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Experimental study on the ignition characteristics of cellulose, hemicellulose, lignin and their mixtures

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1 **Experimental Study on the Ignition Characteristics of Cellulose,**

2 **Hemicellulose, Lignin and Their Mixtures**

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6 **Abstract**

7 Ignition behaviour of biomass is an essential knowledge for plant design and process control
8 of biomass combustion. Understanding of ignition characteristics of its main chemical
9 components, i.e. cellulose, hemicellulose, lignin and their mixtures will allow the further
10 investigation of ignition behaviour of a wider range of biomass feedstock. This paper
11 experimentally investigates the influences of interactions among cellulose, hemicellulose and
12 lignin on the ignition behaviour of biomass by thermogravimetric analysis. Thermal properties
13 of an artificial biomass, consisting of a mixture of the three components will be studied and
14 compared to that of natural biomass in atmospheres of air and nitrogen in terms of their ignition
15 behaviour. The results showed that the identified ignition temperatures of cellulose,
16 hemicellulose and lignin are 410°C, 370°C and 405°C, respectively. It has been found that the
17 influence of their interactions on the ignition behaviour of mixtures is insignificant, indicating
18 that the ignition behaviour of various biomass feedstock could be predicted with high accuracy
19 if the mass fractions of cellulose, hemicellulose and lignin are known. While the deficiencies
20 of the determined mutual interactions would be further improved by the analytical results of
21 the activation energies of cellulose, hemicellulose, lignin, their mixtures as well as natural and
22 artificial biomass in air conditions.
23

24 **Keywords:** *biomass; ignition temperature; kinetics; cellulose; hemicellulose; lignin*

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26 **1. Introduction**

27 Biomass is considered to be a carbon-neutral and renewable fuel, which holds a great potential
28 to act as an alternative energy resource to address the challenging of global warming and
29 worldwide energy crisis ^[1]. Compared with other thermal conversion technologies, direct
30 combustion is known as the most efficient approach of biomass utilization for heat and power
31 generation ^[2]. However, firing biomass in modified fuel boilers or co-firing biomass with coal
32 in existing coal-fired boilers is a complicate process ^[3], an optimal operation of the biomass
33 combustion process requires essential knowledge of its combustion performances, especially
34 flame properties and ignition behaviour. Ignition plays a crucial role in combustion, having a
35 significant impact on the boiler operation, energy efficiency, as well as in the gas emissions ^[4].
36 Ignition temperature and ignition delay time are known as two important operational indicators
37 to initialise combustion processes ^[5]. Most ignition studies were conducted to control and
38 minimise the self-ignition risks during transport, handling and processing biomass materials
39 ^[6], but ignition mechanism with regard to improvement of combustion performances are rarely
40 reported.

41 Previous studies have attempted to investigate the ignition behaviour of biomass with the aim
42 of improving and making the biomass co-firing performance comparable with that of coal.
43 Rianza et al. ^[7] reported that ignition behaviour of coal could be improved by adding biomass
44 in an air or oxy-firing atmosphere, especially remarkable for high rank coals. Shan et al. ^[8]
45 investigated the ignition and combustion of single biomass pellets in a vertical heating tube
46 furnace, and identified two possible ignition behaviours: homogeneous ignition of volatile and
47 heterogeneous ignition on the biomass particles' surface. More recently, Li et al. ^[3] conducted
48 ignition tests of biomass particles by experimentally detecting the change of luminance inside
49 of a down-fire reactor before and after biomass injection, and results revealed that there is a

50 significant effect of particle size on the ignition temperature and ignition delay time, and
51 suggested that the ignition mechanism of biomass could be switched between homogeneous
52 ignition and heterogeneous ignition. However, biomass feedstock is a highly diverse solid fuel
53 and its chemical composition varies greatly from one source to another, same as their ignition
54 behaviour. Therefore, it is highly essential to develop fundamental knowledge that could
55 potentially be used to predict ignition characteristics of a wider range of biomass feedstock.

56 Due to the major organic substances of biomass can be divided into three main chemical
57 components: cellulose, hemicellulose and lignin ^[9], their distinct thermal characteristics have
58 been often applied as an effective means to provide generalised understandings of various
59 thermal processes of biomass, as well as identify their mutual interactions along thermal
60 conversion processes ^[10-13]. Thermal conversion of biomass has been studied on the basis of
61 these three main components in recent, as well as their interactions, since the mutual
62 interactions can affect their thermal behaviour. Raveendran et al. ^[10] found no detectable
63 interactions among the components during the thermal conversion process through the study
64 of their thermal characteristics on the TGA and packed-bed pyrolyzer. Yang et al. ^[14] also
65 observed negligible interactions among the three components in their studies by using a TGA
66 analyzer, as well as in Wang et al ^[13] study. However, Worasuwanarak et al ^[11] observed
67 significant interactions between the components by studying the yield of liquid productions,
68 similar interactions are also reported by Wang et al. ^[12] and Stefanidis et al ^[15]. **The ignition
69 behaviour of biomass could also be affected by interactions among the major components
70 during combustion process, such research however is rarely reported. Studying the
71 performances of ignition behaviour of different component mixtures will allow a further
72 identification of potential interactions among the major components, and also enables the
73 prediction of the ignition behaviour of biomass feedstock.**

74 Apart from the physical and chemical studies on the interactions, kinetic study on the

75 interactions is rarely reported. Thermal conversion of biomass can be classified as
76 heterogeneous chemical reaction, its reaction kinetics can be affected by its three key
77 components [16,17]. Through the reaction kinetic study, the difference between activation energy
78 (E_a), and pre-exponential factor (A) can be obtained to better understand the interactions among
79 the components.

80 In this paper, first, we will characterise the ignition behaviour of the three main chemical
81 components of biomass. Then, ignition characteristics of various mixtures of these chemical
82 components will be fully discussed to quantify the effects of interactions between the organic
83 components on the overall ignition behaviour. Finally, the ignition properties of mixtures of
84 these chemical components to simulate an artificial biomass will be conducted and compared
85 with that of natural biomass of wheat straw and soft wood, as well as the calculation of kinetic
86 parameters, with the aim of identifying the potential interactions among them with regards to
87 ignition behaviour.

