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Hydro-liquefaction of microcrystalline cellulose, xylan and industrial lignin in different supercritical solvents

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HIGHLIGHTS

- The liquefaction behaviors of cellulose and xylan were different from that of lignin.
- Methanol and ethanol showed a better miscibility with subcomponents via molecular simulation.
- The product compositions highly depended on three subcomponents.
- The quality of bio-oil was improved in methanol.

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ABSTRACT

The influences of solvent on hydro-liquefaction of cellulose, xylan, and lignin were investigated using micro-autoclave. The maximum conversion and bio-oil yield obtained from cellulose and xylan liquefaction were achieved in methanol, whereas similar liquefaction characteristics of lignin were observed in methanol and ethanol. The molecular simulation of interactions between solvents and subcomponents indicated that methanol and ethanol were highly miscible with raw materials. GC–MS and FT-ICR MS characterization revealed that the chemical compositions of liquid products highly depended on the utilized feedstocks. Esters, ketones, and aldehydes were mainly produced from cellulose and xylan conversion, whereas aromatic compounds were primarily derived from lignin conversion. EA results showed that methanol favored the hydrogenation and deoxygenation, resulting in the heating value increased. It could be concluded that the oil quality was highly improved in supercritical methanol.

1. Introduction

The energy and environmental crisis such as rapid declined reserves of fossil fuels and global warming issues are the dominant concerns (Höök and Tang, 2013; Dhillon and von Wuehlisch, 2013). Consequently, growing efforts are made to search the alternative and sustainable sources for fuel production. Woody biomass is considered as the preferred raw material due to its abundance, availability, and carbon neutral (Cambero and Sowlati, 2014; Beauchet et al., 2011). Especially, due to lower amounts of sulfur and nitrogen, harmful emissions are hardly detected during the burning process (Ndibe et al., 2015). Among the common thermo-chemical technologies, liquefaction of woody biomass has been reported as a promising pathway to produce the liquid fuel and value-added chemicals (Lu et al., 2016; Huang and Yuan, 2015). Cellulose, xylan, and lignin are the main components, which make up a large portion of woody biomass (Stefanidis et al., 2014).

Numerous studied based on the main components liquefaction have been reported. However, most researches are emphatically focused on the influences of different process variables on the liquefaction behavior, to explore the reaction mechanism and kinetics. Yin and Tan (2012) found the different reaction pathways from hydrothermal liquefaction of cellulose under acidic, neutral, and alkaline conditions. Koriakin et al. (2014) studied the thermo-chemical liquefaction of microcrystalline cellulose in various organic solvents. It was reported that the production distributions and chemical structure of solid residues strongly depended on the employed solvents. Cheng et al. (2012) investigated the effects of reaction parameters on hydrothermal degradation of alkali lignin in water-ethanol co-solvents, and found that solvent and temperature played vital roles on alkali lignin conversion. Brand and Kim (2015) studied the liquefaction characteristics of major biomass constituents in supercritical ethanol, and observed

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that the chemical compositions of liquefaction-derived bio-oils from each sub-component were completely different. Particularly, commercially available hemicellulose was hardly found. Therefore, xylan was generally used as the representative model compound (Khelfa et al., 2013). In comparison with cellulose and lignin, few studies on the xylan liquefaction were provided.

It should be noted that the employed solvents have great influences on the reaction behavior and chemical composition of products derived from biomass liquefaction. Due to the severe conditions from supercritical water, large numbers of organic solvents such as alcohol, phenol, acetone, and tetralin have been applied as reaction mediums to enhance the bio-oil yield and quality (Li et al., 2014a,b; Wang et al., 2009; Jin et al., 2014; Li et al., 2015a,b). However, no single study has been conducted to explore how solvent affects the liquefaction behavior of three sub-components, and a deeper investigation on the interactions between solvents and sub-components via molecular simulation was rarely reported.

In the present work, hydro-liquefaction of cellulose, xylan, and lignin was conducted in different solvents. Different types of solvents including alcohols (methanol, ethanol, propanol and i-propanol), ketone (acetone), and alkane (heptane and cyclohexane) were utilized in the major sub-components liquefaction. Moreover, to better understand the solvent effects, Monte Carlo method based on the random molecular cluster model was employed to investigate the interaction between solvent and feedstock. The elemental and chemical compositions of bio-oils obtained from raw materials hydro-liquefaction were characterized through elemental analysis (EA), gas chromatography-mass spectrometry (GC–MS), and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS).

