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The effect of ethanol on hydroxyl and carbonyl groups in biopolyol produced by hydrothermal liquefaction of loblolly pine: ^{31}P-NMR and ^{19}F-NMR analysis

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HIGHLIGHTS

- For the first time, ^{31}P-NMR and ^{19}F-NMR were employed to understand the effect of ethanol on the formation bio-oil.
- Ethanol significantly increased the bio-oil and decreased the residue yield.
- Addition of ethanol increased the hydroxyl concentration while decreased the carbonyl concentration.
- More aliphatic and less phenolic type OH was obtained when ethanol was used as a co-solvent.

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ABSTRACT

The goal of this study was to investigate the role of ethanol and temperature on the hydroxyl and carbonyl groups in biopolyol produced from hydrothermal liquefaction of loblolly pine (*Pinus* spp.) carried out at 250, 300, 350 and 390 °C for 30 min. Water and water/ethanol mixture (1/1, wt/wt) were used as liquefying solvent in the HTL experiments. HTL in water and water/ethanol is donated as W-HTL and W/E-HTL, respectively. It was found that 300 °C and water/ethanol solvent was the optimum liquefaction temperature and solvent, yielding up to 68.1 wt.% bio-oil and 2.4 wt.% solid residue. ^{31}P-NMR analysis showed that biopolyol produced by W-HTL was rich in phenolic OH while W/E-HTL produced more aliphatic OH rich biopolyols. Moreover, biopolyols with higher hydroxyl concentration were produced by W/E-HTL. Carbonyl groups were analyzed by ^{19}F-NMR, which showed that ethanol reduced the concentration of carbonyl groups.

1. Introduction

Lignocellulosic biomass is being used as an alternative feedstock for the production of bio-based polyols (biopolyols) in order to reduce our dependency on petroleum. Polyol is a compound that has multiple hydroxyl groups in its structure and is essential for the synthesis of a variety of polymers such as epoxy, polyurethane, polyester, polycarbonate, and phenolic resin. However, today the major source for polyols is petroleum. Researchers have thus focused on biopolyol in the face of depleting petroleum reserves, increased greenhouse effect, as well as an increasing demand by the consumers for bio-based products. Moreover, the U.S. Department of Energy (DOE) and the U.S. Department of Agriculture (USDA) have prioritized the development of bioenergy and bioproducts with the goal to produce 18% of the current U.S. chemical commodities from lignocellulosic biomass by 2020, and 25% by 2030 (Perlack et al., 2005).

Bio-oil, the black liquid produced by degradation of lignocellulosic biomass through thermomechanical processes, has attracted interest to be used as a biopolyol because of its high hydroxyl concentration. Gas chromatography–mass spectrometry (GC–MS) analysis of bio-oil showed that bio-oil is a highly complex mixture, mainly composed of carbohydrates, furans, phenols, guaiacols, syringols type of compounds (Thangalazhy-Gopakumar et al., 2010). Hydrothermal liquefaction (HTL), also known as direct liquefaction, is a thermomechanical conversion technique to produce

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bio-oil where lignocellulosic biomass is converted into liquid (bio-oil), gas and solid products using subcritical or supercritical water at elevated temperature (250–370 °C) and pressure (2–24 MPa). Bio-oil produced by the HTL process has a significant potential for commercialization in terms of price and life cycle assessment (Elliott et al., 2015). The effect of process parameters such as temperature, pressure, reaction time and feedstock type on the bio-oil yield in HTL process has been intensively studied and valuable literature reviews can be found elsewhere (Akhtar and Amin, 2011; Toor et al., 2011). Approximately 30–40 wt.% bio-oil (based on dry mass of biomass) is obtained from the hydrothermal liquefaction of lignocellulosic biomass (Akhtar and Amin, 2011). Recently, ethanol has received attention to be used as a co-solvent in the HTL process due to its high hydrogen solvent capability. Yuan et al. (2007) proposed that the highly reactive free radicals generated from the HTL of biomass were stabilized by the ethanol which acts as a hydrogen-donor solvent, and Cheng et al. (2010) reported that bio-oil yield could be increased from 40 to 65 wt.% when ethanol was used along with water in a sub-critical condition. In another study, alkaline lignin was liquefied in hot compressed water/ethanol medium, and found that addition of ethanol increased the degradation of lignin which resulted in a lower amount of solid residue (Yuan et al., 2010). This improvement may be due to the low dielectric constant of ethanol which facilitates dissolving of high molecular weight lignin at supercritical temperatures (Krammer and Vogel, 2000). The synergistic effect of water/ethanol mixture in the liquefaction of rice husk for bio-oil production via the HTL process was also observed by Liu et al. (2013). Besides the high bio-oil yield, the addition of ethanol to water also affects the distribution of phenolics such as phenol, ethylphenol and guaiacols, ethylguaiacol and syringol in the bio-oil as well (Ye et al., 2012; Ouyang et al., 2015). Recently, Kosinkova et al. (2015) reported that aqueous ethanol improved the higher heating value (HHV) of bio-oil to be used in the field of biodiesel applications. Moreover, the addition of medical stone as a catalyst into aqueous ethanol could further increase the yield of bio-oil produced by HTL of cotton seed (Yan et al., 2015).

