



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Influence mechanism of torrefaction on softwood pyrolysis based on structural analysis and kinetic modeling

Shurong Wang*, Bin Ru, Gongxin Dai, Haizhou Lin, Li Zhang

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:

Received 25 September 2015

Received in revised form

7 February 2016

Accepted 8 February 2016

Available online xxx

Keywords:

Biomass

Torrefaction

Pyrolysis

Kinetic model

¹³C CP/MAS NMR

ABSTRACT

The influence mechanism of torrefaction on biomass pyrolysis was studied in detail. ¹³C CP/MAS NMR was employed to characterize the evolution of functional groups during torrefaction, indicating that hemicellulose was extensively deacetylated and depolymerized; the crystalline structure of cellulose was destroyed; and the aryl ether linkages and propyl side branches in lignin were cleaved. A distributed activation energy model with three combined Gaussian functions was introduced to analyze the pyrolysis kinetics of biomass. The mean activation energies for three parallel reactions remained unchanged after torrefaction, while the weighing factors proved that their contributions to devolatilization largely changed. Acetic acid yield significantly decreased after torrefaction, with reduction of the yields of 5-hydroxymethylfurfural and levoglucosan because of the depolymerization of carbohydrates during torrefaction. Due to the dissociation of propyl branches and the demethylation of methoxyls in lignin, pyrolysis of torrefied biomass yielded more guaiacol and catechol and less phenols with C4-propyl groups.

Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Production of biofuels from renewable biomass through thermochemical conversion has attracted increasing attention as an alternative to substitute fossil fuels [1–4]. It has been proved that pyrolysis technology could effectively convert biomass into liquid fuels, known as bio-oil [5]. However, the crude bio-oil has some unfavorable properties, including high oxygen and water contents, low heating value and strong acidity, which limit its direct application [5–8]. Using

pretreatments to reduce the oxygen content of raw biomass is a promising strategy to improve the bio-oil quality [9].

Torrefaction is one of the promising approaches to enhance the quality of raw biomass [10]. It is usually performed at low temperature (200–300 °C) under inert atmosphere [11]. Torrefaction could lower the content of oxygen in biomass via dehydration and deacetylation. Boateng and Mullen [12] found that the main products formed in biomass torrefaction were water and acetic acid, as well as a few of acetol and levoglucosan. In addition, torrefaction could also improve raw biomass properties in terms of energy density,

* Corresponding author. Present address: State Key Laboratory of Clean Energy Utilization, Zhejiang University, Zheda Road 38, Hangzhou 310027, China. Tel.: +86 571 87952801; fax: +86 571 87951616.

E-mail address: srwang@zju.edu.cn (S. Wang).

<http://dx.doi.org/10.1016/j.ijhydene.2016.02.082>

0360-3199/ Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

hydrophobicity, grindability and so on, making it more favorable for further utilization. Therefore, torrefaction has received great attention in many biomass processes, such as combustion, gasification and so forth [13]. However, researches focused on the combination of torrefaction and pyrolysis in biomass conversion are limited, and the effect of torrefaction on subsequent pyrolysis behavior of torrefied biomass is not well understood [14]. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, as well as a small amount of extractives and inorganic minerals. The composition distribution and chemical structure of biomass are considerably changed after torrefaction. However, the fundamental research on the evolution of functional groups in biomass torrefaction was inadequate. Rousset et al. [15] found that torrefaction greatly increased the carbon content in bamboo. And the element composition of torrefied biomass was close to that of lignite. Melkior et al. [16] proposed that ^{13}C solid-state cross-polarization/magic angle spinning (CP/MAS) NMR was a powerful tool to investigate the evolution rules of typical functional groups during torrefaction. Brosse et al. [17] torrefied beech heartwood and its isolated components, holocellulose and lignin, at 230 °C for 7 h, finding that hemicellulose underwent a significant degradation during torrefaction, and the β -aryl-ether linkages in lignin structure were cleaved.

