



Hydropyrolysis characteristics and kinetics of potassium-impregnated pine wood



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ABSTRACT

Pine wood biomass (WB) samples impregnated with different potassium contents have been investigated to determine the influence of potassium on their hydropyrolysis behavior. The experiments were carried out using a thermogravimetric analyzer under both N₂ and H₂ atmosphere, and at the heating rate of 10 °C/min from room temperature to 700 °C. Results demonstrated that potassium effected on the biomass pyrolysis significantly, as evidenced by the changes in char content and characteristic parameters such as the maximum weight loss rates and the corresponding peak temperatures. The mass of char remaining after pyrolysis significantly increased with the impregnation of potassium acetate, but it did not increase proportionately to the potassium content. The temperature at which the maximum degradation rate occurs shifted to lower temperature, and this effect was more prominent for potassium-impregnated biomass pyrolysis under H₂. It was also shown that the potassium had significant catalytic influence on the biomass pyrolysis, but this ability varied with the potassium content. The kinetic analysis indicated that both unimpregnated and potassium-impregnated biomass exhibited two-stage characteristics which could be kinetically described by two consecutive first order reactions. Moreover, the apparent kinetic compensation effect (KCE) has been observed for biomass pyrolysis under both N₂ and H₂.

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1. Introduction

In the past decades biomass has become more attractive to industry since it is a low CO₂, alternative energy source, which can therefore make significant contributions to meeting renewable energy obligations [1]. Processes such as combustion, gasification and pyrolysis have been identified as possible routes for energy and transport fuel production. The inorganic constituents of biomass can include more than 19 metals (including alkali metals), some of which act as catalysts that can determine the rate of degradation and yield of char in pyrolysis. It has been shown that certain chemical elements which affect pyrolysis degradation are sodium, potassium, magnesium and silicates [2]. Furthermore, in combustion, sulfur, sodium, chlorine and potassium in particular, influence the ash chemistry and hence dictate corrosion, slagging and fouling characteristics [3].

Of all the metals present in biomass, it is potassium that has the greatest influence on its thermal conversion properties, catalyzing both the pyrolysis and the combustion/gasification stage [4,5]. Potassium

catalyses both volatile combustion and char burn-out reactions, at least under low temperature combustion [6].

Transformation and release of potassium have been studied during the pyrolysis processes of biomass [7]. The results reveal that the potassium evolves during decomposition of the organic matrix at 200–400 °C from the original binding sites and may redeposit as discrete particles (mainly potassium) or disperse in the organic char matrix. Further evaporation of potassium to the gas phase occurs at approximately 700 °C, and evaporation of deposited potassium particles contributes to this.

The effect of alkali and other metals on the decomposition behavior of biomass have been investigated by some researchers [3–10]. Most of them suggested that the inorganic species present in biomass (which are necessary for plant growth) became one of the decisive factors which determined the behavior of biomass under thermal degradation, and this in turn affected the kinetic and conversion during pyrolysis, combustion, and gasification. Nowakowski et al. [4] reported that potassium-catalyzed pyrolysis increased the char yields greatly. Shimada et al. [8] claimed that alkali and alkaline earth metal chlorides affected cellulose pyrolysis in different ways. Pan and Richards [9] examined the effect of ion-exchanged cations on wood pyrolysis and reported that potassium, but not calcium, acted as a catalyst in pyrolytic reactions. A catalytic effect due to the presence of potassium in the biomass samples (willow SRC, wheat straw) was observed during combustion experiments in a DTA and methane-air flame [3].

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Alkali metals' catalytic effects on biomass pyrolysis have been known from early times, but have not been as much clarified in terms of the reaction mechanism as in the case of no alkali presence. Nishimura et al. [11] argued that K^+ acts as an initiator for biomass pyrolysis. The main components of biomass such as hemicelluloses and cellulose, are composed of numerous glucose units connected by glycosidic linkage with covalent bond of 300–400 kJ/mol and have crystalline structures stabilized by OH...O hydrogen bonds. When the temperature for biomass pyrolysis reaches over 200 °C, the degradation of hemicellulose and cellulose is initiated from the cleavage of the glycosidic linkage in its amorphous phase, where the weaker hydrogen bonds (about 25 kJ/mol) are present relative to its crystal phase (about 75 kJ/mol) [12]. The cleavage of glycosidic linkage is followed by the ring-opening of the glucose units. It is then possible that the ring-opening of $-C-O-C-$ bonds in the glucose unit is accelerated by the addition of K salts [11].

Since the presence of potassium plays important roles during biomass pyrolysis, it is important to clarify the influence of potassium on the pyrolysis behavior of biomass. On the other hand, the accurate knowledge of the reaction kinetics is essential for modeling of the pyrolysis process as well as designing a suitable reactor. For this reason the present work focuses on the kinetics of biomass pyrolysis in the presence of potassium.

Hydropyrolysis is an important technique for improving the quality of bio-oil produced from biomass pyrolysis. Preliminary work with *Euphorbia rigida* wood [13], pine wood chips [14] has established that bio-oils can be obtained in higher yield and with lower oxygen contents via hydropyrolysis compared to normal pyrolysis. Hydrogen is a reducing gas and the cracking of biomass in the presence of hydrogen can reduce the oxygen content in bio-oil [14]. Hydropyrolysis has also been described as a potentially rapid procedure for obtaining lignin-enriched residues from wood pyrolysis for either simply estimating lignin content or for performing stable isotope ratio measurements [15]. Therefore, it is interesting to investigate the hydropyrolysis characteristics and kinetics of biomass. It should be noted that the pyrolysis process refers not only to the thermal decomposition of the initial biomass but also to the secondary reactions among the primary pyrolysis products. Fig. 1 shows the decomposition routes for biomass pyrolysis [16].

