Cornstalk liquefaction in sub- and super-critical ethanol: Characterization of solid residue and the liquefaction mechanism

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ABSTRACT

Cornstalk liquefaction in sub- and super-critical ethanol was carried out in an autoclave at various temperatures. The characteristics of solid residue were investigated by XRD and sugar analysis. Milled solid residue fraction was isolated from the solid residue, and its chemical characteristics were comparatively investigated with milled wood lignin of cornstalk by gel permeation chromatography, FT-IR, and 2D HSQC NMR. The results showed that the structure of xylan in cornstalk was not broken down completely under the reaction temperatures and those liquefaction conditions were unable to break effectively apart the inter/intra chain hydrogen bonding in cellulose fibrils. Characterization of milled solid residue showed that the de-polymerization of lignin was more dominant than the re-polymerization as reaction temperature increased from 180 to 300 °C. The β-O-4, ferulate, tricin sub-structures almost disappeared from the spectrum of milled solid residue, which indicated the re-polymerization or decomposition of those bonds in lignin during cornstalk liquefaction process. The result showed that characterization of solid residue fractions provided some new information of the mechanisms about cornstalk liquefaction in ethanol.

1. Introduction

Biofuels have attracted much attention in the past decades because of increased carbon dioxide emission from fossil fuel combustion and the depletion of crude oil [1]. Biomass is one of the most abundant sources of renewable energy, and will be an important part of a more sustainable future energy system [2]. Liquefaction of biomass with proper solvents is process that can prospectively be integrated with optimized conditions to simultaneously produce fuel additives and valuable chemicals [3].

The use of ethanol in supercritical technology can be carried out under relatively mild conditions. Also, it acts as a hydrogen donor solvent in supercritical media and can react with acidic components in bio-oil by esterification to obtain fatty acid ethyl esters similar to biodiesels [4,5]. Therefore, ethanol has been widely adopted as solvent for liquefaction of various biomasses [6—8]. Investigation on the characteristics of bio-oil and solid residue is good for understanding the mechanism of biomass liquefaction in sub- and supercritical ethanol. In recent years, although bio-oil and solid residue have been analyzed by GC—MS, FT-IR, and NMR in many reports [9—11], the degradation of biomass cannot be easily described by detailed chemical reaction pathways with well-defined single reaction steps. In addition, the solid residue has not been characterized by ^{13}C NMR and ^{1}H NMR analyses due to the insoluble of solid residue in organic solution. In our previous work, the milled solid residue was firstly isolated from the solid residue remaining from cypress liquefaction in sub- and supercritical ethanol and hot-compressed water [12,13]. Milled solid residue has many advantages for investigation of the mechanism of biomass liquefaction such as (1) being soluble in many organic solutions (2) keeping the final state of liquefaction reaction. The NMR spectra of milled solid residue showed that these were mainly from the decomposition and re-polymerization of lignin [12,13]. Lignin is a complex amorphous polymer composed of phenylpropanoid units consisting primarily of coniferyl, sinapyl, and p-coumaryl alcohols. Although the lignin in wood and non-wood plants shares the basic chemical structure, the structural properties of non-woody

plants are still known to be different from those of softwood and hardwood lignin. Therefore, it is necessary to investigate more characteristics of milled solid residue isolated from non-wood biomass liquefaction in sub- and super-critical ethanol.

Various agricultural non-woody residues can be deemed as abundant and renewable sources, but cornstalk is the only non-woody biomass that was investigated in this paper. In the present work, the cornstalk liquefaction in sub- and super-critical ethanol was carried out in a closed system under identical conditions. The milled solid residue was obtained from cornstalk liquefaction in sub- and super-critical ethanol at various temperatures, and extraction by a Fritsch planetary ball mill, and extraction by dioxane purification. Then the characteristics of various milled solid residue fractions and solid residue were investigated by sugar analysis, elemental analysis, FT-IR, 2D HSQC NMR, and XRD, which could provide more decomposition and re-polymerization mechanism of non-woody biomass liquefaction in sub- and super-critical ethanol.

