# A study on the mechanism research on cellulose pyrolysis under catalysis of metallic salts

**Shurong Wang[†], Qian Liu, Yanfen Liao*, Zhongyang Luo and Kefa Cen**

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China
*Electric Power College, South China University of Technology, Guangzhou 510640, China

**Abstract**−Experimental research on cellulose pyrolysis under catalysis of metallic salts was done on a thermobalance and a rapid pyrolysis system. Thermogravimetric analysis showed that $K^+$ catalyzed the formation of active cellulose strongly and decreased the activation energy of cellulose pyrolysis. Experimental results indicated that $K^+$ would promote the formation of char and restrain the production of bio-oil largely. $Fe^{2+}$ had a similar catalysis effect on cellulose pyrolysis with $K^+$. $Fe^{2+}$ particularly catalyzed the formation of small molecule gaseous product while $K^+$ the formation of char. The addition of $K^+$ or $Fe^{2+}$ resulted in a reduction of levoglucosan formation, and enhanced the production of hydroxyacetaldehyde and other small molecule components. Levoglucosan and hydroxyacetaldehyde were formed by the decomposition of active cellulose in a parallel mode. The secondary cracking of levoglucosan would also produce hydroxyacetaldehyde. A modified cellulose pyrolysis mechanism model was proposed based on the B-S model.

Key words: Cellulose, Pyrolysis, Metallic Salt, Catalysis, Mechanism

## INTRODUCTION

With the concerns over energy shortage and $CO_2$ emission, biomass is now being considered as an inexhaustible and clean energy resource all over the world. Recently, thermochemical conversion was considered to be the most common and convenient method for biomass utilized as a clean energy resource and chemical feedstock [1-3]. Biomass mainly consists of cellulose, hemicellulose and lignin [4]. Also, a very small quantity of inorganic component usually exists in biomass, as refers to alkali, earth alkali and other compounds. Special attention has been paid to alkali metallic salt, which has a strong catalysis on biomass gasification [5]. Besides that, contamination and deposition would appear easily on the equipment surface because of the strong volatility of alkali metallic salt [6,7]. Among many kinds of metallic salts, potassium salt appears to be the most important for its higher content in biomass. Some other transition metallic salts such as ferric and cupric salt have a little effect on the pyrolysis behavior, but might influence the composition of liquid product [8]. Catalysis effect of metallic salt on product distribution has been studied. K and Ca ions might promote the formation of char from wood with the expense of tar and levoglucosan formation. Other metal ions, particularly Fe and Cu, enhanced the yield of levoglucosan and char from wood and newsprint [9].

Pyrolysis is not only the inevitable pathway in the process of gasification or combustion of biomass, but also an independent technology to produce high quality product, such as flash pyrolysis for bio-oil production [10]. Therefore, it is necessary to carry out an in-depth study of the effect of metallic salt on biomass pyrolysis behavior for following optimization of thermochemical conversion technology. In this paper, cellulose was chosen as the representative for biomass, for its simplicity and importance in biomass pyrolysis [11]. Moreover, the behavior of cellulose pyrolysis could reflect that of whole biomass pyrolysis [12]. Kinetic research, which is often carried out on thermobalance, is a fundamental method to reveal the behavior of cellulose pyrolysis. And here, typical metallic salts such as KCl and $FeCl_2$ were used in the present study.

## EXPERIMENTAL

### 1. Thermogravimetric Analysis

Cellulose particles had a size within the range of 50-61 μm, which were obtained directly by pulverizing pure filter paper, having more than 99.99% of cellulose and less than 0.01% ash. Before thermogravimetric analysis, cellulose particles were soaked in a predetermined content solution of selected metallic salt for 12 hours, followed by desiccation at a temperature of 333 K. And the metallic salt content in the dried cellulose particles were measured by atomic absorption spectrophotometry. $K^+$ and $Fe^{2+}$ had a content of 1%wt and 0.4%wt, respectively, in corresponding dried cellulose particles. Then thermogravimetric analysis was processed by recording both the history of mass loss of cellulose particles and corresponding temperature, under a linear temperature increase from the ambient to the final. In order to fully characterize cellulose pyrolysis at an inert atmosphere, nitrogen of the purity over 99.99% at a steady flow of 40 ml/min was selected as the carrier gas. A quantity of cellulose of about 5 mg was used in each experiment.

