



Production of biodiesel with lithium glyceroxide



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ARTICLE INFO

Article history:

Received 15 April 2015

Received in revised form 22 July 2015

Accepted 30 July 2015

Available online 11 August 2015

Keywords:

Glycerol

Lithium hydroxide

Metal alkoxide

Glyceroxide

Lithium soap

ABSTRACT

Alkoxide/hydroxide catalysts were synthesized by heating aqueous solutions of lithium hydroxide with glycerol under vacuum. The dehydration rates for different mole ratios of lithium hydroxide to glycerol were 3:1 < 2:1 < 1:1. Temperature showed a clear effect on dehydration rate while the effect of vacuum was less important. The resulting base catalysts were characterized by X-ray powder diffraction (XRD), Nuclear Magnetic Resonance (NMR), and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Catalysts prepared with 2:1 and 3:1 mole ratios comprised mono and a novel di-lithium substituted glyceroxide, as well as lithium hydroxide. Transesterification reactions of canola oil with methanol were conducted using equivalent mole amounts of sodium methoxide (0.0104 mol, 0.5 wt.%) and glycerol lithium base catalysts (0.0104 mol, 0.2 wt.%). The lithium glyceroxide/hydroxide catalyzed rapid transesterification though the reaction was slower than observed for sodium methoxide. All catalysts resulted in a high methyl ester yield (>99 wt.%). The catalytic activity was 1:1 < 2:1 < 3:1 (lithium hydroxide:glycerol), and was not significantly influenced by conditions used in preparing the catalyst. The crude glycerol remaining after the lithium glyceroxide catalyzed reaction was reacted with free fatty acid to prepare glycerol insoluble lithium soap. A recovery of most of the lithium (85%) as a lithium soap was possible by filtration of the glycerol fraction producing a substantially ion free glycerol solution. This novel reaction afforded glycerol that was substantially free of catalyst and a value added lithium soap suited for use as commercial grease.

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1. Introduction

Depletion of easily recovered petroleum reserves and the need for more environmentally friendly materials has led to a search for alternatives to petroleum based products. Mono-alkyl ester of long chain fatty acids derived from renewable feedstock, such as vegetable oil or animal fats can be used as an alternative to conventional diesel [1]. Biodiesel is an important alternative to petroleum-based fuel that helps reduce atmospheric pollution. One of the critical barriers to the wide application of biodiesel is the relatively high cost of production [2]. Biodiesel can be produced by base-catalyzed transesterification of triacylglycerols (TGs) and low molecular weight alcohols. Potassium and sodium hydroxide are used in biodiesel production. However, these hydroxides produce water when dissolved in alcohol leading to

product loss, catalyst consumption, and the production of soap. Sodium and potassium methoxide also dissolve in methanol releasing methoxide ions; however, no water is released. Therefore, metal methoxides, such as sodium methoxide, are a preferred choice over metal hydroxides for higher reaction rate and yield. Sodium methoxide, used in commercial biodiesel production, is often sold as a 25% (w/v) methanol solution [3]. However, the drawbacks of using methoxide catalysts are hazardous and costly production that demands special facilities as well as increased transportation costs, as methanol and methoxide are flammable and corrosive. Calcium diglyceroxide has been reported as an effective catalyst for transesterification of TGs with methanol for biodiesel production [4]. Fatty acid methyl ester (FAME) yield was limited to approximately 95% at 2 h when employing calcium glyceroxide as the catalyst [5].

Sodium glyceroxide catalyst would be the lowest cost option. However, using lithium glyceroxide catalyst offers a unique opportunity as spent catalyst dissolved in the glycerol is readily converted to glycerol insoluble lithium soaps, which may be sold as lithium grease, a value added product. Removing the catalysts this way simplifies glycerol refining. The objective of this study was to

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produce low cost lithium glyceroxide base catalyst from aqueous solutions of lithium hydroxides and glycerol. The proposed catalyst can be prepared on site and is less costly to transport. Similar catalysts prepared from sodium and potassium can be used in transesterification reactions that achieve the same reaction rate and yield as alkoxides produced by other more expensive and hazardous routes as described by Gok et al. [3] and Pradham et al. [6].

The further advantage of lithium glyceroxide is that crude glycerol can be reacted with free fatty acids that are insoluble in the glycerol. Lithium soap produced from the crude glycerol may be used as a component of lubricating grease, which accounts for approximately 60% of the grease used in the world [7]. Lubricating greases made with lithium grease adhere particularly well to metal, are water resistant and non-corrosive, may be used under heavy loads, and exhibits good temperature tolerance [8].

In biodiesel production plants, 10% of the raw oil mass is released as a glycerol product which contains residual catalyst and must be upgraded before it can be utilized [9]. Typically, the glycerol should have a purity of approximately 85% before being sold to glycerol refiners [10]. However, crude glycerol formed during biodiesel production often contains as little as 66% glycerol after methanol removal. Impurities including soaps, glycerides, and esters [11] must be removed to produce higher quality glycerol. Generally, the lithium soaps are less soluble in inorganic solvents and therefore, glycerol produced by this reaction is largely free of both soap and residual catalyst [12].