Compared with raw biomass, the pyrolysis behavior of torrefied biomass is greatly changed. Torrefaction improved the thermal stability and lowered the reactivity of biomass by removing the thermally unstable fragments. Branca et al. [18] investigated the effect of torrefaction on the pyrolysis of spruce wood chips, and found that compared with raw biomass, pyrolysis of torrefied samples showed a higher char yield and lower liquid products yield. The main compounds in bio-oil included anhydrosugars, guaiacol, phenols and pyrolytic lignin, while some light oxygenates, such as hydroxyacetaldehyde, hydroxypropanone, acids and furans, showed much lower contents. The changes in bio-oil composition resulted from the corresponding modification of biomass chemical structure in torrefaction. Zheng et al. [19] performed two-staged pyrolysis of pine chips, and found that rising temperature in the first stage of torrefaction lowered the bio-oil yield due to the devolatilization, cross-linking, and carbonization occurring in this stage. Additionally, many kinetic studies on the torrefaction process have been carried out [13]. However, there were very few of kinetic studies on the pyrolysis of torrefied biomass. Broström et al. [20] reported a kinetic model containing three parallel reactions corresponding to the decomposition of three pseudo-components, and found that the activation energy for pyrolysis of each pseudo-component rarely changed after torrefaction.

In this study, the effect of torrefaction on the biomass structure and the subsequent pyrolysis behaviors were investigated. ^{13}C CP/MAS NMR was employed to quantitatively characterize the evolution of biomass chemical structure during torrefaction. A distributed activation energy model with three combined Gaussian functions (3G-DAEM) was introduced to assess the pyrolysis kinetics of torrefied biomass. Finally, the distributions of tar-derived compounds from pyrolysis of raw and torrefied biomass were analyzed by

Py-GC/MS, and the correlation between structure evolution and pyrolysis behaviors was discussed in detail.

Materials and methods

Torrefaction

A typical softwood, *Pinus bungeana*, was selected as the raw biomass for torrefaction. The sample was first ground and sieved into 0.18–0.25 mm, then dried at 60 °C for several days. Torrefaction pretreatment was performed at a tube furnace with nitrogen purging. About 10 g sample were treated at required temperatures of 200 °C, 225 °C, 250 °C, 275 °C and 300 °C for 0.5 h, which were denoted as Torr-200 °C, Torr-225 °C, Torr-250 °C, Torr-275 °C and Torr-300 °C, respectively, and the raw sample was denoted as Torr-60 °C. The energy yield for the torrefied biomass was calculated according to the equation used in a previous study [21].

Structural characterization

The ultimate analysis was performed on a Micro Elemental Analyzer (Elementar Analysensysteme, Germany). The high-heating value (HHV) was calculated based on the ultimate composition according to the equation proposed by Demirbaş [22]. Information about the functional groups in the raw and torrefied biomass were quantitatively analyzed by ^{13}C CP/MAS NMR (BRUKER DMX 500, Germany). Carbonyl carbon resonance in glycine was chosen as the external reference. Each spectrum was scanned for more than 1200 times.

Pyrolysis behaviors

The thermal analysis kinetics for the pyrolysis of the raw and torrefied biomass were studied on a thermogravimetric analyzer (TA-Q500, TA Instruments, USA) with non-isothermal method. 2 mg sample was loaded and heated from 25 °C to 800 °C with a constant rate of 10 °C min⁻¹. High purity nitrogen with a flow rate of 40 mL min⁻¹ was used to provide inert atmosphere and sweep the released volatiles. MATLAB software was used to perform the specific calculation in the kinetic modeling. Tar-derived pyrolytic products from raw and torrefied biomass were analyzed by Py-GC/MS. In each run, about 0.5 mg sample was pyrolyzed at 600 °C for 10 s in a micro-pyrolyzer (CDS5200, USA), the products were swept into GC/MS (Thermo Scientific, Trace DSQII) for analysis. The specific analysis method of GC/MS detection was described in our previous study [23].

Results and discussion

Structural characterization

As the torrefaction temperature increased, the molar ratios of O/C and H/C in biomass decreased (see Fig. 1), implying the change of biomass composition after torrefaction. Their variation in temperature range of 225–250 °C was much less than that in 250–300 °C. This phenomenon was also found in

Download English Version:

<https://daneshyari.com/en/article/5147651>

Download Persian Version:

<https://daneshyari.com/article/5147651>

[Daneshyari.com](https://daneshyari.com)