2. Experimental

2.1. Materials and chemicals

Cornstalk was obtained from Guangzhou, Guangdong Province of China. The raw material was air-dried, ground in a universal high-speed smashing machine and sieved to give fractions with a 40 mesh screen. The cornstalk powder was extracted with distilled water and ethanol to remove water-soluble and polar organics, dried at 105 °C for 24 h, and stored in desiccators at room temperature. The characterization of cornstalk has been reported in our previous literature [14]. The cornstalk contained 39.2% cellulose, 35.1% hemicelluloses, 20.2% lignin, and 5.5% ash (on a dry basis). All used chemicals were of analytical or reagent grade.

2.2. Liquefaction

The liquefaction experiments of cornstalk were performed in a 1 L stainless steel reactor (magnetically stirred autoclave), in which 10 g cornstalk sample and 100 mL ethanol were placed. Then the autoclave was sealed and the air inside the autoclave was replaced with high-purity nitrogen. The autoclave was then heated to desired temperature at 4 °C/min by an external electric furnace, and held for desired resistance time. After each run, the autoclave was cooled down to room temperature by means of cool water inside the reactor. The solid and liquid mixture was removed as clean as possible with ethanol from the autoclave, filtrated through a Teflon membrane filter with 0.45 μm of pore size, and washed 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. To further evaluate the effect of reaction temperature on the solid residue, the solid residue was further divided into acid-soluble solid residue (ASSR) and acid-insoluble solid residue (AISR) after treatment with 3% H_2SO_4 at 100 °C for 4 h. All the product yields were calculated on a dry-ash-free basis. Each experiment was conducted in duplicate and the differences between the results of two tests were below 3% of the values.

2.3. Preparation of milled wood lignin and milled wood residue

Milled solid residue and milled wood lignin were isolated after milling of the solid residue and dewaxed cornstalk in a ball mill prior to extraction with dioxane/water according to the classical procedure [15], respectively. Briefly, the ball milled samples (40 g) were extracted twice with dioxane/water (400 mL; 96:4, v/v) for 48 h. After the suspension was removed by centrifugation, the solution obtained was concentrated under reduced pressure to obtain crude milled solid residue or milled wood lignin. Subsequently, the crude samples were dissolved in acetic acid/water (20 mL; 9:1, v/v), and precipitated into water (400 mL). The precipitated fractions were filtered, dissolved in 1,2-dichloroethane/ethanol (10 mL; 2:1, v/v). The 1,2-dichloroethane/ethanol-soluble milled fractions precipitated into ether (200 mL), the ether-insoluble were defined as MSR and MWL, respectively.

2.4. Characterization

The elemental composition, molecular weight, and FT-IR analysis of the samples were conducted as described previously [12]. 2D HSQC NMR spectra were recorded according to the literature [16]. X-ray diffraction patterns of raw cornstalk and solid residues were obtained using an X-ray diffractometer (Shimadzu XRD 6000, Japan). Scans were collected at 40 kV and 30 mA with a step size of 0.02° and step of 2°/min. Cypress crystallinity, as expressed by crystallinity index (CrI), was determined from XRD data using the formula by Segal et al. [17] as follows:

$$CrI = (1 - I_{am}/I_{002}) \times 100$$

In which I_{002} is the intensity for the crystalline portion of biomass (i.e., cellulose) at about $2\theta = 22.6°$ and I_{am} is the peak for the amorphous portion (i.e., cellulose, hemicelluloses, and lignin) at about $2\theta = 18.6°$.

3. Results and discussion

3.1. Yield and sugar composition of solid residue fractions

The effect of reaction temperature on the solid residue yields (A), sugar composition of various solid residue fractions (B), and MSR fraction yields (C) can be inferred from Fig. 1, which presents the results obtained from the liquefaction experiments at various temperatures ranging from 180 °C to 300 °C. In general, biomass was firstly decomposed and de-polymerized to fragments of lighter molecules during the liquefaction process. And then those unstable fragments rearranged through condensation, cyclization and polymerization to form new compounds [18]. Clearly, the ASSR yield decreased slightly from 76.1% to 75.0% as the final temperature increased from 180 to 220 °C. Then,