88 **2. Materials and methods**

89 *2.1 Materials and sample preparation*

90 Cellulose and Xylan (corn cob xylan) powder are purchased from Sigma-Aldrich, and lignin
91 (dealkaline lignin) powder is purchased from Carbosynt. Xylan has been often considered as a
92 representative molecule for hemicellulose [14]. The proximate and ultimate analysis of these
93 samples as well as of the wheat straw and soft wood are presented in Table 1. As it can be
94 observed from the analysis, the contents of volatile matter in cellulose and xylan is higher than
95 in lignin, while lignin has a much higher fixed carbon and ash content. For lignocellulosic
96 biomass, the largest component is cellulose with over 40% of its overall weight, which will be
97 majorly converted to gaseous and liquid products during its thermal conversions;

98 hemicellulose, the least stable component, accounts for approximately 30% by weight of initial
 99 biomass; while lignin normally accounts for approximately 20% by weight, 40% of which
 100 attributes to char yield after pyrolysis [18-20].

101 Table 1. Proximate and ultimate data of biomass samples (wt. %)

	Cellulose	Xylan	Lignin	Wheat Straw	Soft Wood
Moisture <i>ar</i>	2.70	2.90	3.20	2.30	3.50
VM <i>db</i>	89.70	84.80	51.30	74.80	58.36
Ash <i>db</i>	1.70	1.70	15.00	7.40	1.12
FC <i>db</i>	8.60	13.50	33.70	17.80	40.52
C <i>db</i>	42.18	38.41	62.09	45.20	58.28
H <i>db</i>	6.15	6.18	5.88	5.25	4.71
O <i>db</i>	51.66	55.40	30.52	48.84	36.51
N <i>db</i>	0.01	0.01	0.51	0.71	0.50

102 *db: dry basis; ar: as received*

103 2.2 Experiment design

104 Table 2. Summary of testing conditions

		Mixing ratio (%)	Heating rate (°C/min)	Final temp. (°C)
Individual samples	Cellulose	-	20	900
	Xylan	-	20	900
	Lignin	-	20	900
	Wheat straw	-	20	900
	Soft wood	-	20	900
Mixture samples	Cellulose / Xylan	50/50	20	900
	Cellulose / Lignin	50/50	20	900
	Xylan / Lignin	50/50	20	900
Artificial samples*	Wheat straw	Cellulose / Xylan / Lignin 61.3/19.3/19.4	20	900
	Soft wood	Cellulose / Xylan / Lignin 43.1/24.1/32.8	20	900

105 * *The ratio is summarised from the literature [13, 21]*

106 The Coning and Quartering Method [22] is applied to prepare the mixture samples in this study.
 107 This method has demonstrated its advantages for preparation of samples with poor flowability,
 108 which can reduce the sampling size of the powder sample without generating a systematic bias.
 109 Individual samples are mixed in a container according to the predetermined mixing ratio in the
 110 experiment design, as detailed in Table 2, followed by the mixing procedures: 1) pour a cone

111 of the mixture into a plate; 2) divide the cone into halves; 3) divide the cone into quarters; 4)
112 discard the two opposite quarters of the sample; 5) recombine the remaining sample. The
113 procedure is repeated three times to prepare each mixture sample. A total of 10 samples are
114 prepared, as listed in Table 2.

115 *2.3 Estimation of the ignition temperature*

116 Ignition temperature is identified as the lowest temperature at which a solid fuel starts to ignite
117 without the aid of an external ignition sources. In theory, ignition temperature is the
118 temperature to which a fuel-air mixture must be increased so that the heat evolved by the
119 exothermic reactions of the combustion system will just overbalance the rate at which heat is
120 discharged to the surroundings ^[23]. Ignition temperature of solid fuels is often determined by
121 empirical methods through thermogravimetric (TG) and differential thermogravimetric (DTG)
122 curves, such as: (1) identify the temperature at which the mass loss curve in the combustion
123 (oxidative atmosphere) diverges from that of pyrolysis (inert atmosphere) ^[24, 25]; (2) identify
124 the temperature at which it starts the maximum reactivity of devolatilization ^[26]. Considering
125 the replicability and reliability of the results ^[27], method (1) will be employed in this study to
126 determine the ignition temperature in this work. This method is based on the principle that
127 when the fuel sample is ignited, two exothermic peaks appear before and after the turning point
128 at where the TG curves of combustion and pyrolysis are diverged ^[28]. However, there might
129 exist crosses of TG curves of combustion and pyrolysis when the diverging point is
130 undistinguishable; if this turns out to be the case, DTG curves will be used as a complementary
131 information, and the diverging point will be defined as where the second peak of the
132 combustion curve appears.

133 *2.4 Determination of kinetics*

134 The kinetics of biomass thermal conversions can be expressed by following equation:

$$135 \quad \frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (\text{Eq.1})$$

136 where T is the absolute temperature; R is the gas constant; $f(\alpha)$ is the mass conversion function;
137 α is the conversion fraction, which represents the relationship between the initial mass (m_0) and
138 the final mass (m_∞), and the current mass (m) of the sample, as given below:

$$139 \quad \alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (\text{Eq.2})$$

140 When the heating rate ($\beta = dT/dt$) is constant, Eq. 1 can be integrated as:

$$141 \quad g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T dT \exp\left(-\frac{E_a}{RT}\right) \quad (\text{Eq.3})$$

142 where $g(\alpha)$ is an integrate function, consequently, Eq.3 can be approximated by:

$$143 \quad \ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad (\text{Eq.4})$$

