



Thermochemical conversion of crude glycerol to biopolyols for the production of polyurethane foams



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HIGHLIGHTS

- High-quality biopolyols were produced from a sole feedstock of crude glycerol.
- Properties of biopolyols depend on H₂SO₄ loading, reaction temperature and time.
- Polyurethane foam with satisfied performance was produced from the biopolyols.
- The biopolyols were mainly composed of glycerol, monoglycerides, and diglycerides.
- Esterification, transesterification and dehydration are major reactions.

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ABSTRACT

This study aimed to produce biopolyols from crude glycerol via a novel thermochemical conversion process. The effect of operational parameters, including sulfuric acid loading and reaction temperature and time, on the properties of the produced biopolyols was investigated. Biopolyols produced under preferred reaction conditions of 200 °C, 90 min, and 3% sulfuric acid loading showed a hydroxyl number of around 481 mg KOH/g, an acid number of around 5 mg KOH/g, and a viscosity of around 25.0 Pa s. The resulting polyurethane (PU) foams showed a compressive strength of around 184.5 kPa and a density of around 43.0 kg/m³, comparable to those of some petroleum-based analogs. Characterization of the biopolyols via pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), gas chromatography (GC), and thermogravimetric analysis (TGA) showed that the major reactions of this process were the formation of monoglycerides and diglycerides through the esterification and transesterification of different components in crude glycerol.

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1. Introduction

Polyols are compounds containing multiple hydroxyl functional groups. As one of the major feedstocks for polyurethane (PU) production, most polyols used today in the PU industry are petroleum-derived. Concerns about depletion and price increases of the world's petroleum resources, have led to increased research and industrial interests in developing biopolyols (bio-based polyols) from renewable resources as alternatives to conventional petroleum-based polyols.

Vegetable oils have been widely used for the production of biopolyols. Although most vegetable oils, with the exception of castor and lesquerella oils, do not contain hydroxyl groups, the presence of unsaturation sites in vegetable oils provides huge reaction potentials for polymerization and functionalization.

Various processes, including epoxidation followed by the ring-opening of oxirane (Petrovic et al., 2002; Zlatanovic et al., 2002), hydroformylation followed by hydrogenation (Lysenko et al., 2004), ozonolysis with further hydrogenation (Petrovic et al., 2005), and newly developed thiol-ene coupling (Desroches et al., 2011), have been used for the production of vegetable oil-based biopolyols. The produced vegetable oil-based biopolyols exhibited suitable properties for the production of PU foams, e.g., acid numbers below 5 mg KOH/g, and hydroxyl numbers below 500 mg KOH/g, with most ranging from 150 to 300 mg KOH/g (Guo et al., 2000; Hu et al., 2002; Tu et al., 2007; Veronese et al., 2011). PU foams produced from these vegetable oil-based biopolyols also exhibited mechanical properties comparable to their petroleum-based analogs (Guo et al., 2000; Zhang et al., 2007). However, a future of vegetable oil-based biopolyols as major alternatives to petroleum-based polyols may pose a critical issue of competition with food supplies and biodiesel production from vegetable oils.

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Glycerol is a valuable feedstock derived from either petroleum or natural resources, and has extensive applications in food, pharmaceuticals, cosmetics, tobacco, PU, and other industries (Pagliaro and Rossi, 2008). In the PU industry, glycerol is mainly used as an initiator to react with propylene oxide and ethylene oxide to produce polyether polyols for flexible PU foams, and to a lesser extent, rigid PU foams. With the rapid growth in the production of biodiesel worldwide, large volumes of crude glycerol, a byproduct of the transesterification of vegetable oils and/or animal fats with alcohol during biodiesel production, have been produced. Compared to pure glycerol, crude glycerol has a significantly different composition, and contains various impurities such as methanol, water, soap, free fatty acids (FFAs), fatty acid methyl esters (FAMES), and glycerides (Hu et al., 2012a). Although low-value crude glycerol (approximately \$0.1/kg, (Johnson and Taconi, 2007)) can be refined to high-purity glycerol for extended applications by many refining techniques, e.g., vacuum distillation and ion exchange (Carmona et al., 2009), these refining processes are too costly, especially for small- and medium-sized biodiesel producers (Pachauri and He, 2006). Currently, crude glycerol has become a financial and environmental liability for the biodiesel industry (Johnson and Taconi, 2007). Therefore, development of economically viable approaches of converting low-value crude glycerol into value-added products is imperative. Numerous studies have been conducted to develop both biological and chemical catalytic conversions of crude glycerol to produce value-added products such as hydrogen, succinic acid, 1,3-propanediol, polyhydroxylalkanoates, and monoglycerides (Johnson and Taconi, 2007; Pachauri and He, 2006; Dobroth et al., 2011; Yang et al., 2012).