The aims of the present work are to examine the influence of potassium on the pyrolysis characteristics and kinetics of biomass pyrolysis. A comparative study of nitrogen (inert) and hydrogen (10% H_2 in N_2) as a carrier gas was conducted using a thermogravimetric analyzer. The thermal events taking place during pyrolysis of biomass were identified and the kinetic data were obtained to fit thermogravimetric data, the global processes being considered as two consecutive first order reactions according to the initial fast pyrolysis and the subsequent slow pyrolysis.

2. Experimental

2.1. Materials

Pine wood sawdust (collected from New South Wales, Australia) was used as biomass feedstock. The wood biomass was dried at

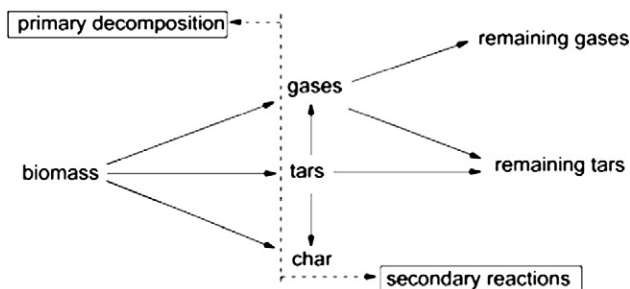


Fig. 1. The decomposition routes for the biomass pyrolysis.

105 °C and ground previously, sieved to obtain a 90–140 μm fraction. The proximate analysis, ultimate analysis, lower heating rate (LHV) and biochemical composition (determined by Klason sulfuric acid digestion procedure [17]) are listed in Table 1.

2.2. Impregnation of the wood biomass (WB)

One gram of biomass (pine wood) samples was demineralized using hydrochloric acid treatment according to the method reported in other literature [5]. The original content of K in the pine wood is 3.8 mg/g, and after HCl washing the K content is <0.1 mg/g. The washed pine wood was then impregnated by potassium (as potassium acetate) to yield a 1.25 wt.%, 2.5 wt.%, 3.75 wt.% and 5.0 wt.% K-impregnated sample. A certain amount of potassium solution (K content 10 mg/mL) was added into the biomass sample, and then the final solution volume for impregnating the biomass was fixed at 10 cm^3 by adding de-ionized water. The biomass samples were mixed for 2 h and then oven dried at 70 °C to constant weight. These samples were labeled according to the salt concentration in which they were impregnated (e.g. WB – 2.5% K).

2.3. Pyrolysis

Pyrolysis was carried out in a ThermoCahn TGA 2121 system. The balance can record accurately the weight loss of 0.001 mg and temperature of 0.1 °C and has provision for passing reactant/inert gas around the sample and heating the sample at heating rates ranging from 1 to 100 °C/min. In the present study, about 10 mg of sample was pyrolyzed under N_2 or H_2 (90% N_2 + 10% H_2 mixture) atmosphere (gas flow 50 mL/min) at heating rate of 10 °C/min from room temperature to 700 °C. The small amount of sample and the slow heating rate ensure that the heat transfer limitations can be ignored. The evolution with temperature of weight loss (TG) and the weight loss rate (DTG) were obtained for pyrolysis. The weight loss rate was calculated by the expression:

$$\frac{dW}{dt} = -\frac{1}{W_0} \left(\frac{dW_t}{dt} \right) \quad (1)$$

The pyrolysis conversion, x , can be calculated by

$$x = \frac{W_0 - W_t}{W_0 - W_f} \quad (2)$$

where W_0 is the original mass of the test sample; W_t is the mass at time t and W_f is final mass at the end of pyrolysis.

3. Results and discussion

3.1. TG curves

For pyrolysis of the biomass materials, the weight loss curves are shown in Fig. 2. It can be seen that the pyrolysis of biomass under both N_2 and H_2 is characterized by an initial rapid decomposition followed by a slow process. The first stage is attributed to the fast decomposition of hemicellulose and cellulose, while the second stage is caused by the slow decomposition of lignin of biomass [10]. In the first stage (<280–300 °C under N_2 and <250–280 °C under H_2), the TG curves have almost overlapped for both the potassium-impregnated and un-impregnated biomass materials under N_2 , while these curves have shifted to lower temperature under H_2 after impregnating potassium. In the second stage (>280–300 °C), the final weight loss decreased by 13–17% under N_2 and 11–15% under H_2 , respectively, as the potassium content in the biomass increased from 1.25% to 5.0%.

Table 1
Some characteristics of the biomass (pine wood sawdust) samples.

Proximate analysis (wt.%)				LHV (MJ/kg)	Ultimate analysis (wt.%)				Biochemical composition (wt.%)			
FC	V	A	M	Q _{net} (MJ/kg)	C	H	O ^a	N	Cellulose	Hemi-cellulose	Lignin	Others ^a
12.4	81.1	2.6	3.9	16.2	49.7	7.4	42.5	0.4	49.9	19.7	24.9	5.5

^a By difference.

3.2. DTG curves and effects of potassium content

The DTG results for the un-impregnated and K-impregnated biomass samples are plotted as Fig. 3 and some characteristic parameters of biomass pyrolysis are shown in Table 2: temperature of initial pyrolysis (T_i), temperature at the end of the reaction (T_f), the maximum weight loss rates $(dW_i/dt)_{max}$, the temperature at which the maximum degradation rate occurs (T_p), and the char content. Due to the release of some volatiles by physical processes before a significant weight loss rate takes place, difference in the baseline of some profiles is found and that makes it difficult to determine T_i . To solve this difficulty, the beginning temperature of pyrolysis, T_i , is defined as temperature at pyrolysis conversion 5%. Similarly, T_f is calculated at pyrolysis conversion 95%. T_i and T_f are related to the difficulty with which the reaction proceeds [18]. For the K-impregnated biomass samples, T_i values (195.7–200 °C) for biomass under H_2 are obviously lower than those (203.4–211.8 °C) under N_2 (Table 2), indicating that the pyrolysis of biomass is facilitated under H_2 .