144 The conversion function $f(\alpha)$ depends on the operating conditions and the stage of the
145 combustion. Combustion is a complicated process, which normally can divided into three
146 different reaction stages ^[29], or two parallel reactions with three reaction stages ^[30], or more
147 recently two-stage reactions with the first step that occurs at lower temperature and the second
148 step that occurs the oxidation of char at higher temperature ^[31]. Thermal decomposition of
149 biomass has been commonly described as first-order reaction ^[32]. In this study, we consider the
150 combustion process with two-stage reaction mechanism, and both stages are governed by the
151 first order reaction law. In this case, $f(\alpha) = (1 - \alpha)$, as a result, $g(\alpha) = -\ln(1 - \alpha)$, and for
152 most system $RT/E_a \ll 1$ ^[33], then Eq.4 can be approximated by:

$$153 \quad \ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] \approx \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT} \quad (\text{Eq.5})$$

154 The left hand side of Eq.5 is plotted against $1/T$ for the data from a single heating rate, which
155 leads to a straight line, from which the activation energy can be obtained as the slope of this
156 line, and the pre-exponential factor is derived from its intercept.

157 3. Results and discussion

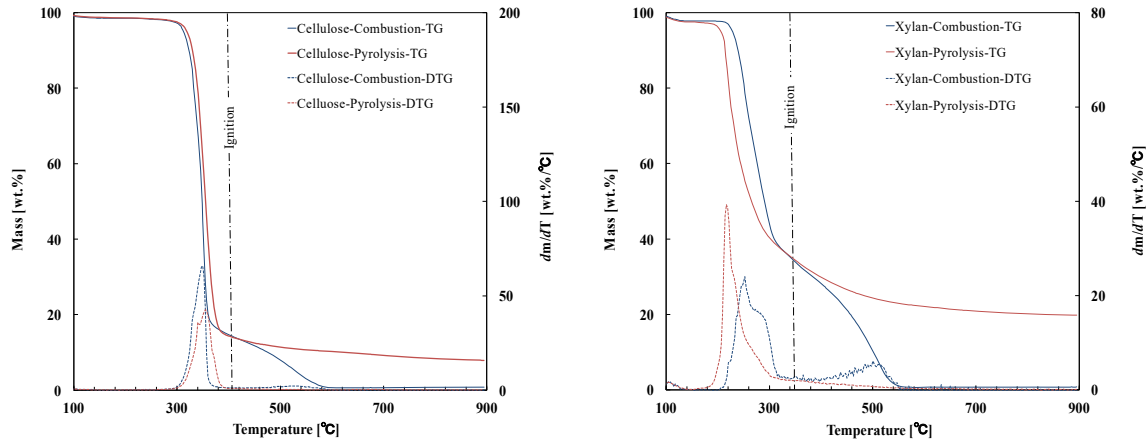
158 3.1 Thermal characteristics of cellulose, xylan and lignin and their ignition temperatures

159 Fig. 1 (a-c) show the mass loss profiles of cellulose, xylan and lignin in air and nitrogen
160 atmospheres at a heating rate of 20°C/min up to a final temperature of 900°C. Due to the
161 different chemical structures of the individual components, substantial differences in the
162 thermal characteristics among them could be expected [34].

163 Fig.1 (a) shows that cellulose starts to decompose at a temperature of 325°C and losses over
164 80% of its mass before 410°C, which is close to the content of its volatile matter as shown in
165 Table 1. When temperature is greater than 410°C, the mass loss curves along its pyrolysis and
166 combustion processes start to diverge, where the pyrolysis curve tends to flatten without further
167 decomposition, and the solid residues account for approximately 8% of its initial mass at the
168 end of the process; while the combustion curve shows that a continuous mass loss occurred
169 until 600°C with less than 1% inert residues left in the end. The difference between the amounts
170 of solid residue after pyrolysis and combustion processes equals to the content of the fixed
171 carbon in cellulose. Fig.1 (b) shows that the decomposition of xylan starts at the temperature
172 of 190°C and the divergence of its pyrolysis and combustion curves occurs at 370°C, where the
173 pyrolysis rate is getting stable while a second drop of mass occurs in combustion process due
174 to char oxidation. The solid residue left after pyrolysis and combustion processes are 18% and
175 1.5% of the initial mass of xylan respectively.

176 In Fig.1 (c), the show shows that the decomposition of lignin starts at 210°C and the curves of
177 pyrolysis and combustion diverged at 405°C. A slow decomposition of lignin is noticed at the
178 temperature ranges from 405°C to 750°C in its pyrolysis, and the remaining accounts for
179 approximately 45% of its initial mass after pyrolysis; while in combustion, lignin loses more
180 than half of its mass at the temperature ranges from 405°C to 600°C, and there is 15% of its

181 mass left in the end, which equals to its ash content.

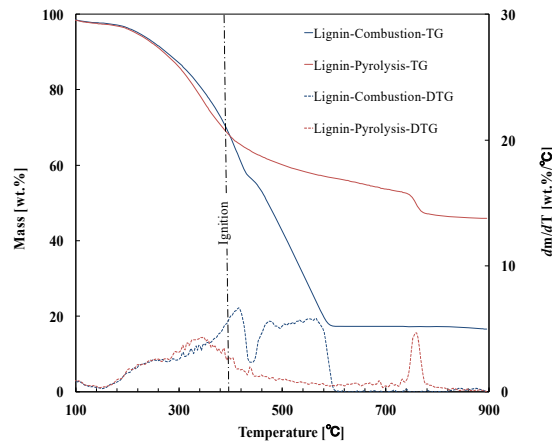


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183

(a) Cellulose

(b) Xylan



184

185

(c) Lignin

186 Fig.1. Thermal characteristics of individual chemical components in air (combustion) and nitrogen (pyrolysis)

187 with identified ignition temperatures

188 By comparing TGA profiles of cellulose, xylan, and lignin in Fig.1, nearly all of their mass

189 loss curves of pyrolysis and combustion processes coincide on top of the each other before

190 the divergence occurred, a slight deviation might be caused by the difference of thermal

191 conductivity of nitrogen and air [3]. This implies that, at the early stage of thermal conversion,

192 temperature is the dominant factor of the reactions, rather than the existence of oxygen.

