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Effects of organic and inorganic metal salts on thermogravimetric pyrolysis of biomass components

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Abstract−Thermogravimetric analyzer (TGA) was employed to elucidate the catalytic effects of organic and inorganic metal salts (K_2CO_3, KAc, Na_2CO_3 and NaAc) on the pyrolysis of three biomass components (cellulose, hemicellulose and lignin). In case of cellulose, TG analysis results showed that all the four metal salts increased the yield of char products and decreased the weight loss rates of cellulose pyrolysis, which followed the order of Na_2CO_3>K_2CO_3>NaAc>KAc. In contrast to cellulose, the four organic and inorganic salts employed had no significant effects on the remaining two biomass components:, hemicellulose and lignin. However, the four metal salts led to the devolatilization reaction of hemicellulose to occur at lower temperature region, and the dehydration reaction of lignin was promoted more or less. An increase in the heating rate might augment the maximum degradation rate. Different mixing ratios had little influence on the progress of catalytic pyrolysis. Based on the observations, the potential mechanism of the catalytic pyrolysis of biomass components with metal salts was discussed.

Keywords: TGA, Biomass, Metal Salts, Catalytic, Pyrolysis

INTRODUCTION

Biomass is generally considered an ideal renewable energy source that is capable of relieving the energy crisis and environmental pollution [1-3]. As a notable energy conversion technology, pyrolysis of biomass produces bio-oil as a substitute for fossil fuels [4-6]. Biomass is mainly composed of cellulose, hemicellulose, lignin, and a small amount of inorganic metals [7-9]. Though many studies about the pyrolysis process of three major biomass components have been conducted, knowing the catalytic effects of different metal salts on biomass pyrolysis is also very important for the application of biomass.

The possible interactions between the organic components of biomass and alkali metal ions were investigated by Gargiulo et al. [10]. They showed that alkali metal ions could affect both the devolatilization and gasification processes, which inhibited the levoglucosan yield while enhancing the production of CO_2 and H_2. Li et al. [11] observed that $ZnCl_2$ shifted the starting point of the pyrolysis reaction of phoenix tree residues to lower temperature, where Na_2CO_3 speeded up the reaction, and CaO moved the starting point of the reaction to higher temperature. Xing et al. [12] studied the catalytic pyrolysis behaviors of wood using copper and potassium over thermogravimetric analyzer (TGA) and pyrolysis-gas chromatograph/mass spectrometry (Py-GC/MS). The presence of both copper and potassium could increase the amount of small molecular compounds (C_2-C_4) and decrease the yield of bio-fuel precursors, the latter of which plays a more dominant role. Eom et al. [13] concluded that potassium had a prominent catalytic effect, which could promote the formation of low molecular weight compounds and suppress the formation of levoglucosan. With an increase in the content of potassium, the amount of formed C_6 and C_2C_6 poplar wood derivatives increased. In summary, the previous research work focused on the effect of alkali and earth alkali metals on biomass pyrolysis confirming that their presence promoted cellulose decomposition, enhanced the production of permanent gases and light oxygenates, and depressed the production of anhydrosugars such as levoglucosan. However, the studied samples were generally biomass and cellulose. Systematic studies on the effect of inorganics on other major biomass components such as hemicellulose and lignin have rarely been reported.

In this context, we investigated the catalytic effects of organic and inorganic metal salts on the pyrolysis of three biomass components (cellulose, hemicellulose and lignin) by using TGA. The potential mechanisms of the catalytic pyrolysis were discussed in detail. The objective was to provide the relative parameters and guidance for the wider use of biomass.

EXPERIMENTAL

1. Materials

Commercial microcrystalline cellulose, beechwood xylan and lignin alkali were purchased from Sigma-Aldrich and were considered as representatives of the three main biomass components: cellulose, hemicellulose and lignin, respectively. The average particle size of cellulose and lignin was about 50 μm, and xylan was about 100 μm. The ultimate and proximate analysis of the three biomass

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[‡] The authors declare no competing financial interest.

