A novel index for the study of synergistic effects during the co-processing of coal and biomass

Jumoke M. OLADEJO [1], Stephen Adegbite [1], Cheng Heng Pang [2], Hao Liu [3], Ashak M. Parvez [1], Tao Wu[2, 4,*]

[1] Department of Chemical and Environmental Engineering, The University of Nottingham Ningbo China, Ningbo 315100, China

[2] Municipal Key Laboratory of Clean Energy Conversion Technologies, The University of Nottingham Ningbo China, Ningbo 315100, China

[3] Department of Architecture and Built Environment, The University of Nottingham, Nottingham NG7 2RD, The UK

[4] New Materials Institute, The University of Nottingham Ningbo China, Ningbo 315100, China

Corresponding author: tao.wu@nottingham.edu.cn

Abstract

In this study, synergistic interaction between coal and biomass and its intensity was investigated systematically using a low rank coal and its blends with different biomass samples at various blending ratios. The catalytic effects of minerals originated from biomass were also studied. It was found that some of the minerals existing in the ash derived from oat straw catalysed the combustions process and contributed to synergistic interactions. However, for the coal and rice husk blends, minimal improvements were recorded even when the biomass and coal blending ratio was as high as 30 wt%. Biomass volatile also influenced the overall combustion performance of the blends and contributed to synergistic interactions between the two fuels in the blends. Based on these findings, a novel index was formulated to quantify the degree of synergistic interactions. This index was also validated using data extracted from literature and showed high correlation coefficient. It was found that at a blending ratio of 30 wt% of oat straw in the blend, the degree of synergistic interaction between coal and oat straw showed an additional SF value of 0.25 with non-catalytic and catalytic synergistic effect contributing 0.16 (64%) and 0.09 (36%) respectively.

This index could be used in the selection of right type of biomass and proper blending ratios for co-firing at coal-fired power stations, which intend to improve combustion performance of poor quality coal by enhancing synergistic interactions during co-processing.

Keywords – Fuel characterisation; synergistic interaction; performance index; synergy index; thermogravimetric analysis

1.0 Introduction

The low cost and carbon lean nature of biomass make it a promising energy alternative for the mitigation of CO_2 emissions [1, 2]. However, the technical, economic and socio-ethical issues associated with the large-scale utilization of biomass have hindered its large-scale development [3, 4]. One of the feasible solutions to mitigate these issues is to cofire biomass with coal. This approach has become a general practice in western countries as it offers significant social and environmental benefits such as energy security, energy sustainability, greenhouse gas emission reduction, and economic developments [1].

In the past few decades, extensive research has been carried out in understanding the suitability of coal/biomass blends in various thermochemical conversion processes [5-7]. Synergistic effect was observed for some blends [1, 8] while insignificant additive behaviour was also observed for some other blends [9, 10]. The synergy observed in coal/biomass fuel blends was mainly attributed to both catalytic and non-catalytic synergistic effect of biomass constituents and their influence on the coal during co-firing. The non-catalytic synergistic effect is mainly associated with the high volatile content in biomass while catalytic synergistic effect is dictated by Alkali and Alkali Earth Metals (AAEMs) in biomass which have catalytic impacts on the reactivity of chars derived from coal [11, 12]. Nonetheless, even though all biomass have AAEM species, the presence of synergy and its

intensity is dependent on the physical/chemical properties of the fuels, especially the AAEM contents [13].

To date, much effort has been made to understand the influence of AAEMs on the catalytic influence on co-processing of biomass with coal. Many researchers have studied the catalytic performance of ash derived from high temperature ashing process ($\geqslant 550^{\circ}$ C) or some ash elements, such as K, Ca and Si [14]. However, some AAEM species are normally released at very low temperatures (<500 °C) [15]. Therefore the use of high temperature ash as catalyst did not show the catalytic effect of AAEMs originated from biomass. So far, not much work has been carried out to show the catalytic effect of minerals in biomass. In addition, although synergistic interactions [1, 8] have been studied greatly in the past few decades, there is not much effort being made to distinguish the contribution of catalytic effect and non-catalytic effect on the overall synergistic interactions occurring, needless to say there is a reliable approach to quantify synergistic interactions and the contribution from catalytic and non-catalytic factors.

This paper focuses on the synergistic interactions between coal and biomass in the blends. Thermogravemetric analysis (TGA) was conducted to understand the catalytic effects of minerals (AAEMs) from biomass and the non-catalytic effects of volatile matters on the co-processing of biomass with coal. A novel indicator was therefore proposed to evaluate the extent of synergistic interactions as well as to quantify the contribution of catalytic and non-catalytic effects to these interactions.

2.0 Experimental

2.1 Coal and Biomass Samples

One coal and two types of biomass were used in this research. The coal, Yunnan (YC), was obtained from Fuyuan town (Yunnan Province, China), which is mainly used for industrial process heating especially in wine-making industry. The biomass samples, Oat Straw (OS) and Rice Husk (RH), were chosen to represent agricultural waste and agro-industrial residue respectively due to their abundance globally.

2.1.1 Sample Preparation

The samples were prepared following standard procedures described elsewhere (BS EN 14780 and ISO 13909) [16, 17]. All the samples were initially reduced to a size smaller than 500 μm using a cutting mill (Retsch SM 2000, Germany), and further milled to be smaller than 106 μm using a Retsch SM 200 mill. Each biomass was blended with the coal in three mass fractions, i.e., 10, 30 and 50 wt%.

2.2 Proximate, Ultimate and Heating Value Analyses

Proximate analysis was performed using the thermo-gravimetric analyser (TGA) (STA 449 F3 Netzsch, Germany) while ultimate analysis of the samples was conducted using a PE 2400 Series II CHNS/O Analyzer (PerkinElmer, USA). In a TGA test, approximately 5 –10 mg of the sample was placed in an alumina crucible following a testing procedure described elsewhere [18, 19] . For ultimate analysis, approximately 1.5 mg of sample was placed in a platinum foil pan. The higher heating value (HHV) of a sample was measured using an IKA Calorimeter C200 (IKA, USA), which utilized approximately 1.0 g of the sample. All experiments were repeated at least three times with the average value used as the final value.

2.3 Mineral Composition of Fuel

Mineral composition of the unblended fuels was determined by using an X-ray Fluorescence (XRF) spectrometer, the procedure adopted is described elsewhere [20].

2.4 Thermal Analysis

Combustion characteristics of individual fuels and their blends were measured following a non-isothermal method, which was amended from elsewhere [21, 22]. In the test, the sample was heated in air (80 vol% Nitrogen and 20 vol% Oxygen) from 50 to 900 °C at a heating rate of 20 °C min^{-1} and a gas flow rate of 50 ml min^{-1}. Characterisation of pyrolysis was also conducted using the same technique under pure nitrogen atmosphere (>99.9%). All experiments were repeated at least three times to ensure repeatability and accuracy.

The initiation temperature (IT) is the temperature at which 0.3 wt% mass loss rate of the sample was achieved after the release of moisture, which is normally used as an indication of the start of fuel decomposition. In fuel characterisation, the peak temperature (PT) is considered inversely proportional to the reactivity/combustibility of the fuel, which was determined as the temperature where the weight loss ($\frac{dw}{dt}$) of the sample reached its maximum. The burnout temperature (BT) represents the end temperature of the burning process, which was determined as the temperature when the rate of burnout (mass loss rate) decreased to less than 1 wt% min^{-1} on weight basis. The ignition temperature at which the fuel burns spontaneously without external heat source was also obtained based on the method adopted by many others [23].