193 Among these three samples, cellulose has the narrowest decomposition temperature range

194 and lost the most of its mass during the decomposition process, while lignin has the widest
 195 decomposition temperature range and generates the most residual. The ignition temperatures
 196 of cellulose, xylan, and lignin are 410°C, 370°C, and 405°C respectively. These temperatures
 197 are identified as the diverging point of TG curves and are the same temperatures at which the
 198 second peak appears in the DTG curves under air conditions.

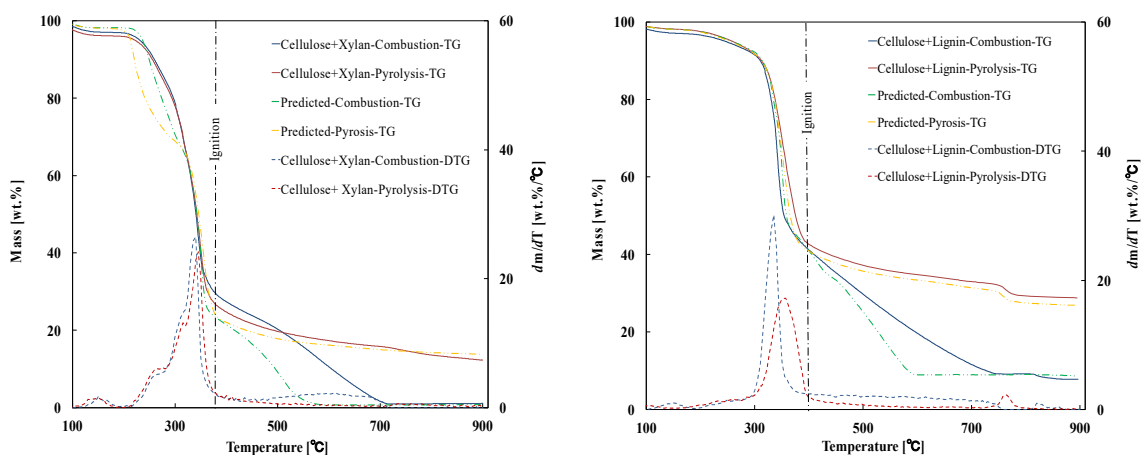
199 3.2 Ignition characteristics of mixtures of xylan, cellulose, and lignin

200 The thermal behaviour (mass loss) of the mixtures could be predicted using the weighted sum
 201 of the partial contributions of individual components [10] as described by the following equation:

$$202 \quad \frac{dm_{mix}}{dt} = \sum_i y_i \frac{dm_i}{dt} \quad (\text{Eq.6})$$

203 where y_i refers to the mass fraction of component i in the mixture. So that the TG and DTG
 204 curves could be drawn based on the calculation results, and then the ignition temperatures of
 205 these mixtures would be predictable. To quantify the interactions of individual components on
 206 the ignition temperature of mixtures, the thermal tests of various mixtures of chemical
 207 components in air and nitrogen are performed and the results along with the predicted thermal
 208 characteristics of the mixtures are shown in Fig.2 (a-c). The potential impacts of interactions
 209 on the determined ignition temperatures will be discussed in this section.

210

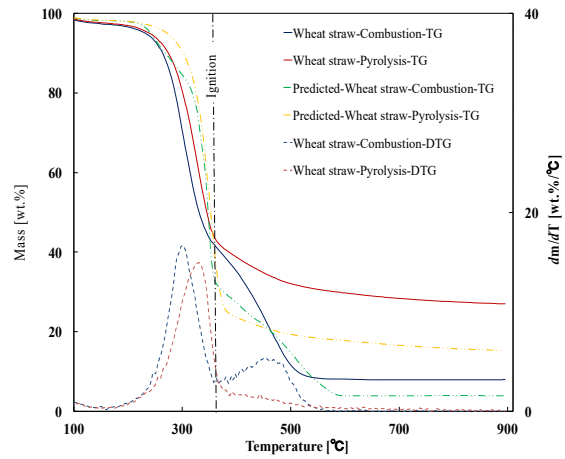
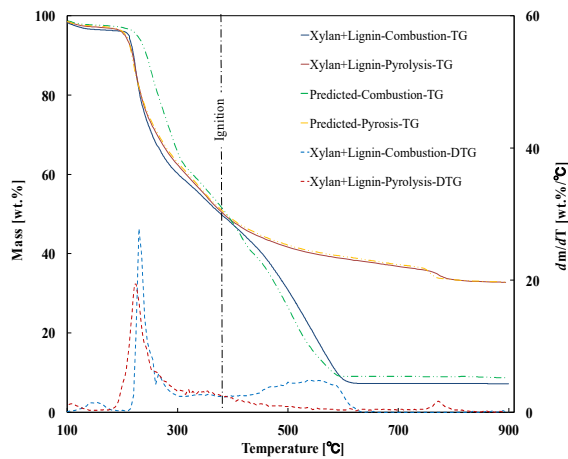


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(a) Mixture of Cellulose and Xylan

(b) Mixture of Cellulose and Lignin



213

(c) Mixture of Xylan and Lignin

214

(d) Mixture of Cellulose, Xylan and Lignin (as a prediction of wheat straw)

215

216 Fig 2. Thermal characteristics of mixtures of components in air (combustion) and nitrogen (pyrolysis) with
 217 identified ignition temperatures along with the prediction results

218 Fig.2 (a) shows the experimental and predicted results of the mixture of cellulose and xylan,
 219 its decomposition starts at a temperature of 250°C, same as the predicted starting temperature.

