Research article

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

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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.

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## 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

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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 $^1$H).

### 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$_2$CO$_3$) 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



## Closed-loop Production of Biodiesel Using Glyceroxide Catalyst
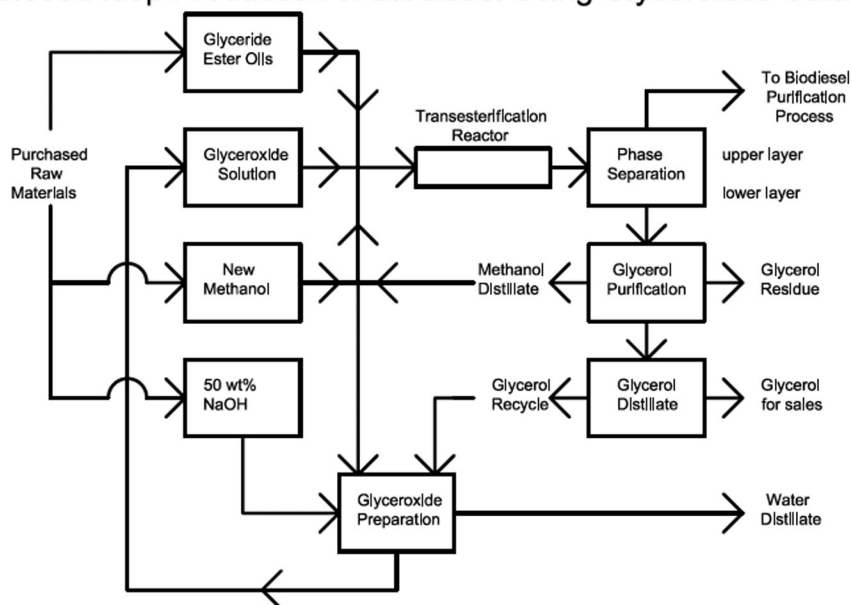
Fig. 1. "Closed-loop" production of biodiesel using glyceroxide catalyst.

piece of glass wool between the reboiler flask and the vapor space leading to the condenser. A second piece of glass wool was placed in the space between the condenser and the vacuum take-off to guide liquid droplets from the condenser into the receiver flask. Approximately 11.8 mL of water was removed by heating to 60 °C at a pressure of 150 Torr. Full vacuum was applied to the system, but due to backpressure the vapor temperature (at 135 °C) prior to the condenser corresponded to 1.8 Torr absolute pressure. The temperature in the round-bottom flask was carefully adjusted to minimize overheating of the crude glycerol. When vapor temperature and pressure reached 135 °C and 1.8 Torr, respectively, glycerol began to distill as a clear viscous solution. The purity of the distilled glycerol was confirmed by $^1$H and $^{13}$C NMR by comparing to commercial glycerol (SI Fig. 1).

### 2.2. Preparation of sodium glyceroxide catalyst

Sodium glyceroxide catalyst was prepared according to published methods [22] by adding 16.0 g of 50 wt.% NaOH aq (0.2 mol) to 18.4 g of glycerol (0.2 mol). The water added to, and produced by, the reaction (approximately 11.6 mL total) was removed by rotary evaporation. Upon cooling to room temperature, the product (NaC$_3$H$_7$O$_3$, FW = 114.03 g/mol) was obtained as a while crystalline solid suitable for characterization by X-ray crystallography.

### 2.3. X-ray crystallography of sodium glyceroxide

A specimen of C$_3$H$_7$NaO$_3$ was used for the X-ray crystallographic analysis (SI Fig. 2). The X-ray intensity data were measured in good agreement with the published structure [26] and showed one sodium ion bonded to the 1-position oxygen atom of glycerol and coordinated by four other oxygen atoms from neighboring glycerol molecules.

### 2.4. Preparation of sodium glyceroxide catalyst formulation

A 1:1 glycerol:sodium glyceroxide catalyst formulation was prepared by adding 16.0 g of 50 wt.% NaOH aq (0.2 mol) to 36.8 g of glycerol (0.4 mol). The water added to, and produced by, the reaction (11.6 g total) was removed by rotary evaporation. Upon cooling to room temperature, the product was obtained as a slightly yellow, highly viscous solution (NaC$_6$H$_{15}$O$_6$) (Scheme 1).