2. Materials and methods

2.1. Preparation of catalyst

Catalysts were prepared through heating aqueous solution of lithium hydroxide and glycerol under vacuum pressure. Lithium hydroxide (EMD Chemicals, Gibbstown, NJ, USA) was dissolved in distilled water to prepare an aqueous solution (10% w/w). Glycerol was added to lithium hydroxide solution at three mole ratios of lithium to glycerol (1:1, 2:1, and 3:1). In order to obtain the desired mole ratios, a constant amount of lithium hydroxide (0.25 g or 0.0104 mol) was mixed with glycerol to prepare 1:1, 2:1, and 3:1 mole ratios. The mixtures were heated at 120 and 140 °C in a short path vacuum distillation Kugelrohr oven (GKR-50, Buchi, Flawil, Switzerland) under 25, 50, 100, and 120 Pa for 3 h to evaporate water. Water loss was determined by weighing the sample flask containing the glycerol and LiOH every 15 min. All determinations were performed in triplicate.

2.2. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

Lithium content of catalyst was determined using Inductively Coupled Plasma-Atomic Emission Spectrometry ICP-AES (Model IRIS Intrepid, Thermo Jarrell Ash, Franklin, MA, USA). Catalysts prepared from 0.75 g lithium hydroxide were dissolved in 100 mL of distilled water, which were then analyzed by ICP-AES. Certified lithium chloride standard solution (10 to 10,000 mg/L, EMD Chemical) and lithium free blank were used to calibrate the ICP. The means of three determinations was reported.

2.3. X-ray powder diffraction

The catalyst prepared at 1:1, 2:1, and 3:1 mole ratios of lithium to glycerol as well as lithium hydroxide were characterized by X-ray powder diffraction (XRD; D8 Advance-II, Bruker Germany). For XRD analysis the source wavelength (λ) was 0.15406 nm

generated by Cu K α radiation produced at 36 kV and 20 mA. The diffraction angle from 5° to 100° was determined with a step length of 0.037° and the step time of 1.77 s.

2.4. Transesterification reactions

Transesterification reactions of refined canola oil (Bunge Canada, Oakville, Canada) with acid value of 0.12 mg KOH/g was conducted at 60 °C with 0.0104 mol (0.5 wt.%) lithium methoxide or sodium methoxide as catalyst using a 6:1 mole ratio of methanol to TG. Only one replicate of each reaction was conducted. The average molecular weight of canola oil was assumed to be the same as molecular weight of triolein, 885.46 g/mol [13]. All glassware was flame dried before use. Transesterification reactions were conducted in a two-necked flask (250-mL) having a reflux condenser and a sampling port. Temperature was maintained using an oil bath capable of maintaining the temperature within 0.1 °C. A magnetic stirrer was used to agitate the reaction mixture at 1000 rpm during transesterification. At first, 114.70 g (0.1295 M) canola oil was added to the flask which was then heated to 60 °C. Methanolic glycerol lithium catalyst solution, prepared with glycerol lithium catalyst (0.0104 mol lithium) and methanol (25.00 g). This solution was then injected into the flask through a septum placed over the sampling port and the reaction was assumed to have started immediately. Samples (1 ± 0.01 mL) were taken with a syringe at regular intervals (0.5, 1, 2, 3, 4, 5, 6, 7, 8, 10, 15, 20, 25, 30, 60, and 90 min) from the time of injection. Each sample was neutralized after sampling by adding hydrochloric acid (1 N) immediately to stop any ongoing reaction. The yield of fatty acid methyl ester (FAME) production at different time intervals was determined by NMR.

2.5. Nuclear Magnetic Resonance (NMR) spectroscopy

Samples were dissolved in deuterated chloroform (CDCl₃) and dried catalyst samples (0.0104 mol) were diluted in 25 mL deuterated water with dimethyl sulfoxide (5 mg/mL) as an internal standard. Solutions (0.5 mL) were transferred to Nuclear Magnetic Resonance (NMR) tubes (5 mm i.d., 500 MHz) and the proton NMR spectra were recorded. The effect of drying conditions on glycerol integrity was determined via catalyst spectra, which were compared to glycerol. Proton NMR spectroscopy spectra were recorded with a 500 MHz Avance NMR spectrometer (Bruker BioSpin Corporation, Billerica, MA, USA) equipped with a ¹H NMR 5-mm probe (spectral width: 10,330.58 Hz; data points: 32,768; pulse width: 6.05 μs at 90°; pulse delay: 1.79 s and number of scans: 16). Fourier transform software (ACD Labs version 11) was used to convert the free induction decay (fid) data into a frequency domain spectrum that was further processed. The ⁷Li NMR spectra were recorded on a 500 MHz Avance NMR spectrometer. The ⁷Li chemical shifts are reported in ppm relative to an external 0.1% LiCl/DMSO-d₆ standard set at 0 ppm. The LiCl/DMSO-d₆ standard is placed into a coaxial capillary (NORELL C-N15CCI-B Insert, Coaxial, 5 mm) and positioned in a 5 mm NMR tube with glycerol/D₂O sample in the tube.

The glycerol content of the catalyst samples was determined according to the area of the selected signal directly as shown in the following equation:

$$X\% = 125 \times \frac{92.09}{78.13} \times \frac{3A_1}{A_2} \quad (1)$$

where X = glycerol content of the catalyst samples, A_1 = area of the proton attached at the sn2 carbon at 3.65 ppm and A_2 = area of the methyl group from dimethyl sulfoxide.

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