Bioresource Technology 151 (2014) 424–427

Contents lists available at ScienceDirect

Bioresource Technology

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

Short Communication

Characterization of milled solid residue from cypress liquefaction in sub- and super ethanol

Hua-Min Liu *, Yu-Lan Liu

College of Food Science and Technology, Henan University of Technology, Zhengzhou 450001, China

HIGHLIGHTS

- MSR was isolated from solid residue.
- Re-polymerization reactions were the main reaction at 220–260 °C.
- The thermal stability of lignin side-chain in cypress has been investigated.

ARTICLE INFO

Article history:
Received 23 September 2013
Received in revised form 10 October 2013
Accepted 15 October 2013
Available online 23 October 2013

Keywords:
Milled solid residue
Liquefaction
Characterization
Cypress

ABSTRACT

Cypress liquefaction in sub- and super ethanol was carried out in an autoclave at various temperatures. Milled solid residue (MSR) was isolated from solid residue remaining from the liquefaction process, and its chemical characteristics was comparatively investigated with milled wood lignin (MWL) of cypress by sugar analysis, elemental analysis, FT-IR analysis, gel permeation chromatography, and NMR analysis. Results showed that there were two reactions (de-polymerization and re-polymerization) during the cypress liquefaction in sub- and super ethanol and the re-polymerization reactions were the main reaction at 220–260 °C. Considering the stability of side-chain, the stability of lignin side-chain in cypress during liquefaction process in ethanol could be sequenced as follows: β-5 > β-β′ > β-O-4′. The MSR were mainly from the decomposition and re-polymerization of lignin. This study suggests that characterization of MSR provides a promising method to investigate the mechanisms of cypress liquefaction in ethanol.
Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Thermo-chemical liquefaction is an effective method for converting biomass into valuable liquid bio-oil and solid fuel at 150–420 °C in the presence of solvents (Behrendt et al., 2008; Liu et al., 2013b). In recent years, super-critical fluids were extensively used as chemical reaction media in biomass liquefaction (Peng et al., 2009). For example, sub- and super-critical water is widely applied to a variety of biomasses liquefaction because it is inexpensive, abundant and environmentally compatible (Yuan et al., 2009; Xiao et al., 2013). Ethanol is a form of biomass energy which can be made from biomass and is widely used as vehicle fuel. Supercritical ethanol was also used as a reaction medium to promote mass and heat transfer during biomass liquefaction (Xu et al., 2008).

Detailed information of liquefaction products is propitious to the investigation of biomass liquefaction. However, the compound distributions in bio-oil and gas products are not well-known for various biomass feeds (Zhang et al., 2007). Some studies available on product identification and simulation (Kruse and Gawlik, 2003; Yang et al., 2011). However, liquefaction of biomass cannot be easily described by detailed chemical reaction pathways with well-defined single reaction steps because of the complex organic compounds in products. Recently, many literatures have been investigated the mechanism of biomass liquefaction in solvents. Lump analysis has been used to investigate the biomass liquefaction by lumping the large number of chemical compounds into groups of pseudo-components, according to their characteristics of material and products (Liu et al., 2012a,b, 2013a). The results show that lump analysis is effective for the investigation of biomass liquefaction. In a preliminary investigation, the physical and chemical characteristics of solid residue obtained from hydrothermal liquefaction cypress have been measured by FT-IR, X-ray diffraction, sugar analysis, and elemental analysis to investigate the mechanism of biomass liquefaction in hot-compressed water (Liu et al., 2013b). However, the solid residue is not characterized by 2D HSQC NMR analysis due to the insoluble of solid residue in DMSO. Therefore, more information from the NMR analysis of solid residue may help to better understand the liquefaction process.

In this study, characteristics of milled solid residue isolated from the solid residue remaining from cypress liquefaction in sub- and super ethanol are measured to obtain more mechanism

* Corresponding author. Tel./fax: +86 0371 67789937.
E-mail address: liuhuamin5108@163.com (H.-M. Liu).

0960-8524/$ - see front matter Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.10.050

information of biomass liquefaction in ethanol. As the first step, the solid residues obtained from biomass liquefaction in ethanol at various temperatures were milled in a Fritsch planetary ball mill followed by dioxane (96%) extraction and purification, respectively. Then the effect of temperature on the characteristics of milled solid residues was investigated to discuss the decomposition and re-polymerization mechanism of biomass liquefaction in sub- and super ethanol.

2. Methods

2.1. Materials

Cypress was collected from Xuchang, Henan province in China. The original sample was air-dried and then milled into fine powder smaller than 40-mesh. The sample powder was dried in an oven at 105 °C for 24 h before use. The main components of cypress were as follows (on a dry weight basis): 43.2% cellulose, 26.3% hemicelluloses, 28.2% lignin, and 2.5% ash (Liu et al., 2013b). The solvents used in this work were all of analytical grade.

