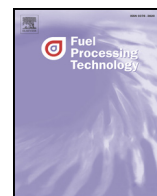




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Research article

Waste glycerol from biodiesel synthesis as a component in deep eutectic solvents

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ABSTRACT

As biodiesel production increases worldwide, so does the generation of its glycerol waste byproduct. Purifying the waste glycerol is difficult and energy intensive; it would be preferable to find a productive use for waste glycerol requiring little to no refining. Herein, we examine the use of waste glycerol from biodiesel production as a component in deep eutectic solvents (DESs). Specifically, we examine mixtures of waste glycerol and choline chloride (ChCl) as prototype simple and inexpensive DESs. The densities and viscosities of the waste glycerol derived DESs are consistent with those measured in DESs prepared with clean glycerol. DESs from waste glycerol are competent solvents for a classical Fisher esterification reaction and show utility in extracting methanol from crude biodiesel mixtures. These DESs therefore show promise as solvent systems, leading to a decrease in waste from the ever-increasing production of biodiesel and also serving as a value-added product for biodiesel manufacturers.

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1. Introduction

As concerns rise over depletion of fossil fuels and their contributions to global warming, biodiesel has grown in popularity and worldwide production is increasing annually. The National Biodiesel Board reports that the United States produced approximately 1.8 billion gallons of biodiesel in 2013. Similarly, the European Union produced slightly more than 1.8 billion gallons in each of the last several years. Other countries, like Brazil, have implemented a mandate to include at least 7% by volume biodiesel in all diesel fuels. While biodiesel offers a myriad of benefits, its production engenders a big waste problem. The production of glycerol generates approximately 10% by volume of a glycerol co-product (see Fig. 1). Consequently, this means that approximately 200 million gallons of biodiesel-waste glycerol was generated in 2013 in the U.S. alone.

Finding a solution to the waste glycerol problem has been a top priority for biodiesel industry for some time [1]. Unlike high purity glycerol valued as a commodity with many uses, including an additive in cellulose films, food and drinks, and pharmaceuticals [2], the glycerol produced as a by-product of biodiesel synthesis is far from pure [3]. It is commonly contaminated with methanol, soaps, and residual catalyst [2]. The level of impurities in this glycerol commonly results in a gelatinous or even solid physical state instead of the clear viscous liquid of clean glycerol.

There are three basic grades of glycerol [4]. Crude glycerol, which is how biodiesel-waste glycerol is classified, contains 70–90% glycerol. For use in industrial application, glycerol must be in technical grade (96.0–99.5% glycerol). To be used in cosmetics, pharmaceuticals, and the food and drink industry, the glycerol must be 99.5–99.7% pure. Refining the crude glycerol into pure glycerol is time and energy intensive [5]. It must go through a process of neutralization, stripping, filtration/centrifugation, and vacuum distillation before it reaches the purity standards required [6]. These purification methods are generally only accessible to larger biodiesel manufacturers because of the time and expense required to perform this purification process.

The aim of the current work is to help ameliorate the biodiesel-waste glycerol glut by developing a process for inexpensively transforming it into a useful product, thus helping to make the biodiesel industry more sustainable. There are some promising biological methods for transforming biodiesel-waste glycerol [7,8]. One possibility is using the waste glycerol as a feedstock for the production of biodegradable polymers [9]. While this technique is promising, the quantity of waste glycerol that would be consumed is minimal compared to the current supply. Additionally, the waste glycerol can be used as an additive for co-digestion and gasification in anaerobic digesters and wastewater treatment plants [10–13]. However, the upper limit to the quantity of crude glycerol that can be added to the sludge is low (sometimes as low as 1% [14]). Some chemical transformations are also under study: for example, glycerol can be converted to ethanol and/or methanol [7,15,16], used as a feedstock in H₂ production [17,18], or be converted into an oxygenated fuel additive [19]. However, all of these methods require high temperatures, use expensive transition-metal catalysts, and suffer from poor atom economy. In an effort to use the crude glycerol “as is”, recent studies have investigated substituting

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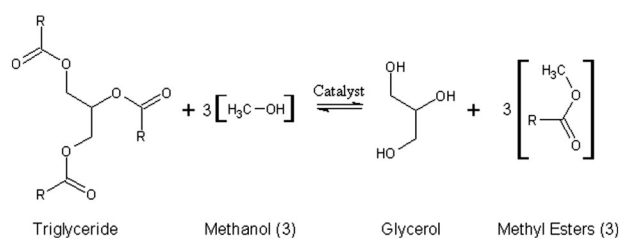


Fig. 1. General fatty acid methyl ester (biodiesel) synthesis from triglycerides producing glycerol.

crude glycerol for corn grain as animal feed [20,21]. Two studies on pigs [22] and catfish [23] have shown the successful introduction of up to 10% crude glycerol into animal feed without detriment to animal growth curves; however, the crude glycerol used as animal feed is limited to vegetable oil feedstocks.

Research has been published using glycerol as a component in deep eutectic solvents (DESs) [24]. DESs are generally prepared with two classes of compounds: hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs). HBDs are generally neutral, small, covalently bonded molecules which are capable of hydrogen bonding, such as sugars, polyols, and carboxylic acids. The HBAs are generally ionic compounds; those studied most commonly thus far have been quaternary ammonium salts [25]. DES solvent systems are similar to ionic liquids (ILs) in many ways, possessing unusually low volatility, interesting chemical and physical properties, reusability, etc. [26]. DESs offer several advantages over ionic liquids, including lower cost, biodegradability, and simple preparation from readily available and inexpensive precursors [25].

