



10th International Conference on Applied Energy (ICAE2018), 22-25 August 2018, Hong Kong, China

Biomass constituents' interactions with coal during co-firing

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Abstract

The importance of biomass in the emerging low carbon economy remains quite crucial especially relating to the co-firing of coal and biomass due to the improvements in thermal properties and its influence on reactivity, burnout and flame stability. In this research, the combustion profile of coal and biomass blends, coal and low temperature biomass ash blends and coal and demineralized biomass blends were studied using thermogravimetric analysis. The results established the presence of both mechanism of synergy in the fuel blends during co-firing. This was substantiated by significant decrease in peak, burnout temperature as well as reduction in activation energy, demonstrating non-additive interaction between the biomass and coal sample. Further deductions reveal a degree of overlap in the function of catalytic and non-catalytic synergy mechanisms in the biomass blends due to competitive reactions among the catalyzing AAEMs and the hydrogen contributing organic constituents of biomass with coal. Finally, this study further establishes a higher degree of catalytic synergy in potassium rich oat straw in comparison to calcium rich gumwood.

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Peer-review under responsibility of the scientific committee of ICAE2018 – The 10th International Conference on Applied Energy.

Keywords: biomass, coal, combustion, synergy, Thermogravimetry.

1. Introduction

The environmental and economic challenges posed by the continued dependence on fossil fuel necessitate the need for finding sustainable alternatives to meet the growing energy demand of the increasing population. Currently, the abundance of coal reserves and the dependence of developing countries like China and India on cheap energy

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resources is basis for predicted increase in coal consumption in the future. Still, the high pollution associated with coal usage demands investigation into ways of improving thermal conversion of coal while reducing the resulting environmental issues. Past researchers have highlighted the role of biomass usage as a supplementary fuel to improving the combustion behaviors of coal [1-2]. As a result, several studies have investigated the influence of co-firing on thermal decomposition profiles using thermogravimetric approaches and their observations highlight the importance of evaluating changes in combustion profiles [4-10]. In addition, the role of catalytic and non-catalytic synergy influencers have also been extensively discussed but only a handful of studies have experimentally approached the isolation of both mechanisms of synergy [2, 12]. In this study, coal was blended with biomass samples, low temperature ash of the biomass samples and demineralized biomass to study the influence of these constituents on co-combustion profile. The biomass samples were representative of potassium and calcium-rich biomass respectively. Investigating these factors will provide more insights into the thermal interactions between coal and biomass constituents, particularly differentiating between the catalytic synergy of K - and Ca- rich samples.

Nomenclature

A	Pre-exponential factor
AC	Australian coal
BT	Burnout temperature
E	Activation energy
GW	Gumwood
HTA	High temperature ash
LTA	Low temperature ash
OS	Oat Straw
PT	Peak temperature

2. Materials and Methods

2.1. Coal and Biomass Samples

Australian coal (AC), Oat straw (OS) and Gumwood (GW) were selected for this research due to their abundant availability as agricultural residue and/or commercially availability. These samples were prepared using the British standard BS EN 14780 and ISO 13909 for the biomass and coal samples respectively [13, 14].

2.2. Proximate, Ultimate and Mineral Analysis

Proximate analysis was conducted using the thermo-gravimetric analyser (TGA) (Netzsch STA 449 F3, German) following the procedures adopted by [4]. The ultimate analysis (CHNS) of the parent fuels was conducted using a PE 2400 Series II CHNS/O Analyzer (PerkinElmer, USA). The results are given in Table 1. Mineral composition of the ash was determined by using an X-ray Fluorescence (XRF) spectrometer as described in [2].

Table 1. Ultimate and proximate analysis of fuel samples

		Oat Straw (OS)	Gumwood (GW)	Australian Coal (AC)
Ultimate Analysis (wt%)	Carbon	47.5	48.9	81.3
	Hydrogen	6.8	6.5	4.9
	Nitrogen	2.3	3.5	1.9
	Sulphur	0.3	0.6	2.2
	Oxygen (by difference)	43.2	40.5	9.7
Proximate analysis (wt%)	Moisture	4.0	4.8	0.7
	Volatile Matter (VM)	72.1	76.3	34.6
	Fixed Carbon (FC)	17.4	13.4	48.2
	Ash	6.5	5.5	16.5

2.3. Preparation of biomass low temperature ash, water leached biomass and characterization

Low temperature ash (LTA) of OS and GW was prepared by using a low-temperature plasma ashing equipment (PR300, Yamato, Japan) using methods detailed in [2]. Oat straw sample was demineralized using the water leaching process (OS_WL) as done in previous study [12] for removing catalytic elements especially potassium. OS_WL, OS_LTA and GW_LTA were blended with AC samples at 10 and 30wt% biomass fraction.