### 2. Cellulose Rapid Pyrolysis System

As shown in Fig. 1, the pyrolysis system mainly consists of a preheating part, a pyrolysis reactor, and a rapid condensation system. The pyrolysis reactor was a quartz glass tube, having a diameter of 30 mm, a thickness of 5 mm and a length of 1,200 mm. A silicon carbide pipe, being concentric with quartz glass tube, supplied the heat required in cellulose pyrolysis by thermo radiation at a maximum electric power of 8 kW. Nitrogen of over 99.99% purity
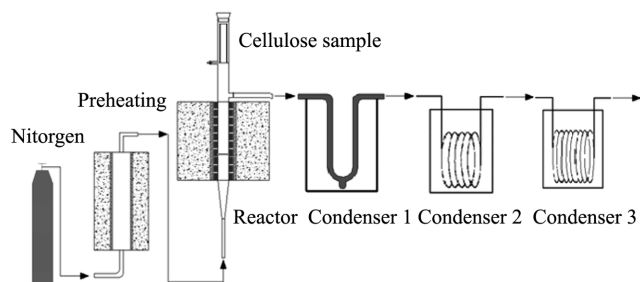
Fig. 1. Cellulose rapid pyrolysis system.

was also adopted here as the carrier gas to ensure that pyrolysis underwent at an inert atmosphere. To reduce the char content in tar, a quartz fiber mesh was located at the exit of reactor and separated most char from the volatile released out during cellulose pyrolysis. The following multi-condensation system could quench the volatile quickly and collect the liquid products, in which the condensation mediums are the mixture of ice and water in the first part, and the mixture of dry ice and acetone in the following two parts.

Similar to the pretreatment of cellulose particles for thermogravimetric analysis, the dried cellulose had $K^+$ and $Fe^{2+}$ content of 0.8%, 2.0%, 3.0%wt and 0.02%, 0.30%, 0.50%wt, respectively. The detailed operating procedure can be seen in the literature [12]. The water content in the collected liquid product (bio-oil) was measured by Karl Fischer method, while the organic components were determined with a GC-MS apparatus.

## RESULTS AND DISCUSSIONS

### 1. Analysis of Thermogravimetic Curves

As shown in Fig. 2 and Fig. 3, cellulose first underwent a dehydration process, followed by a slight weight loss which was ascribed to slow depolymerization or glass-transition, corresponding to the flat region of DTG curves. Then free radicals and some functional groups appeared, accompanied by the release of a little small-molecule volatile. This was followed by the formation of active cellulose, corresponding to the shoulder on DTG curves. When temperature increased more, cellulose would decompose violently and had an obvious peak on DTG curves, as was the main pyrolysis stage
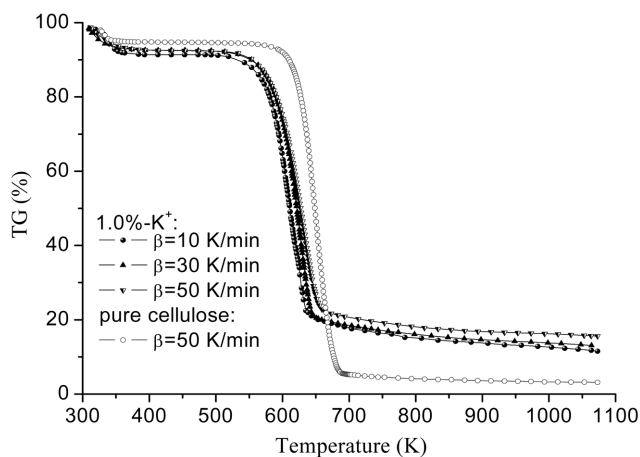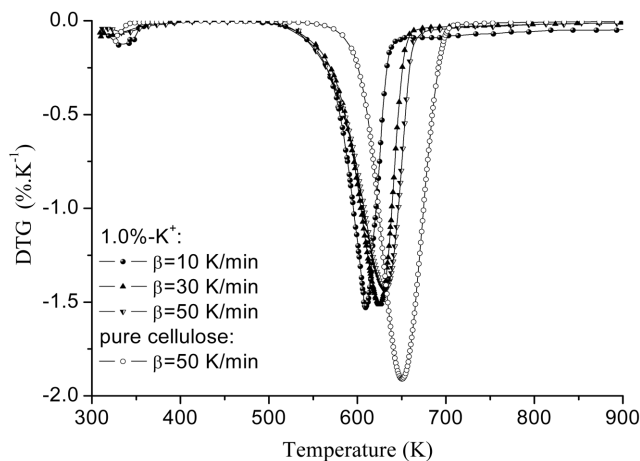


