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Structural evolution of chars from biomass components pyrolysis in a xenon lamp radiation reactor☆

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ABSTRACT

The structural evolution of the chars from pyrolysis of biomass components (cellulose, hemicellulose and lignin) in a xenon lamp radiation reactor was investigated. The elemental composition analysis showed that the C content increased at the expense of H and O contents during the chars formation. The values of $\Delta_{H/C}/\Delta_{O/C}$ for the formation of cellulose and hemicellulose chars were close to 2, indicating that dehydration was the dominant reaction. Meanwhile, the value was more than 3 for lignin char formation, suggesting that the occurrence of demethoxylation was prevalent. FTIR and XRD analyses further disclosed that the cellulose pyrolysis needed to break down the stable crystal structure prior to the severe depolymerization. As for hemicellulose and lignin pyrolysis, the weak branches and linkages decomposed firstly, followed by the major decomposition. After the devolatilization at the main pyrolysis stage, the three components encountered a slow carbonization process to form condensed aromatic chars. The SEM results showed that the three components underwent different devolatilization behaviors, which induced various surface morphologies of the chars.

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1. Introduction

Fast pyrolysis is recognized as a promising thermal–chemical technology for effectively converting biomass into liquid bio-oil, which can be a substitution for fossil vehicle fuels [1,2]. Therefore, the production of bio-oil has aroused extensive attention [3–6]. However, attention on structural evolution of bio-char, a solid by-product, is much limited although it is important to reveal the pyrolysis behavior of biomass. Moreover, bio-char is underutilized, and it is very critical to the high value-added utilization of bio-char before elucidating its structural characterization [7].

Biomass mainly consists of three major components, namely 40 wt%–50 wt% cellulose, 20 wt%–40 wt% hemicellulose and 15 wt%–30 wt% lignin [8,9]. The formation of bio-char is deeply influenced by the major components due to their different structures. So knowledge of the char from individual component is important for a better understanding of bio-char properties and biomass pyrolysis mechanism. Pastorova *et al.* [10] found that the char precursor of cellulose was a polymer based on furanoid skeletons and hydroxyaromatic skeletons. Wooten *et al.* [11] analyzed the formation of char from cellulose

pyrolysis by ^{13}C -CPMAS-NMR, suggesting that cellulose firstly converted to an amorphous intermediate cellulose, then to a disordered final carbohydrate, and finally to aromatic carbons. Xin *et al.* [7] indicated that the cellulose char formation involved a series of complex reactions, including dehydration, decarbonylation, ring-opening and aromatization to form a disordered three-dimensional network precursor, and deoxygenation and dehydrogenation to form a highly aromatic char.

In particular, studies on the char properties from hemicellulose and lignin pyrolysis are scarce. Lv *et al.* [12] observed that the surface morphology of hemicellulose char shifted from severe irregular agglomeration to smoothness and porousness with temperature increasing by SEM. Xin *et al.* [13] analyzed the surface property of xylan char by BET, and suggested that the relatively high average pore size of the char could be ascribed to the branched structure in xylan. Sharma *et al.* [14] performed the structural characterization of lignin char by FTIR and ^{13}C -CPMAS-NMR and found that high temperature could reduce the content of hydroxyl and methoxyl groups, leading to the improvement of aromaticity. Lou and Wu [15] characterized the pyrolysis char of EMAL lignin by FTIR, and the results showed that the aromatic substitution decreased gradually with the temperature increasing, and the aromatic nature of char completely disappeared at 700 °C.

Although there are some studies on the structural analysis of the chars from biomass components as mentioned above, the structural evolution of component chars during the whole pyrolysis process is rarely analyzed. Additionally, the structural differences of the chars from biomass components are seldom compared. In this study,

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the chars (solid residues) of biomass components (cellulose, hemicellulose and lignin) pyrolysis at different pyrolysis stages in a xenon lamp radiation reactor were collected. Then the structural evolution of chars was analyzed and compared using elemental analysis, FTIR, XRD and SEM, aiming at providing a comprehensive understanding of the formation of chars from biomass components pyrolysis.

2. Experimental

2.1. Materials

Microcrystalline cellulose, xylan and organic lignin were used as the model compounds of cellulose, hemicellulose and lignin, respectively. These materials were purchased from Sigma-Aldrich Corporation.

2.2. Apparatus

The diagram of the xenon lamp radiation reactor is shown in Fig. 1. The radiation source was a spherical high pressure short arc xenon lamp (3 kW). The xenon lamp was located on the inner focus of the ellipsoidal speculum to converge the light on the other focus after reflection. The diameter of the ellipsoidal speculum was 360 mm, and the focal lengths were 60 mm and 800 mm, respectively. A plane speculum was arranged between the two focuses to change the light path, so that the light was gathered in the quartz glass reaction tube (inner diameter of 40 mm) to realize the radiation heating of the sample. A rotating shutter at a response time of 0.01 s was arranged between the plane speculum and the reaction tube to control the heating time. After reaction, the sample was quenched by liquid nitrogen immediately. The operation of the reaction system was controlled by a programmable logic controller (PLC). In the pyrolysis experiments, 0.1 g sample was put on a quartz glass slice in the reaction tube. Then the reactor was purged with pure N₂ gas at a flow of 200 ml·min⁻¹ for 3 min to provide an inert atmosphere. The output power of the xenon lamp was kept at 3 kW. The heating time was in range of 15–120 s, which was controlled by the rotating shutter.