2.4 Performance Indices

The ignition (Z_i) and combustion (S) index of the fuel and their blends were calculated based on the Equations (1) and (2) [23].

$$Z_i = \frac{\left(\frac{dw}{dt}\right)_{max}}{t_i t_{max}} \times 10^2 \quad (1)$$

$$S = \frac{\left(\frac{dw}{dt}\right)_{max}\left(\frac{dw}{dt}\right)_{av}}{T_i{}^2 T_b} \times 10^6 \quad (2)$$

Where:

$(\frac{dw}{dt})_{max}$ is the maximum rate of mass loss (% min^{-1});

$(\frac{dw}{dt})_{av}$ is the average rate of mass loss (% min^{-1});

t_{max} is the time at which the peak mass loss rate is attained (min);

t_i is the ignition time (min);

T_i is the ignition temperature (°C);

T_b is the burnout time (min).

2.5 Low Temperature Ashing

The low temperature ashing of biomass samples was performed using a PR300 Plasma Cleaner (Yamato Scientific, Japan). This device was used to burn off the carbonaceous components of the sample at low temperatures (less than 150^{o}C) under which the presence of minerals in biomass remains unchanged. The plasma was generated at a power of 200 W. Approximately 0.5 g of a sample was loaded on a glass crucible, placed in the ashing chamber, and exposed to pure oxygen at a flow rate of 100 ml min^{-1} to ensure minimal reflection of the plasma beam. Each ashing experiment required 30 hours for the complete burning of carbonaceous materials.

133 **2.6 Catalytic Effect of Biomass-Derived Ash**

134 To understand the influence of minerals from biomass on combustion process, low
135 temperature ash of each biomass was blended with Yunnan coal at a blending ratio
136 equivalent to 30 wt% biomass in blend. The intrinsic reactivity of these blends was carried
137 out.

138 **3.0 Results and Discussion**

139 **3.1 Proximate, Ultimate and Heating Value Analyses**

140 Results of ultimate and proximate analyses of the samples are shown in Table 1. The coal
141 sample showed the highest heating value, which suggests that the blending of coal with
142 biomass of lower energy content would normally lead to the reduction in combustion
143 temperature in existing utility boilers [24]. The Rice Husk had very similar sulphur content
144 (0.4 wt%) but significantly different ash content (21.2 wt%) compared with Oat Straw. Oat
145 Straw had the highest volatile matter (72.1 wt%).

146 **Table 1 – Ultimate and proximate analysis of samples**

	Rice Husk (RH)	Oat Straw (OS)	Yunnan Coal (YC)
Ultimate analysis (wt%, daf)			
Carbon	50.1	47.5	86.2
Hydrogen	7.4	6.8	5.1
Nitrogen	1.7	2.3	1.0
Sulphur	0.4	0.3	1.1
Oxygen (by difference)	40.4	43.2	6.6
LHV (MJ Kg^{-1})	19.6	17.6	33.5
Proximate analysis (wt%)			
Moisture	4.1	4.0	4.5

Volatile Matter (VM)	62.8	72.1	27.2
Fixed Carbon (FC)	11.9	17.4	57.3
Ash	21.2	6.5	11

Mineral composition of the samples is illustrated in ***Table 2***. The biomass samples had relatively low sulphur content, which helps mitigate the environmental impacts associated with the emission of sulphur oxides (SOx). Normally, the reaction of AAEMs originating from biomass with SOx could lead to the formation of sulphates which contributes to the capture of gas phase sulphur [25]. This is an important advantage of co-firing of coal with biomass, especially for coals of relatively high sulphur content, such as Yunnan coal.

Normally, alkali metals, such as potassium (K) and sodium (Na), and alkali earth metals (AAEMs), such as calcium (Ca) and magnesium (Mg), are known to have catalytic effect to the thermal decomposition of fuels [26]. Table 2 shows the elemental composition of low temperature ash derived from all samples studied. The OS, RH and YC had high AAEM of 61.6 wt%, 26.9 wt% and 25.5 wt% respectively. The high potassium content in the OS and RH and the high content of calcium in YC suggest their likelihood of enhancing combustion performance. Another interesting element that has been known to aid the release and activation of these catalytic AAEMs is Cl, which was very high in OS (24.2 wt%) [27]. This further supports the high potential in catalytic effect when OS is blended with YC. However, it was reported that the enhancement could be weakened by the reaction between the catalytic minerals, such as AAEMs, with silicates and/or alumina-silicates [28]. This means that the high Si content in RH (45%) and YC (26.2%) might hinder the catalytic effects of AAEMs. Nonetheless, the potential of enhanced catalytic effects of the YC and OS fuel blends remained positive due to the high AAEM-to-Si ratio. However, the high Si content of

RH might still hinder such improvements for YC and RH blends. In addition, it must be noted that agglomeration and clinkering may arise when a biomass fuel has high Na and K contents as observed in OS due to the formation of sticky low temperature melts of silicate eutectics [29].

Table 2 – Mineral composition of the samples (wt%)

Elements	Rice Husk (RH)	Oat Straw (OS)	Yunnan Coal (YC)
Fe	5.4	1.5	21.0
K	20.2	47.4	4.8
Si	45.0	8.8	26.2
P	15.8	3.1	-
Ca	4.6	14.2	20.7
S	-	-	20.5
Cl	5.0	24.2	-
Na	0.6	-	-
Al	0.3	0.3	1.4
Ti		-	3.8
Mg	1.5	-	-
Mn	1.6	-	-
Br		0.4	1.6

3.2 Intrinsic Reactivity

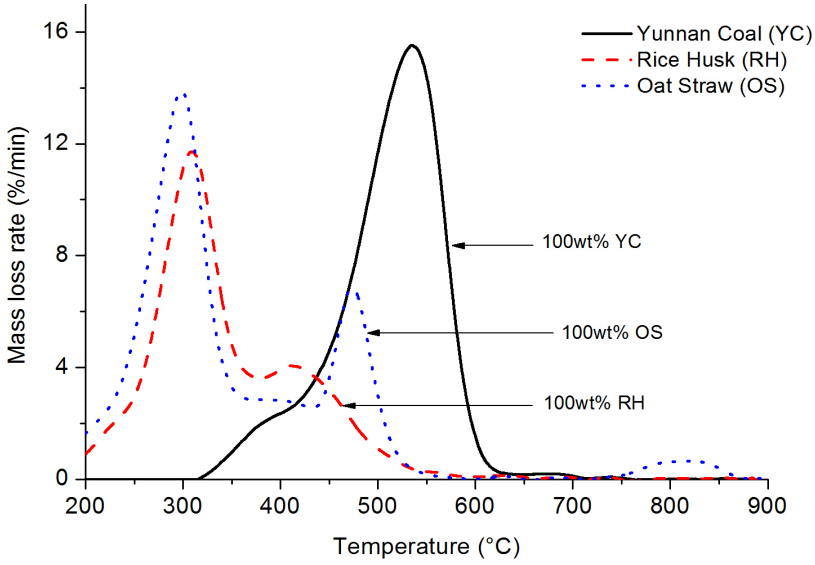
3.2.1 Reactivity of Individual Fuels

The thermal decomposition curves of OS, RH and YC is shown in Figure 1 with key features extracted and summarized in Table 3. It is evident that YC had one major decomposition stage with a strong peak for char burnout while the biomass samples were featured with two main mass loss stages representing the decomposition of organic compounds in the fuel. For the biomass samples, the first stage in the range of 144 – 420 °C represented the

179 decomposition of hemicellulose, cellulose and partial decomposition of lignin [30]. The
180 second stage represented mainly char burnout as well as the decomposition of lignin and
181 fell in the range of 378 - 518°C.

182 It is showed that the degradation of OS and RH began at 144 and 166 °C respectively. Both
183 samples exhibited an initial slow mass loss from initiation till about 255 °C due to the slow
184 decomposition of lignin content. When temperature was raised above this point, the mass
185 loss rate increased rapidly and reached the peak temperatures of 299 and 309 °C, for OS and
186 RH respectively, attributed mainly to the decomposition of hemicellulose and cellulose.

187 As shown in the DTG curve of RH, the mass loss rate increased immediately after the first
188 reaction zone, while for OS, a flat mass loss region was observed before the second reaction
189 zone which showed a sharp increase in DTG rate. This suggests a lower reactivity of the OS
190 char particles and higher mass loss rate at higher temperatures.