As shown in Fig. 3, the DTG curves for both un-impregnated and potassium-impregnated biomass exhibit one clearly defined peak,

with a long tailing throughout and towards the end of pyrolysis. The main peak (at 280.0–298.3 °C under N_2 and 249.3–283.4 °C under H_2) is attributed to hemicelluloses and cellulose decomposition, due to their less stable structure. The pyrolysis of hemicellulose and cellulose occurred quickly, with the weight loss mainly happening at 200–350 °C [19]. Lignin degrades over a wide temperature range and there is no clear peak. Because of its cross-linked structure and aromatic nature, the polymeric lignin matrix is capable of withstanding temperatures greater than 500 °C [20]. In other works, the pyrolysis of *Festuca mairei* exhibited two separated peaks at 230 °C and 325 °C [10], and the pyrolysis of Eucalyptus wood demonstrated three peaks at 305 °C, 486 °C, and 625 °C, respectively [21]. However, the pyrolysis of cotton stalk, shea meal [22], and oak trees [23] was characterized by only one single peak at 200–450 °C followed by continuous but much slower mass loss, which demonstrated similar trends for biomass pyrolysis in our work. Obviously, different compositions of biomass have various effects on the thermal behavior during the pyrolysis process. The biomass used in this work is characterized by the composition of higher hemicellulose and lower cellulose, which leads to the overlapped or emerged peaks from both hemicellulose and cellulose.

Moreover, the pyrolysis of biomass under H_2 (compared to N_2) demonstrated that the main peak for the decomposition of hemicellulose and cellulose shifted to lower temperatures for both the un-impregnated and potassium-impregnated biomass samples, and also exhibited higher DTG peaks and $(dW_i/dt)_{max}$ values for WB, WB-1.25% K, and WB-2.5% K, but not for WB-3.75% K and WB-5.0% K (Table 2). Probably high potassium content in the biomass can drastically change the char structure and lead to the limitation of releasing volatiles during biomass pyrolysis [24].

The T_p (the temperature at which the maximum degradation rate occurs) value for biomass pyrolysis shifted to lower temperature after impregnating potassium, decreasing by 14.0–18.3 °C under N_2 and 20.8–34.1 °C under H_2 , respectively (Table 2 and Fig. 4(a)). This indicated that the potassium present in biomass had significant catalytic effect, and this catalytic effect was more prominent for biomass pyrolysis under H_2 . On the other hand, the non-linear decrease of T_p with potassium content indicated that the critical point (or critical effect) existed for biomass pyrolysis. For instance, the T_p decreased with the increase of potassium content before reaching 3.75%, but after that T_p increased slightly. As well as shifting temperature, the potassium-impregnating treatment also changed the pyrolysis temperature range and the maximum weight loss rate (Table 2), indicating changes in decomposition pathways for biomass pyrolysis.

The influence of potassium content on char yield in pyrolysis is illustrated in Table 2 and Fig. 4(b). The results indicated that the effect of impregnating potassium was to increase the amount of char or to decrease the yield of the organic vapors. However, this conclusion is tentative because there are two possibilities which could result in the increase of char content. One is that obviously the potassium in the residue after pyrolysis could lead to the increase of char weight; and the other is that potassium may facilitate the polycondensation reaction for char formation. To distinguish these two possibilities, the potassium-free-basis weight loss of the samples was also calculated and the final residues were included in Table 2. It could be seen that the char content increased significantly even with impregnating 1.25% potassium into the biomass, but the further increase of potassium content only slightly changed the char content. In addition, the

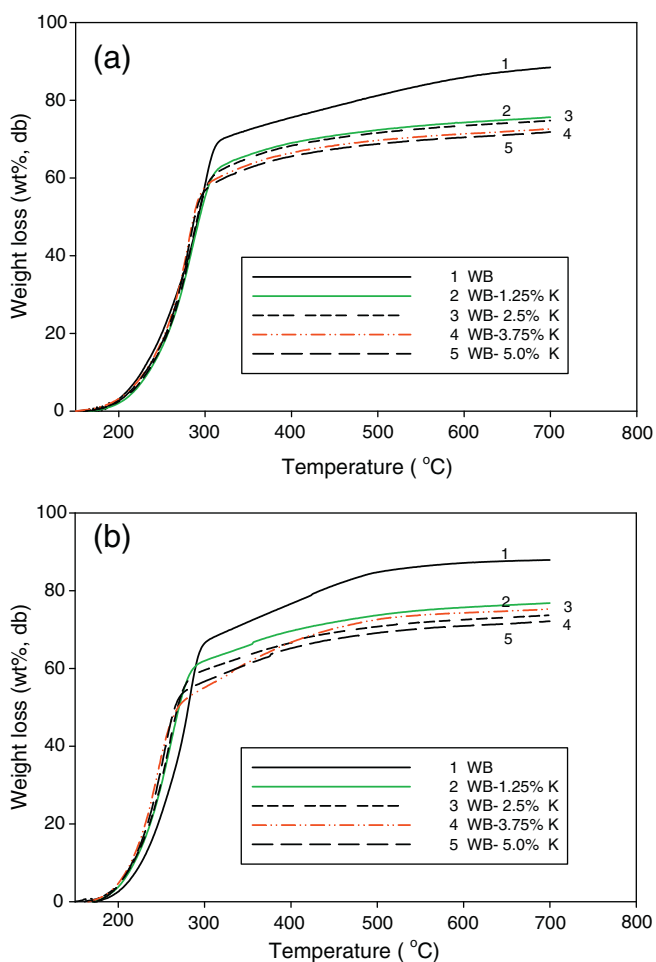


Fig. 2. Weight loss vs temperature of different biomass (SW) samples pyrolysed under (a) N_2 and (b) 10% H_2 in N_2 atmosphere.