2.4. Combustion characteristics and Kinetic study

Using a non-isothermal technique, the combustion characteristics of samples were studied using a TGA from 50 – 900°C at a heating rate of 20°C min⁻¹ and airflow rate of 50 mlmin⁻¹ and the PT and BT were extracted from the thermal profile. The kinetics of combustion process was studied adopting the model free method suitable for non-isothermal kinetics as detailed elsewhere [12]. With the assumption of first order reaction kinetics, the reaction rate constant method was used to derive the kinetic parameters obtained from equations (1) and (2):

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

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

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 degree of thermal conversion; n is the reaction order (= 1) and t is time.

3. Results and Discussion

3.1. Fuel Thermal Properties

The biomass samples is represented by devolatilization and char oxidation PT of 299/474°C and 318/456°C for the 100wt%OS and 100wt%GW respectively. Similarly, the BT of 100wt% OS and 100wt%GW were 518°C and 488°C. The PT and BT of 100wt% AC was 533°C and 636°C indicating the slow burnout of coal char. The AC/OS and AC/GW fuel blends have devolatilization PT in the range of 301 - 323°C representing the decomposition of hemicellulose and cellulose in the biomass. This is shown in Fig. 1. Interestingly, the char burnout stage revealed reductions in PT with increasing biomass. About 12 - 29°C reductions in char PT was observed in AC/OS blends while AC/GW blends showed 53°C reduction for both blends. Likewise, the BT of the blends revealed 11 - 30°C and 63 - 67°C reductions for the AC/OS and AC/GW blends respectively. This is linked to increase in char reactivity from the co-blending. Irrespective, this shift in char oxidation stage to lower temperatures were higher in the GW blends. Past studies have attributed such synergy to either catalytic (from volatile inorganic alkali and alkali earth metals (AAEMs) present) and/or non-catalytic (from biomass organic constituents) influencers [11, 15].

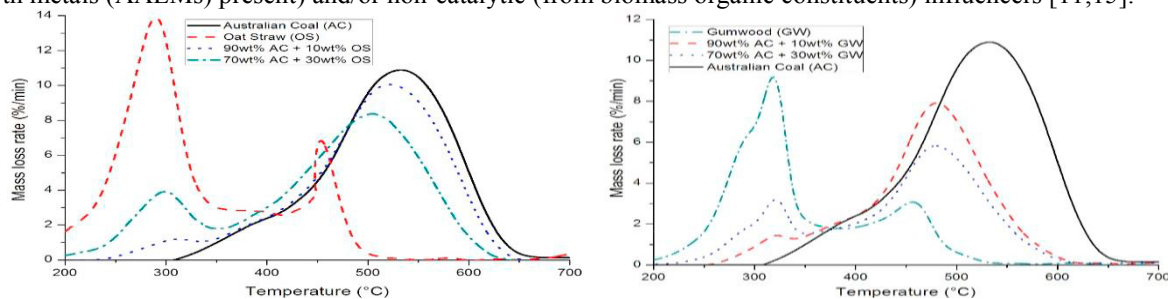


Fig. 1. Heating profile of Australian coal, gumwood, oat straw and their blends

3.2. Synergy induced by biomass inorganic constituents

In support of the cause of synergy, low temperature ash of both biomass samples were prepared and the mineral constituents are listed in Table 2 which indicates AAEMs fraction of 66.5% and 83.9wt% for OS_LTA and

GW_LTA respectively. The comparison of the low and high temperature ash constituents shows volatilisation of alkali metals i.e. potassium, sodium whose volatility increases with high chlorine content as in these samples [5].