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192 **Figure 1: DTG curves oat straw, rice husk and Yunnan coal**

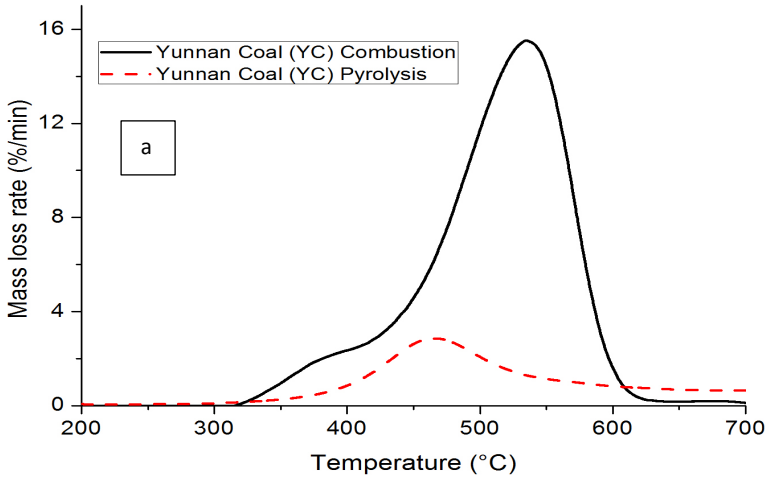
193 The difference in the 2nd stage reactivity could be linked to the catalytic influence of the
194 mineral contents of OS. It was found [31] that catalytic effect of potassium contributed to
195 the clear distinction of the two devolatililization peaks and shifted the first peak
196 temperature to a lower temperature. In this study, it is believed that the high potassium
197 content in OS (as shown in ***Table 2***) enhanced the complete decomposition of lighter
198 volatile species and the release of more volatiles, which subsequently led to the formation
199 of more porous char with higher overall burnout reactivity.

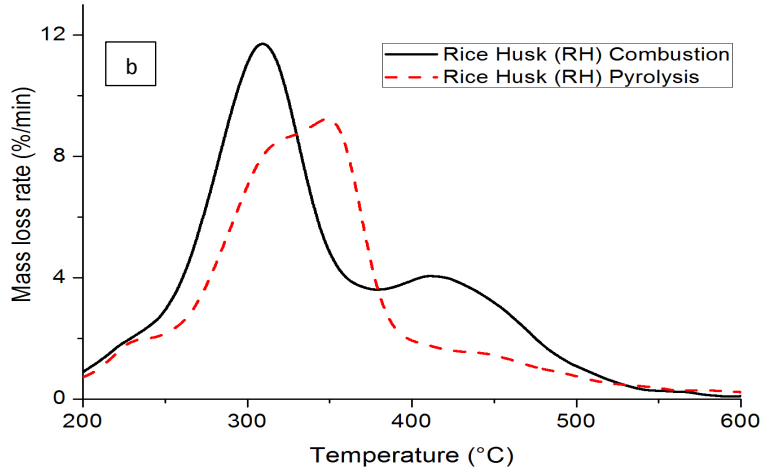
200 YC decomposed at a temperature range between 329 and 605 °C with its only peak
201 appearing at 535 °C and exhibited a more synchronized mechanism of thermal
202 decomposition. In this study, the comparison of the combustion and pyrolysis profiles
203 showed that 83 wt% (RH) and 97 wt% (OS) of total volatiles in biomass samples were burnt
204 during the first reaction stage as an indication of its homogenous (gas-phase) ignition
205 mechanism. This is relatively unclear for YC due to its singular peak as its degradation curve
206 could be indicative of the simultaneous combustion of both volatiles and char over a wider
207 temperature range.

208 From the pyrolysis profiles shown in Figure 2, it is evident that the devolatilization of YC
209 occurred at higher temperatures (355 – 571 °C) compared with OS (146-489 °C) and RH (168
210 – 486 °C). The low pyrolysis rate and the high temperature required for YC could signify an
211 increase in resistivity of volatile release in the organic structure. The pyrolysis mass loss rate
212 of the biomass samples remained close to that of the combustion profile, which can be
213 explained by their high combustibility and reactivity of the volatile matter [32].

214 The decreasing peak temperatures of the biomass samples during combustion as shown in
215 Figures 2b-c suggested the enhanced reactivity during combustion compared with pyrolysis.

However this reduction in the peak temperature is not obvious in Figure 2a because of its low volatile content of YC.





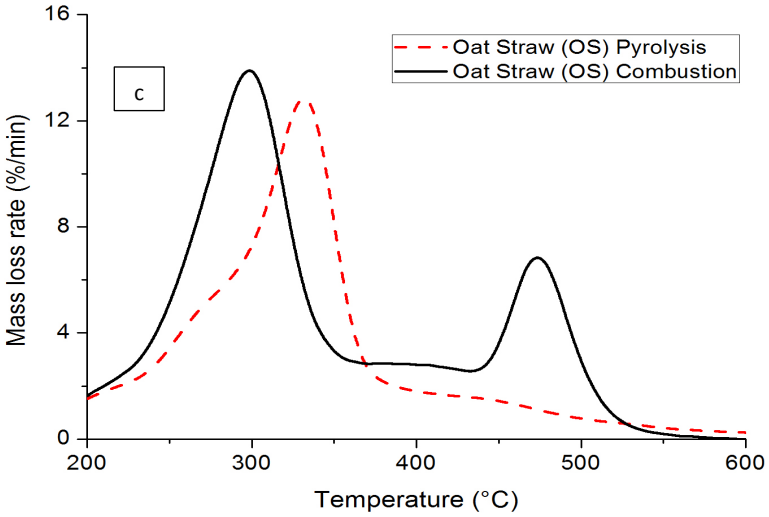


Figure 2: Pyrolysis and combustion profiles of (a) Yunnan coal, (b) Rice Husk, and, (c) Oat Straw

Normally, higher oxygen content of the biomass samples is an indicator of their high reactivity [33]. Among these three fuels studied, the most reactive fuel is OS with oxygen content of 43.2 wt% as shown in ***Table 1***. The high oxygen content and high oxygen/carbon ratio led to the formation of char with higher reactivity [19]. Likewise, the high volatile and low fixed carbon content of biomass resulted in the yield of a small amount of highly porous char, which subsequently contributed to the high overall reactivity of the fuel.

For RH, OS and YC, the ratio of volatile matter to fixed carbon, another indicator of combustion reactivity, is 5.3, 4.2 and 0.48 respectively. This ratio is an indicator of the fuel's volatility, a ratio >4 suggests homogenous oxidation of the volatiles while a ratio smaller than 1 indicates heterogeneous gas-solid reactions [22]. Therefore, the combustion of RH and OS was predominantly the gaseous phase oxidation of its volatiles while for YC it was the simultaneous oxidation of both volatiles and char.

