [49]. In RW, calcium-based compounds make up more than 60 wt% of the inorganics. The influence of Ca during co-firing has been previously studied by other researchers [50], which suggest that catalytic activity of Ca is restricted to its ability to migrate and react with the organic species in the carbon matrix of coal. Consequently, the transformation of calcium increases its catalytic effect on the coal char's matrix during combustion [18, 51]. The secondary elements that play a catalytic role include potassium and chlorine-based

elements[39, 52] in RW (13.8 wt% K₂O and 1.5 wt% Cl). These elements help catalyse the combustion of the MC/RW blends, leading to the disparity of MC/RW and MC/mRW TGA profiles as shown in Figure 4.

4. Conclusions

In this research, it was found that the synergistic effects between xylan-cellulose and cellulose-lignin led to up to 5% non-additive reduction in peak and burnout temperatures. Minerals in biomass show some inhibition effects during the devolatilization of the blends, however the presence of catalytic effects of minerals in biomass during co-firing was also evident, which result in the reduction in the ignition (≤ 20 °C), peak temperature (≤ 12 °C) and burnout temperature (≤ 6 °C). The promoting/synergistic effects of Rosewood minerals on the burnout of the blends were found to be affiliated to the catalytic influence of potassium and calcium on char reactivity. Similarly, improvement in the reactivity of the biomass/coal blends is associated with the catalytic effects of ash in biomass. The synergistic competition between biomass organic and inorganic constituents was observed.

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References

- [1] Varol M, Atimtay A, Bay B, Olgun H. Investigation of co-combustion characteristics of low quality lignite coals and biomass with thermogravimetric analysis. *Thermochimica Acta*. 2010;510(1–2):195-201.
- [2] Loo SV, Koppejan J. *The hand book of biomass combustion & Co-firing*. London: Earthscan, 2008.
- [3] Gil MV, Casal D, Pevida C, Pis JJ, Rubiera F. Thermal behaviour and kinetics of coal/biomass blends during