### 2.5. Relative viscosity of sodium glyceroxide catalyst formulation in methanol

The bubble-time viscosity experiment [27] was modified to determine the optimum viscosity for pumping a methanol solution of the sodium glyceroxide catalyst formulation. The latter (1.67 g) was dissolved in increasing amounts of methanol and 500 μL of each solution was pipetted into separate glass tubes (length = 18 cm, OD = 5 mm) and capped. Five concentrations (0.17 M, 0.19 M, 0.23 M, 0.27 M, 0.35 M) of the methanolic catalyst formulation were tested in triplicate at room temperature. The error bars represent average standard deviation in the measurements. The catalyst formulation was assigned a formula weight of 206.08 g/mol for NaC$_6$H$_{15}$O$_6$. Each tube was held in the vertical position, and then flipped 180° to allow the solutions to flow the length of the tube. The time required for each solution to travel the

length of the tube was recorded. The data are presented in Fig. 2 and show a correlation between concentration and viscosity whereby the less concentrated solutions are also the most viscous.

At room temperature, solutions of sodium glyceroxide in methanol exhibit opposite viscosities as compared to solutions of similarly sized inorganic salts as well as glycerol dissolved in methanol [28,29]. Interestingly, at identical temperatures and concentrations, ionic solutions of glycerol can have lower viscosities than non-ionic glycerol solutions and the effect is enhanced when the solution contains larger ions, such as methoxide and glyceroxide [30]. The observed effect can be attributed to the fact that the latter are "structure breaker" ions that disrupt the hydrogen bonding network of the solvent and produce solutions with a lower viscosity [31]. From an engineering perspective, the practicality of this phenomenon allows for more concentrated solutions of glyceroxide formulation in methanol to be pumped.

### 2.6. Transesterification of canola oil

Transesterification of triglycerides using the sodium glyceroxide catalyst formulation was performed at three different conditions. The oil to methanol stoichiometry (1:6 and 1:9) and catalyst loading (0.5 wt.% and 1 wt.%) were investigated. Triolein (C$_{57}$H$_{104}$O$_6$, FW = 885.4 g/mol) was used as a proxy for calculations involving canola oil stoichiometry since it represents the major component of the oil [32]. Only the active catalyst (NaC$_3$H$_7$O$_3$, 114.03 g/mol) was considered when calculating the 0.5 wt.% and 1 wt.% catalyst loadings, however the reactions were performed using the catalyst formulation (NaC$_6$H$_{15}$O$_6$). All reactions were performed in a 250 mL, 3-neck round-bottom flask equipped with a reflux condenser. The temperature was maintained at 60 °C and the reaction was stirred vigorously with a magnetic stir bar (Table 1).

**Reaction 1.** The 1:1 glycerol:sodium glyceroxide catalyst formulation (3.37 g, 1 wt.% of active catalyst) was dissolved into 48.5 mL of methanol (38.4 g, 1.2 mol, 6 eq) and added to 176.8 g (0.2 mol, 1 eq) of virgin canola oil (Best Way Food Products). The reaction mixture was refluxed for 120 min.
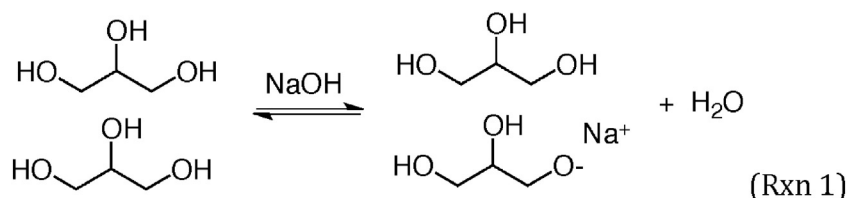
**Reaction 2.** The 1:1 glycerol:sodium glyceroxide catalyst formulation (1.67 g, 0.5 wt.% of active catalyst) was dissolved into 48.5 mL of methanol (38.4 g 1.2 mol, 6 eq) and added to 176.8 g (0.2 mol, 1 eq) of virgin canola oil. The reaction mixture was refluxed for 120 min.

**Reaction 3.** The 1:1 glycerol:sodium glyceroxide catalyst formulation (3.37 g, 1 wt.% of active catalyst) was dissolved into 72.7 mL of methanol (57.6 g 1.8 mol, 9 eq) and added to 176.8 g (0.2 mol, 1 eq) of virgin canola oil. The reaction mixture was refluxed for 120 min.