Fig. 3. Catalysis effect of KCl addition on DTG curves.

of cellulose. The stage was then followed by a slight decomposition of residue. Along with the increase of heating rate, the main weight loss stage widened and moved slightly towards higher temperature.

After cellulose was added with KCl, char yield at the end of main pyrolysis stage increased largely from 5%wt for pure cellulose to 20%wt. The final char yield also remained at a value of 15-18%wt at the end of the pyrolysis. KCl had an obvious promotion in char production during cellulose pyrolysis [5,9]. Moreover, KCl also influenced the thermo-decomposition behavior of cellulose. It could be seen that the shoulder of TG and DTG curves appeared earlier in a lower temperature region under the catalysis of KCl. And the peak of DTG curves also had a shift in the direction of lower temperature. All of these indicated that KCl strongly catalyzed the formation of active cellulose. Comparing the DTG curves of pure cellulose with that of cellulose after KCl addition, the weight loss rate of the former gradually exceeded that of the latter with a temperature increase at the same heating rate. This might be attributed to the fact that the addition of KCl decreased the activation energy of cellulose pyrolysis. Fig. 4 and Fig. 5 showed the thermo-decomposition behavior of cellulose after being added with $FeCl_2$. The residue continued to decompose after the main pyrolysis stage, as led to a final char yield about 5%wt. It is clear that $FeCl_2$ had a similar
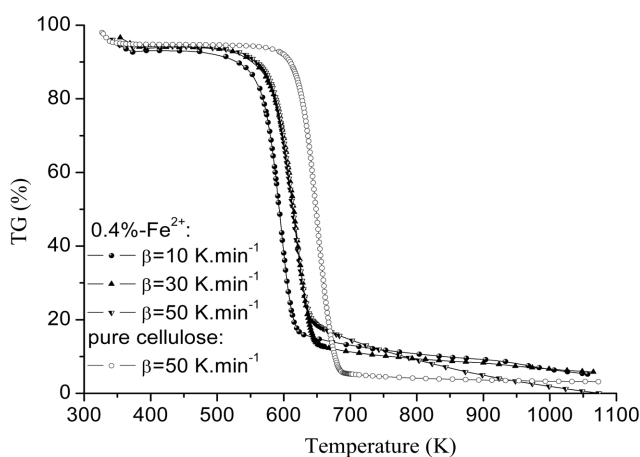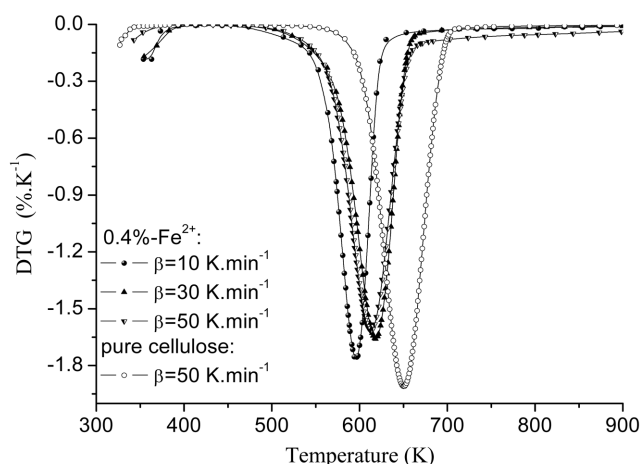


