



Biobutanediol-mediated liquefaction of empty fruit bunch saccharification residues to prepare lignin biopolyols



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HIGHLIGHTS

- Empty fruit bunch lignin residues were converted into liquid lignin polyols.
- Liquefaction of lignin was performed using bio-butanediol to prepare biopolyols.
- Isomers of butanediol with PEG differently affected the liquefaction efficiency.
- The highest liquefaction efficiency was obtained with 2,3-butanediol levo-form.
- Resulting biopolyols were suitable monomers for biopolyurethane synthesis.

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ABSTRACT

Saccharification residue from empty fruit bunch (EFB) was liquefied with bio-butanediol to produce lignin biopolyols for the preparation of biopolyurethane. To substitute petroleum-derived polyhydric alcohols, butanediol isomers (1,4-butanediol, levo-2,3-bio-butanediol, and meso-2,3-bio-butanediol) or PEG#400-blended butanediol isomers were used as liquefaction solvents in the presence of sulfuric acid catalyst. Lignin biopolyols with a conversion of 63.3%, a hydroxyl number of 582.7 mg KOH/g and an acid number of 21.7 mg KOH/g were obtained under the optimal condition consisting of 25% biomass loading, 3% acid loading, and a temperature of 150 °C for 120 min when liquefied with 1,4-butanediol/PEG#400 blended solvent (9/1, w/w). When the levo-2,3-bio-butanediol solvent was used in the absence of PEG#400, the highest conversion, 68.9%, was obtained. Lignin biopolyol-based biopolyurethanes were synthesized with toluene diisocyanate. FT-IR analysis revealed that EFB lignin biopolyols liquefied with bio-butanediols were suitable monomers for the preparation of biopolyurethane.

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1. Introduction

Empty fruit bunch (EFB) lignocellulose containing 37.3–46.5% cellulose, 25.3–33.8% hemicellulose, and 27.6–32.5% lignin is produced largely as a byproduct of the crude palm oil production process (Sudiyani et al., 2013). Many studies investigating the utilization of EFB byproducts report on EFB saccharification via biological conversion to produce biosugar for the production of bioethanol, biofuels and L-lactic acid (Wang et al., 2014; Eom et al., 2015). However, a large amount of EFB lignin residue is produced as additional byproduct in these processes (Raman and Gnansounou, 2014).

Recently, solvothermal liquefaction of EFB saccharification residue containing lignin for the purpose of preparing bioplastics has attracted the attention of researchers with the aim of converting the lignin residue to a value-added product (Li et al., 2013;

Ouyang et al., 2015). In general, liquefaction via the solvolysis reaction has been performed under mild conditions (100–200 °C and 1 atm) in the presence of acid or base catalysts. However, there are problems associated with the excessive use of petroleum-derived polyhydric alcohols such as ethylene glycol (EG), polyethylene glycol (PEG), phenol, and glycol. It is difficult to classify these plastics derived from lignin biopolyols as “bioplastics” because a major component (more than at least 70%) in their production is usually a petroleum-derived solvent (Jin et al., 2011).

Butanediol (BD) is a major commodity chemical and is manufactured at a scale of over 2.5 million tons annually for applications in plastics, polyester, spandex fibers, rubber, biosynthetic building blocks, and fuel additives (Yim et al., 2011; Park et al., 2015). To replace petroleum-derived BD, considerable research has been conducted on the biological production of BD involving its four isomers: 1,4-butanediol (1,4-BD) and 2,3-butanediol in the forms of levo (2,3-BDL), meso (2,3-BDM), and dextro (2,3-BDD). To this end, the biosynthetic pathways of recombinant *Escherichia coli* have been developed for the selective production of 1,4-bio-BD

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from glucose, xylose, sucrose and sugar mixtures (Yim et al., 2011), 2,3-bio-BDL from glucose (Park et al., 2015), and 2,3-bio-BDM from crude glycerol (Lee et al., 2012).

Compared to polyhydric alcohol as a liquefaction solvent, the use of bio-BDs as a liquefaction solvent for EFB saccharification residues containing lignin can allow for the production of lignin biopolyol-derived bioplastics via the solvothermal liquefaction process. In order to produce totally bio-based lignin biopolyol, we aimed to substitute conventional petroleum-derived solvent to bio-BD that can be produced biologically from biosugar. In this study, the saccharification residue of EFB, which contained 49.7 wt% lignin, was liquefied in the presence of sulfuric acid catalyst. In our previous study, the liquefaction efficiency of EFB saccharification residues was improved when using crude glycerol solvent containing polyethylene glycol (Lee et al., 2016). Considering this point, three forms of bio-BD isomers (1,4-BD, 2,3-BDL, and 2,3-BDM) or PEG#400-blended bio-BDs were employed as liquefaction solvents to substitute petroleum-derived polyhydric alcohols and improve the liquefaction efficiency. The effect of PEG#400-blended 1,4-BD solvents, biomass loading, acid loading, temperature, and liquefaction time were analyzed to produce lignin biopolyols with higher conversion. Then, the effects of using various bio-BD isomers and the mixing of PEG#400 as a co-solvent were analyzed based on biomass conversion, hydroxyl number, acid number, and FT-IR spectra. Finally, lignin biopolyols-derived biopolyurethanes were synthesized with toluene diisocyanate (TDI) and the presence of polyurethane bonds was confirmed by FT-IR analysis.