Table 1. Ultimate and proximate analysis of the three biomass components

Sample	Ultimate analysis^{daf}/%					Proximate analysis^{ad}/%			
	C	H	O	N	S	M	V	A	FC
Cellulose	44.06	5.98	49.49	0.41	0.06	6.59	88.85	0.21	4.35
Xylan	40.25	5.76	53.62	0.32	0.05	6.51	76.16	5.02	12.31
Lignin	58.70	5.45	35.43	0.37	0.05	6.87	67.10	2.94	23.09

daf: dry ash free basis; ad: air dried basis; M: moisture; V: volatile; A: ash; FC: fixed carbon

Table 2. Detail method used for the ultimate and proximate analysis

Content	Method	Content	Method
Carbon	GB/T [a] 476-2008	Moisture	GB/T [a] 212-2008
Hydrogen	GB/T [a] 476-2008	Volatile	GB/T [a] 212-2008
Nitrogen	GB/T [a] 19227-2008	Ash	GB/T [a] 212-2008
Sulfur	GB/T [a] 214-2007	Fixed carbon	GB/T [a] 212-2008

[a]National standard of China

components is shown in Table 1. The analysis method was based on the National standard of China, which is shown in Table 2. For comparison, the air dried basis, which was based on the samples losing the external moisture at a room temperature of 20 °C and a relative humidity of 60%, was chosen for the proximate analysis. Four organic and inorganic salts, namely, Na_2CO_3 and K_2CO_3 (≥98.0%, anhydrous, granular), NaAc and KAc (≥99.0%, powder), were purchased from Shanghai Huaheng Chemical Plant. All of the above reagents were of analytical grade.

2. Pyrolysis Experiment

For the pyrolysis experiments, the three biomass components physically mixed with 10% of four metal salts were carried out on a thermogravimetric analyzer (SETSYS-1750 CS Evol, Setaram). About 10 mg of the sample was pyrolyzed at a constant heating rate of 10 °C/min in the temperature range of 30 to 800 °C. Inert nitrogen (>99.999%) was chosen as the carrier gas with a flow rate of 120 mL/min. In addition, four mixing ratios (0%, 5%, 8% and 10%) and three heating rates (10 °C/min, 20 °C/min and 40 °C/min) were selected to investigate their effects on the pyrolysis of cellulose added with organic metal salt (KAc) by using the TGA.

3. Kinetic Theory

The TGA curves represent the overall weight loss rate of biomass during pyrolysis. For non-isothermal process, the kinetic law for biomass pyrolysis combined with the Arrhenius equation can be described by the following Eq. (1) [14]:

$$\frac{d\alpha}{dt}=K(1-\alpha)^n=A\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{1}$$

where, A is the pre-exponential factor, E is the activation energy, T is the absolute temperature, and R is the gas constant, n is the reaction order, and α is the conversion fraction, which can be defined by the following Eq. (2):

$$\alpha=(m_0-m)/(m_0-m_z) \tag{2}$$

where, m_0 is the weight of initial sample, m is the weight of sample at time of t, and m_z is the final sample weight. Here, the constant heating rate, β, can be described by the following Eq. (3):

$$\beta=\frac{dT}{dt} \tag{3}$$

Combining Eqs. (1) and (3), Eq. (4) can be obtained, which gives a different form of kinetic law:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{4}$$

The activation energy and pre-exponential factor are calculated by the Coats-Redfern integral method [15-17], which is based on Eqs. (5) and (6) as shown in the following:

For the 1st order of reaction,

$$-\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=-\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]+\frac{E}{RT} \tag{5}$$

For the nth order of reaction,

$$-\ln\left[\frac{-\ln(1-\alpha)^{(1-n)}}{T^2(1-n)}\right]=-\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]+\frac{E}{RT} \tag{6}$$

where, $\frac{2RT}{E}$ is far less than 1 and $-\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]$ is almost a constant, E and A can be obtained from the slope and intercept of the straight line by plotting $-\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ (n=1) or $-\ln\left[\frac{-\ln(1-\alpha)^{(1-n)}}{T^2(1-n)}\right]$ (n≠1) vs. $\frac{1}{T}$. The advantage of non-isother- mal experiment is that it allows shorter experimental time and eliminates the technical difficulties associated with an isothermal method which requires an initial heating period [12].

RESULTS AND DISCUSSION

1. Catalytic Effects of Metal Salts on the Pyrolysis of Biomass Components

1-1. Effects of Different Kinds of Metal Salts on Catalytic Pyrolysis

The TG and DTG pyrolysis curves of cellulose, xylan and lignin mixed with different metal salts are shown in Fig. 1. The experimental results revealed that the catalytic pyrolysis process consisted of three stages: dehydration, primary pyrolysis reaction, and a slower decomposition of residues [18]. During the main pyrolysis process, there was a dramatic decomposition of cellulose (325 to 425 °C) and xylan (220 to 320 °C), as well as a slower degradation of lignin

