



Contribution of dehydration and depolymerization reactions during the fast pyrolysis of various salt-loaded celluloses at low temperatures



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HIGHLIGHTS

- Mg/Ca are more effective than Na/K in catalyzing cellulose dehydration during heating-up.
- Most of Mg/Ca (but little Na/K) become water insoluble during cellulose heating-up.
- Cellulose dehydration is significantly catalyzed by Na/K but not Mg/Ca during isothermal pyrolysis.
- Depolymerization is trivial during cellulose heating-up but important during isothermal pyrolysis.

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ABSTRACT

The loaded salts (NaCl, KCl, MgCl₂, and CaCl₂) have significantly different influence on the contribution of dehydration and depolymerization reactions to the decomposition of sugar structures during cellulose fast pyrolysis at 325 °C. The structures of salt-loaded celluloses already become cross-linked during heating-up period, largely due to the enhanced dehydration reactions catalyzed by inorganic species. As stronger Lewis acids, the alkaline earth metal ions (Mg²⁺ and Ca²⁺) are more effective than the alkali metal ions (Na⁺ and K⁺) to catalyze the dehydration reactions of sugar structures, leading to the formation of more cross-linked cellulose for the alkaline earth metal chloride-loaded celluloses. As a result, the majority of Mg and Ca are transformed into water-insoluble forms during the heating-up period, largely reducing the catalytic effects of these species on the dehydration of sugar structures during the subsequent isothermal pyrolysis. Rather, the dehydration of non-sugar structures is enhanced because the catalytic species are already bonded with non-sugar structures. In contrast, the dehydration of sugar structures during the heating-up period is less significant for the NaCl-loaded and KCl-loaded celluloses. The majority of Na and K are water-soluble after the heating-up period so that the dehydration of sugar structures is further enhanced during isothermal pyrolysis. The loaded salts have less influence on the depolymerization reactions. The contribution of depolymerization reactions to sugar conversion is relatively small during the heating-up stage, but increases substantially during isothermal pyrolysis.

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1. Introduction

Biomass is considered to be an important source for biofuels production, especially via the technical route of bio-oil production from fast pyrolysis followed by biorefinery [1,2]. However, bio-oil as a feedstock suffers from several key undesired features including high acidity [2,3], low heating value [3] and high viscosity [1,4,5]. Therefore, fundamental understanding on biomass

pyrolysis chemistry and mechanisms is essential to realizing the production of high-quality bio-oil.

Lignocellulosic biomass has complex macromolecular structures which consist of three major oxygen-containing organic polymers including cellulose, hemicellulose, and lignin [6]. The pyrolysis of biomass and its model compounds (cellulose, hemicellulose and lignin) experiences complex chemical reactions during pyrolysis [7–10]. The formation of a liquid intermediate during the pyrolysis of biomass or its model compounds (such as cellulose) is an important phenomenon which has not been clearly understood yet [11–13]. Such a liquid intermediate as the precursors of volatiles strongly determines the properties of produced

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bio-oil. Biomass also contains abundant inherent inorganic species (e.g., alkali and alkaline metallic species) which can have significant effects on biomass pyrolysis and bio-oil production [14]. Our recent study [15] revealed the fundamental mechanism of the MgCl_2 loading in weakening the hydrogen bonding network within the macromolecular structures of cellulose during pyrolysis. Significant dehydration reactions take place even during the heating-up period, leading to the formation of a highly cross-linked cellulose during the subsequent pyrolysis. The nature of salts added into cellulose is widely known to be a critical factor that alters the reaction mechanism and the properties of pyrolysis products [16–20]. Unfortunately, no study has been carried out to investigate the effect of different alkali and alkaline earth metal species on the contribution of dehydration and depolymerization reactions during the fast pyrolysis of salt-loaded celluloses.

Therefore, this paper continues the work reported in our recent study [15] and aims to understand the significantly different contribution of dehydration and depolymerization reactions during the fast pyrolysis of cellulose samples loaded with various alkali and alkaline earth metal chlorides including NaCl, KCl, MgCl_2 and CaCl_2 .

2. Experiments

2.1. Materials and fast pyrolysis experiments

Cellulose was purchased from a commercial supplier (Sigma–Aldrich, Avicel PH-101) and sieved to a size fraction of 75–106 μm . The size-fractioned cellulose sample was then washed by deionized water to remove water-soluble components that may exist originally. This washed cellulose is hereafter referred to as “raw” cellulose. A set of salt-loaded cellulose samples were prepared from the raw cellulose via wet impregnation using a suitable amount of each salt (NaCl, KCl, MgCl_2 or CaCl_2) at ~ 0.025 mol salt per mole of glucose unit. A drop-tube/fixed-bed quartz reactor (carrier gas: Argon), described elsewhere [21,22], was used for the conduction of fast pyrolysis experiments of the raw and salt-loaded cellulose samples. In each experiment, the pyrolysis reactor was firstly preheated to 325 $^\circ\text{C}$. Approximately 0.3 g of sample was then fed into the reactor in one shot, followed by holding the reactor at the temperature for various holding times. Once the pyrolysis experiment is finished, the reactor was taken out of the furnace and rapidly cooled down to room temperature with argon continuously flowing through the reactor. For the pyrolysis experiment at zero holding time, the reactor was taken out of the furnace immediately after the sample bed temperature reached 325 $^\circ\text{C}$, as monitored by a thermocouple. The initial heating rate is estimated to be ~ 150 $^\circ\text{C s}^{-1}$, according to a method detailed elsewhere [23]. The solid residue after pyrolysis was then collected and the weight loss of the sample during pyrolysis was also determined.

