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New materials from solid residues for investigation the mechanism of biomass hydrothermal liquefaction

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ABSTRACT

Advanced analysis technologies cannot be applicable to structural characterization of solid residue from biomass hydrothermal liquefaction due to its insoluble characteristics in organic solution. In this investigation, the milled solid residue fractions were isolated from the solid residues producing during cypress hydrothermal liquefaction at 220, 260, and 300 °C. Their fractions structural characteristics were comparatively investigated by advanced analysis technologies such as liquid state Nuclear Magnetic Resonance. Dichloroethane/ethanol insoluble fractions were firstly found during the liquefaction process at 260–300 °C and results showed that the fractions were the intermediate component of biomass carbonization and mainly produced from the re-polymerization reactions of lignin during hydrothermal liquefaction process. The presence of crosslinking reactions between carbon-carbon which lead to the formation of a highly crosslinked structure resulting in the formation of milled solid residue fractions, which made the fractions be not insoluble in dichloroethane/ethanol and have high thermal stable and molecular weight. Ether structures scission, de-methylation reactions, re-polymerization between carbon-carbon, and fragmentation of large molecular fractions have been occurred in lignin during hydrothermal liquefaction process. The result showed that characterization of milled solid residue fractions provided some new information of the mechanisms of biomass hydrothermal liquefaction.

1. Introduction

Over the past few decades, the environmental concerns on greenhouse gases and the depletion of fossil fuel reserves have urged out society to seek sustainable, renewable, and environmentally friendly energy sources (Wu et al., 2016). Among the alternative resources, biomass is constituted by lignin, hemicelluloses, and cellulose and presents the greatest potential to produce optional liquid fuels (Wu et al., 2016). The utilization of biomass via thermo-chemical conversion has received increased attention due to the rapid increase in the global energy demand and environmental pollution. There are five typical themo-chemical processes to convert biomass, which included liquefaction, gasification, pyrolysis, hydrothermal hydrolysis, and combustion (Wang et al., 2013, Xiao et al., 2014; Xiao et al., 2013). Among the four typical themo-chemical processes, liquefaction can break down biomass into light fragments in various solvents (such as water, methanol, acetone, and their mixtures) under high pressure and low temperature firstly, and then these small fragments re-polymerize into oily compounds with different molecular weights (Zhang et al., 2010).

Hydrothermal liquefaction (also called hot-compressed or sub/supercritical waters) has many advantages, such as environmental compatibility, high liquefaction effective, and does not require drying pretreatment for wet biomass before liquefaction (Thiruvenkadam et al., 2015). The oily compounds from biomass liquefaction cannot be directly used as transportation fuels because of complex mixtures of more than 400 various compounds, which included ketones, carboxylic acids, carbohydrates, alcohols, aldehydes, phenols, ethers, and furans (Zhu et al., 2015). In addition, those complex mixtures of oily compounds make the liquefaction process be not easily described by well-defined single chemical reaction pathways. The cellulose, hemicelluloses and lignin components in biomass form an insoluble three-dimensional network which makes the biomass more difficult to convert due to the very complex structure (Lange, 2007). Another reason for the difficulty in defining the single chemical reaction pathways is due to the heterogeneous reactions which occurred on and inside the biomass particles surface during liquefaction process (Kruse and Gawlik, 2003). Recently, characterization of solid residue remaining in biomass liquefaction has carried out by, sugar analysis, X-ray diffraction, FT-IR, and elemental analysis to obtain the mechanism information of liquefaction process (Kruse and Gawlik, 2003). In addition, the

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solid residues were also divided into acid-soluble and acid-insoluble residues, and some new mechanism information such as carbohydrate degradation process and polymerization reactions at low temperatures were found (Liu et al., 2013). However, the major problem on characterization of solid residue was that all those reports can't solve the soluble characteristics of solid residue in organic solution.

Therefore, the advanced liquid state NMR spectroscopy cannot be applicable to structural characterization of solid residue due to its insoluble characteristics in organic solution. In the previous work, the milled solid residue was firstly obtained from the solid residue of cypress liquefaction in ethanol (Liu and Liu, 2014). Milled solid residue has many advantages for investigation the mechanism of biomass liquefaction such as (1) being soluble in many organic solutions and (2) keeping the final state of liquefaction reaction. The NMR spectra of milled solid residue showed that there were mainly from the lignin fraction by degradation or re-polymerization reaction (Liu and Liu, 2014).

Various forestry and agricultural byproducts could be considered as renewable and abundant biomass sources, but cypress was deemed as a representative biomass that was studied in this report. Therefore, the objective of this investigation was characterized the structural characteristics of milled solid residue remaining in cypress hydrothermal liquefaction and to study the mechanism of cypress hydrothermal liquefaction. As the first step, the milled solid residue fractions were isolated from the solid residue at various liquefactions, respectively. Then the temperature effect on the physical and chemical characteristics of those milled solid residue fractions was studied to help understand the mechanism of biomass hydrothermal liquefaction.