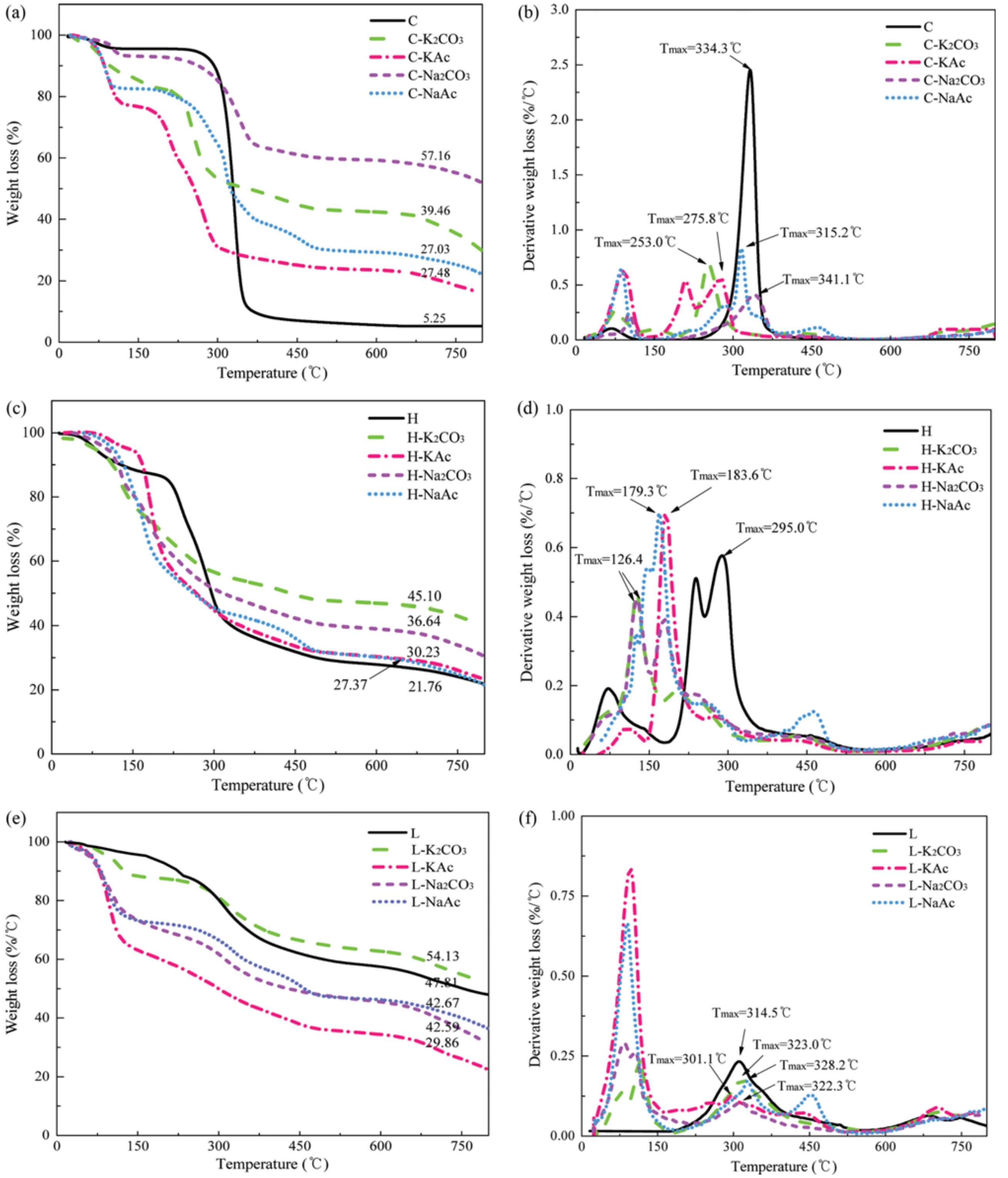

Fig. 1. TG and DTG pyrolysis curves of cellulose, xylan and lignin mixed with different metal salts.
(a) TG curve of cellulose+10% metal salts, (b) DTG curve of cellulose+10% metal salts, (c) TG curve of xylan+10% metal salts, (d) DTG curve of xylan+10% metal salts, (e) TG curve of lignin+10% metal salts, (f) DTG curve of lignin+10% metal salts

(200 to 500 °C). The non-condensable gases produced from the pyrolysis process were mainly consisted of H_2, CH_4, CO and CO_2 [19]. The amounts of solid products generated by cellulose, xylan and lignin were 5.35%, 27.73% and 47.81%, respectively.