2.2. Liquefaction

The liquefaction experiments were carried out with a batch reactor system (Parr, USA). The detail of the liquefaction and separation experiments have been described previously (Liu et al., 2013b). Briefly, once the reactor was cooled to room temperature, the gas was vented. The solid and liquid mixture was removed from the autoclave and the solid residue extracted with water and acetone to remove water-soluble oil and heavy oil until the solvents in the thimble became colorless. Acetone and water insoluble fraction was designated as solid residue.

2.3. Preparation of milled wood lignin and milled wood residue

The extractive-free ground cypress and the solid residues obtained from cypress liquefaction in sub- and super ethanol were milled (5 h) in a Fritsch planetary ball mill followed by dioxane (96% v/v) extraction and purification according to Li et al. (2012). The samples obtained from the purification experiments were defined as milled wood lignin (MWL) and milled solid residue (MSR), respectively.

2.4. Characterization

The neutral sugar composition of MSR and MWL was determined by hydrolysis with 6% H_2SO_4 for 2.5 h at 105 °C. The liberated neutral sugars were analyzed by high performance anion exchange chromatography (Dionex ICS-3000, USA) using a Dionex GP50 gradient pump, ED50 electrochemical detector, and a carbopac™ PA1 column (Xiao et al., 2013). The elemental compositions (C, H and N) of the solid residue were determined with Elemental Analyzer Vario EL (Germany). The composition of oxygen (O) was estimated by difference. Fourier transform infrared spectrometry (FT-IR) experiments were conducted with the Thermo Scientific Nicolet iN10 FT-IR Microscope (USA). The instrument was equipped with a liquid nitrogen cooled MCT detector and the spectra were recorded in the region of 4000-650 cm^{-1} at a resolution of 4 cm^{-1}. The weight-average (Mw) and number-average (Mn) molecular weights of MWL and MSR were determined by GPC with THF as the mobile phase and calibrated with polystyrene standards. NMR spectra were recorded on a Bruker AV-III 400M spectrometer (100 Mr/z) at 25 °C in DMSO. 2D HSQC NMR spectra were recorded according to the literature (Li et al., 2012).

3. Results and discussion

3.1. Yield and chemical composition of MWL and MSR

The yields of MWL and MSRs obtained from before and after cypress liquefaction in sub- and super ethanol were expressed as a percentage of dry starting material. Table 1 gives the yields of MSRs and MWL. As can be seen, with an increase of temperature from 220 to 260 and 300 °C, the yield of MSR increased from 0.66 to 1.6% and 0.76%, respectively. Although MWL is low yield and has some modifications during the milling process, it is considered to be a representative of the native lignin in lignocelluloses. To obtain detailed compositional and structural features, the three MSRs were further characterized as compared to MWL of cypress. It is important to note the hot-compressed ethanol treatment increased the MSR yield as compared to the cypress MWL yield (0.48%). The higher yield of MSR is probably due to thermal treatment of biomass under anoxia condition can greatly enhance its grindability, since the energy consumption for milling is 3–7 times lower than that of untreated biomass (Prins et al., 2006; Arias et al., 2008). The content of associated hemicelluloses in the MSRs and MWL was determined as the results of neutral sugar (Table 1). The result indicated that all of the samples contained rather low amounts of bound polysaccharides as shown by a neutral sugar content of 0.11–0.91%, suggesting that the thermal treatment of cypress in ethanol could not entirely decompose the neighboring polysaccharide moieties. The elemental composition of the MSRs and MWL are presented in Table 1. Clearly, the result reveals that MSRs-260 and 300 °C have higher C content and lower O content as compared to that of MSR-220 °C and MWL. This may be due to the polymerization reaction of lignin was mainly present in biomass liquefaction in higher temperature.

3.2. FT-IR characterization

Fig. S1 in supplementary data shows FT-IR spectra of MSRs obtained from hot-compressed ethanol treatment at various temperatures and MWL of cypress. As can be seen from the diagram, the relative intensities of the bands for aromatic skeleton vibrations at 1592, 1504, 1454, 1419 cm^{-1} in FT-IR spectra of MSRs and MWL showed minor changes, which confirmed that the "core" of the lignin structure in MSRs does not change significantly during the liquefaction process. Interestingly, unconjugated ketone and carboxyl group stretching (1713 cm^{-1}) in MSRs were remarkable increased, which indicated that the formation of new structure

Table 1
Yield, neutral sugar composition, and elemental analysis of MSRs and MWL.

Samples	Yield (%)	Sugar analysis (wt%)					Elemental analysis (wt%)				
		Ara	Gal	Glu	Xyl	Man	C	H	S	N	O
MWL	0.48	0.34	0.24	0.62	2.2	0.05	60.6	6.2	0.17	0.39	32.6
MSR-220 °C	0.66	0.21	0.17	0.12	0.52	0.04	59.9	6.0	0.24	0.44	33.4
MSR-260 °C	1.6	0.22	0.18	0.23	0.68	0.21	61.9	5.2	0.15	0.45	32.3
MSR-300 °C	0.76	0.11	0.30	0.98	0.91	0.66	65.4	5.7	0.17	0.41	28.3

Download English Version:

https://daneshyari.com/en/article/7079976

Download Persian Version:

https://daneshyari.com/article/7079976

Daneshyari.com