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Value-added conversion of waste cooking oil and post-consumer PET bottles into biodiesel and polyurethane foams

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ABSTRACT

A sustainable process of value-added utilization of wastes including waste cooking oil (WCO) and post-consumer PET bottles for the production of biodiesel and polyurethane (PU) foams was developed. WCO collected from campus cafeteria was firstly converted into biodiesel, which can be used as vehicle fuel. Then crude glycerol (CG), a byproduct of the above biodiesel process, was incorporated into the glycolysis process of post-consumer PET bottles collected from campus to produce polyols. Thirdly, PU foams were synthesized through the reaction of the above produced polyols with isocyanate in the presence of catalysts and other additives. The characterization of the produced biodiesel demonstrated that its properties meet the specification of biodiesel standard. The effect of crude glycerol loading on the properties of polyols and PU foams were investigated. All the polyols showed satisfactory properties for the production of rigid PU foams which had performance comparable to those of some petroleum-based analogs. A mass balance and a cost analysis for the conversion of WCO and waste PET into biodiesel and PU foams were also discussed. This study demonstrated the potential of WCO and PET waste for the production of value-added products.

1. Introduction

Biodiesel (fatty acid ester) produced by transesterification of renewable feedstocks such as vegetable oils and animal fats with alcohol, has been widely considered as an alternative to petroleum diesel. Despite many advantages over petroleum diesel, such as biodegradable, non-toxic and low CO_2 emission profiles, the extensive commercialization of biodiesel is mainly limited by its high manufacturing cost (Meher et al., 2006; Camobreco et al., 1998). Waste cooking oil (WCO), which is abundant available and about 2.5–3.0 times cheaper than virgin vegetable oils (Demirbas, 2009), can largely reduce the biodiesel production cost. It is estimated that about 0.7–1.0 million tons of WCO is generated in EU each year (Supple et al., 2002), and an average of 10 kg of total waste grease per person were produced annually in the U.S. (Wiltsee, 1998).

The production of biodiesel from WCO is mainly performed under the catalysis of alkalis, acids, or enzymes. Alkaline catalysts such as NaOH, KOH, and $NaOCH_3$, are more commonly used due to their higher reaction rate in comparison with acid and enzymatic catalysts. However, alkaline can react with free fatty acid (FFA) present in WCO feedstocks, resulting in soap formation and thus reducing biodiesel yield (Kulkarni and Dalai, 2006). A two-step process, involving the acid-catalyzed esterification of FFA with methanol and traditional alkali-catalyzed transesterification, has been developed to produce biodiesel with improved yield from WCO, when its FFA content was higher than 1 wt% (Meng et al., 2008). The optimum parameters for biodiesel production, such as methanol/oil molar ratio, alkaline catalyst loading, reaction time, and reaction temperature, varied with WCO sources.

Crude glycerol (CG) is a byproduct of the biodiesel production process. Basically, the production of every 10 kg of biodiesel yields approximately 1 kg of CG (Kongjao et al., 2010). Depending on the feedstock and the process used for biodiesel production and the post-treatment methods used, CG contains various impurities such as alcohols, water, salts, and soap and has a low value (approximately $0.11/kg) (Johnson and Taconi, 2007). The refining of crude glycerol to pure glycerol is an important way for its value-added

Abbreviations: CG, crude glycerol; DEG, diethylene glycol; FFA, free fatty acid; PET, polyethylene terephthalate; pMDI, polymeric methylene diphenyl diisocyanate; PU, polyurethane; TPP, titanium isopropoxide; WCO, waste cooking oil.

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processing as glycerol is a versatile platform chemical in the industries of foods and beverages, pharmaceuticals, cosmetics, textiles, etc. However, the refining processes are costly (approximately $0.44/kg (Werpy et al., 2004)), especially for small- and medium-sized biodiesel plants (Pachauri and He, 2006). Crude glycerol has become a potential financial and environmental liability for biodiesel producers (Johnson and Taconi, 2007). Considerable studies have been recently focused on the development of biological or chemical methods of converting CG into value-added products, such as 1,3-propanediol (Mu et al., 2006; Oh et al., 2008), citric acid (Rywińska and Rymowicz, 2010), hydrogen (Sabourin-Provost and Hallenbeck, 2009), poly(hydroxyalkanoates) (Mothes et al., 2007), succinic acid (Scholten et al., 2009), polyols, and polyurethane (PU) foams (Hu et al., 2012; Luo et al., 2013).