2. Experimental

2.1. Materials and instruments

The microcrystalline cellulose (purity of >99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Xylan (purity of >90%) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Additionally, the industrial lignin (purity of >90%) was available from Changzhou Peaks Chemical Co., Ltd. The schematic diagram of 20-mL stainless steel autoclave is displayed in Supplementary Fig. S1. All the organic solvents used in the experiment were analytical grade and used as received.

2.2. Hydro-liquefaction process and products separation

In each experiment, 1 g of raw materials (cellulose, xylan and lignin) with 10 mL of tested solvents and 300 μg/g Ni-based catalyst ($NiCl_2$) were charged into the reactor. The air inside was completely removed since the autoclave was purged with high purity hydrogen. Subsequently, the initial pressured was elevated to 4.0 MPa. Following the adjusted hydrogen pressure, the reactor was then heated to the desired temperature and kept for the required time. After the reaction, it was cooled down to room temperature rapidly in a water bath.

The Supplementary Fig. S2 shows the separation procedures of products from feedstock-based hydro-liquefaction. After releasing the gas inside, the resulted suspension was thoroughly rinsed out of the reactor with acetone. Then, the liquid/solid mixtures were filtered through a pre-weighed filter paper to obtain the filtrate and residue. The solid sample remaining on the filter paper was dried in a vacuum oven at 110 °C for 24 h before weighing, and the dried fraction was named as solid residue. The filtrate was evaporated with removal of solvents and formed water during the liquefaction process, and the resulted liquid sample was designated as bio-oil.

The yields of bio-oil, solid residue, and gas were all expressed in wt.%. The bio-oil and solid residue yields were calculated as the ratio of the corresponding product to the raw material. Especially, it should be noted that gaseous yield was acquired by difference, and thus some mass losses were included.

2.3. Model construction and simulation method

According to the structural characteristics of three sub-components, the corresponding models of molecular structure are displayed in Supplementary Fig. S3. The structural units in the polymers were shown with head-to-tail non-contacted mode. The geometric structures for these molecular models were optimized through dreiding force field from Forcite mode. Besides, the density functional theory (DFT) of $DMol^3$ mode was applied to the energy optimization of structural units (Li et al., 2014a,b). Additionally, the solvent molecular models were built with the same method, and then the structures and energies were optimized, respectively.

The Material Studio software from Accelrys Company was employed in the simulation (Fan and Yuen, 2007; Peng et al., 2007). The GGA (Generalized gradient approximation)-PBE (Perdew, Burke, and Emzerhof) functional and DNP (Double numeric with polarization) basic set were utilized as the optimization methods (Perdew et al., 1996). The atom core process was utilized with all electron method. The DIIS (Direct inversion in an iterative subspace) and smearing methods were chose to accelerate the convergence of self-consistent field (Császár and Pulay, 1984). Especially, the COSMO (Conductor-like screening model) effect was negligible in the simulation calculation (Diedenhofen et al., 2003).

The Monte Carlo method based on the random molecular cluster model was utilized to investigate the interactions between solvents and sub-component molecular models (Li et al., 2014a,b). As the distance between two molecular models was a lattice, it could be assumed as a couple of molecular interaction conformation. A pair of model conformation from cellulose and ethanol is displayed in Supplementary Fig. S4. One hundred conformations with the lowest energies were exported in the simulation results, and then the energy of mixing between sub-components and solvent molecular models could be obtained.

2.4. Characterization of liquefaction product

The Elementar Vario EL III analyzer was carried out to determine the elemental compositions including carbon (C), hydrogen (H), and nitrogen (N) in the bio-oils produced from different solvent treatments. The oxygen (O) content was evaluated by difference. The high heating value (HHV) was estimated according to the Dulong formula (Li et al., 2015a,b):

$$\mathrm{HHV\ (MJ/kg)} = 338.2\mathrm{wt.\%(C)} + 1442.8(\mathrm{wt.\%(H)} - \mathrm{wt.\%(O)}/8) \quad (1)$$

The compositions of bio-oils were characterized via gas chromatography-mass spectrometry (GC–MS, Thermo Fisher Scientific, and TRACE) with a DB-35 MS column (30 m × 0.25 mm × 0.25 μm). The carrier gas was helium with a constant flow of 1.0 mL/min. The temperature was set from 45 °C (kept for 4 min) to 280 °C with the heating rate of 25 °C/min, and then held for 20 min. The identification of chemical compounds were accomplished by comparison with the mass spectra from NIST (National Institute of Standards and Technology) database, and quantified through the area normalization method.