2. Methods

2.1. Materials

Lignin residue derived from EFB in the form of a fine powder was provided by the Research Institute of Chemical Technology in Korea. Polyethylene glycol #400 and 1,4-butanediol of reagent grade were purchased from Dae-jung Co. (Korea) and were used as an additive solvent and the main solvent, respectively. Two forms of liquid bio-butanediol isomers (2,3-BDL and 2,3-BDM) produced by biological conversion were supplied from GS Caltex Co. in Korea (kindly gifted from Dr. Hyo Hak Song) (Lee et al., 2012; Park et al., 2015). Sulfuric acid with 98% purity (Sigma–Aldrich Co.) was used as an acid catalyst. To analyze lignin biopolyols for the hydroxyl and acid number, various solvents were used, such as pyridine (Sam-Chun Co.), phthalic anhydride (TCI Co.), imidazole (Sigma–Aldrich Co.), ethanol (Dae-Jung Co.), and standard sodium hydroxide solutions of 0.1 N and 1 N (Sigma–Aldrich Co.). To polymerize biopolyurethane, toluene diisocyanate (TDI, Sigma–Aldrich Co.) was used in the same equivalence ratio. All other chemicals were of reagent grade and used without further purification or alteration.

2.2. Composition analyses of EFB lignin residue

The provided EFB lignin residue was a byproduct from an enzymatic saccharification process with EFB lignocellulosic biomass via the enzymatic hydrolysis reaction after hydrothermal pretreatment (Lee et al., 2016). The principal components of the EFB lignin residue were found to be 49.7% lignin, 22.1% cellulose and 2.7% hemicellulose.

2.3. EFB lignin residue liquefaction

The EFB lignin residue was liquefied in a 100 mL three-neck flask under mild temperatures (100–170 °C) and atmospheric pressure with stirring at 200 rpm, using a heating mantle equipped

with a controller (Thermo Electron Corp., Madison, WI). Reaction solutions with 30 g of solvent and EFB lignin residue (biomass loadings on the solvent weight ranging from 5–35 wt%) were preheated for 1 h. Three forms of bio-butanediol (1,4-BD, 2,3-BDL, 2,3-BDM) were used as the main liquefaction solvent, and PEG#400 was introduced as the blending solvent (10 wt%). Sulfuric acid was added to initiate the reaction to account for the 98% purity (acid loadings on the solvent weight ranging from 0 to 7 wt%). The liquefaction time was investigated over a range of 5–180 min. The reaction was terminated by cooling the reaction solution to room temperature with a flow of cold water.

2.4. Biomass conversion analyses

Lignin biopolyol samples (approximately 10 wt% on the amount of the used solvent) were used without a purification process and were dissolved in 50 ml of ethanol (95%). The solid residue was collected by centrifugation at 10,000 rpm and then washed with 50 ml of ethanol twice and DDW once. After washing the lignin biopolyol product, the solid lignin residue was recovered using filter paper (Whatman #4) and then dried at 105 °C for 24 h. Afterward, the weight of the residue was measured twice to calculate the exact biomass conversion via the following formula (Hu et al., 2012):

$$\text{Biomass conversion ratio (\%)} = 100 - ((W_1 - W_2)/W_3) * W_4/W_5 * 100,$$

where

- W_1 : total weight of filter paper with residue after drying;
- W_2 : dry weight of the filter paper without residue;
- $W_1 - W_2$: net dry weight of the residue;
- W_3 : weight of lignin biopolyol used for the biomass conversion analysis;
- W_4 : total weight of lignin biopolyol obtained from the liquefaction process;
- $((W_1 - W_2)/W_3) * W_4$: total weight of the residue in the lignin biopolyol;
- W_5 : weight of EFB lignin residue initially used in the liquefaction process.

2.5. Hydroxyl and acid number analysis

The hydroxyl number analysis of the lignin biopolyol sample (2 g) was conducted according to ASTM D4274-05D. An esterification reagent of 25 ml was added to each lignin biopolyol solution and the esterification reaction was performed at approximately 100 °C with agitation for 15 min. Samples were titrated to pH 8.0 using a 0.5 N sodium hydroxide solution after cooling to room temperature. The acid number was analyzed with 1 g of the lignin biopolyol sample according to ASTM D4662-08. Each sample was dissolved in 50 ml of ethanol and titrated to pH 8.0 with a 0.1 N standard sodium hydroxide solution. All samples were measured in duplicate.

2.6. Bio-polyurethane synthesis

Polyurethane derived from lignin biopolyol was synthesized in a 50 ml beaker. Herein, 5 g of lignin biopolyol was preheated to 100 °C using an oil bath. To initiate the polymerization reaction, TDI was added dropwise to the stirred solution at the same equivalent ratio of the hydroxyl and isocyanate groups. All samples were transferred and cured at 105 °C for 12 h to form crosslinking bonds, at which point the stirrer could no longer move.

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