Applied Energy 121 (2014) 1–9

Contents lists available at ScienceDirect

Applied Energy

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

Understanding the chemical and structural transformations of lignin macromolecule during torrefaction

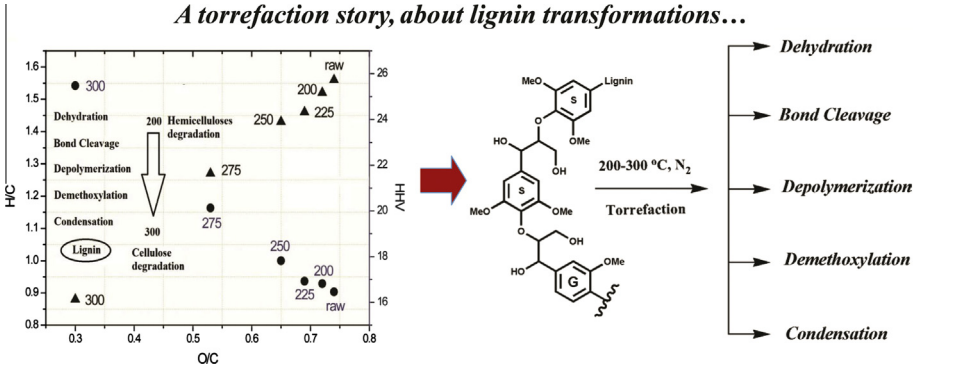
Jia-Long Wen [a], Shao-Long Sun [a], Tong-Qi Yuan [a], Feng Xu [a], Run-Cang Sun [a,b,*]

[a] Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, China
[b] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China

HIGHLIGHTS

- The terrified bamboo has a high energy yield of 85.7% and a HHV of 20.13 MJ/kg.
- The structural changes of hemicelluloses, cellulose, and lignin were investigated.
- First study on the structural transformations of lignin during torrefaction.
- The mechanism of structural changes of lignin has been proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 September 2013
Received in revised form 17 December 2013
Accepted 4 February 2014
Available online 19 February 2014

Keywords:
Bamboo
Bioenergy
Lignin
NMR
Structural transformations
Torrefaction

ABSTRACT

Torrefaction is an efficient method to recover energy from biomass. Herein, the characteristics (mass yield, energy yield, physical, and chemical characteristics) of torrefied bamboo at diverse temperatures (200–300 °C) were firstly evaluated by elemental analysis, XRD, and CP–MAS ^{13}C NMR methodologies. Under an optimal condition the terrified bamboo has a relative high energy yield of 85.7% and a HHV of 20.13 MJ/kg. The chemical and structural transformations of lignin induced by thermal treatment were thoroughly investigated by FT-IR and solution-state NMR techniques (quantitative ^{13}C NMR, 2D-HSQC, and ^{31}P-NMR methodologies). The results highlighted the chemical reactions of the native bamboo lignins towards severe torrefaction treatments occurred, such as depolymerization, demethoxylation, bond cleavage, and condensation reactions. NMR results indicated that aryl-ether bonds (β-*O*-4) and *p*-coumaric ester in lignin were cleaved during the torrefaction process at mild conditions. The severe treatments of bamboo (275 °C and 300 °C) induced a dramatic enrichment in lignin content together with the almost complete disappearance of β-*O*-4, β-β, and β-5 linkages. Further analysis of the molecular weight of milled wood lignin (MWL) indicated that the average molecular weights of "torrefied MWL" were lower than those of control MWL. It is believed that understanding of the reactivity and chemical transformations of lignin during torrefaction will contribute to the integrated torrefaction mechanism.

1. Introduction

Bioenergy has been considered as one of attractive renewable energy alternatives in the future [1]. Among the existing technologies to enhance lignocellulosic biomass for renewable energy

* Corresponding author at: Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, China. Tel./fax: +86 10 62336903.
E-mail address: rcsun3@bjfu.edu.cn (R.-C. Sun).

http://dx.doi.org/10.1016/j.apenergy.2014.02.001
0306-2619/

production, torrefaction was regarded as a simple and efficient method. Torrefaction is a thermo-chemistry process that enables energy densification of biomass and biomass homogenization, which usually conducted in an inert atmosphere and low temperatures of 200–300 °C [2]. In fact, the basic principle of torrefaction is the removal of oxygen and enrichment of carbon of the final solid product. The torrefied biomass has a lower O/C ratio as compared to the original biomass [2]. Besides, the torrefied biomass has a higher energy density and grindability, which enhance the combustion performance. Due to the aforementioned advantages of torrefaction, research and development activities in biomass torrefaction for energy applications worldwide were very active in these years [3–15].

Up to now, different methods and various feedstock types employed in torrefaction have been reported [3–15]. Among the existing feedstocks employed for torrefaction, bamboo will be an excellent feedstock for future torrefaction industry [11]. Bamboo is a promising biomass for future energy production because of its high growth rate and a number of major fuel characteristics, such as low ash content and high heating value [16]. Bamboo species widely distributed in Asian countries and their traditional applications are well known. Nevertheless, it is of great importance to use efficient biomass conversion technologies to take advantage of bamboo's characteristics (high contents of cellulose and lignin) under the context of biomass utilization [11].