**Control Reaction.** Sodium hydroxide (0.65 g, 0.37 wt.% of active catalyst) was dissolved into 48.5 mL of methanol (38.4 g, 1.2 mol, 6 eq) and added to 176.8 g (0.2 mol, 1 eq) of virgin canola oil. The reaction mixture was refluxed for 120 min.

## 3. Results and discussion

Reference spectra of canola oil (0.2 mol) and methanol (1.2 and 1.8 mol) were used to observe the respective reactions at t = 0. Upon

Scheme 1. Synthesis of the 1:1 glycerol:sodium glyceroxide catalyst formulation prepared from 2 eq of glycerol:1 eq of sodium hydroxide.
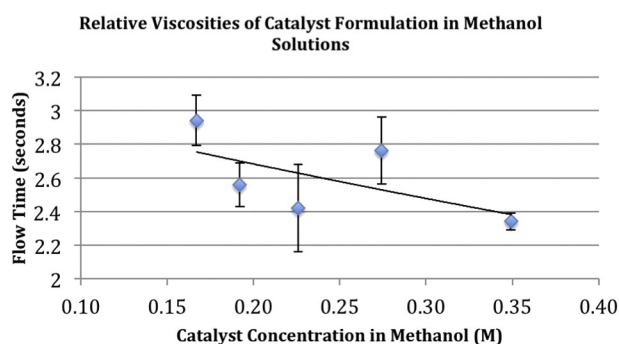
**Fig. 2.** Relative viscosities (as flow times) of increasing concentrations of catalyst in methanol. Error bars indicate standard deviation.
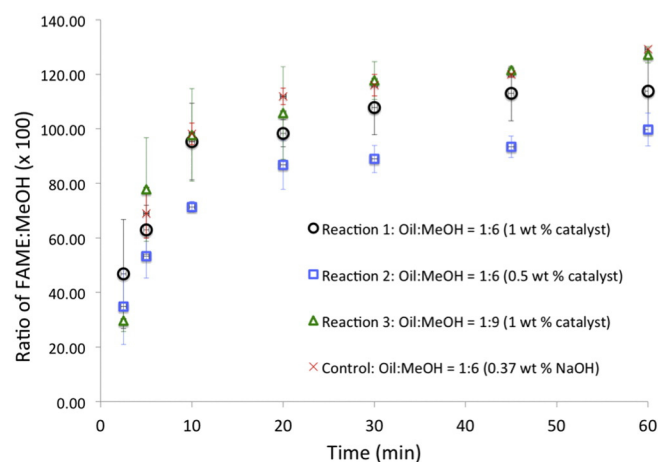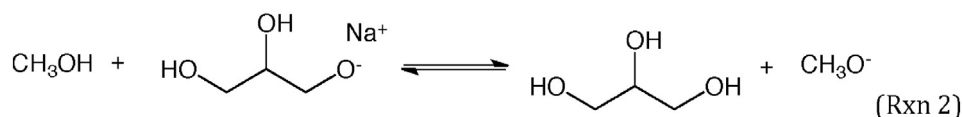


**Fig. 3.** Transesterification reaction kinetics of canola oil using different concentrations of methanol and catalyst formulations.

addition of the catalyst formulation, with vigorous mixing, 100 μL aliquots were removed from the reaction mixture at t = 0, 2.5, 5, 10, 20, 30, 45, and 60 min. The aliquots were placed in NMR tubes, cooled in an ice bath, and diluted with 400 μL of CDCl$_3$ and 20 μL of tetramethylsilane (TMS). The distinct $^1$H resonances of the methanol CH$_3$ group ($\delta$ = 3.46 ppm) and the FAME ester CH$_3$ group ($\delta$ = 3.66 ppm) allowed for analysis of transesterification reaction kinetics [33]. Spectral chemical shifts were referenced using TMS ($\delta$ = 0.00 ppm). In each spectrum, the olefin protons ($\delta$ = 5.17–5.43 ppm) were integrated as 1.00, since the concentration and chemical shift range of these atoms remains constant throughout the transesterification reaction (SI Fig. 3). The peak areas of FAME and methanol were converted to a ratio to determine reaction progress. To plot the reaction kinetics as a percentage of the final equilibrium concentration of FAME and methanol, the aforementioned methyl group peak area ratios multiplied by a factor of 100 (Eq. (1)). The results are presented in Fig. 3.

$$\text{Reaction progress} = \frac{\text{peak area of FAME ester CH}_3(\delta = 3.66 \text{ ppm}) \times 100}{\text{peak area of methanol CH}_3(\delta = 3.46 \text{ ppm})}.$$

(1)

Eq. (1) is the equation used to calculate transesterification reaction progress observed by $^1$H NMR.