2. Experimental sections

2.1. Materials

Cypress was obtained from Henan province, China. The sample was dried in an oven at 105 °C for 24 h, then ground into small particles to obtain the fractions below 40 meshes. The proximate and ultimate analysis results showed that the sample contained 28.2% lignin, 26.3% hemicelluloses, 43.2% cellulose, 0.3% nitrogen, 6.0% hydrogen, 44.8% oxygen, 48.9% carbon, and 2.5% ash (on a dry weight basis) (Liu et al., 2013). All solvents and chemicals used were analytical grade.

2.2. Liquefaction

The experiments of liquefaction were carried out in a 1 l stainless autoclave (Parr, USA) with a type J thermocouple and an external electrical furnace, and the temperature controlled to ± 1 °C. After liquefaction reaction was completed and the autoclave was cooled to 25 ± 1 °C by water, the reaction gas was vented without further analysis and then the reaction mixture was removed from the autoclave. The solid residue was obtained after extraction by water and acetone to remove water-soluble and acetone-soluble compounds, respectively. The solid residue was then dried at 105 °C for 12 h before used. The solid residues obtained from the hydrothermal process at 220, 260, and 300 °C were 64.7%, 36.2%, and 39.5%, respectively (Liu et al., 2013).

2.3. Isolation of milled solid residue and milled wood lignin

Milled solid residue (MSR) and milled wood lignin (MWL) were isolated after milling of the solid residue and dewaxeds cypress in a ball mill before extraction with dioxane/water on the base of the classical procedure, respectively (Björkman, 1954). The scheme for fractional isolation of MWL or MSR is shown in Fig. 1. For a type run, 40 g of sample after ball mill was extracted by dioxane/water (400 ml; 96:4, v/v) for 48 h. The suspension was removed by centrifugation and then crude MSR was obtained by concentrating under reduced pressure to remove the solvent. Subsequently, the crude MSR was dissolved in 20 ml acetic acid/water (9:1, v/v), and precipitated into 400 ml water. The precipitated MSR was filtered and dissolved in 10 ml 1,2-dichloroethane/ethanol (2:1, v/v). The 1,2-dichloroethane/ethanol-insoluble MSR was defined as MSR-B. The 1,2-dichloroethane/ethanol-soluble milled solid residue precipitated into ether (200 ml), and the ether-insoluble was defined as MSR-A.

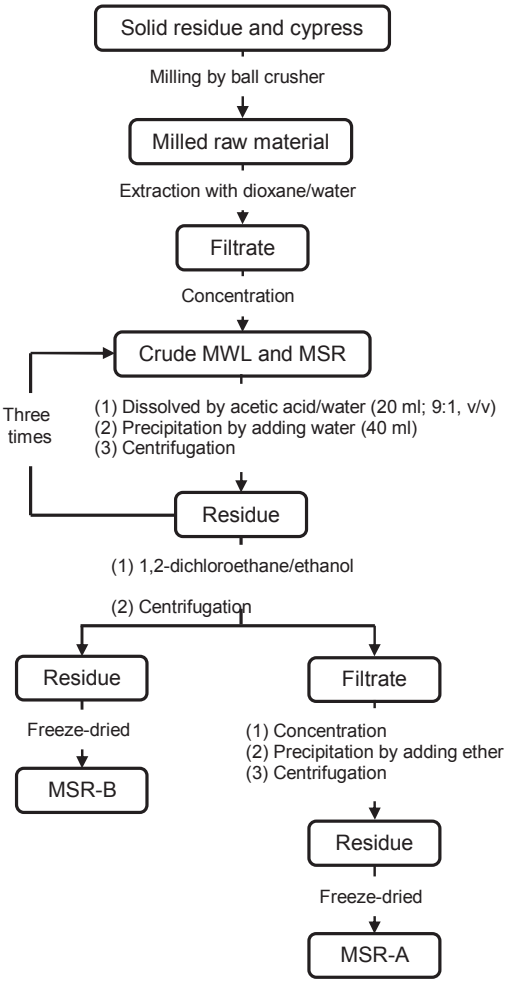

Fig. 1. Scheme for fractional isolation of Cypress MWL and MSR fractions.

2.4. Characterization

The functional groups in milled solid residue and milled wood lignin were determined by a Nicolet iN10 FT-IR Spectrophotometer (Madison, WI, USA) equipped with a liquid nitrogen-cooled MCT detector. Ultraviolet (UV) spectroscopy analysis was carried out in ethanol solution by UV 2300 (Shanghai Tianmei Science and Technology Co., Ltd., China) using 1 cm cells.

Molecular weights of the milled solid residue and milled wood lignin were measured by gel permeation chromatography (GPC) and the process was same as those described by previously (Li et al., 2012a,b). The elemental compositions (C, H, N, S, and O) of the MSR, MWL, and cypress were measured by an Elementar Vario EL analyzer. The oxygen content was calculated by difference.

Thermal degradation of all samples was evaluated by thermogravimetric analyzer (Shimadzu, Japan) from 30 to 640 °C at 10 °C/min heating rate under nitrogen protection. The mass of the samples used varied from 3 to 5 mg.

The solution-state heteronuclear single quantum correlation (HSQC) and ^{31}P NMR spectra of the MWL and MSR fractions were acquired on a