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Investigation of biomass torrefaction based on three major components: Hemicellulose, cellulose, and lignin

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ABSTRACT

In this work, torrefaction of hemicellulose, cellulose, and lignin were studied at a series of torrefaction temperatures (210, 240, 270, and 300 °C) based on the properties of their three-phase products, namely solid, liquid (water and tar), and gaseous products. Among the three biomass components, significant difference of torrefaction characteristics was found due to their different molecular structures. For the solid product, hemicellulose presented lowest yield from 85.65% to 41.54% as the temperature increased because of the poor thermostability, thereby showing obvious variations in carbon and oxygen contents. For the gaseous product, CO_2, followed by CO, were the dominant gaseous components in all torrefaction conditions including different feedstock and temperatures; also a small number of other components (H_2 and CH_4) were produced during torrefaction of lignin. The liquid product was composed of water and a small amount of tar. For the tar product, acids and ketones were the dominant components in the torrefaction of hemicellulose, while anhydrosugar in the torrefaction of cellulose, and phenols in the torrefaction of lignin. As the temperature increased from 210 °C to 300 °C, about 19.76–71.11%, 5.85–33.27%, and 16.28–44.89% of oxygen from hemicellulose, cellulose, and lignin, respectively, was transformed into the liquid and gaseous products. Dehydration reaction and volatilization of the oxygenated gaseous product were the two dominant deoxygenation pathways, and the water, CO_2, and CO were the dominant carriers of oxygen migration. In contrast to oxygen, only a small amount of carbon was transferred into tar product, followed by gaseous product, consequently the solid samples still retained most of the energy.

1. Introduction

Torrefaction pretreatment of biomass (also known as torrefaction deoxygenation pretreatment) is generally carried out under inert conditions at a temperature range of 200–300 °C [1,2]. In recent years, torrefaction has been considered for an effective method to improve the quality of biomass raw materials, and for a subsequent application of biomass in the pyrolysis, gasification, and combustion [3]. During the 2003–2017, over 400 papers have been published on the research area of biomass torrefaction (via the Web of Science), which mainly include the following aspects: (i) fuel characteristics and physical–chemical properties of the solid product [4–7]; (ii) torrefaction kinetics and process modeling [8,9]; (iii) economics and techno-economic evaluation [10,11]; (iv) application and thermochemical conversion utilization [12–15]; (v) combined pretreatment methods of torrefaction with other pretreatment processes [16–18]. The advantage of torrefaction has been widely reported, including effective reduction of the oxygen-containing functional groups [19], improvement in the carbon content and high heating value (HHV) [20], and enhancement in the grinding performance [21] as well as hydrophobicity [22,23].

Cellulose, hemicellulose and lignin are three major components of biomass. Generally, the contents of cellulose, hemicellulose, and lignin can reach 40–60%, 15–30%, and 10–25%, respectively [24], depending on the type of biomass [25]. The properties of the three biomass components would significantly affect the characteristics of torrefaction process and product quality of the biomass feedstock. Therefore, an extensive effort should be made on the study torrefaction of cellulose, hemicellulose, and lignin. However, based on the review of the literature published over the past 15 years, the result indicated that most of the studies were still focused on biomass itself, and only few researches have been carried out on the three biomass components, which are listed in Table 1.

Several studies focused on one of the three biomass components [26–30]. Lv et al. [26] carried out cellulose torrefaction at 220–280 °C

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Table 1
The studies concerning torrefaction of the three biomass components (cellulose, hemicellulose, and lignin) reported in literature.