TG and DTG pyrolysis curves of cellulose with 10% metal salts at a heating rate of 10 °C/min are presented in Figs. 1(a) and 1(b), respectively. All the four additives increased the yields of char products greatly, and decreased the temperature of maximum degradation rates. By adding Na$_2$CO$_3$ to cellulose, the amount of carbon increased from 5.35% to 57.16%, which indicated the decomposition pathway was different and the presence of salts favored the reactions for the formation of char. Furthermore, organic and inorganic metal salts affected the pyrolysis of cellulose in different ways. Organic metal salts had a distinct catalytic effect in prompting the formation of char, the increasing effect of which was in the following order: Na$_2$CO$_3$>K$_2$CO$_3$>NaAc>KAc. Inorganic metal salts might be beneficial for the dehydration reaction, whereas the organic metal salts had less significant effects on it. All the salts except Na$_2$CO$_3$ led to devolatilization to occur at lower temperature regions during the pyrolysis of cellulose. Compared to sodium additives, the potassium additives had a more significant effect. The maximum degradation rate could be achieved when the temperature shifted from 334.3 to 253.0 °C in the presence of 10% K$_2$CO$_3$. The DTG curve of the pyrolysis of cellulose with KAc had two weight loss peaks, which was also observed by Nowakowski et al. [20]. It indicated that the pyrolysis of cellulose in presence of KAc was more complicated, which needed further study.

Figs. 1(c) and 1(d) clearly showed that the TG and DTG curves had obvious changes when the pyrolysis of xylan was conducted in the presence of four metal salts. Although all the four metal salts shifted the starting point of primary pyrolysis reaction to lower temperature, each catalyst had different impact on the weight loss rate of the xylan pyrolysis. Organic metal salts (KAc and NaAc) increased the maximum weight loss rate from 0.58 to 0.72 °C/min, while the inorganic metal salts (Na$_2$CO$_3$ and K$_2$CO$_3$) had a little effect on the weight loss rate where it decreased from 0.58 to 0.46 °C/min. In addition, the yield of char increased when inorganic salts were added to xylan and slightly decreased in the presence of organic salts. Especially, K$_2$CO$_3$ played a dominant role in increasing the amounts of solid products during the catalytic pyrolysis of xylan (21.76% to 45.10%). An overlapping phenomenon existed in the temperature ranges of the two degradation processes (dehydration and devolatilization). The molecular structure of xylan was composed of two main units, which led to the existence of two weight loss peaks in the DTG curves. The addition of metal salts made the boundary of the two weight loss peaks become blurred.

Figs. 1(e) and 1(f) show the catalytic effects of four metal salts on the pyrolysis of lignin. During the initial decomposition stage (100 to 120 °C), there was a remarkable dehydration reaction when lignin was added with 10% of the metal salts. The moisture content was substantially increased with the addition of organic metal salts, which was in the following order: KAc>NaAc>Na$_2$CO$_3$>K$_2$CO$_3$. When KAc was added to lignin, the maximum dehydration rate increased from 0.19 to 0.85 °C/min. However, it was not clear whether the moisture came from the biomass component or the surrounding absorbed in the metal salts. In contrast to the dehydration stage (200 to 500 °C), the primary pyrolysis stage was suppressed slightly with the addition of four metal salts. Organic and inorganic metal salts did not change the weight loss behavior in the stage of slow decomposition of residues. On the whole, organic and inorganic metal salts except K$_2$CO$_3$ had a distinct catalytic effect in promoting the formation of aquo-compounds and suppressing the formation of char products. However, K$_2$CO$_3$ had no obvious influence not only on the yield of residues but also on the degradation rate of lignin. Note that the phenomenon of weight loss observed in the TGA of all the doped components occurred at higher temperature regions (after 600 °C), which was due to the thermal cracking of metal salts.

1-2. Effects of Different Mixing Ratios on Catalytic Pyrolysis

The TG and DTG curves of cellulose with different mixing ratios of KAc at a heating rate of 10 °C/min are shown in Figs. 2(a) and 2(b), respectively. The amounts of char products increased significantly in the presence of KAc, while the influence of organic metal salts was almost independent of the mixing ratios. Furthermore, all the catalysts with different mixing ratios had negligible influence on the weight loss rate of cellulose pyrolysis, where the maximum degradation rates were observed to be similar. However, a change in the mixing ratios had different effects on the dehydra-