220 The significant release of volatile matter of the mixture occurred at the temperature range of
 221 250°C to 350°C, nearly the same as the predicted temperature range. Although there is an
 222 obvious burnout delay in the experimental combustion curve compared to that from prediction,
 223 where the sample in the experimental curve keeps decomposing till reaching 700°C, which is a
 224 much higher temperature than the ending decomposition temperature of the predicted curve,
 225 that is 550°C, however, this does not affect the identification of ignition temperature. The
 226 decomposition of xylan particles at lower temperatures could potentially form a charred film
 227 that, acted as a barrier, warps nearby cellulose particles, so that the mass and heat transfer of
 228 and between the particles is limited, as stated in Stylianos et al. [15] and Wang et al. [13] studies.

229 There are two detectable diverging temperatures observed in the TG curves of the mixture of
 230 cellulose and xylan: one is 370°C, and the other is 510°C, leading to a difficult identification of
 231 ignition temperature. To address this, the DTG curves are used as complementary information,

232 and the ignition temperature of the mixture is defined at 405°C, compared with the predicted
233 one at 400°C, indicating that the ignition temperature of the mixture can be predicted from the
234 sum of the individual decomposition data of the mixture component.

235 Fig.2 (b) shows the decomposition performance of the mixture of cellulose and lignin, which
236 agrees well with the predicted decomposition behaviour. When the temperature reaches to
237 400°C, the pyrolysis and combustion curves start to diverge, however, there is an obvious
238 difference in the combustion curve between the experimental and the predicted at the
239 temperature range of 420-730°C. A prolonged combustion is observed in the experimental
240 curve, this might be caused by the melting and forming of agglomeration of lignin particles,
241 and the agglomerated lignin wrapping nearby cellulose particles ^[15], lowering the heat transfer
242 efficiency of the particles. In addition, the structure of lignin consists of phenylpropane coupled
243 with C-C bond and/or C-O-C bond, which covers an extremely wide decomposition
244 temperature range (152-700°C) ^[15]. Accordingly, above reasons may lead to a higher
245 temperature to burnout, while the ignition characteristics are not affected. The diverging point
246 of the curves in the experiment data occurs at 400°C from both TG and DTG results, meaning
247 that the ignition temperature of the mixture is 400°C, the same as the prediction.

248 Fig.2 (c) shows the experimental and predicted thermal performance of the mixture of xylan
249 and lignin, which starts to decompose at 210°C. When temperature exceeds 400°C, the pyrolysis
250 curve becomes flat, while the combustion curve continues to drop till 600°C. Both experimental
251 curves coincide with the predicted ones. The diverging point of the curves in the test occurs at
252 400°C, which can also be identified in the DTG curves, indicating the ignition temperature of
253 the mixture of xylan and lignin is 400°C.

254 **At last, a comparison of experimental and predicted performance of wheat straw is presented**
255 **in Fig.2 (d). The predicted results are similar to that of wheat straw, the decomposition starts**

256 at 230°C. When the temperature reaches 350°C, pyrolysis curves become flat according to both
257 experimental and predicted results. The combustion curves, however, start the second drop,
258 which is known as char oxidation stage. Since compositions in the wheat straw is more
259 complicate than that in pure component of cellulose, xylan or lignin; this leads to a higher
260 amount of remaining solids from the experiment results when compared with the predicted
261 result, both in pyrolysis and combustion tests. The departing point of the curves in the
262 experiment is at 350°C, a same result was obtained from the DTG curve; while there are two
263 diverging points observed in predicted curves, the first point agrees well with the experimental
264 result, indicating the ignition temperature of wheat straw could also be acquired by predictions.

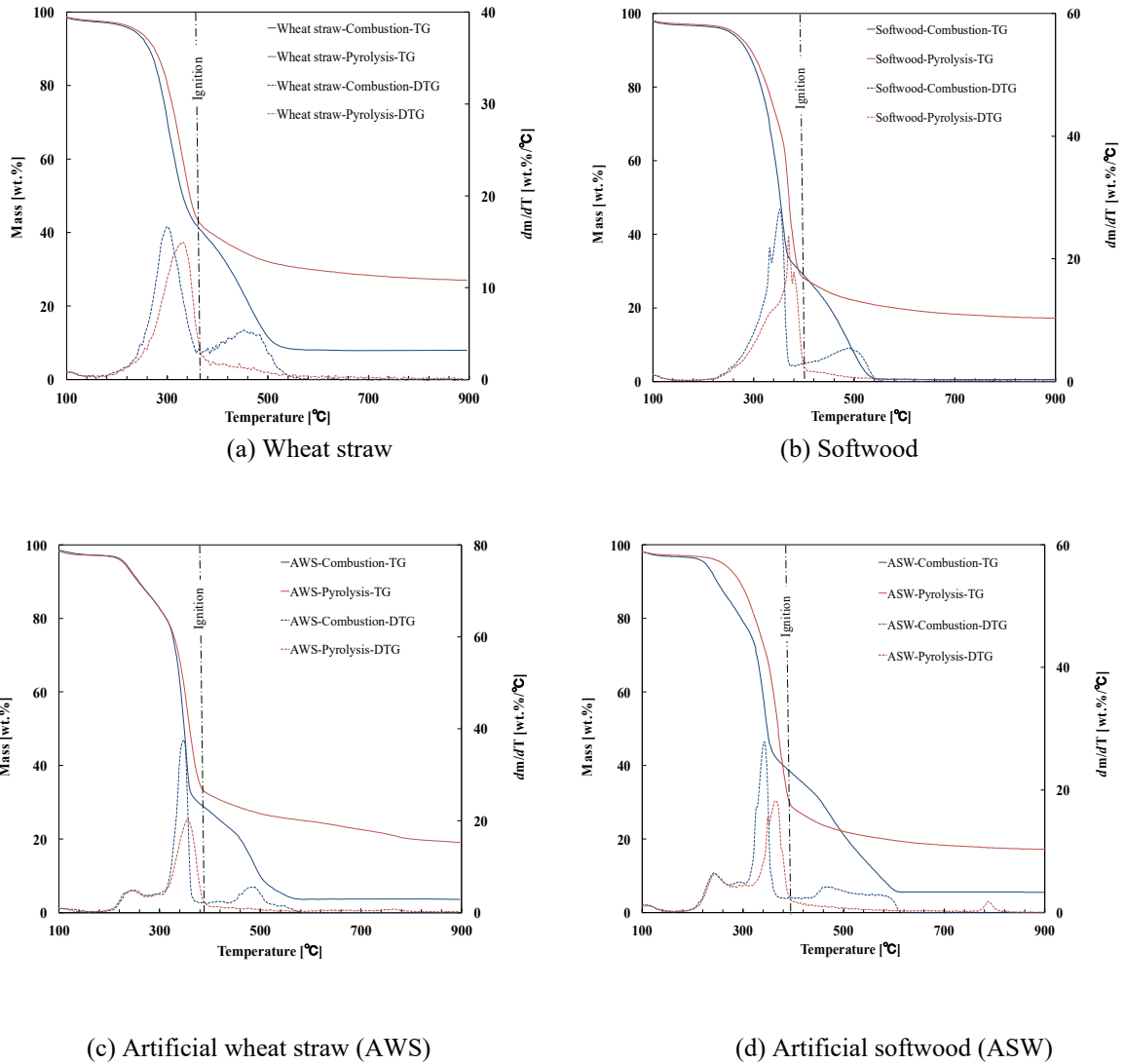
265 As discussed above, the determined ignition temperatures of mixtures (cellulose and lignin,
266 xylan and lignin) are close to the ignition temperature of lignin. Cellulose and xylan have a
267 higher volatile matter content, which means that the major part of them have been released at
268 the pyrolysis stage; lignin, however, has the highest fixed carbon content of all of them, which
269 contributes to the significant amount of char yield after pyrolysis. According to Kai et al. [34],
270 at the combustion stage, the oxidation of the formation of char is characterised by the existence
271 of lignin. This might result in the ignition temperatures of lignin mixtures, being close to the
272 ignition temperature of lignin itself. From the experimental data of all the mixtures, it is
273 observed that the pyrolysis results could be predicted with precision, similar conclusions were
274 also reported by Stylianos et al [15]. The synergistic effects between components are less
275 significant but can be observed through the study of combustion curves. There is no significant
276 influence on the ignition behaviour when physically mixing cellulose, xylan and lignin.