Table 3 – Combustion characteristics of Rice husk, Yunnan coal and their blends

Property		**RH**	**50 wt%YC+ 50 wt%RH**	**70 wt%YC+ 30 wt% RH**	**90 wt%YC+ 10 wt%RH**	**YC**
Initiation Temperature (°C)		166	192	222	222	329
Zone	Temperature range (°C)	166 - 370	192 - 369	222 - 356	286 - 608	329 - 605
	Peak Temperature (°C)	309	308	313	532	535

	Total mass loss (wt%)	49.3	24.4	13.1	85	88
	Average mass loss rate (wt% min^{-1})	4.8	2.8	1.9	5.3	6.4
	Maximum mass loss rate (wt% min^{-1})	11.7	4.9	3.2	13.4	15.5
Second Reaction Zone	Temperature range (°C)	378 - 503	378 - 601	364 - 601		
	Peak Temperature (°C)	411	519	531		
	Total mass loss (wt%)	18.8	53	66.5		
	Average mass loss rate (wt% min^{-1})	3	4.8	5.6		
	Maximum mass loss rate (wt% min^{-1})	4.1	7.8	11.1		
Burnout Temperature (°C)		503	601	601	608	605
Residual Weight at burnout (wt%)		26.7	18.4	16.5	13.1	11.9

236 **Table 4 – Combustion characteristics of Oat straw, Yunnan coal and their blends**

		OS	**50 wt%YC+ 50 wt%OS**	**70 wt%YC+ 30 wt%OS**	**90 wt%YC+ 10 wt%OS**	**YC**
Initiation Temperature (°C)		144	162	201	244	329
First Reaction Zone	Temperature range (°C)	144 - 420	162 - 346	201 - 345	244 - 334	329 - 605
	Peak Temperature (°C)	299	299	301	305	535
	Total mass loss (wt%)	65	27.4	13.1	6	88
	Average mass loss rate	4.7	3	1.8	1.3	6.4

	(wt% min^{-1})					
	Maximum mass loss rate (wt% min^{-1})	13.9	7.2	2.9	1.8	15.5
Second Reaction Zone	Temperature range (°C)	432 - 518	349 - 564	353 - 583	339 - 591	
	Peak Temperature (°C)	474	456	483	515	
	Total mass loss (wt%)	17.6	58.1	68.7	79.9	
	Average mass loss rate (wt% min^{-1})	4.1	5.4	5.9	6.3	
	Maximum mass loss rate (wt% min^{-1})	6.8	8.7	11.1	13.9	
Burnout Temperature (°C)		518	564	583	591	605
Residual Weight at burnout (wt%)		11.8	11.2	14.2	10.5	11.9

3.2.2 Combustion Characteristics of the Blends

Combustion characteristics of the YC/RH blends are presented in Figure 3 and Table 3.

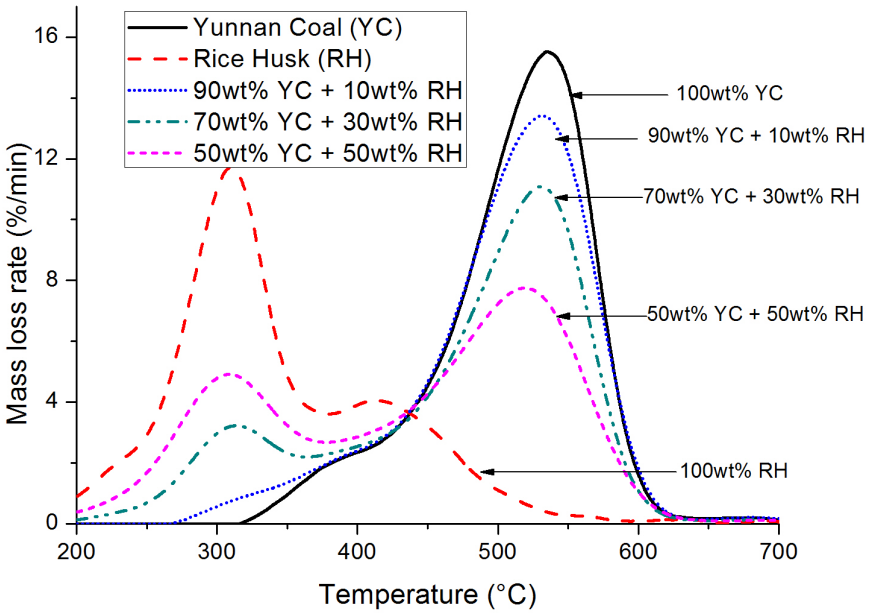


Figure 3: DTG curve of Yunnan coal/Rice husk blends

241 Generally speaking, the blends featured two peaks. However, the first peak was not fully
242 developed for the blend with 10 wt% RH. As previously described by others [34], the first
243 peak temperature of the blend was similar to the first peak temperature of the biomass, i.e.
244 rice husk (309°C), while the second peak temperature and burnout temperature were
245 similar to the peak (535 °C) and burnout temperatures (605 °C) of the Yunnan Coal with
246 minimal deviations. The maximum rate of degradation of the first peak increased with the
247 increase in the RH, while for the second stage, the rate reduced with the increase in RH. This
248 occurrence was due to the combustion of biomass volatiles prevailing in the first reaction
249 zone, while the coal char burning dominated the second reaction zone [35]. It was also
250 observed that the residual weight at burnout temperature increased with the increase in RH
251 due to the high ash content, which might present extra barrier for heat and mass transfer.

252 Similar to YC/RH blends, the YC/OS blends, as shown in Figure 4 and Table 2, had two distinct
253 peaks. However, there was a noticeable decrease in the peak temperature with the increase
254 in oat straw. Since the peak and burnout temperature of OS were lower than those of YC.
255 This reduction in the 2^{nd} peak temperature indicated improved combustion reactivity as a
256 result of synergistic interactions between coal and biomass as shown in in Figure 4b. To
257 further prove the presence of synergy, the experimental results were compared with the
258 theoretical values calculated using the weighted sum of the pure feedstock [36]. The result
259 obtained for the oat straw blend showed distinct shift of the 2^{nd} reaction stage towards
260 lower temperatures compared with theoretical values. However, the theoretical and
261 experimental values of rice husk blends were similar when the blending ratio was below 30
262 wt%, while for 50 wt%, the shift towards lower temperatures did become noticeable.

263 Synergistic interactions can be associated with catalytic and/or non-catalytic mechanisms.
264 The latter involves the formation of free radicals and hydrogen transfer from biomass to coal
265 while the former is based on catalytic effect of alkali and alkali earth metals present in
266 biomass or coal [37]. Consequently, the synergy observed in YC/OS blends could be partially
267 attributed to the catalytic effect of mineral matters in oat straw due to its high alkali metal
268 content, a common occurrence in herbaceous biomass [14, 31, 38]. This could be
269 supplemented by the non-catalytic improvement caused by the interactions of biomass
270 volatiles with coal char as well as the differences in morphology [39]. The release of volatiles
271 from biomass could result in the formation of free radicals during thermal reaction to
272 promote the breakdown of the dense and heat-resistive coal structural components
273 (polycyclic aromatic hydrocarbon bonded by aromatic rings) at lower temperatures [40, 41].
274 Therefore, the higher hydrogen-carbon mole ratio (H/C) of biomass in blends contributed to
275 the improvements observed in coal decomposition [42, 43]. The existence of synergy was
276 quite contentious, as synergistic interaction is not observed in all coal/biomass blends in the
277 first place. However synergistic enhancement was observed in coal and biomass fuel blends
278 even after the demineralisation of its biomass, eliminating catalytic effect of ash as the only
279 cause of synergy [31].

280 At low blending ratios, such as 10 wt% to 30 wt%, peak temperature of each reaction zone
281 was dominated by the fuel fraction with the higher mass loss. This mechanism of
282 decomposition is an indication of independent decomposition of both fuels, which suggests
283 the additive behaviours instead of synergistic interactions between YC and RH, which is
284 similar to what was reported by others [44]. However, slight reduction in the peak
285 temperature of the second reaction zone was observed in the 50 wt% RH blend, which

suggested some interactions between YC and RH. This can only be attributed to the increase in volatiles available from 50% RH and its impacts on non-catalytic synergy mechanism.