Fig. 2. Catalysis effect of KCl addition on TG curves.



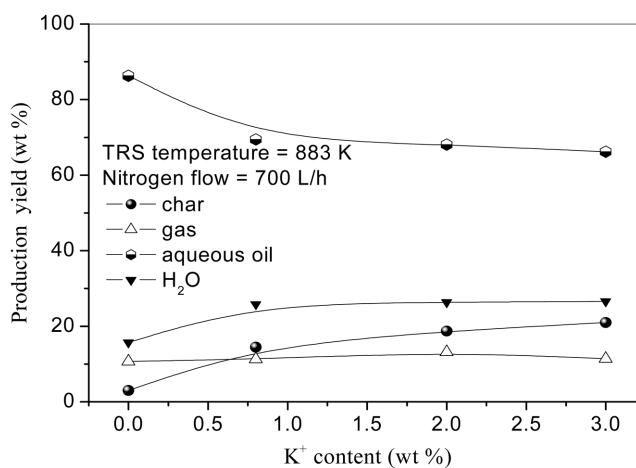Fig. 4. Catalysis effect of $FeCl_2$ addition on TG curves.

**Fig. 5. Catalysis effect of FeCl₂ addition on DTG curves.**



**Fig. 6. Product distribution at different content of K⁺ addition.**
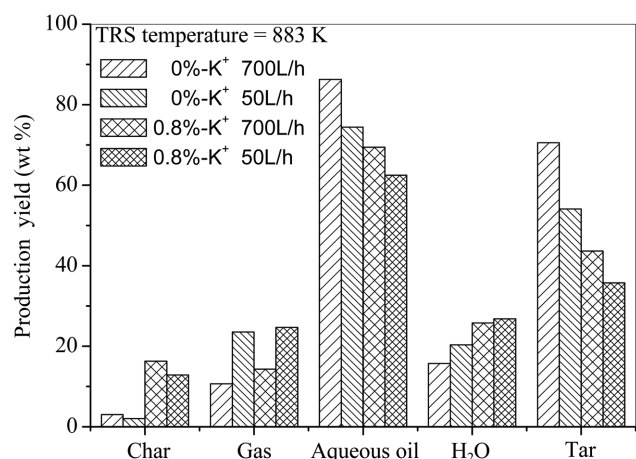


**Fig. 7. Product distribution before and after K⁺ addition.**

but some weaker catalysis with KCl.

## 2. Products' Distribution in Cellulose Rapid Pyrolysis

As shown in Fig. 6 and Fig. 7, high concentration of K⁺ would promote the formation of char and largely restrain the production of bio-oil. Also, the gas yield was improved comparatively, but the

trend was much slighter than that of char. Therefore, the catalysis of K⁺ had a higher selectivity on the formation of char rather than gas. At the same time, the yield of water increased sharply from 15.7%wt to 26%wt after the addition of K⁺, indicating that the dehydration reaction was promoted largely. Correspondingly, the content of organic compounds in bio-oil decreased obviously. The bio-oil produced form pure cellulose was somewhat sensitive to secondary cracking, occurring easily at a long residence time [13,14]. However, after KCl addition, the volatile was little sensitive to temperature and would not decompose intensively at a long residence time. Similarly, the water yield increased smoothly with the increase of residence time under the catalysis of K⁺.