- co-combustion. *Bioresource Technology*. 2010;101(14):5601-8.
- [4] Li XG, Lv Y, Ma B G, Jian S W, Tan H B. Thermogravimetric investigation on co-combustion characteristics of tobacco residue and high-ash anthracite coal. *Bioresource Technology*. 2011;102(20):9783-7.
- [5] Wu T, Gong M, Lester E, Hall P. Characteristics and synergistic effects of co-firing of coal and carbonaceous wastes. *Fuel*. 2013;104:194-200.
- [6] Sahu SG, Chakraborty N, Sarkar P. Coal–biomass co-combustion: An overview. *Renewable and Sustainable Energy Reviews*. 2014;39:575-86.
- [7] Singh K, Zondlo J. Characterization of fuel properties for coal and torrefied biomass mixtures. *Journal of the Energy Institute*. 2017;90(4):505-12.
- [8] Haykiri-Acma H, Yaman S. Effect of biomass on burnouts of Turkish lignites during co-firing. *Energy Conversion and Management*,. 2009(50):2422- 7.
- [9] Haykiri-Acma H, Yaman S. Effect of co-combustion on the burnout of lignite/biomass blends: A Turkish case study. *Waste Management*. 2008(28):2077-84.
- [10] Sjoström K, Chen G, Yu Q, Brage C, Rosen C. Promoted reactivity of char in co-gasification of biomass and coal: synergies in the thermochemical process. *Fuel*. 1999(78):1189 - 94.
- [11] Park DK, Kim SD, Lee SH, Lee JG. Co-pyrolysis characteristics of sawdust and coal blend In TGA and a fixed bed reactor. . *Bioresource Technology*. 2010(101):6151-6.
- [12] Jones JM, Kubacki M, Kubica K, Ross AB, Williams A. Devolatilization characteristics of coal and biomass blends. *Journal of Analytical and Applied Pyrolysis*. 2005(74):502-11.
- [13] Sahu SG, Chakraborty N, Sarkar P. Coal-biomass co-combustion: An overview. *Renewable and Sustainable Energy Reviews*. 2014(39):575 - 86.
- [14] Idris SS, Rahman NA, Ismail K, Alias AB, Rashid ZA, Aris MJ. Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA). *Bioresource Technology* 2010;101:4584 - 92.
- [15] Vuthaluru HB. Investigations into the pyrolytic behaviour of coal/biomass blends using thermogravimetric analysis. *Bioresource Technology* 2004;92(2):187-95.
- [16] Gil MV, Casal D, Pevida C, Pis JJ, Rubiera F. Thermal behaviour and kinetics of coal/biomass blends during co-combustion. *Bioresource Technology*. 2010(101):5601-8.
- [17] Jones JM, Nowakowski DJ, Brydson RMD, B. RA. Potassium Catalysis in the Pyrolysis Behaviour of Short Rotation Willow Coppice. *Fuel*. 2007(86):2389-402.
- [18] Jones JM, Stojanowska G. Influence of Minerals and Added Calcium on the Pyrolysis and Co-pyrolysis of Coal and Biomass. *Journal of Energy Institute*. 2016;3(78):126-38.
- [19] Tchpada AH, Pisupati SV. A Review of Thermal Co-Conversion of Coal and Biomass/Waste. *Energies*. 2014(7):1098-148.
- [20] Vamvuka D, Pitharoulis M, Alevizos G, Repouskou E, Pentari D. Ash effects during combustion of lignite/biomass blends in fluidized bed. *Renewable Energy*. 2009;34(12):2662-71.
- [21] Steenari BM, Lindqvist O. Fly ash characteristics in co-combustion of wood with coal, oil or peat. *Fuel*. 1999;78(4):479-88.
- [22] Saddawi A, Jones JM, Williams A. Influence of alkali metals on the kinetics of the thermal decomposition of biomass. *Fuel Processing Technology*. 2012;104:189-97.
- [23] Vassilev SV, Baxter D, Vassileva CG. An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types. *Fuel*. 2014;117:152-83.
- [24] Vassilev SV, Vassileva CG. Composition, properties and challenges of algae biomass for biofuel application: An overview. *Fuel*. 2016;181:1-33.
- [25] Olanders B, Steenari B-M. Characterization of ashes from wood and straw. *Biomass and Bioenergy*. 1995;8(2):105-15.
- [26] Liu Y, Cheng L, Zhao Y, Ji J, Wang Q, Luo Z, et al. Transformation behavior of alkali metals in high-alkali