Torrefaction is a thermochemistry process, which not only removes water and low molecular-weight organic volatile components, but also induces chemical transformations of the polymers in the plant cell wall, and thus affects the mechanical strength of the material [15]. For example, the major components in biomass (cellulose, hemicelluloses, and lignin macromolecules) are variously affected by torrefaction process, depending on their respective chemical reactivity. Although most researches focus on the physical characteristics (mass yield, ultimate analyses, and grindability) of the torrefied biomass, however, as a very important issue, the chemical and structural transformations of components in biomass have not been thoroughly understood during torrefaction process.

Lignocellulosic biomass is a natural bio-composite, mainly formed by cellulose, hemicelluloses, and lignin. The transformations of chemical and structural features during torrefaction process have a direct influence on the quality of the final product. Lignins are complex natural polymers with various phenolic structures, which significantly affect the final properties of the torrefied bimass. The native lignins of bamboo (*Phyllostachys*) are essentially composed of *p*-hydroxyphenyl (H, 1–2%), guaiacyl (G, 21–31%), and syringyl (S, 67–78%) units associated with abundant *p*-coumarates and ferulates [17]. The main substructures of native lignins are the aryl ether bonds (β-*O*-4 linkages), which are mainly composed of S-type lignin units, while the proportion of carbon–carbon bonds in native lignins is less. It was reported that the lignin degradation starts at temperatures above 200 °C, with a slower kinetics than that of the hemicelluloses degradation [18]. The effect of severe thermal treatment (220–280 °C) on spruce and beech wood lignins has been investigated by thioacidolysis method [19]; however, the understanding of the composition and structure of the lignin macromolecule is traditionally conducted by wet chemical methods, such as thioacidolysis (TA), nitrobenzene oxidation (NBO), and derivatization followed by reductive cleavage (DFRC). These methods are effective in analyzing "native lignin" in plant cell wall. However, they will be ineffective when investigating the structurally changed lignin because that they only considering the ether linkages, but not regarding the changes of carbon–carbon bonds in lignin. Thanks to recent advances in nuclear magnetic resonance (NMR), our knowledge of this natural polymer has been improved and expanded [20–22]. Most of the ether linkages (β-*O*-4 ones) were expected to be cleaved at 200–350 °C via thermal analysis [23]. However, the reactivity and chemical transformations of lignins during torrefaction have been less studied and poorly understood. As a method for upgrading biomass for fuels, it is desired to obtain more solid with lower O/C ratios during torrefaction. Therefore, it is expected that the structural evolution of lignin macromolecule could provide indications for optimizing the torrefaction conditions and hence improve the quality of torrefied biomass.

In the present study, the torrefied bamboo samples under different conditions have been investigated by component analysis, elemental analysis, energy yield, XRD, and CP–MAS ^{13}C NMR techniques. In addition, milled wood lignin (MWL), which is considered to be an ideal representative of "native lignin", extracted from the control and torrefied bamboo and thoroughly analyzed using FT-IR spectra, quantitative ^{13}C NMR, 2D-HSQC NMR, and ^{31}P NMR spectra. Moreover, gel permeation chromatography (GPC) was also used to investigate the effects of torrefaction temperatures on the molecular weight of the lignins. It is believed that the effects of different torrefaction temperatures on the lignin macromolecules and the concomitant chemical transformation of lignin could be observed in a resolved and observable manner.

2. Experimental

2.1. Material

Bamboo (*Phyllostachys pubescens*) was obtained from Shangrao, Jiangxi, China. The culms were manually separated before dried at 50 °C, and the particles with a size between 450 and 900 μm (20–40 mesh) were collected. The dewaxed material (toluene/ethanol, 2:1, v/v; Soxhlet extractor; 12 h) was dried at 60 °C for 16 h.

2.2. Torrefaction process

The torrefaction of bamboo was conducted in a tubular furnace (Furnace 1200C, Central furnace, Tianjin, China). After drying of the bamboo particles in an oven at 105 °C for 24 h as a pre-treatment process, in which the moisture was completely eliminated, the dried samples were put into sample box of furnace. For every torrefaction experiment, a feedstock amount of 25 g of bamboo was used. The feedstock was placed in the sample cup, which was then mounted to the inner cylinder of the reactor. The bamboo was torrefied at 200, 225, 250, 275, and 300 °C for 1 h in the absence of oxygen, respectively. The flow rate of nitrogen was 0.5 L/min. The reaction was processed in two stages. In the first stage, the temperature was risen up to the required torrefied temperature in a desired time (40–60 min, 5 °C/min); in the second stage, the bamboo sample stayed at setting torrefied temperature for the setting residence time (60 min). After torrefaction, the torrefied bamboo samples were collected and weighed.

2.3. "Milled wood lignin" from torrefaction biomass

The crude "milled wood lignin, (MWL)" sample was prepared from bamboo according to classic procedures [24]. The ball-milled of bamboo (control and torrefied bamboo) was prepared with a planetary ball mill for 2 h as previously reported [25].

2.4. Physicochemical characterization of the torrefied bamboo

The compositions of the polysaccharides and lignin in the torrefied bamboo samples were analyzed using the Laboratory Analytical Procedure (LAP) for biomass provided by the NREL [26]. Elemental analysis (C, H, and O) was carried out in an elemental