After $Fe^{2+}$ addition, char yield increased slightly about 4-5%wt (seeing Fig. 8). And $Fe^{2+}$ restrained the formation of bio-oil and promoted the production of gaseous product. Fig. 9 shows that $Fe^{2+}$ had the similar catalysis on water production with K⁺. However, $Fe^{2+}$ particularly catalyzed the formation of small molecule gaseous product while K⁺ the formation of char.

On the basis of the observation of metallic salt distribution with electron microscopy, combined with the content determination of metallic ion in aqueous oil and char, the catalysis of K⁺ or $Fe^{2+}$ mainly occurred in solid phase. Only little metallic ion was released out of
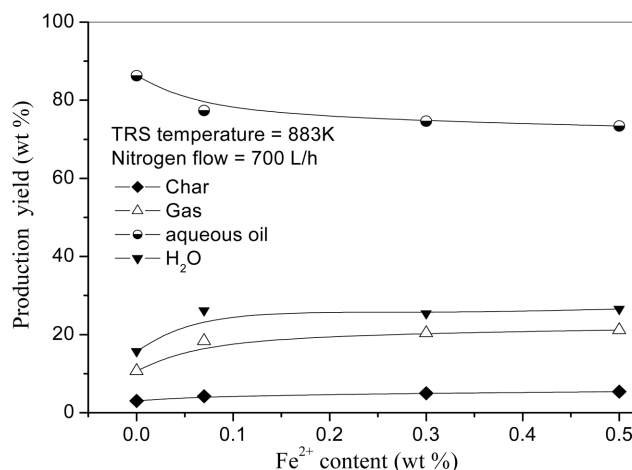


**Fig. 8. Product distribution at different content of $Fe^{2+}$ addition.**
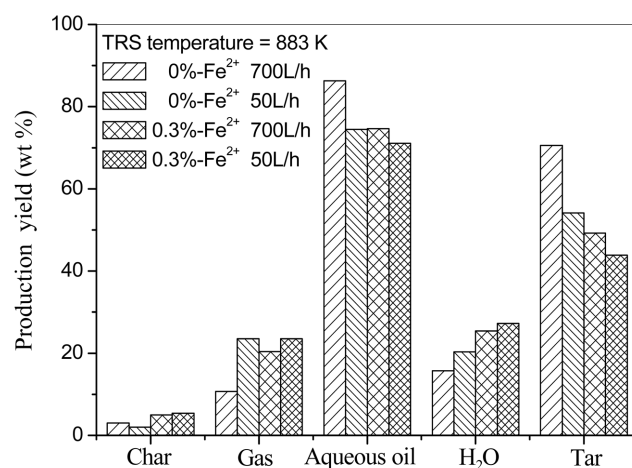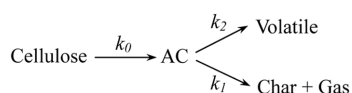


**Fig. 9. Product distribution before and after $Fe^{2+}$ addition.**

solid particles and entered into the liquid or gaseous product. Though metallic salt restrained the formation of liquid product in biomass pyrolysis, it could selectively enhance or restrain the formation of some compounds and changed the component distribution. Similar to the results of other researchers [9,13], the addition of $K^+$ or $Fe^{2+}$ resulted in a reduction of levoglucosan formation, and improved the production of hydroxyacetaldehyde, acetol and other small molecule components, such as alcohols, ketones and aldehydes. After 0.8%wt $K^+$ addition, levoglucosan had a decrease in content from 71.8% to 14.1%, while hydroxyacetaldehyde and acetol increased from 6.2% and 1.7% to 8.7% and 2.9% separately. The trend would be more obvious in the case of high concentration $K^+$ addition. $Fe^{2+}$ had a similar but somewhat weaker catalysis effect on the bio-oil component compared with $K^+$. Therefore, it is possible to change or optimize bio-oil component by selecting appropriate operation conditions and metallic salts.