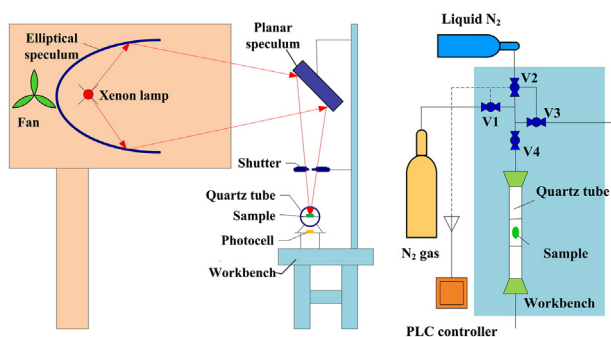


Fig. 1. Xenon lamp radiation pyrolysis apparatus.

2.3. Structural characterization

The elemental composition of the sample was measured on a Vario MICRO Elemental Analyzer (Elementar Analysensysteme GmbH, Germany). The functional groups of the sample were analyzed on a Nicolet 5700 FTIR spectrometer (Thermo Fisher Scientific Corporation, USA). The spectra were recorded from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ by averaging 36 scans. The surface morphology of sample was analyzed by a scanning electron microscope (SEM) (SIRION-100 FEI). The sample was pretreated by coating an Au film prior to scanning.

The accelerating voltage was 20 kV and the magnification was 2500. The crystalline index (CrI) of sample was calculated from X-ray diffraction patterns via Eq. (1) [16].

$$\text{CrI} = \frac{(I_{002} - I_{\text{am}})}{I_{002}} \times 100\% \quad (1)$$

where I_{002} was the peak intensity of 002 lattice plane (at $2\theta = 22.5^\circ$), and I_{am} was the peak intensity of the amorphous phase (at $2\theta = 18.5^\circ$).

3. Results and Discussion

3.1. Evolution of elemental composition

As shown in Fig. 2(a)–(c), the evolution of elemental composition for the chars from the three major components presented similar tendency. The C content increased while the H and O contents decreased with the heating time prolonging. The elemental composition of cellulose chars changed slightly before heating time of 95 s, indicating that cellulose needed relatively long time to preheat the sample prior to initiating decomposition. Subsequently, the C contents increased sharply from 44.68% at 95 s to 80.14% at 100 s, while the corresponding H and O contents decreased from 6.26% and 49.06% to 3.72% and 16.14%, respectively. This suggested that cellulose suffered severe decomposition in a very short time, releasing a large amount of oxygenic volatiles such as acids, ketones, and aldehydes. After that, cellulose underwent a carbonization process, showing that the C content increased slowly at the expense of H and O contents. This was consistent with the TG result of cellulose pyrolysis that the DTG curve appeared a single sharp peak at about 350 °C [4]. In comparison to cellulose, hemicellulose and lignin needed shorter preheating time as their elemental composition changed obviously at heating time less than 15 s. This might be due to the existence of weak branches and linkages in their structure. For example, the acetyl groups in hemicellulose and β -O-4 linkage in lignin were easy to decompose at low temperature [5,6]. In addition, the loose structure and deep color of the hemicellulose (yellow) and lignin (brown) made their radiation absorption efficiency much higher than that of the white crystal cellulose. Therefore, hemicellulose and lignin could absorb a lot of heat within a short time to initiate the pyrolysis. The elemental composition for hemicellulose and lignin mainly changed at the heating time of 15–30 s, suggesting that the matrix of hemicellulose and lignin decomposed at a relatively long time compared to cellulose. Correspondingly, the C contents of hemicellulose and lignin increased from 37.40% and 66.63% at 15 s to 58.06% and 79.87% at 30 s, respectively. These changes of elemental composition for hemicellulose and lignin were not as severe as that for cellulose at the main pyrolysis stage. This was consistent with the appearance of low and wide peak in DTG curve for hemicellulose and lignin [17]. When the heating time was beyond 30 s, both hemicellulose and lignin underwent a slow carbonization process. Due to the aromatic nature of lignin structure, the C content of lignin char was as high as 86% at 120 s, which was much higher than that of hemicellulose char (less than 70%).

From the van Krevelan diagram (Fig. 2(d)), it could be easily found that the ratios of H/C and O/C for the chars decreased with the heating time increased, revealing that the aromaticity of char was gradually strengthened. The values of $\Delta_{\text{H/C}}/\Delta_{\text{O/C}}$ for cellulose and hemicellulose were 1.74 and 1.94, respectively, which were close to 2. This indicated that dehydration was primary during the char formation due to the abundant hydroxyl groups in the sugar units of cellulose and hemicellulose [18]. Meanwhile, the decarbonylation and decarboxylation to form CO and CO₂ were the main reason for the $\Delta_{\text{H/C}}/\Delta_{\text{O/C}}$ value of less than 2 [19]. The value of $\Delta_{\text{H/C}}/\Delta_{\text{O/C}}$ for lignin was 3.04, which was much higher than that for cellulose and hemicellulose. This was due to the abundant methoxyl groups and aliphatic branch chains in the lignin structure and they could decompose during lignin pyrolysis via demethylation and demethoxylation [20,21]. In addition, the condensation of the aromatic

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