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Vapor–solid interaction among cellulose, hemicellulose and lignin

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ABSTRACT

Secondary reactions, including those caused by interactions between vapor and solid phases, are unavoidable during biomass pyrolysis. In this study, the vapor–solid interaction between biomass components (cellulose, hemicellulose, and lignin) was investigated in a two-stage fixed-bed reactor. The results indicated that volatiles from hemicellulose promoted the breakdown of cellulose glycoside bonds and pyran rings as well as the removal of branched aliphatic chains and O-containing functional groups of lignin at 280 °C. Moreover, volatiles from cellulose produced abundant anhydrosugar, which was more prone to re-polymerization and to form aromatic rings on the lignin structure at 315 °C. As a result of the vapor–char interactions at 650 °C, the secondary decomposition of cellulose volatiles to gas products (decreasing by ~8 wt%) was inhibited, but carbonized products (increasing by ~3 wt%) tended to form, whereas hemicellulose vapor was more prone to decompose into low-molecular-weight liquid compounds, resulting in a high liquid yield (increasing by ~6 wt%). In addition, vapor–solid interactions accelerated the removal of O-containing functional groups of lignin volatiles, such as carbonyl and carboxyl, but inhibited the decomposition of H-containing functional groups, such as methyl and methylene. The finding is conducive to the understanding of the interactive mechanisms of biomass pyrolysis.

1. Introduction

Due to its sustainability, abundance, and near-zero CO_2 emission, biomass will play a significant role in future energy supply. As the only renewable carbon source, biomass has attracted attention from researchers regarding its conversion into value-added chemicals and functionalized carbon materials [1]. Pyrolysis is an important process in energy, chemical, or material production from biomass, as it converts biomass into products in three states (biochar, liquid oil, and gas products) [2]. To control the yields and quality of the pyrolysis products, great efforts have been made to clarify the mechanism of biomass pyrolysis [2,3].

The complicated transformation process during biomass pyrolysis is considered to be caused by the complex composition and structure of biomass, which is composed of cellulose, hemicellulose, and lignin [1,2]. Hence, the mechanism of biomass pyrolysis is often simplified by investigating the pyrolysis mechanism of cellulose, hemicellulose, and lignin individually, and summarizing biomass pyrolysis with superposition of the main components as the assumption that no interactions among cellulose, hemicellulose, and lignin. Under this hypothesis, the approach of superposition rule appeared to behave well in some cases [4–7]. However, Couhert et al. [8] pointed out that simple superposition via the component additivity rule fails to predict the gas yield of biomass in flash pyrolysis at 950 °C because of the interactions between pyrolysis components. Furthermore, several studies have clarified the influences of the interactions between cellulose, hemicellulose, and lignin. With the three components simply mixing, Wang et al. [9] found that the interaction of hemicellulose or lignin upon the pyrolysis of cellulose extended the temperature range of levoglucosan and cellulose-lignin interactions enhanced the formation of 2-furfural and acetic acid. Based on simplex-lattice design method, Liu et al. [10] synthesized 15 biomass samples to investigate interactions between components and reported that hemicellulose-cellulose interactions decreased the yield of levoglucosan and largely promoted the formation of hydroxyacetaldehyde, while the presence of lignin decreased the yield of 2-furaldehyde and C=O containing compounds. With the comparisons of pyrolysis products from physical mixture and native mixture, Wu et al. [11,12] reported that cellulose-hemicellulose interactions

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promoted the formation of hemicellulose-derived products but inhibited cellulose-derived products, while cellulose-lignin interactions enhanced the formation of low weight molecular products but inhibited the formation of anhydrosugar. In terms of the interaction intensities of the different components, Hosoya et al. [13] found that cellulose-lignin interacted more intensely than cellulose-hemicellulose. Without a premixed feedstock, Chen et al. [14] investigated volatiles interaction between variant components and found that hemicellulose volatiles enhanced the decomposition of cellulose volatiles, while the decomposition of lignin volatiles was inhibited by cellulose volatiles.

The interactions between these components start to be recognized, which is important for the integral comprehension of biomass pyrolysis. However, more attention is paid to the interactions between volatiles, and the interaction among volatiles and char or solid components is lacking. As a typical multiphase reaction, pyrolysis involves significant vapor–solid interactions. In biomass pyrolysis, Song et al. [15] reported that volatile–char interactions significantly decreased the amount of tar from biomass pyrolysis, especially at relatively high temperatures (e.g. > 800 °C). While during volatile–char interactions, steam–char reactions can produce additional active sites on the char to facilitate tar reformation [16]. Keown et al. [17] reported that volatile–char interactions could also lead to the additional volatilization of alkali and alkaline earth metallic species. However, vapor–solid interactions between cellulose, hemicellulose, and lignin is rarely reported. Furthermore, the influence of vapor–solid interaction on the pyrolysis behavior of biomass components is still unclear.