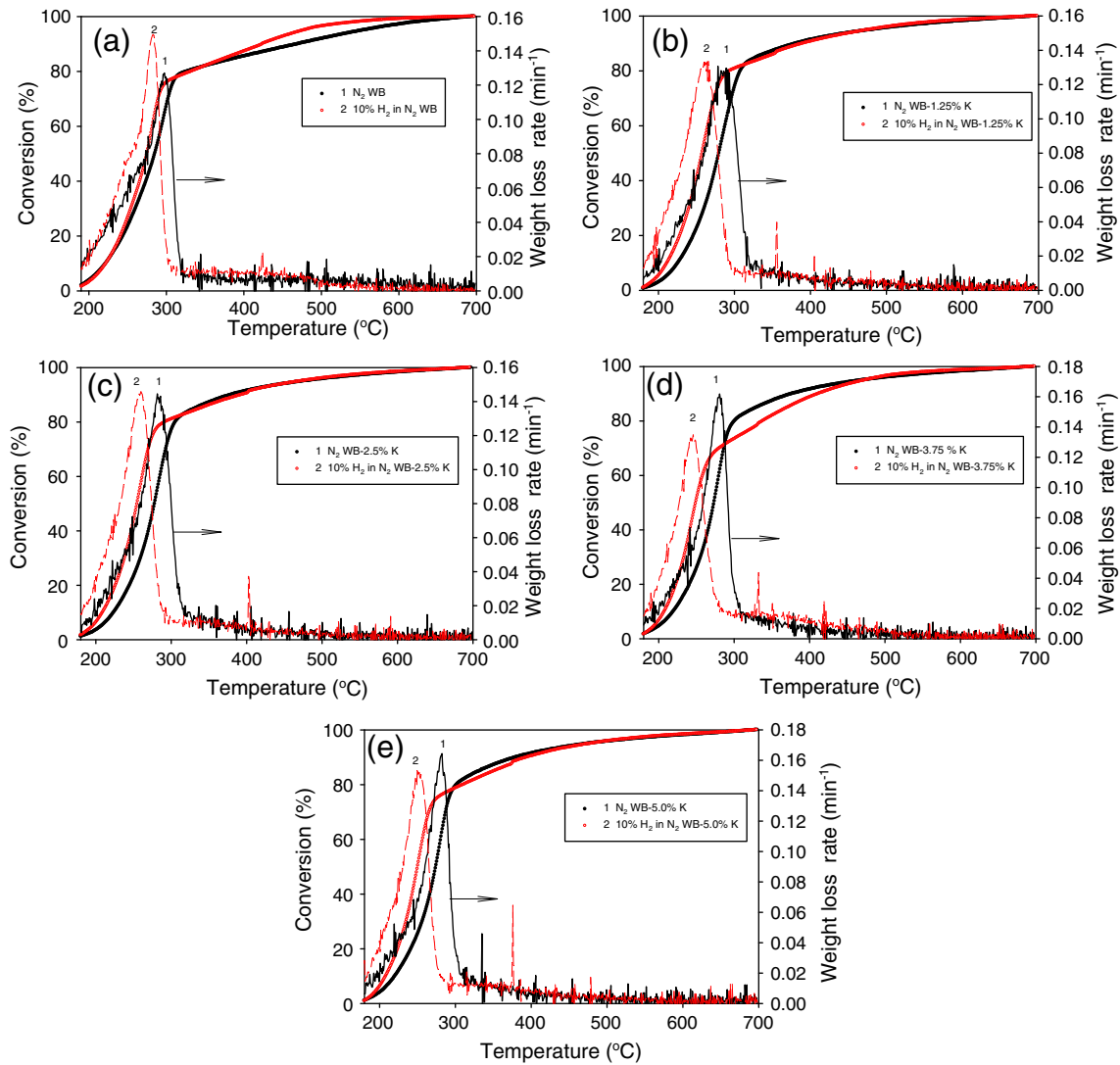


Fig. 3. TG and DTG curves for (a) WB; (b) WB-1.25% K; (c) WB-2.5% K; (d) WB-3.75% K; and (e) WB-5.0% K pyrolysis.

results in Table 2 indicated that the increase of the char content was mainly due to the polycondensation reaction facilitated by impregnating potassium, which resulted in the char content increasing by nearly 8–10% (calculated from potassium-free-basis residues). The increased char production is probably attributed to the alteration of reaction pathways by the alkali metal salts [4,7]. Moreover, it should be noted that char yield did not increase proportionately to the potassium content; a great effect on the relative char yield was observed in the lower potassium content (<1.25%). These results help in the prediction of the quantity of volatile and char produced from biomass. On the other hand, the pyrolysis of biomass under H₂ (compared to N₂) produced less char for all the potassium-impregnated biomass

samples, although this effect is not very prominent. The reason for this will be further explained.

The inorganic mineral matter present in biomass has previously been found to catalytically promote char-forming and secondary tar cracking reactions while concomitantly suppressing additional tar formation [25]. Nassar [26] concluded that the presence of alkaline salts in biomass (i.e., rice straw and bagasse), whether added or innate, acted to lower the apparent activation energy of thermal reactions and promoted the formation of char. Shafizaadeh et al. [27] realized that the yield of organic matter to gas and char changed with the inorganic content, and that higher inorganic contents promoted secondary reactions for breaking down higher molecular

Table 2
Characteristic temperatures and the maximum weight loss rates of biomass samples determined by TGA.