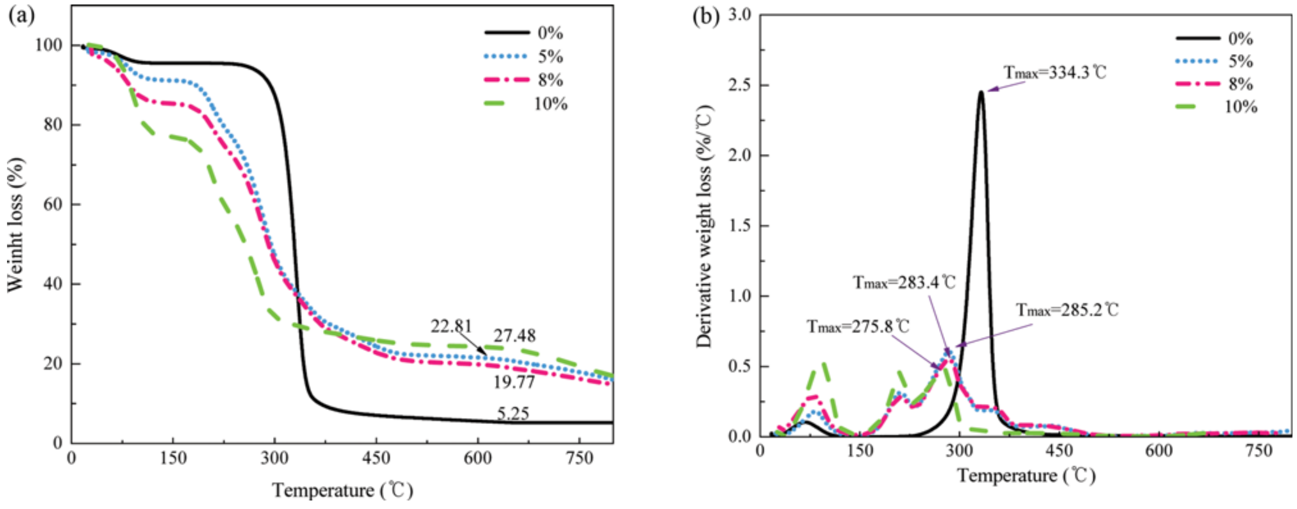

Fig. 2. TG and DTG curves of cellulose with different mixing ratios of KAc at a heating rate of 10 °C/min.
(a) Cellulose+KAc TG, (b) Cellulose+KAc TG

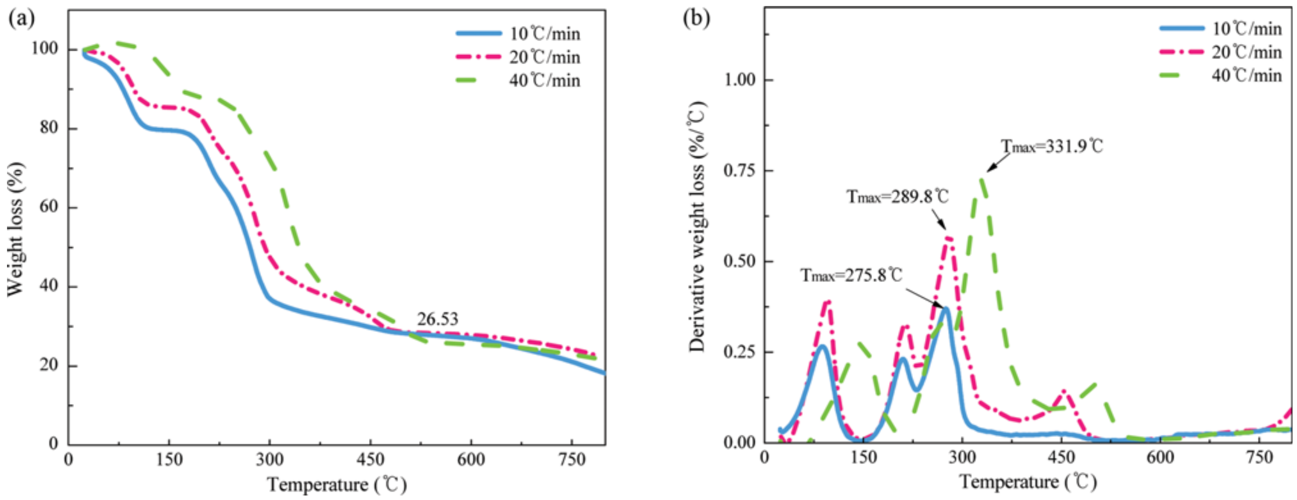

Fig. 3. TG and DTG pyrolysis curves of cellulose with 10% KAc at different heating rates.
(a) TG curve of cellulose+10% KAc, (b) DTG curve of cellulose+10% KAc

tion reaction, the increasing effect of which was in the following order: 10%>8%>5%>0%. All the organic metal salts shifted the starting point of primary pyrolysis reaction to lower temperature (about 280 °C). In addition, two peaks (peak 1 at 210 °C and peak 2 at 290 °C) were clearly observed in the DTG curves of primary pyrolysis reaction.