277 *3.3 Thermal characteristics and ignition temperatures of natural and artificial biomass*

278 To further identify the interaction of chemical components on the ignition properties of
279 biomass, natural and artificial samples (artificial wheat straw (AWS) and artificial soft wood

280 (ASW)) are tested. The mass fraction of cellulose / hemicellulose / lignin in AWS and ASW
281 that we assumed are 61.3/19.3/19.4 and 43.1/24.1/32.8 respectively. Thermal characteristics of
282 the samples of pyrolysis and combustion are examined by using TGA at the heating rate of
283 20°C/min, the results are presented in Fig. 3.

284 The decomposition of wheat straw starts at 250°C and softwood starts at 255°C, and wheat
285 straw lost 60% of its mass when temperature reaches 350°C, while softwood lost nearly 70%
286 of its mass when temperature reaches 405°C, the mass loss is caused by the release of moisture
287 and volatile content in the mixture, after these temperature points, the pyrolysis and combustion
288 curves start to diverge. When temperature exceeds the diverge points, the pyrolysis curve keeps
289 flatter till ending, and there is 25% of its initial mass left as solid residue for wheat straw
290 while it is 20% for softwood, the residue consists of fixed carbon and ash; however, the
291 combustion curve shows a second mass drop, and wheat straw ends at 520°C, while softwood
292 finishes at 510°C, leading to a further mass loss ending with an 18% and 39% of its initial mass
293 of wheat straw and softwood respectively, corresponding to the fixed carbon content. In DTG
294 curves, two obvious peaks appear before diverge temperature for both samples, the first one at
295 100°C, caused by the evaporation of moisture, and as for the second one, it is 300°C for wheat
296 straw and 330°C for soft wood, due to the release of the volatile matter. Then pyrolysis curve
297 becomes stable, while combustion curve shows a third peak at 460°C for wheat straw, and
298 500°C for soft wood, due to the oxidation of char. In consequence, the ignition temperature of
299 wheat straw and softwood is 350°C and 405°C respectively, which can also be observed from
300 the DTG curve in Fig. 3 (a) and (b), similar ignition temperatures can also be obtained from
301 the studies of [3, 35],



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Fig.3. Thermal characteristics of biomass samples in air and nitrogen with identified ignition temperature:

(a) wheat straw; (b) soft wood; (c) artificial wheat straw (AWS); (d) artificial softwood (ASW)

Fig. 3 (c) and (d) show the thermal decomposition results for artificial biomass with the similar trends as that of natural biomass. The first phase decomposition of artificial wheat straw (AWS) starts at 220°C and ends at 365°C, two step decreasing of mass occurred during this phase, both in pyrolysis and combustion curves. The first decrease starts from 220°C to 340°C in TG curves, reaching its peak at 260°C in DTG curves, this is mainly caused by the decomposition of xylan, the least thermally stable component in biomass ^[36], due to the breakdown of its C-O-C and some pyranose C-C bonds ^[37]. According to the individual component tests, xylan

313 starts to decompose at 180°C and sharply loses 65% of its mass before 300°C, while partial
314 cellulose and lignin start to decompose at lower temperatures, this implies that the existence of
315 cellulose and lignin doesn't affect the thermal behaviour of xylan significantly. The second
316 decrease starts from 340°C to 380°C in the TG curves, and as can be seen in the DTG curve, it
317 reaches its peak at 355°C. As illustrated in Fig. 1, during this temperature range, cellulose loses
318 nearly 90% of its initial mass, lignin loses 15%, and xylan loses only 4%, indicating that
319 cellulose and lignin are the main components that attribute the mass loss during this stage. The
320 pyrolysis and combustion curves of AWS start to diverge at 375°C. After that, in the pyrolysis
321 scenario, AWS continues to lose mass very slowly with a remaining of 20% of its initial mass
322 at the end of the test, which is the same as the sum of partial contributions of fixed carbon and
323 ash contents of each component. While for the combustion scenario, most of the mass loss at
324 the char oxidation stage is attributed to lignin and xylan, since both of them have higher fixed
325 carbon contents (33.7 wt.% in lignin; 13.5 wt.% in xylan) compared to cellulose (8.6 wt.%).
326 As shown in both TG and DTG curves, the ignition temperature of the AWS is 375°C.