As seen in Fig. 3, Reaction 2 proceeded slowest due to the lowest catalyst loading (0.5 wt.%) and ratio of oil:methanol (1:6). Reaction 1 (1:6 oil:methanol ratio and 1 wt.% catalyst loading) was slightly faster, likely due to increased catalyst loading. Reaction 3 had the most solvent (oil:methanol ratio = 1:9), highest glyceroxide catalyst loading (1 wt.%), and was the fastest. Reactions 1 and 3 were comparable in speed to the NaOH catalyzed reaction and were nearly complete after only 10 min. These data are statistically significant when accounting for error in measurements (see Supplemental information for discussion of measurements and error).

### 3.1. Reaction equilibria and mass transfer considerations

From an analysis of the mechanism, methoxide ions are reactants that are consumed in the transesterification reaction between methanol and glyceride (fatty acid-glycerol) esters. The immediate product is the FAME ester and the by-products are glyceroxide anions (e.g. diacylglycerol glyceroxide, monoacylglycerol glyceroxide and glyceroxide anions). A glyceroxide ion then equilibrates with excess methanol to form glycerol and methoxide. In a biodiesel reaction using 0.5 wt.% sodium methoxide as the catalyst, the glyceroxide–methoxide cycle occurs over 36 times. Therefore, because the majority of the FAME synthesis occurs via the glyceroxide–methoxide equilibria cycle, the reaction can be catalyzed by commercially available methoxide solutions (i.e. sodium methylate) or methoxide ions that are made from the equilibration of sodium glyceroxide and methanol.

Upon deprotonation by the glyceroxide catalyst, methanol (as methoxide) functions as a reagent for the triglyceride transesterification reaction (Scheme 2).

The transesterification of a triglyceride with methoxide in methanol is a set of equilibrium reactions with monoglyceride and diglyceride intermediates (Scheme 3). Because methanol is sparingly soluble in triglyceride, the reaction is mass transfer limited in its initial stages. Studies have shown that the rate of reaction can be increased if a co-solvent such as tetrahydrofuran is employed to make a single phase reaction medium [34,35].

The theoretical methoxide:glyceroxide molar ratios were calculated to visualize the course of a model transesterification reaction, and are shown on the y-axis of Fig. 4. Three possible scenarios of the initial catalyst formulation were examined (methoxide; a 1:1 M solution of glycerol:sodium glyceroxide (1:1 Gly:NaGx); or a 2:1 M solution of glycerol: glyceroxide (2:1 Gly:NaGx). Four possible scenarios for oil:methanol ratios were examined (1:6 oil:methanol; 1:7 oil:methanol; 1:8 oil:methanol; and 1:9 oil:methanol). The 1:1 glycerol:sodium glyceroxide catalyst formulation is prepared from 2 mol of glycerol and 1 mol of NaOH, and the 2:1 glycerol:sodium glyceroxide catalyst formulation is prepared from 3 mol of glycerol and 1 mol of NaOH. The excess glycerol serves as the reaction solvent and it maintains the glyceroxide base solubility prior to its addition into methanol. These graphs are based on calculations using the reciprocal of K$_{eq}$ (25.12) for the ratio of methanol to glycerol basicities (see SI Eq. (1)). As can be seen, as glycerol is produced in the reaction, more glyceroxide and less methoxide ions are present, and thus the concentration of methoxide becomes lower relative to that of glyceroxide. After approximately 20% of the reaction is complete, the ratio of methoxide ion to glyceroxide ion is very similar, whether the starting catalyst used was only sodium methoxide or a glycerol–sodium glyceroxide formulation. An increase in methoxide ion to glyceroxide ion ratios occurs over the majority of the reaction extent, especially from 20% to 100% completion. As compared to a triglyceride transesterification using only sodium methoxide as the initial reaction catalyst (with 1:6 mol ratio of methanol to oil), this trend shows that greater concentrations of methoxide reagent can be generated when a

**Table 1**
Reaction conditions for transesterification of canola oil with 1:1 glycerol:sodium glyceroxide catalyst formulation.