- coals. *Fuel Processing Technology*. 2018;169:288-94.
- [27] Olsson JG, Jäglid U, Pettersson JBC, Hald P. Alkali Metal Emission during Pyrolysis of Biomass. *Energy & Fuels*. 1997;11(4):779-84.
- [28] Liu S, Qiao Y, Lu Z, Gui B, Wei M, Yu Y, et al. Release and Transformation of Sodium in Kitchen Waste during Torrefaction. *Energy & Fuels*. 2014;28(3):1911-7.
- [29] Hanaoka T, Inoue S, Uno S, Ogi T, Minowa T. Effect of woody biomass components on air-steam gasification. *Biomass and Bioenergy*. 2005;28(1):69-76.
- [30] CEN/TS 15443:2006. Solid recovered fuels - Methods for the preparation of the laboratory sample.
- [31] ISO 17246: 2010. Coal - Proximate analysis.
- [32] Avila C, Pang CH, Wu T, Lester E. Morphology and reactivity characteristics of char biomass particles. *Bioresource Technology*. 2011;102(8):5237-43.
- [33] Omar R, Idris A, Yunus R, Khalid K, Aida Isma M I. Characterization of empty fruit bunch for microwave-assisted pyrolysis. *Fuel*. 2011;90(4):1536-44.
- [34] Fierer N, Schimel J P, Cates R G, Zou J. Influence of balsam poplar tannin fractions on carbon and nitrogen dynamics in Alaskan taiga floodplain soils. *Soil Biology and Biochemistry*. 2001;33(12–13):1827-39.
- [35] Sun RC, Sun X F, Wang S Q, Zhu W, Wang X Y. Ester and ether linkages between hydroxycinnamic acids and lignins from wheat, rice, rye, and barley straws, maize stems, and fast-growing poplar wood. *Industrial Crops and Products*. 2002;15(3):179-88.
- [36] Oladejo JM, Adegbite S, Pang CH, Liu H, Parvez AM, Wu T. A novel index for the study of synergistic effects during the co-processing of coal and biomass. *Applied Energy*. 2017;188:215-25.
- [37] Oladejo J, Adegbite S, Gao X, Liu H, Wu T. Catalytic and non-catalytic synergistic effects and their individual contributions to improved combustion performance of coal/biomass blends. *Applied Energy*. 2018;211:334-45.
- [38] Pang CH, Gaddipatti S, Tucker G, Lester E, Wu T. Relationship between thermal behaviour of lignocellulosic components and properties of biomass. *Bioresource Technology*. 2014;172:312-20.
- [39] Fuentes ME, Nowakowski DJ, Kubacki ML, Cove JM, Bridgeman TG, Jones JM. Survey of influence of biomass mineral matter in thermochemical conversion of short rotation willow coppice. *Journal of the Energy Institute*. 2008;81(4):234-41.
- [40] Lu J-J, Chen W-H. Investigation on the ignition and burnout temperatures of bamboo and sugarcane bagasse by thermogravimetric analysis. *Applied Energy*. 2015;160:49-57.
- [41] Hosoya T, Kawamoto H, Saka S. Cellulose–hemicellulose and cellulose–lignin interactions in wood pyrolysis at gasification temperature. *Journal of Analytical and Applied Pyrolysis*. 2007;80(1):118-25.
- [42] Yu J, Paterson N, Blamey J, Millan M. Cellulose, xylan and lignin interactions during pyrolysis of lignocellulosic biomass. *Fuel*. 2017;191:140-9.
- [43] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*. 2007;86(12–13):1781-8.
- [44] Wu D, Wang Y, Wang Y, Li S, Wei X. Release of alkali metals during co-firing biomass and coal. *Renewable Energy*. 2016;96:91-7.
- [45] Biagini E, Cioni M, Tognotti L. Development and characterization of a lab-scale entrained flow reactor for testing biomass fuels. *Fuel*. 2005;84(12-13):1524-34.
- [46] Hurt R, Sun J K, Lunden M. A Kinetic Model of Carbon Burnout in Pulverized Coal Combustion. *Combustion and Flame*. 1998;113(1–2):181-97.
- [47] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. *Fuel*. 2013;105:40-76.
- [48] Mahadevan R, Adhikari S, Shakya R, Wang K, Dayton D, Lehrich M, et al. Effect of Alkali and Alkaline Earth Metals on in-Situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass: A Microreactor Study. *Energy & Fuels*. 2016;30(4):3045-56.
- [49] Suárez-García F, Martínez-Alonso A, Fernández Llorente M, Tascón JMD. Inorganic matter characterization

in vegetable biomass feedstocks. *Fuel*. 2002;81(9):1161-9.

[50] Yuan S, Zhang N, Qu X, Bi J, Cao Q, Wang J. Promoted catalysis of calcium on the hydrogasification reactivity of iron-loaded subbituminous coal. *Fuel* 2017. p. 153-61.

[51] Perander M, DeMartini N, Brink A, Kramb J, Karlström O, Hemming J, et al. Catalytic effect of Ca and K on CO₂ gasification of spruce wood char. *Fuel*. 2015;150:464-72.

[52] Banks SW, Nowakowski DJ, Bridgwater AV. Impact of Potassium and Phosphorus in Biomass on the Properties of Fast Pyrolysis Bio-oil. *Energy and Fuels*. 2016;30(10):8009-18.