



Two-step sequential liquefaction of lignocellulosic biomass by crude glycerol for the production of polyols and polyurethane foams



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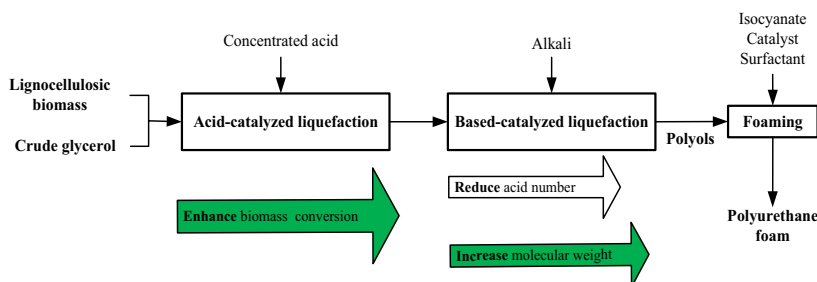
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HIGHLIGHTS

- Two-step sequential liquefaction of lignocellulosic biomass by crude glycerol.
- Acid-catalyzed first liquefaction step enhanced biomass conversion.
- Base-catalyzed second liquefaction step further improved polyol properties.
- Polyols and PU foams exhibited better or comparable properties to literature values.

GRAPHICAL ABSTRACT

Polyols were produced via a sequential two-step liquefaction of lignocellulosic biomass using biodiesel-derived crude glycerol as a liquefaction solvent. This two-step process combines the virtues of both acid- and base-catalyzed biomass liquefaction processes. The produced polyols are suitable to prepare high-quality rigid or semi-rigid polyurethane foams that are commonly used as insulation materials.



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ABSTRACT

A two-step sequential biomass liquefaction process was developed to produce bio-based polyols and polyurethane (PU) foams using crude glycerol as a liquefaction solvent. The first step, acid-catalyzed liquefaction, was highly effective in liquefying biomass, while the second step, base-catalyzed liquefaction, featured extensive condensation reactions. By using the developed two-step liquefaction process, the polyols produced from lignocellulosic biomass and crude glycerol containing 26–40% organic impurities showed hydroxyl numbers ranging from 536 to 936 mg KOH/g, viscosities from 20.6 to 28.0 Pa s, and molecular weights (M_w) from 444 to 769 g/mol. The PU foams produced had densities ranging from 0.04 to 0.05 g/cm³, compressive strengths from 223 to 420 kPa, and thermal conductivities from 32.2 to 38.9 mW/m K. Polyols and PU foams produced from the two-step liquefaction process had improved properties over their analogs derived from a one-step biomass liquefaction by crude glycerol process catalyzed by acid or base.

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1. Introduction

Polyurethanes (PUs) are one of the most versatile polymer groups and have been used for a wide range of applications.

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Flexible and rigid foams are two predominant uses of PUs with coatings, sealants, elastomers, and adhesives being other common applications (Petrovic, 2008). Currently, the PU industry is heavily petroleum-dependent because its two major feedstocks, i.e. polyols and isocyanates, are largely petroleum-derived. Due to concerns over the depletion of fossil resources, there has been a great deal of interest in developing bio-based polyols and PUs from

renewable resources. Lignocellulosic biomass, such as wood and agricultural crop residues, is considered to be the world's most abundant renewable materials. Its main structural units are cellulose (30–35%), hemicellulose (15–35%), and lignin (20–35%) (Behrendt et al., 2008), all of which are highly functionalized materials rich in hydroxyl groups that make them promising materials for the production of bio-based PUs. However, lignocellulosic biomass needs to be liquefied into polyols before it can be used to produce PUs.

One common method used to produce polyols from lignocellulosic biomass is the atmospheric liquefaction of lignocellulosic biomass by polyhydric alcohols. The liquefaction processes are usually conducted at elevated temperatures (150–250 °C) under atmospheric pressure and use polyhydric alcohols, such as polyethylene glycol (PEG) and/or glycerol, as liquefaction solvents (Chen and Lu, 2009; Lee et al., 2000; Hu et al., 2012b; Yan et al., 2008). The liquefaction can be either acid- or base-catalyzed, with the former being much more commonly used. During the liquefaction processes, biomass is degraded and decomposed into smaller molecules by polyhydric alcohols via solvolytic reactions. The produced polyols are largely a mixture of different compounds rich in hydroxyl groups and can be used directly to produce various PU products such as foams (Yan et al., 2008; Hu et al., 2012b; Gao et al., 2010), adhesives (Lee and Lin, 2008), and films (Kurimoto et al., 2000). Various kinds of lignocellulosic biomass, such as wood (Yamada and Ono, 1999; Kunaver et al., 2010) and agricultural residues (Hassan and Shukry, 2008; Wang and Chen, 2007; Chen and Lu, 2009; Hu et al., 2012b; Liang et al., 2006; Lee et al., 2000; Yan et al., 2008, 2010; Briones et al., 2012; Zhang et al., 2012), lignin (Jin et al., 2011), and industrial and bio-refinery byproducts (Briones et al., 2011, 2012; Lee et al., 2002), have been liquefied for the production of bio-based polyols and/or PU foams. Generally, the produced polyols and PU foams show properties comparable with their petroleum analogs (Alma et al., 2003; Chen and Lu, 2009; Lee et al., 2000). A review on this topic has been published recently (Hu et al., 2014).