Compounds containing hydroxyl and carbonyl groups in bio-oil play a major role in its utilization as a biopolyol. There are a variety of polymers synthesized using bio-oil including phenolic resin (Choi et al., 2015), polyurethane (Hu and Li, 2014), epoxy (Kuo et al., 2014) and polyester (Yu et al., 2006), and the hydroxyl groups in bio-oil are utilized to synthesize these polymers. Wei et al. (2014) used bio-oil to modify an epoxy resin, and found that hydroxyl number (OHN) of the bio-oil had a significant effect on the glass transition temperature (Tg) of the modified epoxy resin. In another study, bio-oil was used to synthesize a new adhesive system for application in particle boards. Here, the hydroxyl groups in bio-oil contributed to the condensation reactions with melamine–formaldehyde and melamine–urea–formaldehyde resin precursors which ultimately affected the properties of the resulting resin system (Kunaver et al., 2010). Zou et al. (2012) synthesized a polyurethane foam using bio-oil, and reported that a high number of primary hydroxyl groups from the bio-oil was necessary to increase the mechanical and thermal properties of polyurethane foam. Thus, it could be hypothesized that the reaction behavior and the mechanical/thermal properties of the resulting polymer depend on the interaction between hydroxyl groups in bio-oil and the formaldehyde for phenol formaldehyde resin, isocyanate for the polyurethane, epoxide groups for epoxy resin, and ester groups for polyester production.

Compounds containing carbonyl groups in the bio-oil such as aldehydes, ketones and quinones are found to play a major role in the aging of bio-oil during storage (Czernik et al., 1994). Reactions between compounds containing carbonyl and hydroxyl groups in the bio-oil have been reported to be a reason for bio-oil aging which results in the polymerization and consequently a change in viscosity (Czernik et al., 1994). The production of carboxylic acid as a result of oxidation of carbonyl groups is another problem which may cause equipment corrosion. Most recently, our group has studied the curing reaction of a commercial epoxy resin (EPON828) with a bio-oil, and found that carbonyl groups in the bio-oil contributed the curing of epoxy resin along with the hydroxyl groups as well (Celikbag et al., 2015). Therefore, the characterization and quantification of hydroxyl and carbonyl groups in the bio-oil is crucial to determine its quality as well as optimization for bio-oil based polymer synthesis.

The literature on liquefaction of lignocellulosic biomass in water/ethanol mixture via HTL process lacks specific information regarding the source and variation of hydroxyl and carbonyl groups in the bio-oil. Characterization of these functional groups plays an important role in the improvement of bio-oil for its effective utilization as a biopolyol. Therefore, a comprehensive hydroxyl and carbonyl group analysis is necessary to understand the source and variation of bio-oil hydroxyl and carbonyl group content which will make it possible to engineer the properties of bio-based polymers and their synthesis in future studies. To the best of our knowledge, this is the first study that has used the ^{31}P-NMR and ^{19}F-NMR analytical tools to partition out the hydroxyl and carbonyl groups to understand the role of ethanol in the HTL process of lignocellulosic biomass. Thus, the objectives of this study were to (i) investigate the effect of ethanol and liquefaction temperature and on hydroxyl and carbonyl groups, and (ii) analyze the variation and source of these functional groups in the bio-oil using ^{31}P-NMR and ^{19}F-NMR.

2. Materials and methods

2.1. Materials

Loblolly pine wood chips that are free from bark and leaf were obtained from a local chipping plant in Opelika, AL, USA. Loblolly pine composition (48.5% cellulose, 31.3% hemicellulose, 25.8% lignin and 4.5% extractives) was determined using standard wet chemistry analysis protocol. All chemicals were purchased from VWR; except the phosphorylating agent for ^{31}P-NMR analysis, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), purchased from Sigma Aldrich. All chemicals were reagent grade and used as received.

2.2. Hydrothermal liquefaction (HTL) of loblolly pine

Loblolly pine was ground by a hammer mill (New Holland grinder model 358, New Holland, PA) using 40 mesh sieve size for particle size reduction, and the pine passed through 40 mesh were used. HTL was carried out in 1 L high pressure/high temperature Parr® Reactor (Parr Instrument Company, Model 4577 HP/HT pressure reactor, Moline, IL, USA) equipped with mechanical stirrer and reactor controller (Parr Instrument Company, Model 4848, Moline, IL, USA). The reactor was charged with 25 g of 40 mesh loblolly pine and 250 g of solvent (biomass/solvent = 1/10, wt/wt) which consisted of either DI water or DI water/ethanol mixture (1/1, wt/wt). The HTL process with water and water/ethanol is denoted as W-HTL and W/E-HTL, respectively. Before heating up the reactor, high purity nitrogen was purged into the reactor to remove the air, and then reactor was pressurized to 2 MPa with nitrogen to force all the reactive materials into the liquid phase. Hydrothermal liquefaction was carried out at 300 rpm for 30 min at four different conditions: 250 °C (far-critical), 300 °C (sub-critical), 350 °C (near-critical), and 390 °C (super-critical). HTL time was started once the set temperature was reached. For the 390 °C