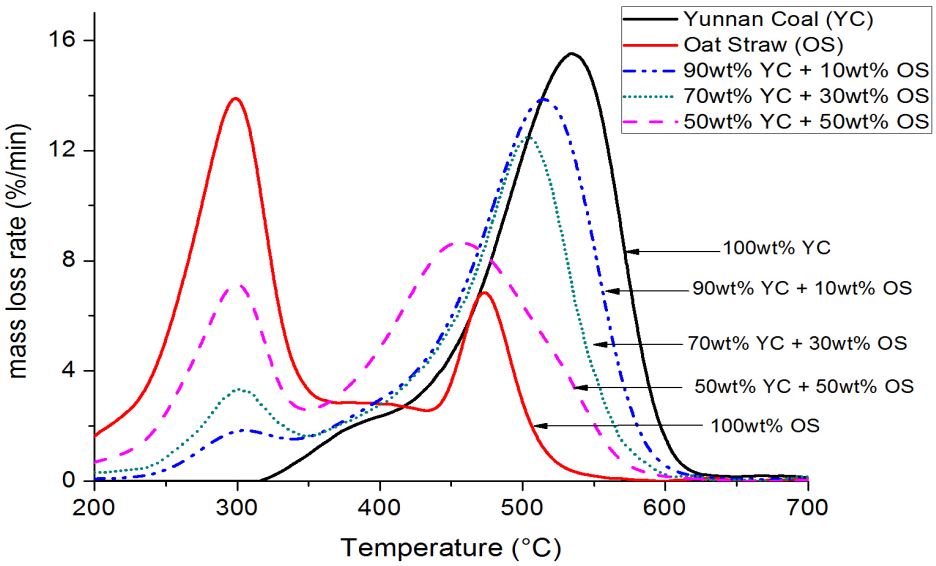


Figure 4: DTG curve of Yunnan coal /oat straw blends

Taking into account the findings for both biomass blends, it can be concluded that the presence of synergy, its extent and the mechanism are dependent on biomass types, blending ratio and properties.

3.3 Ignition Temperature

The ignition temperatures (T_i) of the fuels are shown in Table 5, which were determined following the method described elsewhere [8]. The ease of ignition of the biomass samples is a consequence of their high volatile content (>80 wt%) as shown in Table 1. The ignition temperature of YC was almost 200 °C higher than those of the biomass samples, which might be due to the hetero-homogeneous ignition mode of this coal [11].

However the main mass loss of the blends was characterised by the 2nd peak temperature, which more accurately depicted the effect of biomass addition on the oxidation of coal. Hence, a "trigger temperature" was also extracted from the TGA profiles for the 2nd reaction stage to characterise the ignition of the char oxidation, which is the temperature corresponding to the intersection of the tangent line of the initial mass loss curve (before the sharp drop in mass) and the tangent line that is drawn at the intersection of the vertical line through the 2nd Peak temperature and the mass loss curve [23].

The ignition points of YC/RH and YC/OS blends were slightly higher (<20 °C) than the ignition temperature of the OS (256 °C) and RH (266 °C) in the blend. This suggests weak interactions between fuels in the blends. The 10 wt% RH blend remained close to the ignition temperature of YC due to the immature first peak as seen in Figure 3a. However, the trigger temperatures reduced significantly compared with that of YC (459 °C). The changes in trigger temperature with blending ratio are shown in Figure 5 with the dotted lines representing predictions based on additive behaviours. The blends exhibited a slow drop between 10 and 30 wt%, followed by a sharp drop in this temperature between the 30 and 50 wt%. The 50 wt% OS blends exhibited the largest temperature decrease. These changes in ignition parameter are the result of interactions between individual fuels in the blends.

Table 5 – Ignition temperature of individual fuels and their blends

Sample	Main Ignition Temperature (°C)	Char Trigger Temperature (°C)
100%RH	266	
90 wt% YC+10 wt% RH	451	451
70wt% YC+30 wt% RH	272	438
50 wt% YC+50 wt% RH	268	386

100%OS	256	
90 wt% YC+10 wt% OS	271	439
70 wt% YC+30 wt% OS	256	403
50 wt% YC +50 wt% OS	259	301
100 % YC	459	

The char trigger temperatures were also compared with theoretical values calculated from ignition temperatures of the parent fuels assuming that additive property applies. These calculated values are presented as the dashed lines in Figure 5. For YC/RH blends, the actual trigger temperature was higher than predicted values. For YC/OS blends, the change of trigger temperature of 10-30 wt% blends were relatively linear while for the 50 wt% blend, it exhibited some improvements and lead to a lower temperature.

The changes in the ignition and char trigger temperatures were believed to be the consequence of the interactions between the organic elements of the different fuels in the blend [8, 23]. This non-catalytic synergy might be linked to the increase in volatile matter content of the blends due to biomass addition.

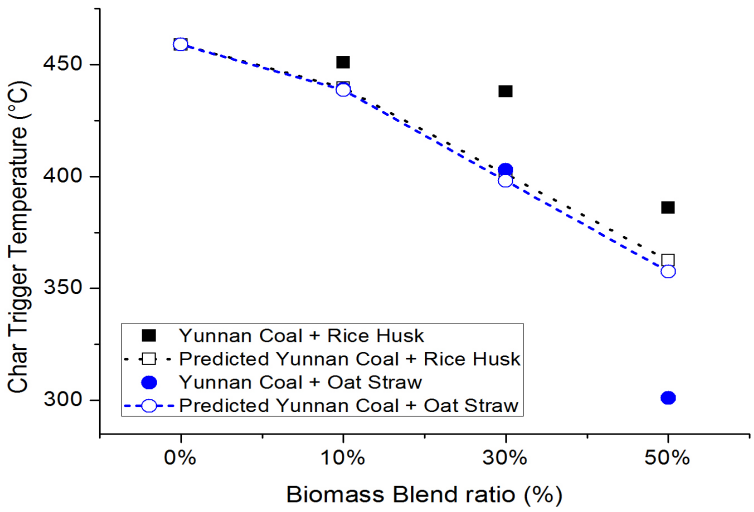


Figure 5: Evaluating additive trend in second reaction zone trigger temperature

To quantify the influence of blending on ignition and combustion performance, the ignition (Z_i) and combustion (S) index of individual fuels and their blends were calculated using Equations (1) and (2) and are presented in Table 6. As shown in Table 6, OS showed the best ignition property while YC was the most difficult to ignite. The ignition index increased with the increase in biomass percentage for all oat straw blends and the 30 wt% RH blend, this is in line with the decrease in ignition temperature and ignition time. This suggests that the ignition properties of Yunnan coal were improved by blending with oat straw or rice husk at certain blending ratios due to the interaction between the fuels. However, insignificant improvement in ignition index was observed for 10 wt% and 50 wt% RH blends.

As can be seen in Equation (2), the combustion index was dependent on peak mass loss rate, peak and Ignition time; hence for the 10 wt% RH blend, it had similar ignition and peak time with YC. However, the peak mass loss rate was reduced. Similarly, the reduction in the peak mass loss rate of the 2nd reaction zone of the 50 wt% RH blend hindered the increase in the ignition index. In comparison to the OS blend, this trend for RH blends could be associated with the high ash content of RH, which reduced the amount of organic matter available for interaction with YC. It can be seen that among the blends, the 10 wt% OS blend had the best ignition index while the 10 wt% RH blend had the worst. This is consistent with what was found for coal and tobacco residues blends, a nearly linear increase in ignition index with increase in biomass due to the high volatile content of the biomass [53].

Table 6 – Performance Parameters of Individual fuels and their blends

	RH	OS	YC	90% YC+10 wt% RH	70% YC+30 wt% RH	50 wt% YC+ 50 wt% RH	90% YC+10 wt% OS	70% YC+30 wt% OS	50 wt% YC+ 50 wt% OS
Zi (%/min^3)	8.4	10.9	3.1	2.8	4.2	3.0	5.4	5.0	4.1
S	1.4	1.8	0.8	0.6	1.1	0.7	1.6	1.2	1.0

$(\%^2/°C^3min^2)$									

The combustion index also suggested that OS was the most reactive. Improvement in combustion performance was observed for the 30 wt% RH and all YC/OS blends. The reduction in combustion index observed in the 10 wt% RH blend can be explained by Equation (2). As mentioned earlier, the 10 wt% RH blend was featured with a single reaction stage at 286 – 608 °C. This indicates a longer residence time required for attaining a desired burnout in comparison with Yunnan coal which burnt out completely between 329 – 605 °C. This suggests the absence of improvement in the combustion performance for 10 wt% RH in comparison with Yunnan Coal. The reductions in the maximum (7.8 wt% min^{-1}) and average mass loss rate (3.8 wt% min^{-1}) of the 50 wt% RH blend due to its double peaks could be interpreted as a reduction in the overall fuel reactivity if this combustion index was used for comparison. This is explained by the high value of the mass loss rates for YC with a peak of 15.5 wt% min^{-1} and a mean mass loss of 6.4 wt% min^{-1}.