Samples	Pyrolysis temperature range T ₁ – T _F (°C)		(dWi/dt) _{max} (min ⁻¹)		Peak temperatures (°C)		Residue (wt.%) (dry basis)		Residue (wt.%) (K-free-basis)	
	N ₂	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂	H ₂
WB	206.8–554.3	208.5–478.5	0.1257	0.1468	298.3	283.4	12.1	11.6	12.1	11.6
WB-1.25% K	211.8–482.6	200.0–477.6	0.1276	0.1324	284.3	262.6	24.4	23.2	22.4	21.2
WB-2.5% K	208.5–475.1	196.6–472.6	0.1419	0.1438	282.2	260.3	25.3	24.7	21.3	20.4
WB-3.75% K	203.4–471.7	195.7–474.3	0.1586	0.1329	280.0	249.3	27.4	26.3	21.5	18.6
WB-5.0% K	205.9–476.8	197.5–479.3	0.1640	0.1511	283.3	252.6	28.2	27.9	20.2	19.8

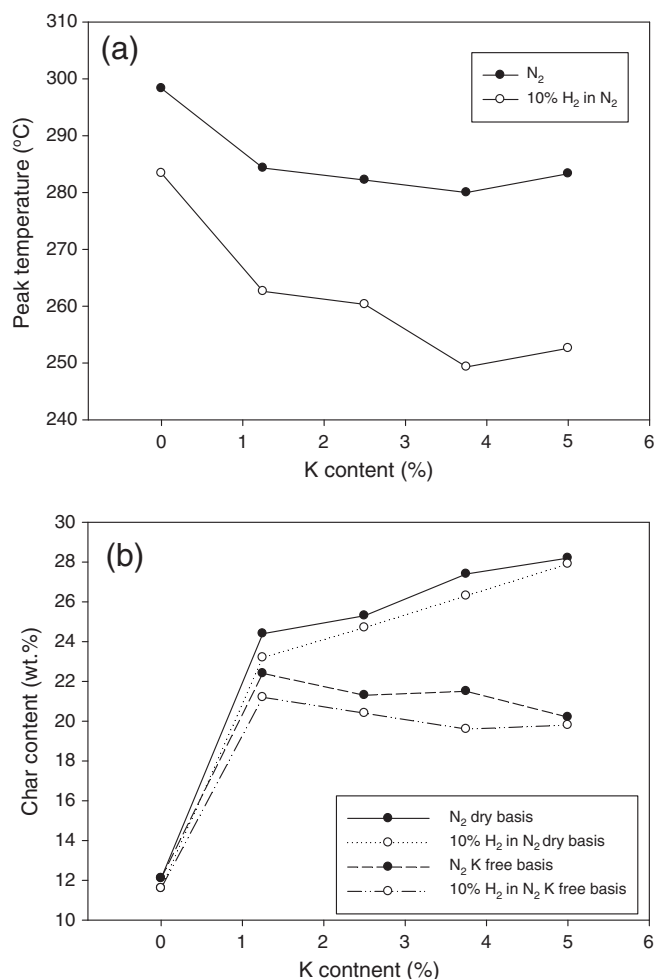


Fig. 4. Relationship between (a) the peak temperature of DTG curves; and (b) char yield against K contents for the K-impregnated biomass.

compounds into smaller ones. Liden et al. [28] developed the “Waterloo model” in which cellulose had two major alternative routes for degradation depending on the amount of alkali metals present. If high levels of alkali metals are present the degradation mechanism favors fragmentation (ring scission) producing lower molecular weight compounds such as hydroxyacetaldehyde, while lower alkali metal contents promotes a de-polymerization mechanism resulting in higher molecular weight compounds such as levoglucosan and beta-D-fructose. From the results of these investigations as well as our experiments, a conclusion can be drawn that the potassium in the biomass samples apparently has a significant catalytic effect on the biomass pyrolysis, however, the degree of catalytic effect varies with the potassium contents in the biomass samples.

The observed effects of inorganic metals on thermal degradation can be summarized as follows: (1) char formation significantly increased for the investigated range of potassium content while the temperature at which the maximum degradation rate occurs shifted to lower temperature; (2) the pyrolysis of biomass under H₂ environment (compared to N₂ environment) demonstrated that both the potassium-impregnated and un-impregnated biomass samples degraded at lower temperature and led to less char; and (3) the potassium apparently has a significant catalytic effect on the biomass pyrolysis, as evidenced by the changes in characteristic parameters in the DTG curves.

The increase of char yield with the increase of K salt addition implies the acceleration of polycondensation for char formation as discussed in the previous parts. Wooten et al. [29] reported that the

tar yield decreased with the increase of K salts addition for cellulose pyrolysis, probably some tars were converted into chars in the presence of K salts. K⁺ ions assist in transforming the hemicelluloses and cellulose molecules structure in the biomass from crystalline to amorphous by weakening hydrogen bonds [11]. Accordingly, the presence of K⁺ ions that can reduce the strength of hydrogen bonds must result in lowering the pyrolysis temperature.

The improved volatile yields (less char yield) for biomass pyrolysis under H₂ are ascribed to the fact that hydrogen and potassium catalyst could mediate hydrocracking and heteroatom removal reactions. Results for eucalyptus wood and sugar cane bagasse have demonstrated the potential of hydrolysis for producing bio-oils with much lower oxygen contents than by traditional pyrolysis processes [30]. Zhang et al. [31] investigated the pyrolysis of corncobs in a fluidized bed reactor and found that more oxygen could be converted into H₂O and CO₂ with the existence of abundant H₂. And they argued that the presence of H₂ generated highly reactive H radicals which can potentially react in the biomass conversion step to produce more light components such as H₂O and CO₂.

3.3. Kinetic analysis

According to Arrhenius law, the kinetics of biomass pyrolysis can be generally described by a differential equation:

$$\frac{dx}{dt} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(x) \quad (3)$$

where A is pre-exponential factor, β is temperature ramping rate, E_a is activation energy, T is temperature, t is time, and x is pyrolysis conversion which can be calculated by Eq. (2).

Assuming the reaction order is 1, the reaction mechanism can be expressed by Eq. (4):

$$f(x) = 1 - x \quad (4)$$

For a constant temperature ramping rate β during pyrolysis, $\beta = dT/dt$. Rearranging Eq. (2) and integrating give

$$1n\left[\frac{-1n(1-x)}{T^2}\right] = 1n\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \quad (5)$$

Since it may be shown that for most values of E_a and for the temperature range of the pyrolysis, the expression $\ln[AR(1 - 2RT/E_a) / \beta E_a]$ in Eq. (5) is essentially constant, if the left side of Eq. (5) is plotted versus $1/T$, a straight line may be obtained if the process can be assumed as a first order reaction. From the slope, $-E_a/R$, the activation energy E_a can be determined, and by taking the temperature at which $Wt = (W_0 + W_f) / 2$ in the place of T in the intercept term of Eq. (5), the pre-exponential factor A can also be determined.