In this work, two kinds of vapor–solid interaction were investigated. Firstly, the influence of the volatiles initially released from hemicellulose or cellulose on the structure of cellulose or lignin were investigated at the low temperature, and the pyrolysis characteristic after vapor–solid interaction was conducted. The second kind of vapor–solid interaction investigated is between volatile and char from components pyrolysis. The effect of char on volatile reformation was investigated at high temperature (650 °C). The study should contribute greatly to the understanding of biomass pyrolysis process.

2. Materials and methods

2.1. Materials

Cellulose, hemicellulose, and lignin were obtained as indicated in our previous study. The results of proximate and ultimate analyses of the samples are shown in Table 1. Before each trial, the sample was dried for 12 h at 100 ± 5 °C.

2.2. Experimental setup and method

The experimental apparatus mainly consisted of a two-stage fixed-bed reactor (inner diameter: 20 mm; thickness: 2 mm; height: 600 mm), a quartz tube sample holder (external diameter: 19 mm) in a carrier (height: 40 mm), a temperature controller system, an ice–water mixture for condensation, and gas purification and drying equipment followed by a gas analysis system to test the gas composition (Fig. 1). One end of the carrier was sealed with a perforated quartz plate. The experiments (Fig. S1) were divided into two parts described in Sections 2.2.1 and 2.2.2.

2.2.1. Vapor-solid interaction

The first part of the experiment was designed to investigate the vapor–solid interactions between the biomass components at lower temperatures. The specific experimental procedure was as follows: Prior to each trial, two zones were heated up to the same designated temperature (280 °C or 315 °C) with N_2 (99.999% 500 mL/min) as carrier gas, which was kept constant for 10 min. After that, 500 ± 5 mg hemicellulose or cellulose was placed in the bottom of the sample holder, and with quartz fibers separating the materials, the same mass of cellulose or lignin was placed on top of the quartz fibers. The inhibition of solid–solid interactions was consequently guaranteed. Finally, quartz fibers were placed on top of the sample holder in case the particles spilled during the reaction process. Once the temperature had stabilized at the selected value, the carrier was rapidly pushed to the center of the first heating zone (Fig. 1) with the N_2 flow rate adjusted to 250 mL/min. Since the vapor was released from the bottom reactants and contacted the upper stage, vapor–solid interactions occurred. Simultaneously, the cellulose or lignin samples were pyrolyzed individually at 280 °C or 315 °C for comparison. After 30 min, the upper and lower samples were weighed. The upper solid samples were named HC280, HL280, and CL315, where for example, HC280 represents that the solid sample derived from cellulose pyrolysis and interacted with hemicellulose vapor at 280 °C and H is for hemicellulose, C is for cellulose, and L is for lignin while the solid samples from without vapor–solid interactions were named C280, L280, and L315, where C280 represents solid products from cellulose pyrolysis at 280 °C. All abbreviations are defined in Table S1.

The second part of the experiment was designed to investigate the vapor–solid interactions between the volatiles and chars at high temperatures. In this part, the char of the biomass components was pre-prepared in a fixed-bed reactor with 1 g each of cellulose, hemicellulose, or lignin, a temperature of 650 °C, an N_2 flow rate of 200 mL/min, and a pyrolysis time of 15 min. The chars were subsequently crushed to smaller than 42 μm. Then, 500 ± 5 mg pre-prepared char was placed in the sample holder (height: 20 mm), which was then moved to the center of the upper heating zone. Then, 500 ± 5 mg of the cellulose, hemicellulose, or lignin sample was placed in another sample holder, which was placed at the bottom heating zone. The interaction procedure was similar with that of the first part at lower temperature. However, in case additional volatiles was released of the char, it is worth noting that the interaction temperature was set at 650 °C. To ensure the accuracy of the data, each trial was repeated three times with an error of less than 5%, and the measured data presented herein are the average values.

2.2.2. Pyrolysis behavior of samples after interactions

The solid sample derived from low temperature interaction were further pyrolyzed at 500 °C to investigate the influence of the vapor–solid interaction on the pyrolysis behavior. Once the temperature stabilized at 500 °C, the sample holder with 500 mg of the collected solid sample was pushed to the center of the first heating zone. The volatiles were then swept into the ice–water condenser so that the condensable volatiles could be collected as liquid products. After

Table 1
Proximate and ultimate analysis of biomass components.

	Proximate analysis (wt%, db.)			Ultimate analysis (wt%, daf.)					LHV (MJ/kg)
	V	FC	A	C	H	N	S	O^d	
Cellulose	95.50	4.50	0.00	42.70	6.20	0.03	0.05	51.02	15.47
Hemicellulose	76.80	21.40	1.80	41.60	5.70	0.02	0.03	52.65	15.31
Lignin	58.90	36.90	4.20	48.30	4.90	0.10	3.10	43.60	19.31

Notes: d: O was obtained from the difference; db: dry basis; daf: dry and ash free basis; LHV: Low heating value; V: Volatile; FC: Fixed carbon; A: Ash.