Normally, the combustibility of any fuel is inversely proportional to the maximum decomposition rate temperature [45]. Similarly, the decrease in the 2^{nd} peak temperature of the OS blends illustrated an improvement in combustion performance. The enhancement in the burnout of the fuels was represented by the small decrease in the burnout temperatures with the maximum decrease of 6.7% for the 50 wt% OS blend, which is consistent with what was reported by many others [34, 46].

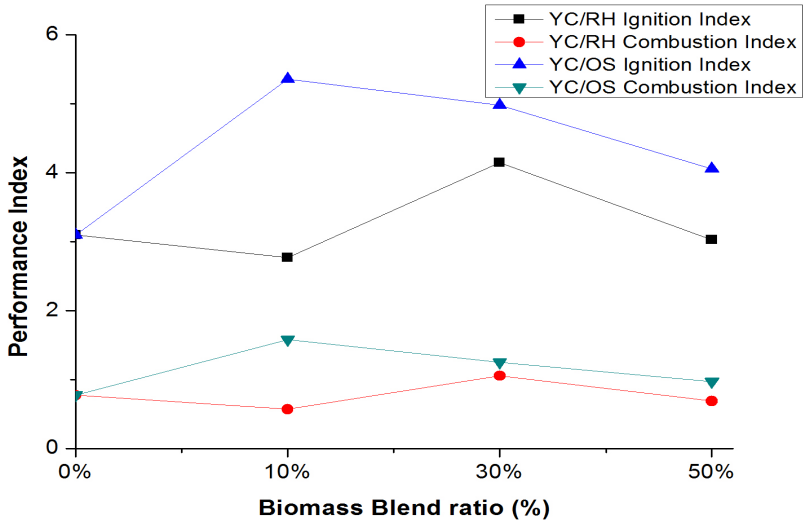


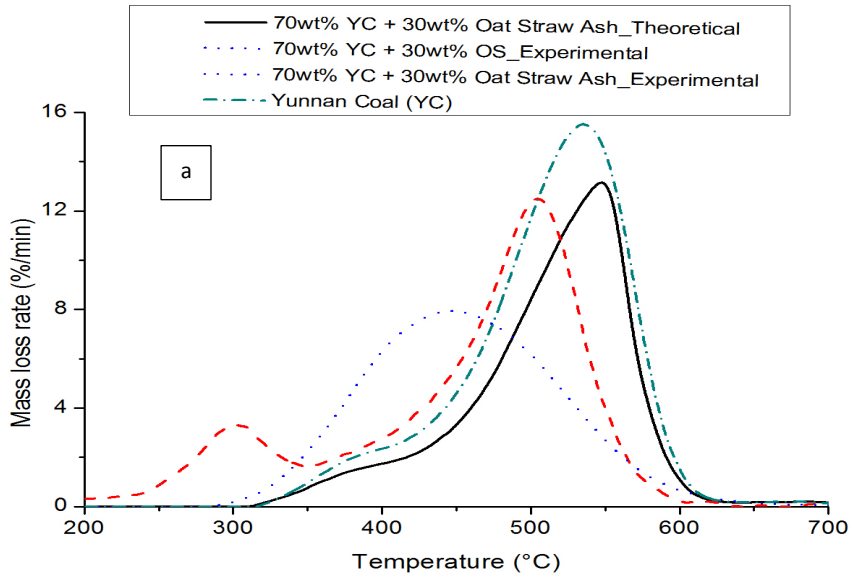
Figure 6: Changes in performance index of fuel blends

Although the combustion and ignition indices (as shown in Figure 6) can be used to show the interactions between individual fuels during co-processing, the accuracy of these indices may be compromised due to the split of the weight loss into two reaction zones as the average and maximum weight loss reduces more rapidly with the increase in blending ratio compared with time and temperature. Therefore, there is a need to develop a novel index to take into account the two reaction zones or the reaction zone exhibiting more synergistic characteristics, thereby improve its reliability and ensure the results are representative of the entire combustion process.

3.4 Catalytic Effect of Biomass Minerals

In this study, the influence of the minerals from biomass on the co-combustion characteristics of the blends was studied. Low temperature ash of Oat Straw and Rice husk were blended with YC to compare with the curve obtained for 30 wt% biomass and 70 wt% YC, as shown in Figure 7 and Table 7. The 70 wt% YC and 30 wt% biomass was chosen as a reference due to the improvement in ignition and combustion index were noticed in the performance index for both YC/OS and YC/RH blends (as illustrated in Figure 6).

The results clearly showed changes in the characteristics of the 30 wt% OS ash blend which led to a lower ignition temperature of 403 °C, a lower peak temperature of 486 °C and a lower burnout temperature of 575 °C compared with those of 100% YC. The PT and BT vary significantly from the additive data.



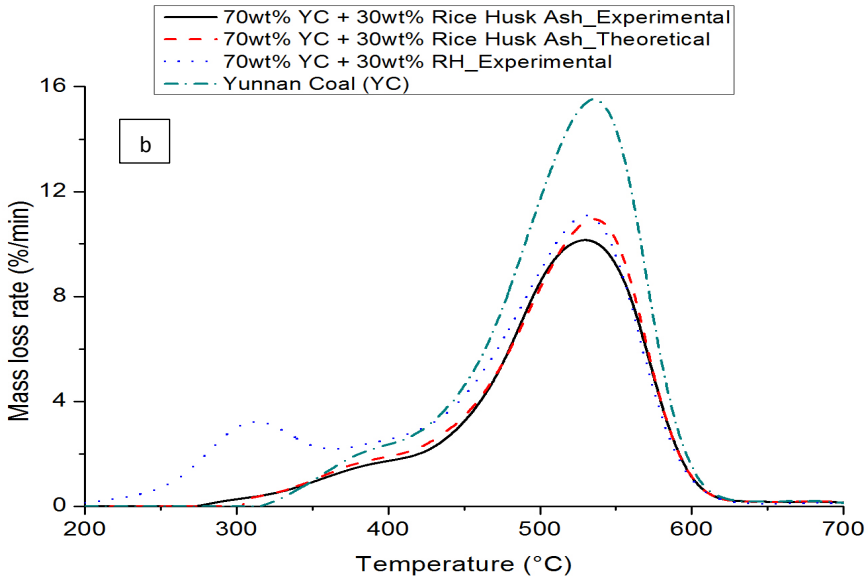


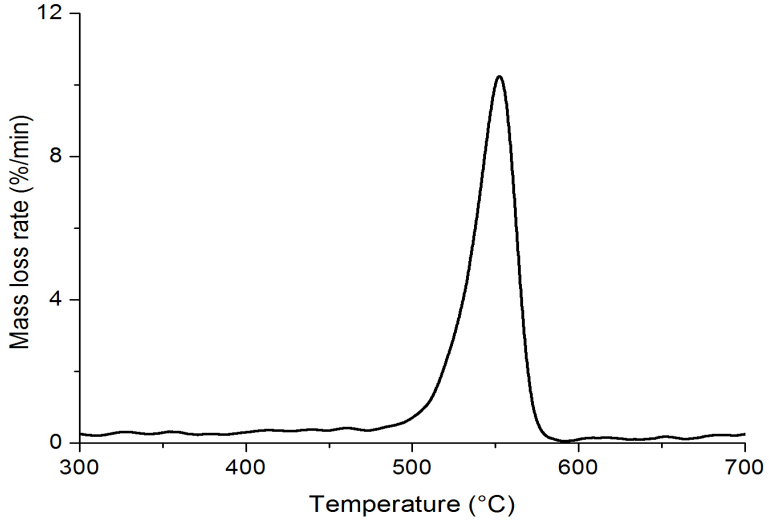
Figure 7: DTG curves of experimental and theoretical data of 100% YC and (a) 30 wt% Oat Straw ash & 30 wt% Oat Straw; (b) 30 wt% Rice Husk ash & 30 wt% Rice Husk