| Reaction | Canola oil | Methanol | Catalyst load |
|---|---|---|---|
| 1 | 176.8 g (0.2 mol, 1 eq) | 38.4 g (1.2 mol, 6 eq) | 1.00 wt.% |
| 2 | 176.8 g (0.2 mol, 1 eq) | 38.4 g (1.2 mol, 6 eq) | 0.50 wt.% |
| 3 | 176.8 g (0.2 mol, 1 eq) | 57.6 g (1.8 mol, 9 eq) | 1.00 wt.% |
| Control | 176.8 g (0.2 mol, 1 eq) | 38.4 g (1.2 mol, 6 eq) | 0.37 wt.% |

$$(Rxn\ 2)$$

Scheme 2. Reaction of sodium glyceroxide and methanol.

glyceroxide catalyst is employed. Interestingly, increasing the molar ratio of methanol from 6 to 9 equivalents enhances this trend.
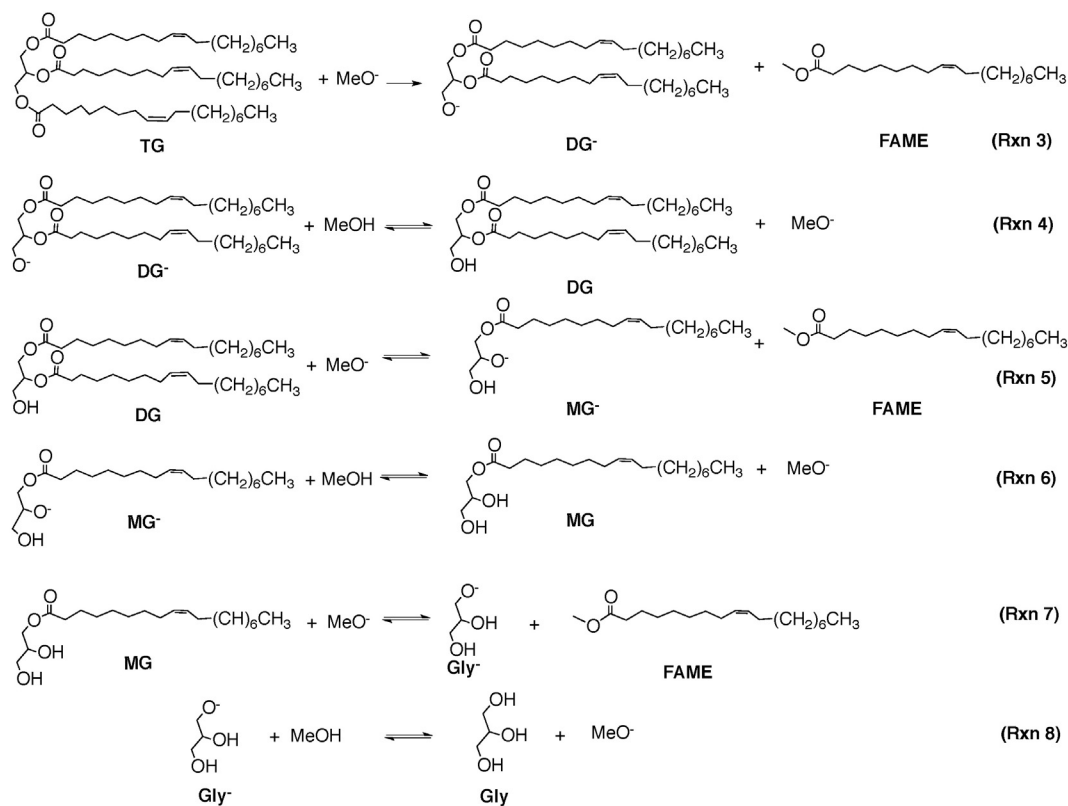
The transesterification reaction equilibria model predicts that the late stages of the reaction have the slowest rate because, at this point, most of the methanol and triglyceride reactants have been consumed and there is a higher ratio of glyceroxide ions to methoxide ions present. Therefore, by exploiting the slightly greater acidity of glycerol relative to methanol, a glyceroxide catalyst formulation used initiate the reaction will have little effect on the overall transesterification rate. Any rate slowing effects that do occur can easily be overcome by using a slightly higher methanol to triglyceride ratio. The equilibria model's prediction

was indirectly proven by the observed percent reaction progress in our kinetic experiments (Fig. 3).