1-3. Effects of Heating Rates on Catalytic Pyrolysis

The TG and DTG pyrolysis curves of cellulose added with 10% KAc at different heating rates (10 °C/min, 20 °C/min and 40 °C/min) are presented in Figs. 3(a) and 3(b). The yield of char products in the co-pyrolysis at different heating rates was similar (around 26.53%), which indicated that heating rate had no obvious effect on the amount of char produced. The observed changes in the TG or DTG pyrolysis curves with different heating rates showed a good consistency. However, the varying heating rates had different influence on the weight loss rates and the initial pyrolysis temperatures. As the heating rate increased, the characteristic pyrolysis temperature of cellulose also increased. There was a backward-shift of the pyrolysis rate curve, and the weight loss rate gradually increased (from 0.40 to 0.75%/°C). Briefly, an increase in the heating rate speeded up the reaction rate, which shifted the initial point of pyrolysis reaction to higher temperature. The two weight loss peaks could also be observed clearly from the DTG curves in the main pyrolysis region.

The results of thermogravimetric experiments were the performance under the comprehensive control of the dynamic mechanism together with the heat and mass transfer mechanism [21]. Hence, at the same pyrolysis temperature, as the heating rate increased, the time for pyrolysis reaction decreased. Furthermore, the heating rate had a profound influence on the temperature gradient between the inside and outside of samples or between the measuring point and the sample. These led to the phenomenon of thermal hysteresis, which shifted the curves of primary pyrolysis reaction to the higher temperature regions.

2. Thermal Degradation Kinetic Analysis

The correlation coefficient (R) and activation energy (E) could be obtained by the Coats-Redfern integral method on the basis of drawn regression lines [19,22]. The calculated results for the biomass components with various contents of metal salts are shown in Table 3. It was found that the correlation coefficients were higher than 0.9655, which indicated the accuracy of this method. With adding 10% of the metal salts, the values of activation energy and pre-exponential factor in the cellulose pyrolysis reaction decreased significantly, which showed that the reaction rates decreased. An enhancement in the reaction order indicated an increase in the complexity of cellulose pyrolysis reaction. Different metal salts had different impacts on the kinetic parameters of the pyrolysis reaction of xylan. The values of activation energy and pre-exponential factor decreased slightly in the presence of potassium, whereas they increased slightly in the presence of sodium. Therefore, potassium promoted the decomposition of xylan. The four metal salts played a vital role in promoting the dehydration reaction of lignin, but had a negligible effect on the kinetic parameters of the overall pyrolysis reaction. The observed trends of kinetic parameters in the pyrolysis reaction of cellulose had no obvious changes with a change in the mixing ratios. However, the values of activation energy and pre-exponential factor increased obviously with an increase in the heating rates, which indicated that the pyrolysis reactions were speeded up.

3. Potential Mechanisms of the Catalytic Pyrolysis

Cellulose, hemicellulose and lignin were the three basic components of crude biomass. Cellulose was composed of a linear chain of different number of β(1→4) linked with D-glucose units, which was a polyhydroxy polymer containing a large number of adjacent hydroxyls. Xylan derived from beechwood was regarded as the substitute of hemicellulose, which had a branched structure consisting of both pentose and hexose. The degree of polymerization of hemicellulose was lower than that of cellulose [23]. Alkaline lignin was chosen as the representative of lignin, the basic monomeric units of which were p-hydroxyphenyl, guaiacyl, and syringyl [14-27]. It was apparent that both cellulose and hemicellulose contained numerous hydroxyl units. Lignin was characterized as

Table 3. Thermal degradation kinetic parameters for the three biomass components added with metal salts