393 The variations in the ignition, peak and burnout temperatures could be explained to some
394 extent by the catalytic effect of the AAEMs originated from biomass such as Oat Straw. The
395 catalytic effect of AAEMs was found to be in order of Na > K > Ca [47]. As shown in ***Table 2***
396 OS contained significant amount of AAEMs, which was greater than that of RH. The
397 investigation on the thermal behaviour of the low temperature ash derived from Oat Straw
398 (as illustrated in Figure 8) showed a mass loss of 17.6 wt% in a temperature range of 473-
399 573 °C, which peaked at 552 °C. This mass loss was attributed mainly to the release of
400 volatile AAEMs compounds at high temperatures such as K^+, KCl and or KOH. The initial
401 volatile inorganic release temperature (552 °C) is lower than the burnout temperature of OS
402 (518 °C), which suggests that AAEMs acted as catalyst for the burnout of OS. Even at a
403 temperature higher than 573°C, there was still significant amount of AAEMs remaining as
404 catalyst for YC char combustion (burnout temperature is 605 °C) as only 17.6 wt% mass loss
405 upon heating while the initial mass fraction of potassium for OS low temperature ash was
406 47.4 wt% (as shown in ***Table 2***). This is consistent with what was reported [15] that the
407 release of a small fraction (<20 wt%) of the organically bonded alkali metals occurred at
408 temperatures up to 800 °C. In this study, the high potassium and calcium content in OS
409 explains the reduction in the burnout temperature of 30 wt% Oat Straw ash blend from 605
410 to 575 °C. This reduction in burnout temperature was also evident in all the YC/OS blends.
411 The high AAEMs content in both OS and RH contributed to the reduction in char burnout
412 temperature of the fuel blends.

413 **Table 7 – Combustion characteristics of YC blended with low temperature ash of biomass**

Sample	Ignition Temp (°C)	Peak Temp (°C)	Total degradation (wt%)	Average degradation (wt%/min)	Maximum degradation rate (wt%/min)	Burnout Temp (°C)

Yunnan Coal	459	535	88	6.4	15.5	605
70%YC + 30 wt% Rice Husk ash	454	529	61.7	4.2	10.1	601
70%YC + 30 wt% Oat Straw ash	403	486	64.2	5.2	10.0	575



414

415 **Figure 8: DTG of Oat Straw low Temperature ash**

416 The peak temperature and burnout temperature of the 30 wt% RH Ash blend was
417 comparable with that of 100 wt% YC. Likewise, the ignition temperature of the 30 wt% RH
418 ash blend was similar to that of 100 wt% YC. This confirmed the absence of catalytic
419 improvement when YC was blended with RH ash. Therefore, the synergistic interactions
420 observed for RH (reductions in trigger temperature as shown in Table 3) could not be
421 attributed to catalytic synergy for RH and are closely related to non-catalytic effects
422 primarily linked to high volatile content and subsequently high char porosity.

423 Nonetheless, results of the 30wt% oat straw and coal blend did not distinguish the effect of
424 volatiles and minerals although it proved the existence of strong synergy between the two
425 fuels. Therefore, ash derived from oat straw (equivalent to 2 wt% ash) was used to reveal

the influence of minerals originated from oat straw on co-firing. A PT of 528 °C and a BT of 588 °C were observed as shown in Figure 9, which were 7 °C and 17 °C lower than those of the coal respectively. This demonstrated a modest catalytic of the minerals in oat straw. As previously mentioned, the PT and BT were 483 °C and 583 °C respectively for the 30 wt% OS blend, it can therefore be concluded that for 30 wt% OS blend, the significant synergistic effect could be attributed to the non-catalytic synergy by the organic content of the oat straw and the catalytic activity of ash.

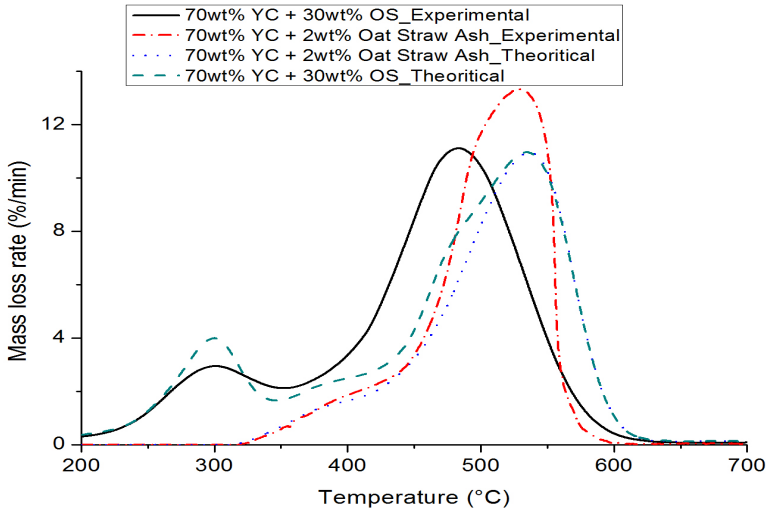


Figure 9: DTG of experimental and theoretical 30wt% oat straw and 2wt% oat straw ash blend

3.5 Synergy Indicator

In this study, it is clear that factors, such as biomass blending ratio, biomass ash properties, volatile content, contributed to strong synergistic interactions between coal and biomass. Each factor affects the synergy observed in the blends to some degree. To select proper biomass for co-processing with coal and to determine the proper blending ratio to enhance synergistic interaction and therefore improve overall combustion performance, there is a

need to develop a novel index, which can also be used to evaluate the different impacts of catalytic and non-catalytic effects.

Synergy index [48] proposed by others was solely a function of the reaction time to reach 95% conversion where larger magnitude of the index indicates greater degree of synergy. In this study, it is clear that the main synergistic improvement include the reduced 2nd peak and burnout temperatures, as shown in the line chart in Figure 10. These observations have been linked partially to the catalytic effects of biomass inorganic content as described in section 3.4 and secondarily, to the non-catalytic effects of biomass organics (high volatiles and char structure). Therefore, the three characteristic factors, i.e., peak temperature, burnout temperature and time to peak of the second reaction stage, which have direct influence on combustion performance, are used as the parameters for the novel synergy index.

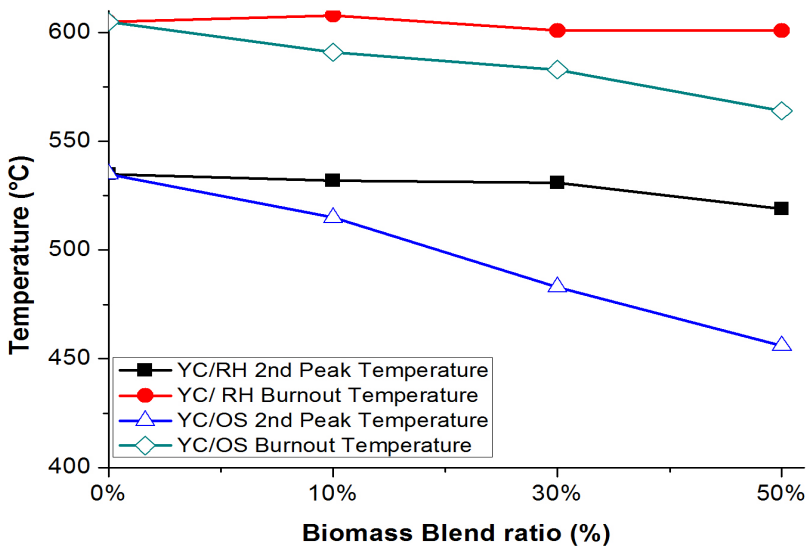


Figure 10: Improvements in peak and burnout temperatures with biomass blending

Consequently, the extent of synergistic interaction between the coal and biomass fuel can be quantified by the formulation of a synergy factor (SF) based on the peak and burnout

458 temperatures of the second reaction zone as well as the time taken. In this study, a novel
459 synergy factor was developed, which is expressed as Equations (3).

