



Crude glycerol-mediated liquefaction of empty fruit bunches saccharification residues for preparation of biopolyurethane



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ABSTRACT

In order to utilize lignin residue from the pretreatment of empty fruit bunch (EFB) and crude glycerol from biodiesel production, lignin residue was solvothermally liquefied using crude glycerol to produce lignol. The optimal liquefaction conditions for lignol production were determined to be 10% biomass loading, 5% acid loading, a liquefaction temperature of 170 °C, and a liquefaction time of 120 min. The biomass conversion at the optimal conditions was 47.9%. The lignols possess hydroxyl number of 1649.3 mg KOH/g and acid number of 8.4 mg KOH/g. Fourier transform infrared spectroscopy revealed that the lignol was suitable for biopolyurethane synthesis.

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Introduction

Palm oil is an edible oil whose production is predicted to increase gradually from the approximately 58 million metric tons per year [1,2]. Higher levels of palm oil production have increased the amount of byproduct residues released from its extraction process. One of the major byproducts from the palm oil industry is empty fruit bunch (EFB) lignocellulose. A large amount of EFBs containing 37.3–46.5% cellulose, 25.3–33.8% hemicellulose and 27.6–32.5% lignin is produced in the processing of fresh fruit bunches (FFBs) into crude palm oil. These residues can be utilized to manufacture bioethanol through a series of pretreatment, saccharification and fermentation [3–5]. During pretreatment and saccharification, large amount of non-fermentable lignin is produced.

Lignin is produced in quantities of over 50 million tons every year in various industries. At present, a significant amount of lignin is used as a fire fuel [6]. While the utilization of lignin in various applications has received significant attention, approximately 2%

of lignin is currently sold as an additive for concrete and a dispersant for dye, surfactants and pesticides processing [7,8]. Thus, various methods of lignin valorization need to be developed to enhance the overall process economics.

Crude glycerol (CG) is being produced from biodiesel manufacturing industries as a cheap byproduct. Effluent containing 70–85% CG is generated up to approximately 10% of the total biodiesel production [9–11]. Although various conversion methods of CG to glycerol derivatives have been developed [12–14], impurities in CG have far prevented its utilization as a high value-added product [15].

Recently, various studies have been conducted to enhance the value of lignocellulosic biomass residues by converting them to monomers for bioplastics synthesis. Many studies have focused on the liquefaction of lignocellulosic residues to prepare polyols for polyurethane (PU) synthesis [16–20]. The liquefaction process usually proceeds with an excess of petroleum-derived chemical solvents (phenol, ethylene glycol, polyethylene glycol, and ethylene carbonate) at 100–200 °C in the presence of sulfuric acid or hydrochloric acid as the catalyst. Recently, the liquefaction of lignin biomass with polyethylene glycol and glycerol has been reported to prepare lignol, lignin polyol [21]. In other researches, supercritical conditions were employed with phenol, formic acid, ethanol or water as the solvent for the liquefaction of lignin

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biomass [22–25]. The biomass liquefaction rate was high in these studies, but the reactions were performed at higher temperatures (more than 200 °C) and pressures.

Compared to chemical solvents such as polyhydric alcohols as liquefaction solvents, the use of CG, a renewable and sustainable bio-solvent of biodiesel byproduct, is advantageous when utilized as a liquefaction solvent because its cost is much lower than chemical solvents. Recently, CG has been applied as a liquefaction solvent for lignocellulosic biomass [26–28]. In this study, EFB-lignin residue obtained as a byproduct from pretreatment and enzymatic preparation of fermentable sugar with EFB lignocellulosic residues was liquefied using CG directly obtained without any pretreatment as a biodiesel byproduct at atmospheric conditions in the presence of sulfuric acid for the production of lignol. Bio-PU was prepared using lignol products with two types of diisocyanate, and confirmed by Fourier transform infrared (FTIR) spectroscopy analysis.

Experimental

Materials

CG was supplied from biodiesel manufacturing company, GS Caltex (Korea). Polyethylene glycol (PEG; #200, #300 and #400) was purchased from Dae-jung Co. (Korea) and used as an additive solvent. Sulfuric acid (Sigma–Aldrich Co., 98%) was used as a catalyst for liquefaction. Phthalic anhydride (TCI Co.), pyridine (Sam-chun Co.), imidazole (Sigma–Aldrich Co.), and ethanol (Dae-jung Co.) were used as analyzing solvents. To determine the hydroxyl and acid numbers of lignol, standard sodium hydroxide solutions (Sigma–Aldrich Co., 0.1 N and 1 N) were employed. Toluene diisocyanate (TDI, Sigma–Aldrich Co.) or methylene diphenyl diisocyanate (MDI, Sigma–Aldrich Co.) was used for the polymerization of biopolyurethane. All other reagents (reagent grade) were used without further purification.

