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Research paper

Cellulose-hemicellulose interactions during fast pyrolysis with different temperatures and mixing methods

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ABSTRACT

In this work, the cellulose-hemicellulose interaction during pyrolysis was investigated to study the impacts of sample preparation, temperature, mixing ratio on the light products distribution. Cellulose-hemicellulose interactions were studied by Py-GC-MS with different temperatures (500, 600, 700 °C), mixing ratios (mass ratio 1:1 and 5:2), and mixing methods (physical and native mixtures). Generally speaking, cellulose-hemicellulose interaction would significantly promote the formation of hemicellulose-derived products and CO_2, while inhibit part of cellulose-derived products, especially the formation of levoglucosan. Moreover, the native cellulose-hemicellulose mixture had the most distinct impact on the product distributions. A statistic method has been used to evaluate the strength of cellulose-hemicellulose interaction and compared with cellulose-lignin interaction, finding that mixing method had the strongest influence on cellulose-hemicellulose interaction, followed by temperature, and mixing ratio had the weakest influence. Most importantly, the interaction between cellulose-hemicellulose was weaker than cellulose-lignin.

1. Introduction

Nowadays, with the fast development of biomass transformation into liquid fuels and valuable platform chemicals, the interactions between the three main components of biomass (cellulose, hemicellulose, and lignin) are receiving increasing attentions [1]. Previously, the interaction between cellulose and lignin has been investigated by TG-FTIR [2] and Py-GC-MS [3], so here, the focus of this work is the interaction between cellulose and hemicellulose.

The interaction between cellulose and lignin could be regarded as the interaction between polysaccharides and lignols, unlike cellulose-lignin interaction, cellulose-hemicellulose interaction is mainly limited to polysaccharides interaction (if the small fraction of polyhexoses in xylan could be neglected, the cellulose-hemicellulose interaction could be regarded as interaction between polyhexoses and polypentoses). Because of this, attention is mainly paid on cellulose-lignin interaction rather than cellulose-hemicellulose interaction.

Previous studies on cellulose-hemicellulose interactions were focused on the effect of interaction on thermogravimetric characteristics. Worasuwannarak et al. [4] tested the cellulose-xylan mixture with a blending ratio of 50:50 by TG-MS, reporting that the experimental weight loss curves seemed to decrease more gradually than the calculated weight loss curves for the cellulose-xylan mixture, this indicated the existence of interaction between cellulose-xylan during pyrolysis process. Wang et al. used xylan as a representative of hemicellulose and checked cellulose-xylan mixture by TG under syngas conditions, finding that the calculated weight loss was higher than that from experiment, and they regarded that the pyrolysis of cellulose and hemicellulose was affected by each other [5]. Liu et al. has investigated cellulose-xylan mixtures with different mixing ratios by TG-FTIR, observed the occurrence of interactions between cellulose and hemicellulose happened when temperature was above 327 °C [6]. Normally, for TG experiment, cellulose-hemicellulose co-pyrolysis would decrease the final tar yield while increase the final char yield.

The gas evolutions under the influence of cellulose-hemicellulose interaction during pyrolysis process were also investigated intensively. From Worasuwannarak et al. experiment, H_2O from the cellulose-xylan mixture was larger than it from the pure component [4]. Fushimi et al. reported the evolutions of gases from cellulose-xylan-lignin mixtures under steam gasification

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conditions at 400 °C for 3 h, concluding that the evolutions of CO_2, CO, CH_4, and H_2 were enhanced after xylan was added to cellulose-lignin mixture [7,8]. Couhert et al. did extensive experiments to predict gas yield from biomass after rapid pyrolysis, but failed to calculate gas yield based on compositions of three main components (cellulose, hemicellulose, and lignin) of biomass [9,10]. Giudicianni et al. carried a series of experiments on biomass three main components mixtures under slow steam pyrolysis conditions, reporting that CO_2 and CO were enhanced under cellulose-xylan co-pyrolysis conditions, besides, they also regarded that strong components interactions could happen on the specific surface area of the solid products [11–13].

Meanwhile, a few references have also mentioned the influence of cellulose-hemicellulose interaction on liquid product distributions. Hosoya et al. mixed cellulose with hemicellulose (glucomannan and xylan) at 2:1 mass ratio and pyrolyzed the mixtures in a tube reactor at 800 °C for 30s, they found cellulose-hemicellulose interaction inhibited the formation of glycolaldehyde and levoglucosan, while slightly promote the formation of furfural. Besides, they also pointed out that interactions observed in cellulose-hemicellulose pyrolysis were weaker than that of cellulose-lignin [14]. Fushimi et al.'s work mentioned that interactions among cellulose, xylan and lignin could increase 5-methylfurfural formation significantly and enhance furfural formation insignificantly [7,8]. Wang et al. checked the product distributions of mixed biomass samples by TG-FTIR and an experimental pyrolyzer, their results showed that the decomposition of levoglucosan was extended over a wider range of temperature when hemicellulose was pyrolyzed together with cellulose, and the existence of cellulose would promote the formation of acetic acid and furfural [15]. Similar results were also reported by Liu et al. based on their TG-FTIR study [6]. Different from previous works, Zhang et al. used an aqueous ammonia and hot water method to remove lignin in biomass to prepare native cellulose-hemicellulose mixture, by comparing the liquid product distribution, they found the cellulose-hemicellulose interaction was much weaker when compared with cellulose-lignin interaction, besides, seeing from their results, the yield of glycolaldehyde was inhibited and the yield of acetic acid was enhanced under cellulose-hemicellulose co-pyrolysis conditions [16].