Table 2. Mineral constituents of biomass samples

	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	K ₂ O	MgO	Cl	Na ₂ O
Oat Straw (OS_LTA)	0.3	9.2	1.5	13.2	49.2	0.5	24.0	2.1
Oat Straw (OS_HTA)	2.1	22.4	2.1	24.5	26.9	3.2	15.2	3.6
Gumwood (GW_LTA)	1.1	2.5	1.1	62.7	11.8	4.7	12.5	3.6
Gumwood (GW_HTA)	1.6	3.1	2.0	88.0	0.6	4.3	0.4	0.0
Oat Straw (OS_WL)	1.1	43.1	-	42.0	8.4	5.4	-	-

The high presence of such catalytic constituents suggests the presence of catalytic synergy. Subsequently, the low temperature ash samples of biomass were blended with the coal sample to verify the presence and influence of the catalytic elements in biomass ash on the thermal decomposition profile of coal as illustrated in Fig. 2. Comparable to the OS blends, the AC/OS_LTA blends revealed 46 - 56°C decrease in PT and 33 - 43°C decrease in BT while the AC/GW_LTA blends had 37 - 44°C and 48 - 56°C reductions in PT and BT respectively. This demonstrates the catalytic influence of the inorganic constituents of biomass on the thermal profile of fuel blends and provides credence to the viability of biomass ash as a means of improving the thermal reactivity of coal in practice[2,9]. In line with theoretical beliefs, the reduction in PT and BT of AC/GW_LTA were lower than that of AC/GW blends, which indicates the presence of both catalytic and non-catalytic synergy contributions to the improvements observed. Contrary to this, the reductions in the characteristic temperatures of the AC/OS_LTA blends were higher than that of AC/OS blends. This indicates the possibility of inhibitive reactions during the AC and OS blends reactions that limits synergy. Hence, indicative of differences in K- and Ca- induced catalytic synergy.

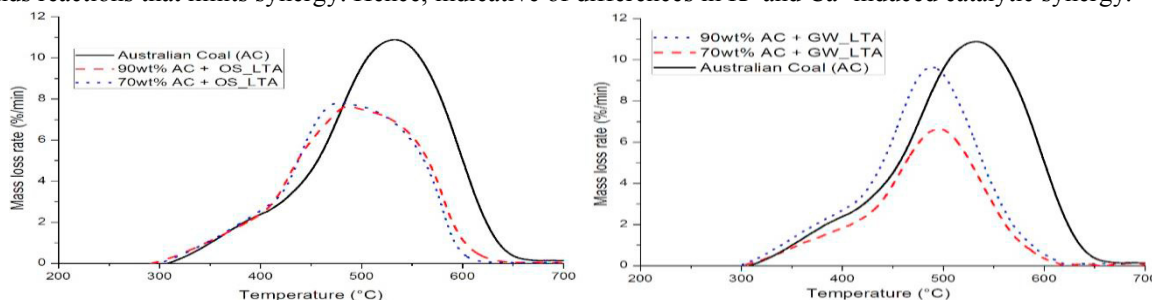


Fig. 2. Heating profile of Australian coal and low temperature ash blends

3.3. Synergy induced by biomass organic constituents

Now that the presence of catalytic synergy have been established in the fuel blends, AC was blended with water leached oat straw (OS_WL) to confirm the existence of non-catalytic synergy and to further investigate possible inhibitive reactions. Mechanism of this synergy is mainly due to the promotion of radicals' formation and their influence on reactivity resulting from the volatile content of biomass [1,9]. The water leaching of oat straw led to the removal of 82.9% of the potassium content, complete removal of the sodium and chlorine content. This leaching method is not effective for calcium-rich biomass like gumwood due to the insolubility of calcium in water. Interestingly, this leaching resulted in minor changes in the thermal profile of OS_WL such as 38°C and 14°C increase in PT and BT respectively, indicating the impact of water-soluble minerals on the thermal decomposition profiles of biomass. The heating profile of AC/OS_WL is shown in Fig. 3 and the result reveals improvements in the char oxidation zone with 20 - 22°C decrease in PT and 25 - 33°C decrease in the BT. This is an indication of the presence of non-catalytic synergy in the char burnout reaction and a confirmation of the existence of synergy competition between the catalytic and non-catalytic constituents of biomass as established in past work [12].

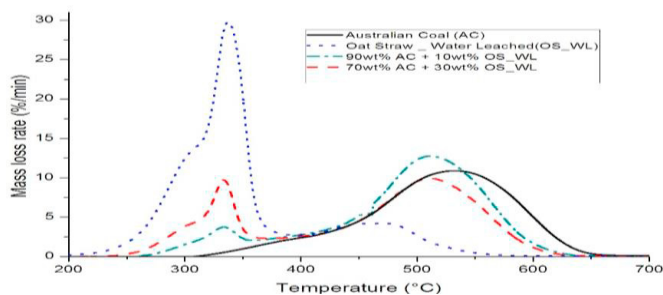


Fig. 3. Heating profile of Australian coal, water leached oat straw and their blends