For these and other reasons, DESs are growing in popularity in the literature [26–28]. The system most relevant to this research is a DES prepared with glycerol as a HBD and choline chloride ((2-hydroxyethyl)trimethylammonium chloride) as a HBA [26,29]. DESs prepared with glycerol and choline chloride (ChCl) have been studied for their utility in CO_2 and SO_2 absorption [30,31], cellulosic biomass pretreatment [32], and biodiesel synthesis [33], just to name a few.

All of the studies of glycerol/ChCl deep eutectic mixtures have been carried out using pure glycerol as a starting material. However, given the glut of waste glycerol on the market from biodiesel preparation, using waste glycerol as the HBD in DESs could reduce waste from biodiesel preparation, provide a value-added product for biodiesel manufacturers, and generate a “green” solvent that could potentially be used in chemical reactions. Herein, we investigate the use of waste glycerol from biodiesel preparations as the HBD in glycerol/ChCl DESs.

2. Materials and methods

2.1. Reagents

Glycerol (Fisher Scientific, 99.8% by volume, $d = 1.261 \text{ g/mL}$ at 20°C [34]), methanol (Fisher Scientific, HPLC grade), sulfuric acid (Fisher, 95–98%), palmitic acid (Aldrich, 98% min by mass) and trifluoroacetic acid (Acros, 99% by volume) were used as received. Choline chloride ($\text{C}_5\text{H}_{14}\text{ClNO}$, Acros, 99% by mass) was dried under vacuum overnight before use. NaOH (Fisher, 95–99% by mass) was ground with a mortar and pestle, dried overnight above 100°C , and cooled in a desiccator before use. Corn oil (Mazola) was purchased at a retail grocery store. Deuterated solvents were purchased from Cambridge Isotope Labs and used as received.

2.2. Analysis

^1H NMR analysis was carried out on a Varian 300 MHz mercury spectrometer. The biodiesel samples were analyzed in CDCl_3 , while glycerol and DES samples were analyzed in D_2O .

2.3. Preparation of biodiesel and waste glycerol samples

Biodiesel was prepared by both acid-catalyzed and base-catalyzed methods. For the acid-catalyzed method, 500 mL (0.531 mol, assuming an average molar mass of 865 g/mol [35]) corn oil was heated to reflux with 150 mL (3.70 mol) methanol and 5.00 g (0.0510 mol) concentrated sulfuric acid. The mixture was refluxed for 48 h, transferred into a separatory funnel, and allowed to separate overnight into a top biodiesel and a bottom glycerol layer. For the base-catalyzed method, approximately 0.60 g (0.015 mol) NaOH was dissolved in 25 mL (0.62 mol) methanol. Next, 100 mL (0.106 mol) of corn oil was heated to approximately 55°C , and the basic methanolic solution was added in one portion with magnetic stirring. The mixture was stirred for 1 h at 55°C , transferred into a separatory funnel, and allowed to cool and separate into biodiesel and glycerol layers overnight. For both methods, some crude biodiesel was reserved for further study, and some biodiesel was purified by washing several times with warm distilled water (a warm water wash removes methanol, glycerol, and soaps from the crude biodiesel). For both methods, the crude glycerol layer contained a significant quantity of unreacted, excess methanol (as evidenced by ^1H NMR analysis). The methanol was removed from the crude glycerol by reduced pressure rotary evaporation. Both the biodiesel and glycerol layers were subjected to ^1H NMR analysis.

2.4. Preparation of DESs

After separating the glycerol from an acid-catalyzed biodiesel synthesis and removing excess methanol as above, DESs were prepared by stirring ChCl in crude glycerol at 80°C for 1 h. Sample volumes of 25.0 mL glycerol were combined with appropriate masses of ChCl to result in final composition ranging between 5–35 mol% ChCl (for example, 4.7853 g ChCl was added to 25.0 mL of glycerol from an acid-catalyzed biodiesel synthesis to prepare a 10% ChCl DES). For these calculations, the density and molar mass of the waste glycerol were assumed to be the same as pure glycerol. Since the measured density of the glycerol from acid-catalyzed biodiesel is similar to that of pure glycerol (1.258 g/mL vs 1.261 g/mL ; see Table A.1), we believe that these assumptions introduce a negligible amount of error to these preparations.

Additionally, a series of experiments were performed to investigate the possibility of preparing a DES prior to allowing the biodiesel reaction mixture to separate. In these experiments, the ChCl was added directly to the biodiesel reaction mixture at the end of the pre-determined reaction time. After addition of ChCl, the reaction mixture was stirred for 1 h at the reaction temperature, then allowed to cool and separate in a separatory funnel. The DESs prepared by both methods were characterized by ^1H NMR.

2.5. Viscosity

Viscosity measurements were made with a Brookfield LVF temperature-controlled rotating cylinder viscometer. The inner aluminum spindle diameter was 1.175 cm, while the outer aluminum cylinder diameter was 1.900 cm. Reference silicone fluids (97.2 cP and 975 cP) were used to calibrate the viscometer at 25.0°C . Viscosity was measured as a function of temperature based on steady-state values at 5°C intervals, as the enclosure temperature was decreased from 65°C to 30°C . As the enclosure was not equipped with a cooling mechanism, the lowest temperature measured was limited by the ambient temperature. Measurements were made at each temperature decrement, at 6, 12, and 30 rpm for kinematic viscosities above 200 cP; values were measured only at 12 and 30 rpm for values below 200 cP. Between three to five replicate measurements were made at each temperature and concentration combination.

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