Fig. 5 shows typical plots of $\ln[-\ln(1-x)/T^2]$ versus $1/T$, indicating that for WB pyrolysis (similar patterns for all other biomass samples), two independent first order reactions should be used to describe the pyrolysis process, which means that Eq. (3) is applied separately to each of the stages. To do so, the conversion x was recalculated for each reaction. The results are shown in Fig. 6. From the slope of each line, the value of E_a and A can be obtained for different stages. Table 3 shows the kinetic parameters of all the samples that were determined by this method. The kinetic parameters are calculated in the range from $x = 0.4$ to 99%, which represented almost the whole pyrolysis region. The good correlation coefficients indicate that the corresponding independent first order reaction model fits the experimental data very well.

From Fig. 6 and Table 3, it could be seen that both biomass pyrolysis and K-catalytic pyrolysis exhibited typical, two-stage characteristics. As discussed earlier, the first stage (temperature <300 °C) is

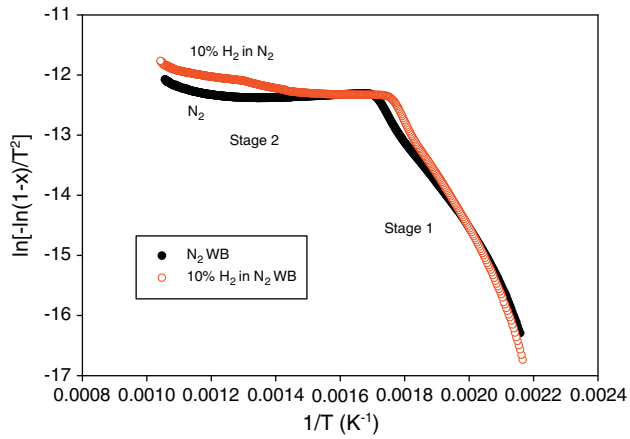


Fig. 5. Plot of $\ln[-\ln(1-x)/T^2]$ vs $1/T$ of biomass (WB) pyrolysis calculated by one-step integral method.

considered to be the decomposition of both hemicelluloses and celluloses, which usually accounts for 60–75% of the conversion during pyrolysis. The second stage (temperature 300–500 °C) is mainly attributed to the degradation of lignin; other reactions in this stage may include the secondary cracking of intermediate compounds to produce small molecules and polycondensation or carbonization reactions to produce char. Park et al. [23] reported that the predominant reaction pathway for biomass pyrolysis was a two-step consecutive first order reaction. Similarly, the pyrolysis of biomass in this work could also be described by two consecutive first order reactions.

The activation energy (E_a) values for biomass pyrolysis were 88–98 kJ/mol (under N_2) and 101–124 kJ/mol (under H_2) in the first stage, while the E_a values decreased sharply to 12–16 kJ/mol (under N_2) and 16–23 kJ/mol (under H_2) in the second stage. Chen et al. [32] reported that the activation energies for cellulose, hemicelluloses and lignin were 127 kJ/mol, 185 kJ/mol, and 31 kJ/mol, respectively, which were higher than the E_a values calculated in the first stage (responsible for the main pyrolysis stage). This is