Polyethylene terephthalate (PET) is a semi-crystalline thermoplastic that has been widely used in the manufacture of fibers, films, and various types of packaging materials-mainly bottles and jars. It was reported that the global consumption of PET in packaging field will grow at a rate of 5.2% to hit about 19.1 million tons by 2017 (Brooks, 2012). Although PET does not create a direct hazard to the environment, its substantially large fraction by volume in the waste stream and its non-biodegradability has led to concerns over its environmental pollution. Chemical recycling is one of the most attractive techniques of recycling PET waste as it can depolymerize PET to generate feedstocks for the production of highly valuable polymers (Sinha et al., 2010). For instance, a series of aromatic polyester polyols were prepared from waste PET and DEG in the presence or absence of functional additives, including adipic acid, glycerol, and poly(propylene glycol)/hexanediol, and showed properties suitable for the production of polyurethane-polyisocyanurate foams (Vitkauskiene et al., 2011). Microwave assisted glycolysis of PET with polyethylene glycol of different molecular weights in the presence of 3% glycerol, has also been conducted to synthesize polyester polyols for PU foam applications (Chaudhary et al., 2013). Our previous study has shown that crude glycerol has potential for the chemical recycling of PET waste to produce polyols and PU foams. As the composition of crude glycerol varies with the feedstock and the process used for biodiesel production, different properties of polyols produced from PET waste and crude glycerol with different composition are expected.

In this study, a sustainable process for value-added conversion of WCO and post-consumer PET bottles into biodiesel and PU foams is developed (Fig. 1). The biodiesel production from WCO and the chemical recycling of post-consumer PET bottles were integrated by CG-a byproduct of the biodiesel process. The produced biodiesel, polyols, and PU foams were characterized and their properties were evaluated to examine the feasibility of designed sustainable process. The effects of CG loading on properties of polyols and the resulting PU foam were also investigated. A mass balance and a cost analysis for the conversion of WCO and waste PET to biodiesel and PU foams were discussed.

2. Experimental

2.1. Materials

WCO and post-consumer PET water bottles were collected from the cafeteria in Ohio State Agricultural Technical Institute (Wooster, OH) and from recycle center in Ohio Agricultural Research and Development Center (Wooster, OH), respectively. After the removal of polyethylene caps and polypropylene labels, the collected PET bottles were washed, dried, and cut into small pieces (5×30 mm) using a shredder. DEG, glycerol, and 0.1 mol/L and 10.0 mol/L NaOH solution were purchased from Fisher Scientific (Pittsburgh, PA). Ethanol and Tetrahydrofuran (THF) in high performance liquid chromatography (HPLC) grade were purchased from Pharmco-AAPER (Shelbyville, KY). Titanium isopropoxide (TPP), HYDRANAL-Composite 5, HYDRANAL-Water Standard 10.0 and HYDRANAL-Methanol Rapid for Karl Fischer titration; glycerin, monoolein, diolein, triolein, butanetriol, tricaprin and N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) for the quantitative analysis of total monoglycerides and free/total glycerol in biodiesel were purchased from Sigma–Aldrich (St. Louis, MO). Standard polystyrene samples were purchased from Agilent Technologies (Santa Clara, CA). Polycat 5, polycat 8, and Dabco DC5357 used in foaming process were obtained from Air Products & Chemicals, Inc. (Allentown, PA). Polymeric methylene-4,4′-diphenyl diisocyanate (pMDI) was obtained from Bayer Material Science (Pittsburgh, PA). All chemical agents were reagent grade, excluding those were specifically mentioned.

2.2. Characterization of WCO

To determine whether any pretreatment was needed, the water and FFA contents of WCO were determined prior to transesterification reaction for biodiesel production. The water content measured by Mettler Toledo volumetric Karl Fisher compact titrator V20

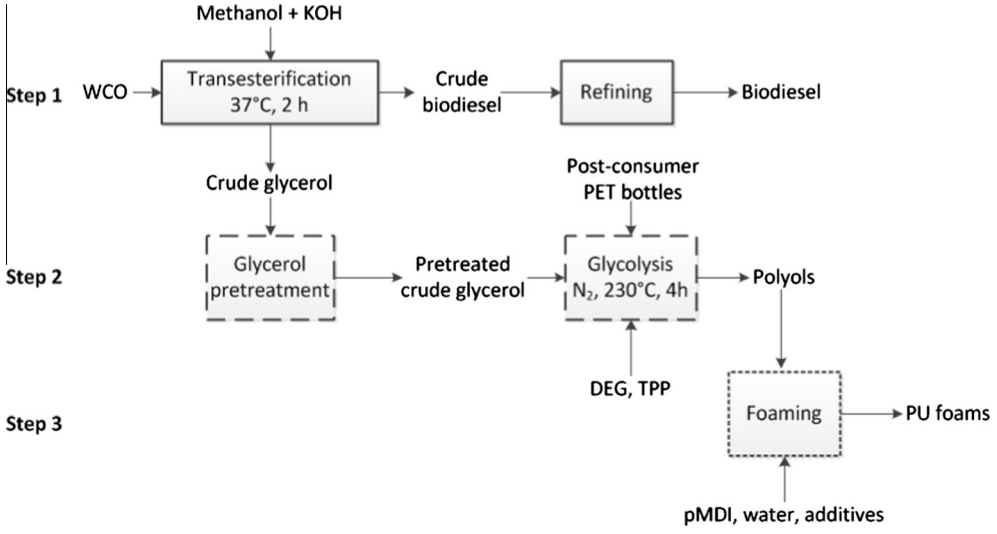

Fig. 1. The value-added conversion of WCO and post-consumer PET bottles into biodiesel and PU foams.