Fuel Processing Technology 146 (2016) 70–75

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Equilibrium studies of canola oil transesterification using a sodium glyceroxide catalyst prepared from a biodiesel waste stream

Dave Bradley [a,*], Erica Levin [a], Christian Rodriguez [b], Paul G. Williard [c], Anina Stanton [d], Aaron M. Socha [b,d]

[a] FYT Fuels, 77 South Street, Dryden, NY 13053, United States
[b] Department of Chemistry and Chemical Technology, Bronx Community College — City University of New York, Bronx, NY 10453, United States
[c] Department of Chemistry, Brown University, Providence, RI 02912, United States
[d] Center for Sustainable Energy — City University of New York, Bronx, NY 10453, United States

ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 7 February 2016
Accepted 7 February 2016
Available online 22 February 2016

Keywords:
Sodium glyceroxide
Biodiesel
Catalyst formulation
Transesterification

ABSTRACT

Crude glycerol is a low value by-product of the biodiesel industry, and its use as an alkaline catalyst component offers a cost-lowering strategy for sustainable fuel production. Sodium glyceroxide can be used to generate methoxide ions in situ, and the latter act as catalysts for the transesterification of triglycerides to fatty acid methyl esters (biodiesel, or FAMEs). Catalytic formulations of sodium glyceroxide were prepared from glycerol, methanol and NaOH, characterized by X-ray diffraction, and used for rapid transesterification of canola oil into biodiesel. The kinetics of the reaction using 6 and 9 M equivalents of methanol and 0.5 wt.% and 1.0 wt.% catalyst loading were studied by ^{1}H NMR spectroscopy. Catalyst formulations prepared from crude glycerol performed transesterification reactions in methanol at a rate comparable to those observed for sodium hydroxide. Analogous to methoxide-catalyzed transesterifications, the reactions using glyceroxide appeared to be rate-limited by mass transfer. The relative viscosities of glyceroxide formulations prepared in methanol are also presented, and show an inverse correlation between viscosity and increasing concentration, a trend characteristic of ionic glycerol solutions.

1. Introduction

As compared to conventional crude oil, North American shale oil contains a smaller fraction of diesel hydrocarbons [1], and thus additional sources are needed to meet domestic demand for this fuel type. Biodiesel, defined as fatty acid alkyl esters, can be used in compression ignition engines with little or no modification to the vehicle [2]. Biodiesel is also termed Bioheat® when used to replace #2 and/or #6 diesel fuel in building furnaces and generators and mandates in New York City require increasing blends of Bioheat® within public and private sectors [3]. Biodiesel has a negligible sulfur and aromatic carbon content, and its combustion produces less sulfur dioxide, carbon monoxide and particulate matter when compared to petroleum-derived diesel fuels [4]. Biodiesel also is less toxic than #2 fuel oil and readily biodegradable [5]. Moreover, the raw materials required to make biodiesel (sodium or potassium hydroxide, alcohols, and triglyceride oil feedstock) are all sourced within the United States. Approximately 60,000 direct and indirect jobs now are supported by the biodiesel industry at present production rates. [6].

In 2014, the United States Department of Energy reported the production of 1.27 billion gallons of biodiesel fuel [7], corresponding to the production of over 120 million gallons of glycerol byproduct. Due to an increasing global supply, the prices of 99.5% pure and crude glycerol have dropped to approximately \$0.25 and \$0.05 per pound respectively [8,9]. Glycerol demand, however, for use in animal feed, personal care products, pharmaceutical applications, and conversion to higher value chemicals remains strong [10] and it has been predicted that the global market for glycerol will reach \$2.1 billion by 2018 [11].

Plant-derived triglyceride oils are the primary starting material for biodiesel fuel production. Triglyceride-derived methyl esters have also found utility as plasticizers in new and emerging markets [12], such as phthalate ester replacements [13] and components of automobile tires [14]. Although solid acid catalytic methods for one-pot processing of fatty acids, virgin, recycled vegetable and animal oils have been reported [15,16], they are often prohibitively expensive at the industrial scale. The majority of biodiesel plants that process less than 10 million gallons per year still largely rely upon base-catalyzed transesterification chemistry. In other cases, heterogeneous catalysts require special designs and often suffer from mass transfer and metal corrosion issues.

To be both environmentally and economically viable, production of fuels and commodity chemicals from plant-based feedstock will require chemical and engineering processes that integrate low-cost feedstock with creative waste and by-product utilization [17–19]. Sodium glyceroxide was discovered over 120 years ago and has since been prepared by dissolving a strong base (NaOH, NaH, NaOMe, NaOEt, or

---

[*] Corresponding author.

http://dx.doi.org/10.1016/j.fuproc.2016.02.009

sodium metal) into glycerol followed by removal of the water, methanol, ethanol or hydrogen gas by-products [20]. Recently, an elegant method for producing biodiesel esters from a glyceroxide catalyst was reported [21,22], and we herein extend these findings to allow for the engineering of a "closed loop" system (Fig. 1). Specifically, we provide a detailed procedure for the preparation and use of a liquid formulation of the sodium glyceroxide catalyst, including viscosity measurements in methanolic solution, and studies of transesterification reaction rates with virgin canola oil.

As compared to typical hydroxide catalysts systems (i.e. NaOH in methanol), water can easily be removed from sodium glyceroxide systems, and thus minimize soap formation during biodiesel production. The raw materials required to prepare sodium glyceroxide (i.e. crude glycerol and 50 wt.% NaOH), could reduce operating expenses for biodiesel manufacturers currently relying upon sodium methylate. A low-cost, plug-in catalytic system thus represents an enabling technology for the biodiesel industry.

