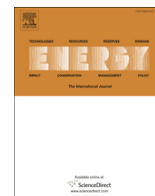




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Influence of torrefaction on the characteristics and pyrolysis behavior of cellulose

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ABSTRACT

The influence of torrefaction on cellulose structural characteristics and the resulting pyrolysis behavior was investigated in this study. Torrefaction reduced O/C ratio in cellulose and increased its high heating value. The crystallinity of cellulose increased slightly first and then decreased sharply with the increase of torrefaction temperature, which could be ascribed to competitive degradation between crystalline region and amorphous region, as indicated by ^{13}C CP/MAS NMR analysis. Besides, the cleavage of β -1,4-glycosidic bond and the dehydration of hydroxyl were the major reactions occurring in torrefaction. Avrami-Erofeev model was found to be the most suitable kinetic reaction model for explaining the thermogravimetric weight loss during the pyrolysis of the raw and torrefied cellulose. A distributed activation energy model based on Avrami-Erofeev model was subsequently used to reveal the pyrolytic kinetics. It was found that the changes in cellulose structure influenced the kinetic parameters greatly. Torrefaction also changed pyrolytic product distribution. The yields of furfural, alicyclic ketones and anhydrosugars increased while that of 5-hydroxymethyl-furfural decreased as torrefaction temperature increased.

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1. Introduction

Fast pyrolysis is a promising technology to efficiently convert renewable biomass resources into liquid bio-fuels, namely bio-oil. However, the quality of crude bio-oil exhibits high acidity, high water content, low heating value and poor stability during storage, which mainly result from the high oxygen content in the biomass feedstock [1–3]. Removal of oxygen in biomass feedstock can reduce water content and acid content, and it can also increase the aromaticity in bio-oil [4]. Therefore, reducing original oxygen content of biomass during pretreatment stage is a feasible method to improve crude bio-oil quality.

As one of the most promising biomass pretreatment technologies, torrefaction is usually carried out in the absence of oxygen at 200–300 °C. The mass density, calorific values and grindability of biomass feedstock are largely improved after torrefaction [5,6]. The hydrophobicity of the torrefied biomass is also enhanced after torrefaction, which is advantageous to keep biomass from fungal

degradation during storage [7]. Additionally, torrefaction could make biomass homogenized, lowering the influence of biomass types and seasonal factors on biomass physico-chemical properties, which is remarkably attractive for process optimization, control and standardization of biomass energy production chain [8]. The chemical structures with poor thermal stability in biomass, such as hydroxyls, ether linkages and O-acetyl branches [9,10], can be cleaved during torrefaction, leading to the formation of some oxygenated compounds. Therefore, torrefaction has a great potential for industrial application and it is getting more and more attention all over the world [11].

The complicated structure of biomass hinders better understanding of torrefaction effect mechanism on biomass pyrolysis behaviors. Since biomass is mainly composed of cellulose, hemicellulose and lignin, individual study of these three components will benefit the understanding of entire biomass. There have been studies of torrefaction effects on hemicellulose [12] and lignin [13], while the studies on cellulose are still missing. Besides, cellulose is the most abundant component of lignocellulosic biomass material and it accounts for almost 50 wt% of biomass [14]. Changes of cellulose chemical structure resulting from torrefaction will considerably influence the biomass pyrolysis behavior. Hence, it is

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necessary to study the evolution of cellulose structure during torrefaction individually.

Since torrefaction is a mild pyrolysis process, the past studies on cellulose pyrolysis behavior at low temperature will be beneficial to the understanding of torrefaction effects on cellulose. Broido-Shafizadeh (B–S) model [15] is the most famous pyrolysis model for cellulose. It considers that cellulose mainly undergoes the reduction in the degree of polymerization (DP) and the formation of active cellulose at low temperature, and the reduction of DP will promote the formation of levoglucosan [16]. Agarwal et al. [17] found that reversible active cellulose existed in the solid state below 260 °C, and it would further undergo depolymerization via ring contraction to yield liquid intermediate cellulose above 260 °C. Basch et al. [18] carried out a vacuum pyrolysis experiment to study the pyrolysis behavior of cellulose and found that the less-ordered region of cellulose decomposed when pyrolyzed at 251 °C, while the crystalline cellulose rarely. Many technologies have been employed to unravel the structural evolution of biomass during torrefaction. Park et al. [19] found that amorphous cellulose was more sensitive to torrefaction than crystalline cellulose via solid state ^{13}C cross-polarization magic angle spinning (^{13}C CP/MAS) NMR analysis. Wen et al. [13] investigated the changes of bamboo structure using XRD and NMR, and found that there was a slight increase for the crystallinity of cellulose with elevated torrefaction temperature before it started to decrease. This phenomenon was further confirmed by Neupane et al. [20] and Rodriguez et al. [21]. Zheng et al. [22] observed cross-linking reaction occurring in the torrefaction of cellulose by using Fourier transform infrared (FTIR) spectroscopy. Ru et al. [23] characterized the changes of typical functional groups in fast growing poplar by two-dimensional perturbation correlation infrared spectroscopy, and found there existed the cleavage of the β -1,4-glycosidic bond during torrefaction. However, some functional group signals of hemicellulose and lignin usually overlap with that of cellulose during the structural characterization of biomass in these studies, leading to some inaccurate judgments about cellulose structure changes.