2.2. Sample characterization and analysis

In this study, the solid residue was separated into water-soluble and water-insoluble portions, which are referred as to water-soluble and water-insoluble intermediates, respectively. As raw cellulose is insoluble in water, the water-soluble compounds in the pyrolyzed solid residue are indeed produced from pyrolysis reactions. The water-soluble portion were obtained via the extraction of the solid residues using deionized water at room temperature according to a procedure detailed elsewhere [24,25]. The concentration of the total organic carbon in the solution after extraction was quantified using a Shimadzu total organic carbon (TOC) analyzer. The yield of water-soluble intermediates (on a carbon basis) was then normalized as the percentage of the total

carbon in the raw cellulose fed into the reactor. The carbon contents of the solid residues were analyzed by a PerkinElmer elemental analyzer for the determination of cellulose conversion based on carbon. The total sugar contents in the liquid and solid samples were determined, via the post-hydrolysis technique described elsewhere [26], for the determination of cellulose conversion based on sugar. The inorganic species in the solid samples were determined using a method detailed elsewhere [27].

3. Results and discussion

3.1. Differences in conversions during the pyrolysis of various salt-loaded celluloses

Fig. 1 presents the results on the cellulose conversions based on weight, sugar, carbon for the raw and various salt-loaded celluloses during pyrolysis under the experimental conditions. The data for the raw and MgCl_2 -loaded celluloses are adapted from our recent work [15]. The conversion on a sugar basis is calculated based on the number of mono-sugar units remained in the solid residue (quantified via post-hydrolysis) as a percentage of those in the initial cellulose. The conversion on a carbon basis is calculated based on the carbon remained in the solid residue as a percentage of the total carbon in the raw cellulose. Similar conversions on bases of weight, sugar and carbon would suggest that depolymerization reactions take place to release anhydro-sugars, while a lower carbon conversion indicates that dehydration reactions play an important role during pyrolysis. The data in Fig. 1 suggest that the addition of salts significantly changes the cellulose conversion during pyrolysis at 325 $^\circ\text{C}$. Compared to the raw cellulose, the cellulose weight conversions of various salt-loaded celluloses are initially higher during the heating-up period, but increase slowly during the isothermal pyrolysis and start to level off at middle conversions (i.e., 40–60%), leading to higher char yields. Significant differences in the cellulose conversions can be found during the pyrolysis of various salt-loaded celluloses. The weight conversions of the salt-loaded celluloses generally follow an order of MgCl_2 -loaded > NaCl-loaded > KCl-loaded > CaCl_2 -loaded. It seems that although MgCl_2 and CaCl_2 are both alkali earth metal chlorides, their effects on cellulose weight conversion during pyrolysis are quite different. The weight conversion of the MgCl_2 -loaded cellulose is much higher than that of the CaCl_2 -loaded cellulose.

In comparison to weight conversion, a considerable degree of sugar conversion takes place in the heating-up period during the pyrolysis of various salt-loaded celluloses (see Fig. 1b). The data in Fig. 1b further indicate that the addition of alkaline earth metal chlorides has a much stronger effect on the sugar conversion than the addition of alkali metal chlorides. For instance, $\sim 50\%$ and $\sim 42\%$ of sugar structures are decomposed during the heating-up period for the CaCl_2 -loaded and MgCl_2 -loaded celluloses, respectively, in comparison to $\sim 22\%$ for the NaCl-loaded cellulose and $\sim 24\%$ for the KCl-loaded cellulose. During the isothermal pyrolysis, although the sugar conversions for salt-loaded celluloses all increase with holding time, some differences still can be observed from various salt-loaded celluloses. For example, in comparison to other salt-loaded celluloses, the sugar conversion for the CaCl_2 -loaded cellulose increases more slowly during the isothermal pyrolysis.

Compared to a high sugar conversion of $\sim 50\%$ for the CaCl_2 -loaded cellulose during the heating-up period, its carbon conversion is only $\sim 3\%$. Obviously, significant dehydration reactions of sugar structures occur during the heating-up period. The depolymerization reactions start to play an important role during the isothermal pyrolysis, as the carbon conversion starts to increase with increasing the holding time. The carbon conversions for various salt-loaded celluloses are all lower than that for raw cellulose.

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