Characterization of EFB lignin residue

The raw lignin of EFB was prepared by hydrothermal pretreatment of EFB at 190 °C for 15 min (Bench Top Reactor, Model 4526, Parr Instruments), mechanical refining of the pretreated slurry with a valley beater (L&W, Norway), enzymatic hydrolysis of the solid fraction of the pretreated EFB with Cellic CTec2 (Novozymes, Denmark), the solid–liquid separation of the hydrolysate with centrifugal filtration, and then followed by washing the solid fraction with 100 times amount of the deionized water. The washed residue was dried and powdered by coffee mill. The content of water-soluble and ethanol-soluble fraction in raw lignin were evaluated by extracting them with Soxhlet apparatus, drying the extractives under the reduced pressure, and assessing them gravimetrically. The phenolics and protein content in water extractives were determined by spectrophotometric analysis and BSA, respectively. Afterward, the water-soluble lignin was calculated by subtracting protein from phenolics. The composition of structural components of the residual solvent-insoluble fraction were determined according to National Renewable Energy Laboratory (NREL) standard procedures. The monosaccharides in water extractives and in acid hydrolysate were determined by HPLC. The acid-soluble lignin was also determined by DU 800 UV/Vis spectrophotometer (Beckman Coulter Inc., USA) at 320 nm. The acid-insoluble lignin on the crucibles was gravimetrically determined, based on the remaining insoluble residue, by subtracting the ash content from them. All compositional analyses were run in triplicate and reported as averages and standard deviations.

The contents of moisture and ash in the EFB lignin residue were determined according to ASTM methods E1755-01 and E1756-01,

2001 [29]. Thermogravimetric analysis (TGA) of 50.0 mg (± 1.0) EFB lignin residue was conducted in each experiment using a Q50 TGA apparatus (TA Instruments). Nitrogen was introduced as a carrier gas at a flow rate of 20 mL/min, while the heating rate was regulated at 5, 15, and 20 °C min⁻¹ over a temperature range of 30–800 °C.

Liquefaction process

The liquefaction reaction of lignin residue was carried out in a 100 mL three-neck flask under atmospheric pressure with stirring at 200 rpm. The reactor was heated by a heating mantle equipped with a temperature controller (Thermo Electron Corp., Madison, WI). Reaction solutions with a total of 30 g solvent and EFB lignin residue (loadings from 5 to 20 wt%) were preheated for 1 h so as to maintain the desired liquefaction temperature (90–190 °C). After preheating, the reaction was initiated by adding 98% sulfuric acid (0–7 wt%). The concentration of acid and biomass loading were calculated by considering the weight content in a fixed amount of liquefaction solvent. The effect of time on the liquefaction efficiency was investigated from 10 to 180 min. Upon completion of the reaction, the heating mantle was removed and the reaction solution was cooled down to room temperature with cold water.

Determination of biomass conversion

Approximately 3 g of lignol products were dissolved without purification in 50 mL of ethanol (250 mL centrifuge tube). The solid fraction was collected after centrifugation at 10,000 rpm for 15 min and then the supernatant was removed. The solid residue was washed with 50 mL ethanol according to the same procedure described above. The washed solid residue was collected and rinsed sufficiently with 50 mL of double distilled water. After filtering this solution through filter paper (Whatman #4), the paper and residue were weighed after drying at 105 °C for 24 h. The biomass liquefaction conversion was calculated according to the following Eq. (1):

$$\text{Biomass conversion ratio (\%)} = 100 - \left(\frac{W_1 - W_2}{W_3} \right) * \frac{W_4}{W_5} * 100 \quad (1)$$

where

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

Determination of acid and hydroxyl number of lignol

The acid number of the lignol was determined according to ASTM D4662-08. Herein, 2 g of lignol was completely dissolved in 50 mL of ethanol (250 mL beaker) and then titrated. The hydroxyl number of lignol was determined according to ASTM D4274-05D. Before adding 25 mL of the esterification reagent to the 250 mL beaker, the weight of the lignol was measured. The esterification reaction was performed in an oil bath at 98 ± 2 °C with stirring for 15 min. Upon completion of the reaction, the solution was cooled

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