Few studies have been reported on the direct utilization of crude glycerol to produce biopolyols and PU foams. Hoong et al. (2011) reported a process of producing polyglycerols from crude glycerol at atmospheric pressure and a preferred temperature of 270 °C, in which the crude glycerol contained 60–90% glycerol, 5–20% methanol, and 10–15% soap on a weight basis. However, the properties of the polyglycerols as polyols were not tested, and the feasibility of using polyglycerols as polyols for the production of PU foam was not investigated. Recently, our research group has utilized crude glycerol as a solvent for the liquefaction of lignocellulosic biomass to produce biopolyols (Hu et al., 2012b; Li and Zhou, 2011). The biopolyols produced under preferential conditions showed suitable properties for the production of PU foams. The PU foams' performances were comparable to those of PU foams obtained from other lignocellulosic biomass liquefaction processes using petroleum-based solvents (Alma et al., 2003; Chen and Lu, 2009; Lee et al., 2000). The research also showed that compared to pure glycerol, crude glycerol as a liquefaction solvent led to the production of biopolyols and PU foams with better material properties. Certain impurities in crude glycerol helped improve the properties of the produced biopolyols and PU foams.

The present study explored the feasibility of using crude glycerol as the sole raw material to produce high-quality biopolyols through an atmospheric thermochemical process. Compared to crude glycerol used in a previous study (Hoong et al., 2011), crude glycerol in this study contained less glycerol and more impurities. This value-added conversion of crude glycerol into biopolyols and PU foams has the potential to improve the economics of biodiesel production as well as the sustainability of the polyol and PU industry. In this study, biopolyols were first produced from crude glycerol using a novel atmospheric thermochemical process, and the effect of different reaction conditions, including sulfuric acid loading, reaction temperature, and reaction time, on the properties of biopolyols was studied. Then, PU foams were produced from biopolyols and characterized to evaluate the suitability of biopolyols in PU foam applications. The reaction

mechanisms among the components of the crude glycerol during the biopolyol production process were also explored, which could help the future scale up and commercialization of this technology.

2. Methods

2.1. Materials

Crude glycerol and biodiesel were obtained from Bio100 Technologies, LLC (Mansfield, OH). Pure glycerol, oleic acid, and sulfuric acid were purchased from Fisher Scientific (Pittsburgh, PA). Chloroform was purchased from Pharmco-AAPER (Shelbyville, KY). Standard stock solutions of monopalmitin, monoolein, diolein, triolein, 1,2,4-butanetriol, tricaprins, and derivatization reagent *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA) were purchased from Restek (Bellefonte, PA). Polycat 5, polycat 8, and DABCO DC5357 used in PU foaming were obtained from Air Products & Chemicals, Inc. (Allentown, PA). Polymeric methylene-4,4'-diphenyl diisocyanate (pMDI) was obtained from Byer Material Science (Pittsburgh, PA). All chemicals used were of reagent grade or higher purity.

2.2. Production process

The production of biopolyols from crude glycerol was carried out in a 500-ml three-neck flask, equipped with stirrer, condenser, and thermometer, under atmospheric pressure with constant stirring. The crude glycerol and sulfuric acid (loading from 0% to 5%, based on the weight of crude glycerol) were added into the flask and then heated to the desired reaction temperature (150–210 °C) using a temperature-controlled heating mantle (Thermo Electron Corp., Madison, WI). Subsequently, the temperature was held constant to conduct the reaction for a predetermined reaction time (60–180 min), after which, the flask was immediately removed from the heating mantle and quenched in tap water. Methanol, water, and other volatiles evaporated during the production process were recovered by a glass Graham condenser connected to the flask.

2.3. Composition analysis of crude glycerol

The composition of crude glycerol was determined according to the methods described in one of our previous publications (Hu et al., 2012a). It was found that the crude glycerol contained approximately 22.9% glycerol, 10.9% methanol, 18.2% water, 26.2% soap, 21.3% FAMES, 1.0% FFAs, and 1.2% glycerides (all on a weight basis).

2.4. Determination of acid and hydroxyl numbers, and viscosities of biopolyols

The acid and hydroxyl numbers of biopolyols were determined in accordance with ASTM D4662-08 and ASTM D4274-05D, respectively. The viscosities of biopolyols were determined in accordance with ASTM D4878-08.

2.5. Determination of the soap content of pretreated crude glycerol and biopolyols

The soap content of pretreated crude glycerol and biopolyols was determined according to the AOCs recommended Practice Cc 17-95. The pretreatment process of crude glycerol using various acid loadings was as follows: sulfuric acid, at loadings ranging from

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