Materials	Experimental apparatus	Torrefaction temperature	Residence time	Main work concerning torrefaction	Ref.
Microcrystalline cellulose	TGA-DSC	220, 250 and 280 °C	48 h	Temperature-duration equivalence regarding thermal degradation of cellulose	[26]
Microcrystalline cellulose	A tube furnace	200, 225, 250, 275 and 300 °C	30 min	Influence of torrefaction on cellulose structural characteristics	[27]
Beechwood xylan (representative of hemicellulose)	A tube furnace	200, 225, 250, 275 and 300 °C	30 min	Effects of torrefaction on hemicellulose structural characteristics	[28]
Organosolv lignin	A tubular reactor	150, 175, 200 and 225 °C	15 min	Structural changes in the lignin macromolecule at different temperatures	[29]
Organosolv lignin	A tube furnace	200, 225, 250, 275 and 300 °C	30 min	Effect of torrefaction on the structure of lignin	[30]
Cellulose, hemicellulose, lignin	TGA	230, 260 and 290 °C	1 h	Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin	[31]
Cellulose, hemicellulose, lignin	TGA	200, 225, 250, 275 and 300 °C	1 h	Isothermal torrefaction kinetics of hemicellulose, cellulose and lignin	[32]
Microcrystalline cellulose, xylan, milled wood enzyme lignin	TGA-FTIR	220, 250 and 280 °C	5 h	Chemical decomposition of lignocellulosic components during torrefaction under isothermal conditions	[33]
Cellulose, xylan (representative of hemicellulose), alkali lignin	A horizontal tubular reactor system	210, 240, 270 and 300 °C	20, 40 and 60 min	Structure changes of hemicellulose, cellulose, lignin during torrefaction	[34]
Microcrystalline cellulose, beechwood xylan (representative of hemicellulose), alkali lignin	A laboratory-scale reactor	210, 240, 270 and 300 °C	30 min	Properties of solid, liquid and gas products from torrefaction; migration characteristics of oxygen and carbon	This study

and investigated the torrefaction characteristics by thermogravimetry-differential scanning calorimetry (TGA-DSC), and the main conclusion was that mass loss could be used as a synthetic indicator of the treatment intensity. Wang et al. [27,28] found that torrefaction could effectively reduce the oxygen content and O/C ratio in cellulose and hemicellulose. As for lignin, torrefaction temperature (200 and 225 °C) can cause polycondensation and de-methoxylation of the aromatic units of lignin [30]; and with the removal of oxygen, the content of C—C and C—H bonds in lignin during torrefaction was enhanced, while that of C—O and O—H bonds was reduced [29]. The other studies involved all the three biomass components [31–34]. Chen et al. [31] investigated co-torrefaction characterization of hemicellulose, cellulose, and lignin in the temperature range of 200–300 °C by TGA, and the results showed that the weight loss of biomass during torrefaction could be predicted from the linear superposition of the weight losses of the individual constituents. Furthermore, the isothermal torrefaction kinetics was developed, and the recommended values of the order of reaction of hemicellulose, cellulose, and lignin were found to be 3, 1, and 1, respectively [32]. Lv et al. [33] reported the products of chemical breakdown of the lignocellulosic components under torrefaction temperature by TGA-FTIR analysis. Zheng et al. [34] pointed out that the rank order of thermal stability during torrefaction was cellulose > lignin > hemicellulose, and their structural changes obviously affected the subsequent catalytic fast pyrolysis behavior. These previous studies achieved remarkable advances in understanding biomass torrefaction. However, the effect of torrefaction on the yields and properties of solid, liquid, and gaseous products using feedstock of cellulose, hemicellulose, and lignin have not yet been thoroughly investigated.

It is well known that deoxygenation is the key step during biomass torrefaction. More importantly, construction of the oxygen migration pathway is helpful for a better understanding of the quality improvement of biomass raw materials and its influence on the subsequent thermochemical utilization. Carbon migration is another important point during biomass torrefaction. In order to establish the above mentioned pathways of oxygen and carbon migration, the evolution and characteristics of solid, liquid, and gaseous products of biomass three major components (hemicellulose, cellulose, and lignin) should be thoroughly investigated at different torrefaction temperatures. However, such useful information, especially the properties of liquid products, is still missed in the torrefaction studies of biomass in the literature, including those summarized in Table 1.

The process flow diagram of this study is shown in Fig. 1. First of all, cellulose, hemicellulose and lignin were torrefied at a temperature range of 210–300 °C, and then the solid, liquid and gaseous products were collected. Afterwards, the physical and chemical properties of these products were analyzed by proximate analysis, ultimate analysis, etc. Some of the data that were difficult to measure were calculated using empirical formula. Finally, the oxygen migration, carbon migration and energy yields of torrefaction were obtained.

2. Material and methods

2.1. Experimental material

Microcrystalline cellulose, beechwood xylan (representative of hemicellulose), and alkali lignin were purchased from Sigma-Aldrich Co., Ltd. (USA). Prior to experiment, the feedstock materials were dried at 105 °C for 2 h.

2.2. Torrefaction deoxygenation experiment

Hemicellulose, cellulose, and lignin were torrefied in a lab-scale reactor for 30 min. More details of reactor can be found in the previous study [35]. In each run, about 5 g sample was loaded into the quartz tube reactor. When the temperature reached the settled value (210, 240, 270, and 300 °C), the released volatiles were swept away by high-