Sample	t/°C	n	E/KJ·mol^{-1}	A/s^{-1}	R
C	200-450	1.8	172.22	8.62E+12	0.9937
C-K_2CO_3	200-450	3.0	118.48	1.89E+09	0.9841
C-KAc	200-450	2.4	94.95	1.69E+05	0.9869
C-Na_2CO_3	200-450	2.2	95.04	8.89E+05	0.9880
C-NaAc	200-450	2.0	89.56	5.28E+05	0.9856
H	100-450	1.2	42.51	35.74	0.9776
H-K_2CO_3	100-450	2.2	36.12	34.23	0.9808
H-KAc	100-450	1.8	30.26	3.00E+03	0.9827
H-Na_2CO_3	100-450	2.2	40.28	36.24	0.9960
H-NaAc	100-450	2.4	41.30	144.29	0.9789
L	150-600	1.8	53.23	47.49	0.9770
L-K_2CO_3	150-600	1.6	49.93	42.61	0.9892
L-KAc	150-600	1.6	44.60	57.03	0.9744
L-Na_2CO_3	150-600	1.4	49.41	49.92	0.9757
L-NaAc	150-600	1.2	47.51	59.6	0.9918
C-KAc-5%	200-450	1.6	92.38	1.05E+05	0.9735
C-KAc-8%	200-450	1.8	93.07	9.50E+05	0.9736
C-KAc-10%	200-450	2.4	94.95	1.69E+05	0.9869
C-KAc-10 °C/min	200-450	2.4	94.95	1.69E+05	0.9869
C-KAc-20 °C/min	200-450	2.4	99.51	5.48E+06	0.9655
C-KAc-40 °C/min	200-450	2.4	105.75	1.26E+07	0.9871

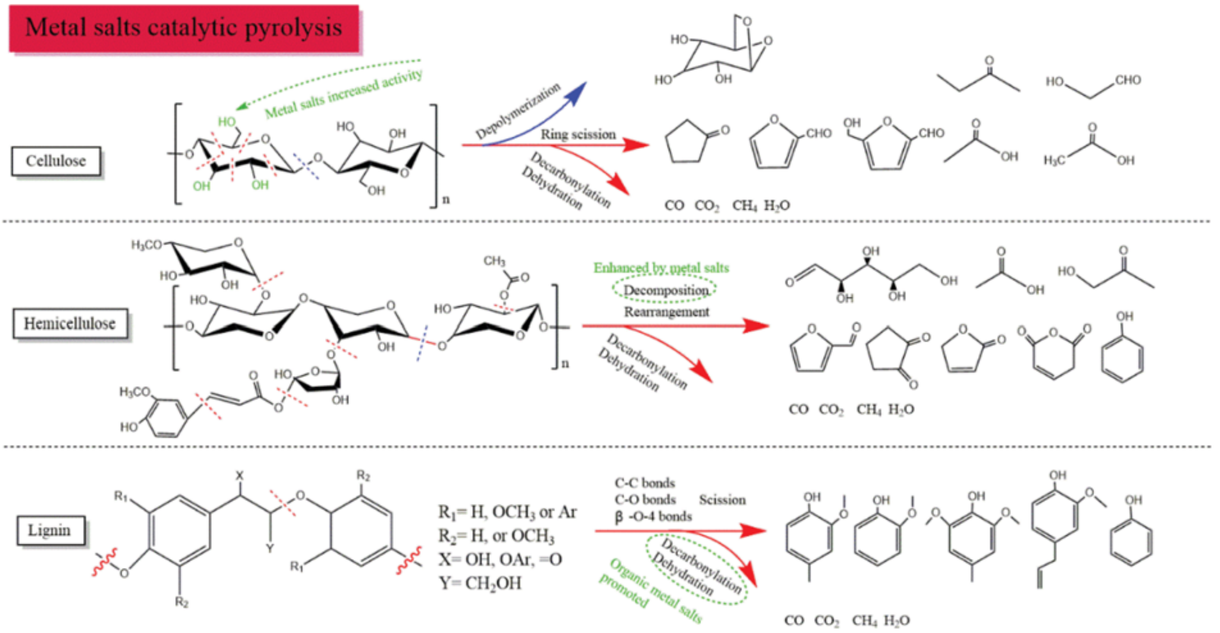

Fig. 4. Potential mechanisms involved in the catalytic pyrolysis of biomass components in the presence of metal salts.

polyaromatic units.

The potential mechanisms that might be involved in the catalytic pyrolysis of cellulose, hemicellulose and lignin with the addition of metal salts are shown in Fig. 4.