327 As for artificial softwood (ASW), similar conclusion can be summarised as AWS, the
328 decomposition of each component is distinguishable. The first phase decomposition begins at
329 210°C, till to 360°C for combustion and it is 240°C-390°C for pyrolysis, two drops of mass
330 occurred during this phase. The first drop starts from 210°C to 330°C in combustion curve,
331 while it is 240°C-350°C for pyrolysis curve. As showed in Table 2, the content of xylan in ASW
332 is similar to that of AWS, which leading to the semblable temperature range of first drop. The
333 second drop of mass happened from 330°C to 360°C in combustion curve and from 350°C to
334 390°C in pyrolysis curve, due to the decomposition of cellulose and lignin. After 390°C, the
335 pyrolysis curve becomes flat and with 20% remaining at the end; while the combustion curve
336 happened the char oxidation phase, and the remaining equals to the sum of partial contributions
337 of ash contents of each component. There are two notable diverging points in Fig 3 (d), one is

385°C, and the other one is 495°C, by complementing the DTG information, the ignition
temperature of ASW is defined at 395°C, similar to that of natural softwood. It can be seen that
the ignition temperature of ASW is close to that of lignin, since the fraction of lignin in ASW
is much higher than that in AWS, indicating that the lignin is the dominant factor that influence
the ignition temperature of the samples.

As discussed above, thermal behaviour of AWS and ASW could be predicted through the sum
of the decomposition behaviour of individual components. As aforementioned, the ignition
temperature and thermal behaviour of the artificial biomass is similar to that of natural biomass,
meaning that the ignition temperatures of various biomass materials are predictable once the
mass fractions of these individual components are certain. Nevertheless, there is a slight
difference between the ignition temperature of natural and artificial biomass can be observed,
reveals the potential interactions among the three chemical components in natural biomass,
which might affect its ignition behaviour; also, the moisture content of the artificial biomass is
different from that of natural biomass, and the variation of moisture content in the samples may
have an influence on the ignition characteristics^[38], a summary of the comparison of moisture
content and ignition temperature is list below in Table 3. It can be seen that the higher the
moisture content, the higher the ignition temperature. The increased moisture content will
increase the thermal properties of materials, like: thermal conductivity and specific heat, as
well as the vaporization and migration of moisture^[39], leading to the delay of ignition as a
function of external heat flux and substantially alters the thermos-physical properties of the
biomass samples^[40].

It also should be noticed that the structures of cellulose, xylan and lignin in biomass differ from
the commercial materials, as well as in the different biomass fuels, and the different structures
would result in varying ignition properties. Besides, the structure of biomass is complicated,
the chemical component cellulose provides the skeletal structure of the biomass that is coated

363 with hemicellulose and cemented by lignin [20, 41], co-existence with the ash and moisture; the
 364 artificial biomass is made by physical mixing of these three components that is unable to mimic
 365 the inner tangles of them precisely. Above results can provide a general perspective of the
 366 ignition behaviour of three chemical components and their mixtures, and to predict the ignition
 367 temperature of natural biomass.

368 Table 3. The summary of moisture content and ignition temperature of natural and artificial biomass.

	Wheat straw	Artificial wheat straw	Softwood	Artificial softwood
Moisture content (wt. %)	2.30	2.84*	3.50	2.91*
Ignition temperature (°C)	350	375	405	395

369 *The moisture content of artificial biomass is the sum of partial contributions of moisture content of each
 370 component.

371 3.3 Kinetic study on the interactions

372 Former study on the ignition behaviour of samples has indicated the possibilities to estimate
 373 the ignition temperature of biomass when the fractions of three chemical components are
 374 certain, but the variation of the ignition temperatures between artificial and natural biomass
 375 illustrates the potential interactions among the chemical components may influence the ignition
 376 behaviour. In order to further understand the mutual interactions, and how they affect the
 377 combustion process, Coats-Redfern method was used to calculate the kinetic parameters of the
 378 combustion of all the samples, and the changes of activation energy (E_a) and pre-exponential
 379 factor (A) will be discussed to investigate the interactions among the cellulose, xylan and lignin.
 380 As discussed in Sec. 2.4, the process of combustion in this study is divided into two steps:
 381 pyrolysis and char oxidation. The combustion kinetic parameters of the studied individual
 382 components and the one from the mixture samples obtained from the calculations are shown in
 383 Table 4, together with the summarised ignition temperatures. At the stage of pyrolysis, the
 384 values of E_a for cellulose, xylan and lignin are 223.32 kJ/mol, 73.85 kJ/mol and 23.41 kJ/mol

385 respectively. Cellulose has the highest E_a value among them, followed by xylan, similar results
386 are also reported by Milosavljevic et al. [42]. This result indicates that the decomposition of
387 cellulose is a crucial step to determine the overall rate of the biomass combustion process [17],
388 while xylan and lignin dominate the initial decomposition.

389 The obtained correlation coefficients (R^2) of cellulose and xylan at their second step are not
390 high enough to be trusted, indicating a completion of decomposition of cellulose and xylan at
391 the early stage of pyrolysis, so that the first order reaction model might not be suitable for the
392 combustion of cellulose and xylan [43]. While the correlation coefficient at the step 2 of
393 combustion of lignin is reliable, indicating the feasibility of first order reaction model on both
394 steps of combustion of lignin. The E_a value for lignin in step 2 is 45.98kJ/mol, higher than that
395 of step 1, this is attributed to the high energy required to decompose inorganic matter [44], since
396 lignin has the highest ash content among these three components.