Among these studies, some aspects that influenced the cellulose-hemicellulose interaction results should be mentioned. First, it has been observed that most studies used xylan as representative of hemicellulose, only Hosoya et al. [14] and Zhang et al. [16] extracted hemicellulose from raw biomass. Though xylose presents the largest amount among the polysaccharides (xylose, mannose, galactose, arabinose) of hemicellulose, using xylose as representative may cause some confusion when compare the results from mixed biomass to natural biomass samples, especially when the research focused on the influence of hemicellulose-involved interaction. In addition, based on Couhert et al.'s experiment, xylan from different origins could lead to very different gas species distributions after pyrolysis [9]. All these suggest that it would be better if hemicellulose could be extracted form biomass for the study of cellulose-hemicellulose interaction.

Another problem is the mixing method. It has been confirmed that mixing method has a significant effect on the research of interaction [3,10]. Most above mentioned studies used physical mixing method, namely, blending cellulose and hemicellulose samples together directly. This mixing method could only represent interactions during pyrolysis processes, while neglect the influence of morphology and covalent linkages between cellulose and hemicellulose in biomass.

Considering the above referred studies and problems, cellulose-hemicellulose interactions have been investigated by Py-GC-MS at fast pyrolysis conditions in this study. The effects of mixing method (physical and native mixture), temperature (500, 600, 700 °C), and mixing ratio (cellulose-hemicellulose mass ratio 1:1 and 5:2) on cellulose-hemicellulose interactions have been checked. Finally, the strengths of interaction under different experimental conditions have been calculated by a statistics method for comparison.

2. Materials and methods

2.1. Sample preparation

For cellulose, according to Blin et al.'s review [17], the structures of cellulose from different sources are similar, so cellulose used here was a commercial product (CAS number 9004-34-6, MDL number MFCD00081512) from Sigma Chemical Co., USA.

Hemicellulose was extracted from China fir wood by aqueous ammonia treatment followed by hot water treatment according to Kim et al.'s suggestion [18]. The detailed preparation process has been illustrated as Fig. 1. To check the polysaccharides in hemicellulose, hemicellulose was analyzed by using the protocol of NREL Chemical Analysis and Testing Standard Procedures: NREL LAP, TP-510-42618, reporting that it contained 1.2 wt% glucan, 75.6 wt% xylan, 0.5 wt% galactan, 5.9 wt% arabinan, 0.6 wt% mannan and 3.7 wt% acid-soluble lignin. It could be concluded that hemicellulose was pure enough for the experiment.

Cellulose-hemicellulose physical mixture was prepared by mixing cellulose and hemicellulose with a mass ratio 1:1 and ground to small particles (around 40 μm). Then the mixture was pressed and agglomerated by using a hydraulic press machine under 20 MPa manually. After that, the mixture was milled to fit through a 100-mesh screen (particle size smaller than 149 μm) to get the physical mixture for experiment.

To make the cellulose-hemicellulose native sample, the delignification process suggested by Liu et al. has been used [19]. In this method, $NaClO_2$ was used to remove lignin. The detailed process could been seen in Fig. 2. To check the composition of cellulose-hemicellulose native sample, the mixture was also analyzed by NREL Chemical Analysis and Testing Standard Procedures, reporting that it contained 64.3 wt% glucan, 25.7 wt% xylan, 0.2 wt% galactan, 0.5 wt% arabinan, 0.1 wt% manna, and 2.8 wt% acid-insoluble lignin. It could be regarded that lignin has

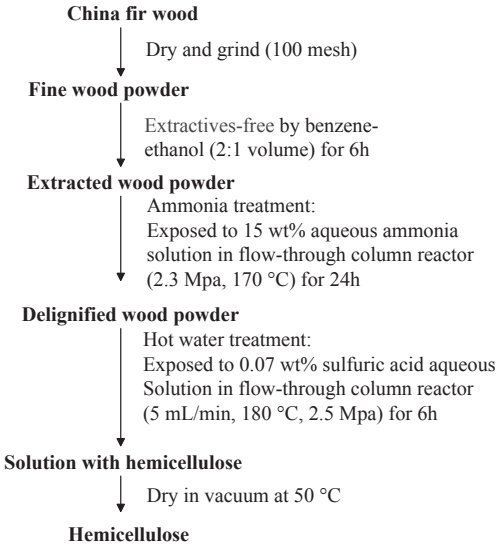

Fig. 1. The preparation process of hemicellulose from China fir wood.