A readily available strong base is needed to deprotonate glycerol in an economical manner. To prepare the catalyst, we employed caustic soda (50 wt.% NaOH in water), which is the lowest cost strong alkaline solution that is commercially available. Besides water, a co-solvent is also needed for the reaction because sodium glyceroxide is a solid that decomposes at 230 °C — a temperature below its melting point [20]. Due to its polarity, we hypothesized that excess glycerol could be used as the reaction solvent, and have established its ability to dissolve the ionic sodium glyceroxide product.

After the glyceroxide catalyst is synthesized, it must be dried prior to use for transesterification — to avoid formation of hydroxide ions. The latter will react with glyceride esters (or FAME esters) to form carboxylate salts (i.e. soaps) and complicate downstream separation of FAME products. Water is present in caustic soda and also is produced by the reaction of NaOH and glycerol, but it is easily separated from glycerol via vacuum distillation. At 100 °C the relative volatility of water to glycerol is approximately 4000:1 (P_{vap} $H_2O = 760$ Torr, P_{vap} glycerol $= 0.19$ Torr), and therefore losses of glycerol during co-distillation with water are minimal.

By contrast, water removal is difficult from sodium methoxide prepared with NaOH and methanol because methanol is more volatile than water and a complex, energy intensive fractional distillation is required. Sodium methoxide is anhydrous and therefore minimizes soap formation, but its preparation from methanol and sodium metal involves handling of very hazardous liquid sodium metal. Moreover, flammable hydrogen gas is generated in the presence of flammable methanol in an exothermic process requiring specialized reactor safety systems. These risk and cost considerations often discourage smaller biodiesel plants from preparing anhydrous sodium methoxide on-site.

We have succeeded in preparing an anhydrous formulation of sodium glyceroxide from purified crude glycerol and inexpensive 50 wt.% caustic soda solution. The glyceroxide formulation readily dissolves in methanol to generate a solution containing a highly efficient sodium methoxide catalyst. We herein report the practical engineering aspects of this sodium glyceroxide catalyst formulation, including its preparation from distilled glycerol, relative viscosities of its methanol formulations, transesterification reaction kinetics and equilibria considerations.

2. Experimental

All chemicals were reagent grade and obtained from Fisher Scientific unless otherwise noted. NMR measurements were performed on an Anasazi-Eft-90 instrument (90 MHz for ^1H).

2.1. Glycerol distillation

A sample of crude glycerol was obtained from Glycerin Traders (LaPorte, Indiana). The assay for the material was determined to be 80.8 wt.% glycerol and 7.5 wt.% water, 6.8 wt.% ash (sodium and/or potassium sulfate/chloride) and 4.8% non-glycerol organics (mono- and diglyceride esters of fatty acids, FAMEs). There was no methanol or soap reported to be present in the sample.

The pH of 50 g of the crude glycerol sample was measured at 4.59. Heating glycerol in acidic conditions can cause dehydration to acrolein [23], and under very basic conditions glycerol polymerizes with heating [24]. Due to the solubility of sodium carbonate and sodium bicarbonate in glycerol [25], an aqueous "trona" buffer was prepared (5.0 mL of water, 284 mg $NaHCO_3$ and 366 mg Na_2CO_3) and added to glycerol pH to obtain a pH of 9.55.

The pH-adjusted glycerol was added to a 250 mL round-bottom flask, equipped with a Vigreux condenser attached to a 3-way adapter fitted to a water-cooled condenser and a catch flask. A demister element was used to coalesce any reboiler droplets by loosely packing a small

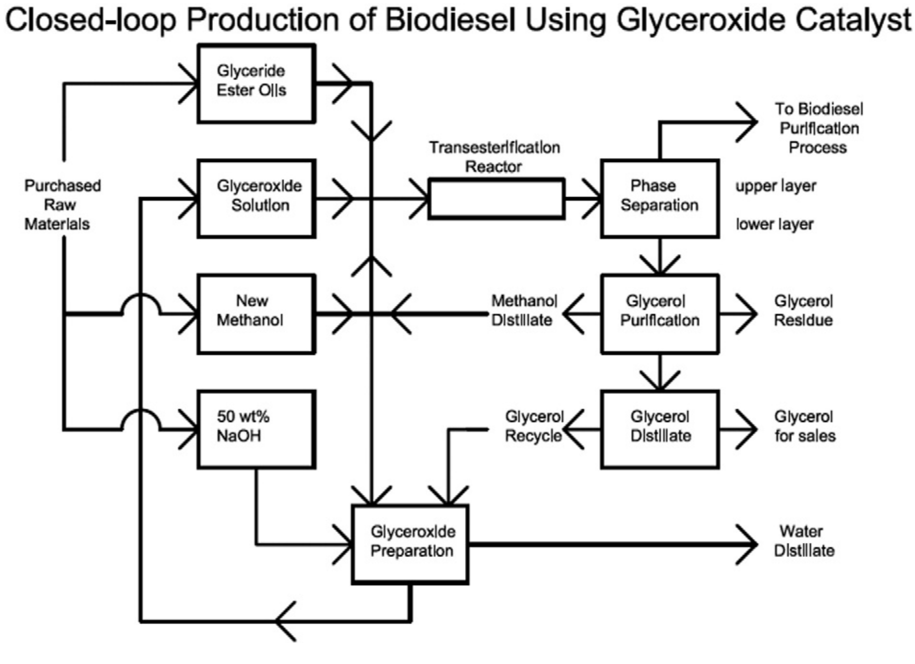

Fig. 1. "Closed-loop" production of biodiesel using glyceroxide catalyst.