397 For the mixture of cellulose and xylan, the E_a value in step 1 is 54.64 kJ/mol which is lower
398 than that of either cellulose or xylan, suggests the potential interactions between them could
399 affect the reaction process during the pyrolysis. At devolatilization stage, xylan begins to
400 decompose prior to cellulose and forming char residues that might cover and wrap around the
401 cellulose surface, which inhibits the release of volatile products and enhances the secondary
402 degradation of macromolecular materials in cellulose. For the mixture of cellulose and lignin,
403 E_a value is 152.74 kJ/mol in step 1, which is placed in between of that of cellulose and xylan.

404 The existence of lignin in the mixture enhances the cellulose to generate small molecular
405 products during the devolatilization process [45], so that the mixture requires lower energy to
406 devolatilize compared to cellulose. And the E_a value for the mixture of lignin and xylan is
407 62.01 kJ /mol in step 1, which is in the range of the activation energy of lignin and xylan.

408 However, for all the three mixtures, correlation coefficients are all rather small in their second
409 step, indicating the first order reaction model is not suitable for describing the combustion of

410 mixtures.

411 Table 4. Kinetic parameters of combustion of individual component.

	Ignition temp. (°C)	Temp. range (°C)	E_a (kJ/mol)	A (1/s)	R^2
Cellulose	410	314-362 ^①	223.32	5.87E+18	0.9967
		382-584 ^②	-	-	-
Xylan	350	230-308 ^①	73.85	2.76E+06	0.9385
		310-550 ^②	-	-	-
Lignin	405	223-453 ^①	23.41	4.03E+00	0.9934
		456-591 ^②	45.98	2.88E+02	0.9329
Cellulose & Xylan	405	245-355 ^①	54.64	1.01E+04	0.9824
		400-700 ^②	-	-	-
Cellulose & Lignin	400	320-350 ^①	152.74	4.27E+12	0.9892
		360-710 ^②	-	-	-
Lignin & Xylan	400	212-269 ^①	62.01	2.89E+05	0.8437
		277-595 ^②	-	-	-
Wheat straw	350	247-352 ^①	62.58	2.69E+05	0.9814
		352-502 ^②	20.31	5.19E+00	0.9746
AWS	375	248-358 ^①	44.93	9.41E+02	0.8753
		361-551 ^②	17.43	2.86E+00	0.7952
Soft wood	405	260-380 ^①	70.46	2.22E+05	0.9889
		390-510 ^②	23.83	9.76E+00	0.9016
ASW	395	227-363 ^①	40.67	4.25E+02	0.9557
		377-570 ^②	13.45	8.14E-01	0.8891

412 Note: ^①step 1 (pyrolysis) of the combustion process; ^②step 2 (char oxidation) of the combustion process

413 The obtained kinetic parameters of the natural and artificial biomass are also listed in Table 4.

414 In step 1, the value of E_a for the natural biomass are all higher than that of the artificial biomass,
 415 with 62.85 kJ/mol and 70.46 kJ/mol for wheat straw and softwood respectively, compared to
 416 44.93 kJ/mol and 40.67 kJ/mol for artificial wheat straw and artificial softwood respectively.

417 Same trends are also observed by the results of step 2, the value of E_a for the natural biomass
 418 are within 20-25 kJ/mol, while it is 13-18 kJ/mol for the artificial biomass. It can be seen, the
 419 activation energy obtained in step 2 are all smaller than that in step 1, meaning that the char
 420 oxidation requires less energy to react than the release of volatile matter. Meanwhile, the values

421 of E_a for artificial biomass are all smaller than that of natural biomass in both two steps. In fact,
422 there exist interactions among cellulose, hemicellulose and lignin in natural biomass, such as
423 the existence of hydrogen bonding between cellulose and lignin ^[46], as well as cellulose and
424 hemicellulose, and also the presence of covalent linkages between cellulose and lignin ^[47],
425 these bonds require more energy to break up, leading to the higher value of E_a for natural
426 biomass than that of artificial biomass. Besides, the chemical and physical interactions within
427 cellulose-hemicellulose-lignin in actual biomass could generate different local reaction
428 conditions ^[46] which cannot be mimicked in a simple physical mixture of the individual
429 components. All these could result in the difference of kinetic results between natural and
430 artificial biomass.

431 For the tests of mixtures and biomass, the calculated E_a are within the approximate range from
432 1 to 180 kJ/mol ^[48]. The obtained kinetic parameters reflect the fact that even when the
433 components are physically mixed, the interactions among them affects the reaction process.

434 **4. Conclusion**

435 In this paper, thermal behaviour of cellulose, xylan, lignin, their mixtures and natural biomass
436 have been studied by using TGA. For all the tested samples, temperature is the dominant factor
437 that influences their thermal behaviour at the pyrolysis stage, regardless of the presence of
438 oxygen. Ignition temperatures of cellulose, xylan and lignin were determined by using TG and
439 DTG curves as 410°C, 370°C and 405°C respectively. Thermal behaviour of the mixtures could
440 be predicted according to that of individual components, and the ignition temperature is
441 dominated by lignin when lignin exists in the mixtures, while cellulose dominates the ignition
442 temperature of the mixture of cellulose and xylan. The ignition temperature of natural wheat
443 straw is 350°C when compared with 365°C of artificial wheat straw, and it is 405°C for natural
444 softwood and 395°C for artificial softwood respectively, **the influence of mutual interactions**

445 among the components on the ignition behaviour is insignificant, and the results demonstrated
446 a similar thermal behaviour between native and artificial biomass. The reaction kinetics of the
447 samples are studied by using Coats-Redfern method, and the results indicate that first order
448 kinetic model was fitted to most of the samples in the tests, especially natural biomass. The
449 study of the changing of activation energy values from the individuals to the mixtures revealed
450 the influence of mutual interactions among the components is significant on the thermal
451 conversion process during the combustion. Future efforts should focus on testing the different
452 kinds of chemical components, monitoring the products yields/evolution and the structure
453 changes of mixtures.

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