## 4. Conclusions

As can be seen from the equilibria model, there should be very little difference in transesterification reaction extents when using either methoxide or glyceroxide as the initial base catalyst. The ability to increase reaction rate by adding more methanol and glyceroxide catalyst was observed in the transesterification kinetics experiments using virgin canola oil.

## Overall transesterification reaction:
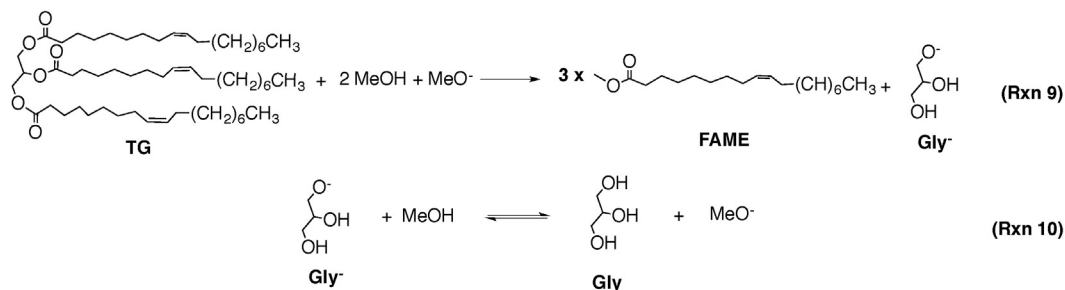


Scheme 3. Transesterification reactions 3–8 showing diglyceride and monoglyceride intermediates (top) and net reactions 9–10 showing glyceroxide catalytic cycle (bottom). TG = triglyceride ester, DG = diglyceride esters, MG = monoglyceride esters, FAME = fatty acid methyl esters, MeOH = methanol, MeO$^-$ = methoxide, Gly$^-$ = glyceroxide, Gly = glycerol, MG$^-$ = monoglyceroxide, DG$^-$ = diglyceroxide.
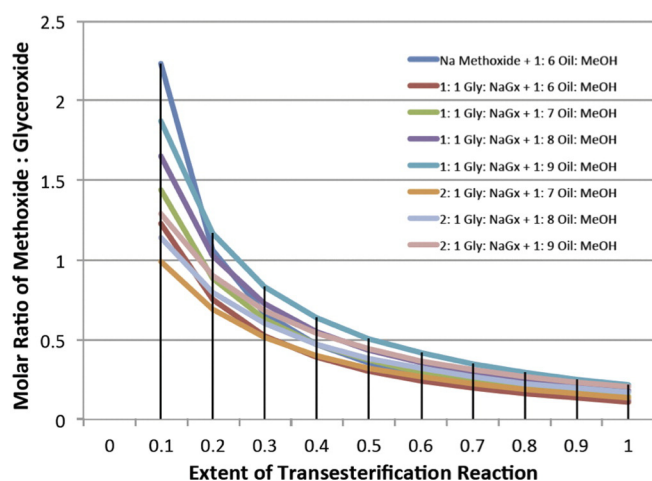
**Fig. 4.** The effect of excess methanol and glycerol on methoxide generation during the course of the transesterification reaction of triglyceride oil.

The glyceroxide process also could also be employed to produce fatty acid ethyl esters via a reaction of triglyceride oil and ethanol, a renewable alcohol. Since the acidities of ethanol (pKa = 15.90), water (pKa = 15.74) and methanol (pKa = 15.54) are similar, a formulation of sodium glyceroxide combined with a large excess of ethanol will produce a sufficient quantity of ethoxide ion. The latter should allow triglyceride transesterification reactions to take place at a somewhat similar rate as compared to those observed with a methanol solvent.

Due to the utility of glyceroxide catalyst formulations for biodiesel production, a closer examination of raw material costs were considered. Glycerol is a by-product of biodiesel synthesis and any glyceroxide formulation used for a triglyceride transesterification reaction could be recovered at rates near 100%. There would be small recurring heat and labor costs to distill glycerol but the capital expenditure of a plug-in glyceroxide generating system would be recouped in approximately 1–2 years on a 38 million liters/year (10 million gallons/year) biodiesel plant (see SI for details). Our initial analysis shows that small industrial biodiesel manufacturers using a glycerol purification system to produce a glyceroxide catalyst formulation could minimize soap formation when compared to using sodium hydroxide catalysts and could significantly increase their net profits when compared to using sodium methoxide catalysts. At a 38 million liters/year scale production rate, this amounts to over $500,000/year of additional net profit.

## Acknowledgments

## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2016.02.009.

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