### 3. Mechanism Analysis

Experimental results showed that the addition of metallic salts clearly influenced the pyrolysis behavior of cellulose, and altered the final products' distribution. However, according to the catalysis fundamental principle, no matter what kind of catalyst doesn't affect the final chemical reaction pathways. The existence of catalyst accelerates some reactions and strengthens them, and correspondingly conceals some other reactions.

$$Cellulose \xrightarrow{k_0} AC \underset{k_1}{\overset{k_2}{<}} \begin{array}{l} Volatile \\ Char + Gas \end{array}$$

As shown above, the widely accepted Broido-Shafizadeh model illustrates the pyrolysis mechanism of cellulose [15]. In the initial stage the polymerization degree falls and active cellulose (AC) forms. Then two competitive reactions take place. Here low temperature is beneficial to the formation of char, while high temperature is to the formation of volatile [16].

However, without reliable experimental support, the existence of active cellulose is always the controversial focus. Therefore, experimental research on flash pyrolysis of microcrystalline cellulose was carried out on a high radiation reactor. An intermediate product was obtained, which was slightly yellow, soluble and solid at ambient temperature. Fig. 10 shows the IR spectra of microcrystal-
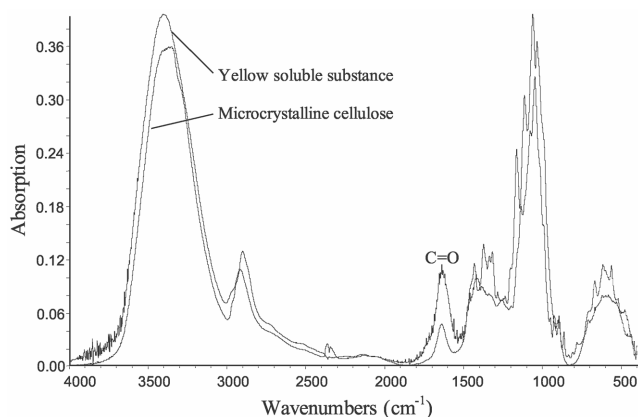
**Fig. 10. IR spectrums of microcrystalline cellulose and yellow soluble substance.**
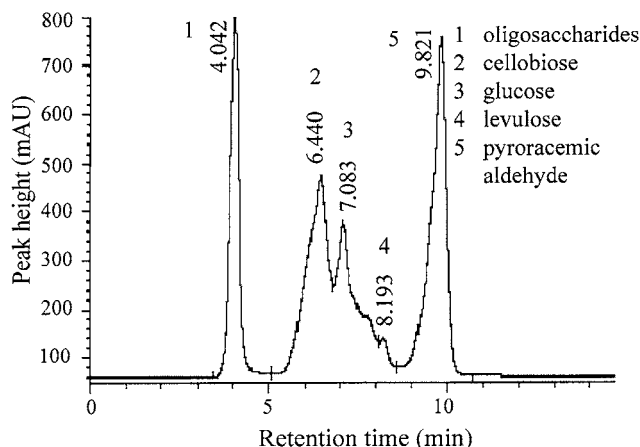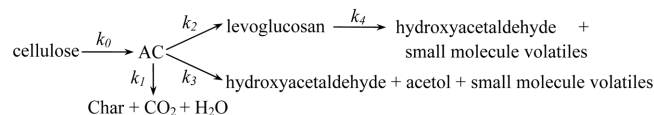
**Fig. 11. HPLC spectrum of yellow soluble substance.**

line cellulose and the yellow soluble substance. Although several changes were noted, the focus here was the intensifying of the absorption band of C=O at 1,650 cm$^{-1}$. It might be the aldehyde groups at C-6, or keto-groups at C-2 and C-3. Most of the active keto-groups underwent further changes, making the cellulose chain susceptible to depolymerization. HPLC analysis showed the main existence of oligosaccharides with an average polymerization degree of about 14 in the yellow soluble substance (Fig. 11). Thus, the reactions in initial stage not only change the structure of cellulose, but also generate a kind of intermediate compound, presumed as active cellulose.