3-1. Potential Mechanisms of Cellulose in the Catalytic Pyrolysis

The results obtained from our investigation clearly showed that even the presence of a small amount of organic and inorganic metal salts in cellulose would alter the TG and DTG pyrolysis curves dramatically. In Figs. 1(a) and 1(b), a significant weight loss between 100 °C and 200 °C was corresponding to the decarbonylation and dehydration processes of cellulose, which released CO, CO_2, CH_4 and H_2O. During the primary pyrolysis process (200 to 350 °C), the pyrolytic products obtained from cellulose could be subdivided into three categories: 1) dehydrated sugars (such as levoglucosan), 2) furan derivatives (such as 2(5H)-furanone, 2-furaldehyde, etc.), 3) low molecular weight linear products (such as acetol, acetic acid, etc.) [28]. These observed results were consistent with the widely proposed pyrolysis mechanisms, where the competition between breaking of glycosidic bond and C-C bond was the primary reaction for the thermal depolymerization and ring scission of cellulose [29-31]. The intensive reaction involving the breaking of glycosidic bond was favored, in which a levoglucosyl end-group was formed [31]. Subsequent glycosidic bond cleavage transferred the chain from the levoglucosyl end-group and generated one molecule of levoglucosan and another levoglucosyl end-group for each of the cleavage event. A second set of reaction pathways producing furan derivatives and lower molecular weight species could compete with this reaction. A number of reactions were possibly involved in this set of competitive pathways [32-34]. The thermal depolymerization and ring scission of cellulose that occurred at the higher temperature region was due to its high degree of polymerization. The three alcoholic hydroxyl groups and seven hydrogen groups in the glucosyl ring had increasing activity in presence of all the four studied metal salts. Furthermore, metal salts promoted the dehydration and condensation reactions of these groups, which were responsible for the formation of char products. Considering the decline in the volatile components and an enhancement in the char products, it appears that the cellulose mixed with metal salts underwent a relative inhibition of the secondary cracking of levoglucosan.

3-2. Potential Mechanisms of Hemicellulose in the Catalytic Pyrolysis

In comparison with cellulose, the observed lower initial decomposition temperature of hemicellulose (Figs. 1(c) and 1(d)) was due to its lower degree of polymerization [27,35]. In contrast to a sharp weight loss of cellulose at ~335 °C, the decomposition and rearrangement of hemicellulose became slow to some extent and lasted from 130 to 300 °C. The DTG results showed that hemicellulose was favorable for the release of CO, CO_2, CH_4 and H_2O at lower temperature (<150 °C) [19]. The weight loss peaks of the two dehydration and decomposition processes were overlapped in the catalytic pyrolysis of hemicellulose added with metal salts. It was speculated that these results were due to the large number of short branched chains and methoxyl groups that existed in the polymer chains of hemicellulose [35]. When the metal salts were introduced in the pyrolysis process, a large number of branched chains in hemicellulose underwent dehydration and condensation among different parent polymers, which indicated the bond cleavage occurred at low temperature easily.

3-3. Potential Mechanisms of Lignin in the Catalytic Pyrolysis

The TG and DTG curves of lignin (Figs. 1(e) and 1(f)) were divided into three stages. The first stage was the removal of physically adsorbed water, which was promoted greatly by the metal salts. The following two stages resulted from the decomposition of lignin [35]. Compared with cellulose and hemicellulose, there was no distinct peak of weight loss during the primary decomposition. It might be due to the stable polyaromatic structure of lignin [36]. Lignin is a three-dimensional amorphous polymer, the structural units of which are p-hydroxyphenyl, guaiacyl, and syringyl connected by β-O-4 ether bond and C-C bond. Most of the oxygen-containing groups in lignin exist in a stable form such as an ether bond or phenolic hydroxyl groups, which are inert to some extent [35]. Therefore, the decomposition of lignin did not change in the presence of metal salts even at a relatively higher temperature. By contrast, the β-O-4 bonds in lignin experienced hemolysis and gave rise to the formation of benzene-containing units, which finally resulted in the generation of carbon materials.

CONCLUSION

Significant influences of metal salts on the pyrolysis of cellulose were found during the primary thermal decomposition process. The yield of char products increased greatly while the weight loss rate clearly decreased in the catalytic pyrolysis of cellulose. The initial point of pyrolysis reaction of hemicellulose moved to a lower temperature in the presence of metal salts. Negligible influence was noted in case of pyrolysis of lignin added with metal salts. All the four metal salts played a dominant role in increasing the moisture content generated from cellulose, hemicellulose, and lignin. The presence of metal salts could promote the dehydration and condensation reactions, which were responsible for the formation of char products. Metal salts also increased the activity of the numerous branched chains in hemicellulose. Overall, the current investigation and the observed results provided an in-depth understanding on biomass pyrolysis besides giving new insights into the mechanism of catalytic pyrolysis.

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