One of the major drawbacks of these atmospheric liquefaction processes is the use of high volumes of petroleum-derived polyhydric alcohols as the liquefaction solvent, i.e., approximately 100–125 g of solvent are required per 20 g of lignocellulosic biomass to obtain high-quality polyols (Lee et al., 2000; Hassan and Shukry, 2008; Chen and Lu, 2009). This high volume use of petroleum-based solvents considerably increases the production cost of polyols and consequently hinders future commercialization efforts. Our previous researches have shown that crude glycerol, a byproduct of the biodiesel production process, can be used as an effective liquefaction solvent for the atmospheric liquefaction of lignocellulosic biomass (Hu et al., 2012b; Hu and Li, 2014a,b). Compared to traditional polyhydric alcohols, crude glycerol has the advantages of being renewable and having a much lower cost, which contributes to the sustainability and cost-reduction of the atmospheric biomass liquefaction processes.

One of the major challenges of using crude glycerol as a liquefaction solvent is its varying composition, which is caused by differences in feedstocks, processes, and post-treatments at biodiesel plants. The varying compositions of crude glycerol could cause problems in the consistency of the properties of the produced polyols and PU products. To address these issues, the effects of crude glycerol impurities on properties of polyols and PU foams derived from acid- and base-catalyzed liquefaction processes were evaluated in our previous reports (Hu and Li, 2014a,b). The results showed that controlling organic impurities in crude glycerol, i.e. free fatty acids (FFAs), methyl esters of fatty acids (FAMES), and glycerides, at optimal levels was critical for the production of high quality polyols and PU foams. Our results also showed that the base- and acid-catalyzed biomass liquefaction processes exhibited

distinct behaviors in terms of liquefaction efficiency and product properties. The base-catalyzed biomass liquefaction process had the advantages of utilizing a wide range of crude glycerol compositions and producing polyols with low acid numbers (<5 mg KOH/g), but suffered from low biomass liquefaction efficiency (i.e., ca. 40–65%) and high polyol viscosities (Hu and Li, 2014a). In contrast, the acid-catalyzed biomass liquefaction process exhibited much higher liquefaction efficiency and produced polyols with lower viscosities (<30 Pa s). However, the acid-catalyzed process had the drawback of producing polyols with high acid numbers, which needed further treatments before PU foam production.

To combine the advantages of both the base- and acid-catalyzed biomass liquefaction processes, this study aimed to develop a novel two-step sequential biomass liquefaction process with crude glycerol to produce bio-based polyols and PU foams. The first step was acid-catalyzed to achieve high biomass liquefaction efficiency, while the second step was base-catalyzed to produce polyols with low acid number and low residual FFA and FAME contents. It was hypothesized that the two-step sequential liquefaction process could produce polyols and PU foams with improved properties over their analogs produced from one-step base- or acid-catalyzed liquefaction processes.

2. Methods

2.1. Materials

Corn stover was harvested from the Ohio Agricultural Research and Development Center (OARDC) farm (Wooster, OH), ground (1 mm mesh screen), and oven-dried at 105 °C for 24 h before being used for liquefaction tests. The components, on a dry basis, were cellulose, hemicellulose, lignin, extractives, and ash at 38.48%, 22.95%, 20.18%, 7.64% and 3.82%, respectively. Chemicals purchased from Fisher Scientific (Pittsburgh, PA) included glycerol, oleic acid, imidazole, NaOH pellets, concentrated HCl (35–38% wt.), and standard NaOH solutions (0.1 N and 10 N). Chemicals purchased from Sigma–Aldrich (St. Louis, MO) included technical grade mono-glycerides (i.e., 40% mono-glyceride, 15–40% diglycerides, and 15–40% triglycerides) and phthalic anhydride. Chemicals purchased from Pharmco-AAPER (Shelbyville, KY) included pyridine, 1,4-dioxane, HPLC-grade THF (tetrahydrofuran), 98% concentrated sulfuric acid, and ethanol. Unless otherwise stated, all chemicals used were of reagent grade or higher purity. Polycat 5, Polycat 8, and DABCO DC5357 used in the PU foaming process were obtained from Air Products & Chemicals, Inc. (Allentown, PA).

The liquefaction solvent used in this study included one model crude glycerol (CG-M) and two industrially derived crude glycerol samples (CG-A and CG-B) obtained from Bio100 Technologies, LLC. (Mansfield, OH). Before being used for liquefaction, biodiesel-derived crude glycerol samples were pretreated to remove salts, water, and methanol according to the procedure described in a previous report (Hu and Li, 2014a). The compositions of the pretreated CG-A and CG-B, determined according to the procedure described in a previous report (Hu et al., 2012a), are shown in Table 1.

Table 1
Compositions of crude glycerol samples used in the crude glycerol-based two-step biomass liquefaction process

Liquefaction solvent ^a	Composition (wt.%)			
	Glycerol	FFA	FAMES	Glycerides
CG-M	60	20	20	0
CG-A	74.0	12.4	11.5	2.1
CG-B	60.8	30.1	7.6	1.5

^a CG-M: model crude glycerol, CG-A and CG-B: industrially derived crude glycerol sample A and B.

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