Being two primary products from cellulose pyrolysis, the formation mechanism of levoglucosan and hydroxyacetaldehyde and the relationship between them becomes a research focus [14,17]. According to the experimental results, both $K^+$ and $Fe^{2+}$ caused a reduction of levoglucosan formation, and improved the production of hydroxyacetaldehyde, acetol and small molecule components. It is obvious that hydroxyacetaldehyde forms in a rather different way compared with levoglucosan [18]. The formation of volatile in cellulose pyrolysis behaves in two competing reactions [9]. The cracking of glucosidic bond in AC produces levoglucosan with its isomeric anhydrosugar, while opening of the acetal structural ring and cracking of internal C-C bond in pyranoid ring lead to the formation of hydroxyacetaldehyde, acetol and other small compounds, regarded as the competitive products compared with levoglucosan. High temperature is beneficial to the formation of competitive products, which has higher activation energy [19]. In the case of metallic salt addition, the cracking of glucosidic bond is restrained but the dehydration and reforming reaction are promoted, resulting in the different changes of levoglucosan and hydroxyacetaldehyde yields.

However, in the early researches levoglucosan was considered as the intermediate product, and its secondary cracking generated all other volatiles [17,20]. Our experimental research showed that in the case of $K^+$ addition, levoglucosan content decreased a little from 14.1% to 10.6%, while the hydroxyacetaldehyde content increased largely from 8.7% to 16.9% when the carrier gas flow was altered from 700 L/h to 50 L/h. Hydroxyacetaldehyde is produced by reforming reaction of saccharides. Also, the secondary cracking of saccharides generates almost all the compounds in bio-oil except themselves. Furthermore, levoglucosan pyrolysis had almost the

same production distribution with cellulose pyrolysis by Fourier Transform Infrared Spectroscopy analysis [14]. So the formation of levoglucosan and hydroxyacetaldehyde behaves both in parallel and continuous reaction mode. Therefore, a modified cellulose pyrolysis mechanism model is proposed as follows:

$$\text{cellulose} \xrightarrow{k_0} \text{AC}$$

with branches:
- $\xrightarrow{k_2}$ levoglucosan $\xrightarrow{k_4}$ hydroxyacetaldehyde + small molecule volatiles
- $\xrightarrow{k_3}$ hydroxyacetaldehyde + acetol + small molecule volatiles
- $\xrightarrow{k_1}$ Char + $CO_2$ + $H_2O$

## CONCLUSIONS

Thermogravimetric analysis showed that $K^+$ or $Fe^{2+}$ reinforced the formation of active cellulose and catalyzed the dehydration reaction. The experimental results on rapid pyrolysis system indicated that $K^+$ or $Fe^{2+}$ restrained formation of aqueous oil and enhanced production of char and gas. The addition of $K^+$ or $Fe^{2+}$ caused a great reduction of levoglucosan production, and improved the production of hydroxyacetaldehyde, acetol and small molecule components. $Fe^{2+}$ had a similar but somewhat weaker catalysis effect on the bio-oil component compared with $K^+$. After the addition of metallic salts, cellulose pyrolysis products had a higher stability and would not undergo secondary cracking easily. It is possible to change or optimize bio-oil components by selecting appropriate operation conditions and metallic salts. Being the primary pyrolysis products, levoglucosan and hydroxyacetaldehyde consumed active cellulose in a parallel reaction mode. Also, the secondary cracking of levoglucosan could produce hydroxyacetaldehyde. A modified cellulose pyrolysis mechanism model was proposed based on the B-S model.

## ACKNOWLEDGMENT

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