Kinetic analysis is a helpful method to study the influence of torrefaction on cellulose pyrolysis. Chen et al. [24] performed thermogravimetric analysis of cellulose torrefaction, and pointed out that the cellulose thermal degradation was slight when the torrefaction temperature was no more than 250 °C. They also found that cellulose torrefaction process was endothermic intrinsically [25]. Ru et al. [23] introduced a distributed activation energy model (DAEM) coupled with three Gaussian functions to explain the kinetics of the torrefied biomass pyrolysis, and found the activation energy corresponding to the cellulose degradation remained nearly unchanged. While the weighting factor relevant to the contribution of cellulose degradation to total biomass devolatilization decreased as a consequence of the dehydration of cellulose during torrefaction.

In this study, XRD and ^{13}C CP/MAS NMR were employed to get insights into the cellulose structure changes during torrefaction. Based on the experimental study of cellulose thermo-degradation, a new kinetic modeling method for pyrolysis of the raw and torrefied cellulose was performed to reveal the influence of torrefaction on the pyrolytic devolatilization behavior. Then, a pyrolyzer equipped with a gas chromatography–mass spectrometer (Py-GC/MS) was applied to investigate the distribution of pyrolytic products.

2. Methods

2.1. Materials and torrefaction process

Microcrystalline cellulose (FMC BioPolymer, Belgium) was

chosen as the cellulose sample and was dried at 60 °C until the weight remained unchanged.

The torrefaction process was carried out in a tube furnace with the required torrefaction temperatures of 200, 225, 250, 275 and 300 °C. Pure nitrogen was adopted to sweep away the released volatiles. In each run, 4 g sample was loaded into the tube furnace when it reached the required temperature, and the torrefaction duration was set to 30 min.

2.2. Structural characterization

The elemental analysis was performed on a Micro Elemental Analyzer (Elementar Analysensysteme, Hanau, Germany). High heating value (HHV) was calculated according to the method proposed by Demirbaş [26]. The energy yield of each torrefied cellulose was calculated by Eq. (1).

$$\text{energy yield} = \frac{\text{HHV}_i}{\text{HHV}_0} \times \text{torrefied yield} \quad (1)$$

where HHV_0 and HHV_i were the high heating values of the raw and torrefied cellulose, respectively.

Powder X-ray diffraction (XRD) analysis was carried out on a PANalytical X'Pert PRO X-ray diffractometer. The diffracted intensity of Cu-K α radiation operated at 40 kV and 40 mA was measured within the diffraction angle of 10°–50°.

Solid-state ^{13}C CP/MAS NMR (BRUKER DMX 500, Germany) analysis was performed to quantitatively characterize the variations of the functional groups in the raw and torrefied cellulose. Each spectrum was scanned for more than 1200 times. Carbonyl carbon resonance in glycine was selected as the external reference.

2.3. Thermogravimetric analysis

Thermogravimetric analysis for the raw and torrefied cellulose were performed on a TA-Q500 (TA Instruments, Newcastle, DE, USA) thermogravimetric analyzer. Samples with initial weight of 2 mg were heated from 25 °C to 800 °C at constant rates of 5, 10, 15 and 20 °C min $^{-1}$. Pure nitrogen with a flow rate of 40 mL min $^{-1}$ was used as the carrier gas.

2.4. Kinetic analysis

The method proposed by Moriana [27] was used to determine reaction model $f(\alpha)$ of the raw and torrefied cellulose pyrolysis before calculating the kinetic parameters. It compared the activation energy values obtained by Coats–Redfern method using various $f(\alpha)$ with the standard activation energy values via Flynn–Wall–Ozawa isoconversional method (FWO), and chose the $f(\alpha)$ which obtained the closest value as the most suitable reaction model. And the most suitable $f(\alpha)$ for the pyrolysis of the raw and torrefied cellulose was Avrami–Erofeev (Am) model (see Eq. (2)), which will be proved in the Section 3.5. Where α was the conversion rate, m is the Avrami exponent, whose change could reflect the variation of the characteristics of nucleation and growth process.

$$f(\alpha) = m(1 - \alpha)[- \ln(1 - \alpha)]^{(m-1)/m} \quad (2)$$

Distributed activation energy model (DAEM) could precisely simulate the biomass pyrolysis over the whole conversion process [28,29]. In this study, the modified DAEM based on the Am model (Am-DAEM) was introduced to perform further calculation of kinetic parameters, as shown in Eq. (3).

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