460 $$SF = \frac{SI_{blend}}{SI_{coal}} \quad (3)$$

461 Where SI is a synergy indicator ($°C^{-3}\ min^{-1/2}$) and can be calculated using Equation (4):

462 $$SI = \frac{1}{t_{p-s}^{0.5} T_b^{\ 2} T_p} \times 10^6 \quad (4)$$

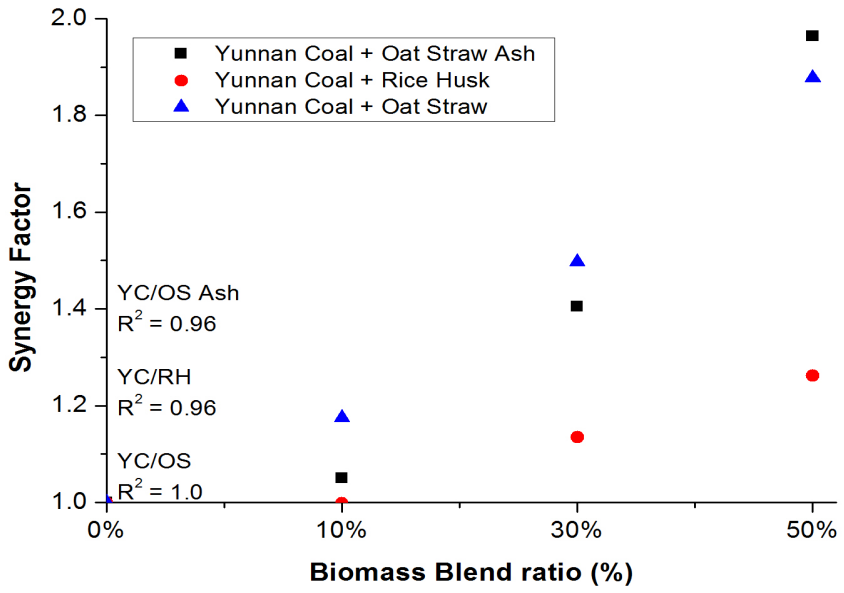
463 Where, t_{p-s} is the time difference between the start and peak of the second reaction zone
464 (min); T_p is the peak temperature (^oC); T_b is the burnout temperature (^oC).

465 Using this index, a comparison baseline was created using the result extracted from the
466 theoretical blends models to determine whether fuel blend establishes a more synergistic
467 effect (SF > 1.15) or additive behaviour (0.8 ≤ SF ≤ 1.15). However, a value of SF ≤ 0.8
468 suggests deteriorated combustion performance after blending. The synergy factors for the
469 Yunnan coal and biomass blends discussed above are shown in Figure 11.

470 It can be seen that the synergy factor increased with the increase in blending ratio; however
471 the rate of increase with biomass blend ratio were different for different blends. For the 30
472 wt% biomass blends (as shown in Figure 6), the most significant synergistic effect occurred
473 for 70 wt% Yunnan coal + 30 wt% oat straw with a synergy factor of 1.50. The 70 wt%
474 Yunnan coal + 30 wt% rice husk blend showed additive behaviour and had an SF of 1.13. For
475 the 10 wt% biomass blends, the YC/RH blend exhibited additive behaviour, which was
476 mainly due to the insufficient amount of AAEMs to catalyse combustion process. Based on
477 these results, it can be concluded that for blends with 30 wt% of biomass, oat straw showed
478 more significantly enhanced reactivity than that of rice husk. The high SF of the 50% OS ash

479 blend was due to the existence of significant amount of catalytic species resulting in greater
480 enhancement in combustion.

481 In this study, assuming an additive behaviour, for 70% YC and 30 wt% OS , the SF is of a
482 value of 1.15. The SF of 70 wt% YC and 2 wt% OS ash was found to be 1.24, which suggests
483 that catalytic synergy resulted in a SF change by 0.09. The difference between the SF value
484 (S.F = 1.40) of 70% YC and 30 wt% OS and that of 70 wt% YC and 2 wt% OS ash (SF = 1.24)
485 could be attributed to volatile effect (non-catalytic synergy) and resulted in a SF change of
486 0.16. Likewise, the non-catalytic synergy detected in the 50wt% RH blend (SF = 1.26) could
487 be attributed to its volatile content, which affected reaction time, and characteristic
488 temperature at higher blend ratio, and resulted in an increase in SF by 0.11 due to non-
489 catalytic synergy.



490

491 **Figure 11: The Synergy indicator of Yunnan coal blends**

492 **Table 8 – Validation of Synergy Factors using Reported Data**

		Biomass blending ratio / Synergy Factor

	Biomass types	0%	10%	30%	50%
Australian Coal (AC) blends[49]	Gumwood (GW)	1.00	1.19	1.27	1.43
	Poplar (PP)	1.00	1.16	1.26	1.38
	Rosewood (RW)	1.00	1.18	1.34	1.57
Mengxi Coal (MC) blends[49]	Gumwood (GW)	1.00	1.18	1.35	1.41
	Poplar (PP)	1.00	1.26	1.39	1.38
	Rosewood (RW)	1.00	1.31	1.80	1.67
Australian Coal (AC) blends [50]	Oat Straw (OS)	1.00	1.11	1.36	
	Printed circuit board (PCB)	1.00	1.03	1.23	
	Rubber	1.00	0.95	1.02	
	Polystyrene (PS)	1.00	1.39	1.40	

Figure 11 shows the synergy factor as a function of the biomass content of the blend (regression function R^2 value ≥0.96). This is in line with past notions that the synergistic interaction that occurred in fuel blends is a function of the organic and inorganic content of the biomass, hence proportional to the portion of biomass introduced into the blend. Nonetheless, the extent of enhancement remained dependent on the constituents of the biomass sample used.

In order to verify this index, combustion data of Australian and Mengxi coal with biomass blends were collated from literature [49, 50], which are illustrated in Table 8. Based on the SF values, for all coal and biomass blends, significant synergistic interactions exist. As for Australian Coal and Rubber, due to the lack of AAEMs in Rubber, which led to lack of catalytic effects for combustion process, there was no noticeable synergistic effects (SF<1.15) being observed. However, for Australian Coal and PCB blends, at high blending ratio, catalytic effects became obvious, which led to significant synergistic interactions (SF>1.15) at higher blending ratios (30 wt%). These findings are consistent with what the

authors found in their study and therefore proved the validity of the synergy factor proposed in this study.

It was also reported [14] that the presence of an optimal improvement level for all fuel blends, beyond which synergy was independent of the biomass blending ratio, which suggests that the improvement of the blended fuels might plateau or even decrease after certain blending ratio [14]. This is also confirmed by the lower SF values for 50 wt% Poplar /MC and 50 % Rosewood/MC blends compared with the blends with only 30 wt% of biomass

4.0 Conclusions .

In this study, the co-firing of Yunnan coal with AAEMs-rich Oat Straw demonstrated strong synergistic interaction by the reductions in 2nd Peak and burnout temperatures. It is found that AAEMs from biomass acted as catalysts for coal combustion, enabling catalytic synergy, which is biomass dependent. Non-catalytic synergistic interactions were also evident at higher blending ratios, which was mainly attributed to the higher amount of volatiles.

A novel synergy factor (SF), which showed a good correlation coefficient, was proposed to quantify the synergistic effects and to distinguish catalytic effect from non-catalytic effect. This index can be used as a tool to predict synergistic effect during co-processing, which is of significant importance for optimizing blending ratio for existing boilers and for the design of new co-firing plant to avoid operation issues. This index also offers opportunities for selecting proper biomass for co-firing with poor quality coal to enhance the overall combustion performance.

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