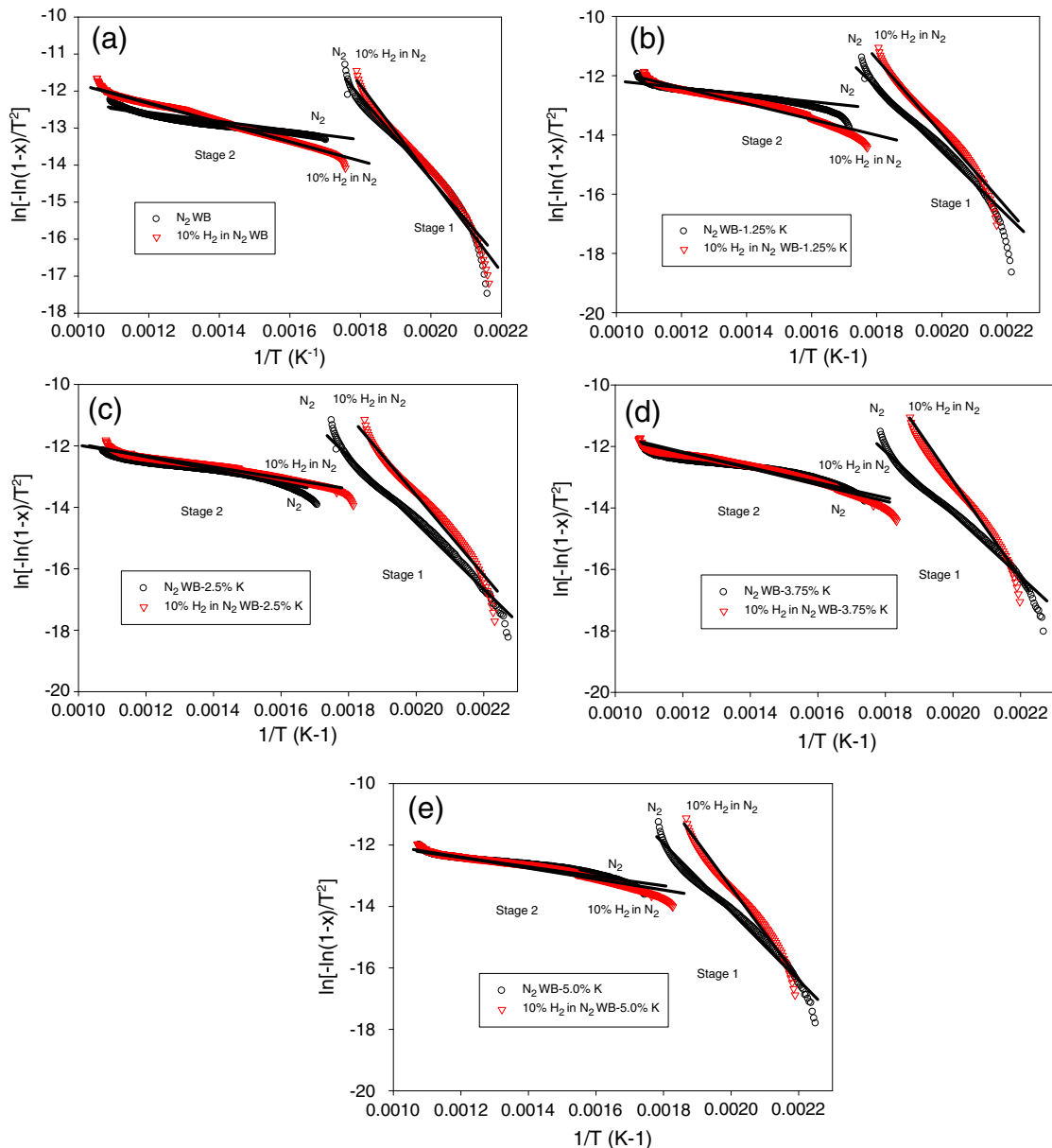


Fig. 6. Plots of $\ln[-\ln(1-x)/T^2]$ vs $1/T$ of (a) WB; (b) WB-1.25% K; (c) WB-2.5% K; (d) WB-3.75% K; and (e) WB-5.0% K pyrolysis recalculated by two-step integral method.

Table 3
Kinetic parameters of biomass (pine wood) pyrolysis.

Samples	Nitrogen atmosphere					Hydrogen atmosphere					
	(kJ/mol)	A(min ⁻¹)	x turning point (%)	T turning point (°C)	R ²	E _a (kJ/mol)	A(min ⁻¹)	x turning point (%)	T turning point (°C)	R ²	
WB	Stage 1	92.45	3.48 × 10 ⁸	63	297	0.9612	101.03	3.01 × 10 ⁹	67	287	0.9791
	Stage 2	11.76	3.22			0.9532	21.84	6.71			0.9936
WB-1.25% K	Stage 1	98.78	1.32 × 10 ⁹	71	298	0.9706	109.05	3.26 × 10 ¹⁰	76	282	0.9810
	Stage 2	13.62	6.88			0.9506	22.71	6.86			0.9732
WB-2.5% K	Stage 1	90.72	2.01 × 10 ⁸	76	298	0.9882	109.87	5.75 × 10 ¹⁰	69	270	0.9775
	Stage 2	16.04	3.46			0.9601	15.68	4.31			0.9701
WB-3.75% K	Stage 1	87.96	1.30 × 10 ⁸	73	287	0.9838	124.44	2.87 × 10 ¹²	62	261	0.9842
	Stage 2	15.02	4.29			0.9563	21.48	7.01			0.9568
WB-5.0% K	Stage 1	91.02	2.84 × 10 ⁸	69	288	0.9807	118.32	5.42 × 10 ¹¹	68	263	0.9806
	Stage 2	12.85	32.74			0.9541	16.83	4.14			0.9629

Note: E_a, activation energy; A, pre-exponential factor; x, conversion; T, temperature.

reasonable because the pyrolysis behavior of biomass, which is composed of cellulose, hemicelluloses and lignin, is different from that of its individual composition; probably some interaction between these three compositions exists for biomass pyrolysis. Moreover, the activation energy for biomass pyrolysis under H₂ increased slightly after impregnating K, this might be partly attributed to the increase of the initial sample mass. It is evident from the results that a change of atmosphere from nitrogen to hydrogen resulted in an increase in the E values (Table 3), which indicated different reaction mechanism for biomass pyrolysis under different gas environment.

Despite the variety in composition of the biomass samples, the activation energies (88–98 kJ/mol under N₂ and 101–124 kJ/mol under H₂) for the main devolatilization stage of biomass in this work fall within the range of the E values reported in other literatures, as shown in Table 4. It should be noted that in the previous work the choice of kinetic model had the potential to affect significantly on the evaluated apparent activation energy. For instance, an overall average E_a value was obtained by normalizing the pseudo-component fractions according to a nominal average lignocellulosic composition of sugarcane bagasse [33]. The mean value of E_a obtained for the eight parallel processes was determined to be 159.6 kJ mol⁻¹, with a standard deviation of 40.5 kJ mol⁻¹. The 121% average increase in E_a that occurs, when the kinetic model is amended from a consecutive to a concurrent reaction scheme, is a stark reminder that inappropriate model selection can have dire implications on the validity of the generated kinetic parameters.

Most of decomposition occurred in the first stage (conversion up to 76%), in which the pre-exponential factors are in the range of 1.32 × 10⁸ ~ 1.32 × 10⁹ and 3.01 × 10⁹ ~ 2.87 × 10¹² for biomass pyrolysis under N₂ and H₂, respectively. The remaining decomposition occurred in the second stage, but in this stage both the activation energy and the pre-exponential factors decreased rapidly. The calculated pre-exponential terms may vary by twenty or more orders of magnitude from literature values [4,33–37], making comparison difficult.

The turning points (the transition between stages) of conversion are 62–76 wt.% for biomass pyrolysis, but the turning points of temperature for biomass pyrolysis under H₂ shifted to lower temperature (compared to N₂), decreasing by 10 °C for WB and 16–28 °C for K-impregnated biomass samples. These results indicated that the pyrolysis of biomass was facilitated under H₂, and this effect was more prominent after impregnating potassium.