3.4. Reaction Kinetics

The values of activation energy (E) and pre-exponential factor (A) of the samples are listed in Table 3. In region 1, E and A of the fuel blends are higher than those of the biomass samples which indicates reduced reactivity of the blends at lower temperature regions which could be associated with the molecular interactions of oat straw or gumwood and coal particles. The small fraction of reactive components from biomass at lower temperature with adequate energy to react will decrease the reaction rates and increase the activation energy as seen in Table 3. In the char burnout stage, the E value remained lower than those of the 2nd reaction zone of the biomass samples and coal. This reduction in E is attributed to the interactions of C-H and C-O bonds of biomass with the C=C bonds of coal char, thereby promoting the breakage of such carbon bonds, accelerating char oxidation and reducing the activation energy [10]. This is reflected by the E value of the char zone, which reduces by a factor of 2 – 10% with increase in the biomass blended with higher reductions in the oat straw blends.

Table 3. Kinetic Parameters of the fuel blends

E (kJ/mol)	GW	OS	AC	90wt% AC + 10wt%OS	70wt% AC + 30wt%OS	90wt% AC + 10wt%GW	70wt% AC + 30wt%GW
Devolatilization							
E (kJ/mol)	82.5	72.1		104.2	95.7	113.8	101.2
A (min ⁻¹)	1.83E+07	1.61E+06		1.83E+09	3.29E+08	2.13E+08	1.57E+08
Char zone							
E (kJ/mol)	167.0	251.1	80.4	77.3	72.0	78.8	76.1
A (min ⁻¹)		3.24E+17	4.67E+04	3.28E+04	2.04E+04	3.71E+04	3.25E+04

3.5. Measure and mode of synergy

As a result, the synergy factor was calculated using formulas derived by [2] and the results are represented in Table 4 to see the extent of synergy of the coal blended with biomass, low temperature ash and water leached oat straw. Interestingly, the synergy index portrays the observations from the characteristic temperature such that the highest improvement is observed in AC/GW blends. Additionally, the presence of catalytic and non-catalytic synergy is confirmed in the AC and OS blends. Non-catalytic synergy occurs from hydrogen transfer and radicals propagation arising from the decomposition of cellulose and hemicellulose content of biomass [1,7]. This enhances the thermal reactivity of coal by the interaction with biomass volatiles. Likewise, catalytic synergy from the interactions and release of volatile AAEMs during devolatilization results in the formation of metal complexes of carbohydrates, which increases, fuel reactivity by promoting dehydrogenation reactions and weakening of bonds [11]. It is also apparent that the catalytic synergy was higher in potassium rich oat straw compared to calcium rich gumwood blends. Finally, a level of overlap in the synergistic roles of the organic and inorganic contents of biomass was observed in the AC/OS blend, which is an indication of competition between the modes of synergy. This highlights the need for further research in both modes of synergy for understanding reaction progression and mechanisms.

Table 4. Synergy Index of the fuel blends

	AC : OS		AC : GW		AC : OS_LTA		AC : GW_LTA		AC : OS_WL	
	90:10	70:30	90:10	70:30	90wt%AC	70wt%AC	90wt%AC	70wt%AC	90:10	70:30
Synergy Index	1.18	1.53	1.66	1.77	1.45	1.60	1.39	1.42	1.41	1.48

4. Conclusion

This study investigates the co-combustion properties of Australian coal with potassium rich oat straw and calcium rich gumwood. The result indicates improvement in combustion properties with reduction of up to 10% the peak and burnout temperatures. In addition, the effect of catalytic synergy was determined by the use of low temperature ash, which also revealed improvement trends in thermal decomposition profiles of both biomass blends. This allows easier progression of thermal reactions at lower temperatures. Furthermore, the influence of organic constituents of biomass was explored using water leached biomass, which not only revealed presence of non-catalytic synergy but also suggests an overlap in the two mechanisms of synergy, which results in competitive synergy. This synergy was detected by increase in reactivity of the fuel blends with reductions in activation energy. The results obtained established more prominent reduction in the characteristic temperatures of the Ca-rich gumwood blends while the improvements in kinetic parameters were higher K-rich oat straw blends. This was further corroborated with the values attained for the synergy index, suggesting the higher degree of catalytic synergy in potassium-rich biomass may be the core influencer of the competitive synergy detected.

Acknowledgements

This work supported by the National Key R&D Program of China (2017YFB0602602 and 2017YFC0210400) and National Natural Science Foundation of China (51606106), Ningbo Natural Science Foundation (2017A610233).

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