3.4. Evaluation of kinetic compensation effect (KCE)

In biomass pyrolysis the apparent activation energy has frequently been observed to increase with the frequency factor. As early as 1980, Chornet and Roy [38] commented that a kinetic compensation effect (KCE) existed in the pyrolysis of various biomass materials as such that there is a definite linear correlation between the variables ln A and E_a. According to the KCE, any alteration in experimental conditions that impels E_a to change will also prompt a complementary

Table 4
Activation energy values for biomass pyrolysis.

Biomasses	Temp. range (°C)	Reaction model	n	E _a (kJ mol ⁻¹)	Refs
Hemicellulose	105–800	Single-step	1	127 (200–350 °C)	[32]
Cellulose				185 (230–380 °C)	
Lignin				31 (283–441 °C)	
Bagasse	25–800	Single-step	0.1–0.6	161.1–169.5	[33]
Cashew shell	RT–900	Parallel (2 reactions)	1	130.2–174.4	[34]
Willow raw	–	Single-step	1	89.0	[4]
Willow K-impregnated				131.7–132.7	
Cotton-stalk	–	Single-step	1	71.055	[35]
Corn stalk				66.518	
Wheat straws	RT–800	Sequential (dual-step)	1	83.6	[36]
				3.74	
Biomass Leucaena	RT–700	Parallel (3 reactions)	0.88	88 (hemicellulose)	[37]
			1.26	203 (cellulose)	
			2.87	75 (lignin)	
K-impregnated biomass	RT–700	Consecutive (two-step)	1	88–98 (Stage 1, N ₂)	This work
				101–124 (Stage 1, H ₂)	
				12–16 (Stage 2, N ₂)	
				16–23 (Stage 2, H ₂)	

Note: °Temp. range for biomass pyrolysis. The E values are obtained for biomass pyrolysis under inert atmosphere unless specified.

compensating response in A . A group of reactions that demonstrate a linear fit of $\ln A$ and E_a values is known as compensation set. The linear relation between $\ln A$ and E_a is a possible explanation for the KCE that arises from the inevitable below:

$$\ln A = \ln k + \frac{E_a}{RT} \quad (6)$$

The kinetic data used to construct the KCE plot in Fig. 7 were from Table 3, where activation energies and frequency factors were evaluated using two consecutive first order models. The remarkably linear relationship between $\ln A$ and E in Fig. 7 (i.e., coefficient of determination equal to 0.9932) would seem to imply the existence of a KCE. The relationship between $\ln A$ and E_a could be expressed as:

$$\ln A = 0.241E_a - 2.289, R^2 = 0.9932$$

A possible explanation for the KCE arises from the inevitable scatter of $\ln A$ and E_a/R values, which occurs when thermoanalytical data is collected over narrow bands of rate and temperature [39]. Garn [40] argued that the KCE was mathematically inevitable because of the reciprocal relationship between A and $\exp(-E_a/RT)$ in the Arrhenius expression. Any change in one of these calculated quantities necessarily demands a compensatory change in the other. Given that the temperature range over which most reactions are studied is so narrow that T may be considered essentially constant and that measured rate constants generally remain within two to three orders of magnitude. Since a satisfactory mechanistic interpretation of such compensation behavior has not yet been established [41], apparently more investigations are needed for the exploration of the mechanism behind the KCE for biomass pyrolysis.

4. Conclusions

Energy crop plants require metals to grow and produce a high yield at harvest. Of all the metals present in biomass, it was reported that potassium had the greatest influence on its thermal conversion properties. The results from this work has demonstrated that the major alkali metal potassium has a significant effect on biomass pyrolysis, as shown by effects on the peak temperature, rate of degradation, chemical degradation mechanisms and yields of char.

It was observed that potassium salts catalyzed biomass pyrolysis and resulted in the decrease of the temperature at which the maximum degradation rate occurs (T_p), especially for biomass pyrolysis under H_2 . For example, the T_p decreased by 14.0–18.3 °C for

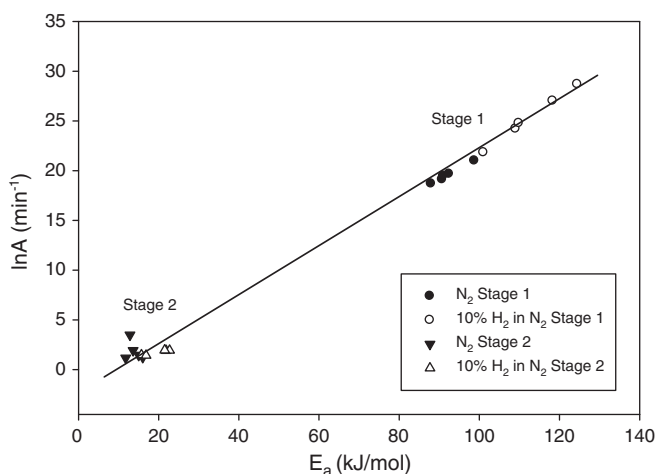


Fig. 7. Compensation plot for Arrhenius parameters obtained from kinetic data.

K-impregnated biomass pyrolysis under N_2 , while this value decreased by 20.8–34.1 °C under H_2 . At the same time, a large increase in char yield was found for all K-impregnated samples. However, it was noted that char yield did not increase proportionately to the potassium content; a great effect on the relative char yield was observed at lower potassium content (<1.25%). DTG analysis revealed that the thermal degradation processes of all biomass samples presented one main peak due to the overlapping effect from the degradation of hemicelluloses and celluloses.

According to the kinetic analysis, the pyrolysis of both unimpregnated and K-impregnated biomass could be kinetically described as two consecutive reactions (two-stage reaction). The activation energy (E_a) values are 88–98 kJ/mol (under N_2) and 101–124 kJ/mol (under H_2) in the first stage, but E_a decreased sharply to 12–16 kJ/mol (under N_2) and 16–23 kJ/mol (under H_2) in the second stage. The remarkably linear relationship between $\ln A$ and E for biomass pyrolysis under both N_2 and H_2 would seem to imply the existence of a kinetic compensation effect (KCE).

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