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Synthesis of potassium glyceroxide catalyst for sustainable green fuel (biodiesel) production

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ABSTRACT

Metal hydroxides and alkoxides are used as base catalysts for biodiesel production. When metal hydroxides are dissolved in alcohol, they produce water, which can react with triglycerides (TGs) and produce free fatty acids (FFAs) rather than the desired fatty acid alkyl esters. Metal alkoxides are more expensive to produce and their transportation is hazardous. In this study, potassium alkoxide catalysts were synthesized from potassium hydroxide (KOH) solution and glycerol, which is by-product of biodiesel production process, by heating 50% KOH solution and glycerol at different mole ratios, temperatures and vacuum pressures. These operating parameters were optimized and their interactive effect on catalyst synthesis was studied by using response surface methodology (RSM). This study also focused on the development of a correlation relating the effects of these variables with drying behavior of reagents during catalyst synthesis.

The results indicated that KOH to glycerol mole ratio and vacuum pressure had the most significant effects ($P < 0.0001$) on free water mass loss during catalyst synthesis. The optimum reaction condition was KOH to glycerol mole ratio of 2:1, reaction temperature 130 °C and vacuum pressure 113 mbar. X-ray powder diffraction showed that glycerol derived alkoxide compounds were predominantly mono-potassium substituted alkoxides that occur as adducts with potassium hydroxide. The glyceroxide catalyst prepared at 3:1 mole ratio of KOH:glycerol has improved biodiesel yield to that of conventional potassium methoxide ($KOCH_3$) catalyst.

Introduction

Biodiesel is a monoalkyl ester of long chain fatty acids, produced from renewable feed stocks, such as vegetable oil or animal fats by reactions with an alcohol in the presence of a base catalyst. This alternative fuel has received favorable attention due to its origin from renewable liquids and its decreased environmental impact when compared to conventional diesel fuel.

Metal alkoxides and hydroxides are used by the biodiesel industry to produce fatty acid esters of lower alkanols by transesterification. However, hydroxides produce water when dissolved in an alcohol. In turn, water molecules react with triglycerides (TGs) to produce free fatty acids (FFA) instead of producing fatty acid ester. In this case, the FFA reacts quickly with the base catalyst to produce soap and, thereby, reduce product yield [1,2]. Alkoxides do not participate in ester hydrolysis and are, therefore, preferred to hydroxides. The major drawback of alkoxide catalysts is that they are more expensive, and their production and transportation is hazardous.

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Glycerol is produced in large amounts as a co-product of biodiesel synthesis processes. In a biodiesel manufacturing plant, ~10 wt.% of triglyceride is released as the co-product glycerol that can be utilized further for value-added products. The oleochemical industry is also a major source of glycerol production, where it is obtained from splitting of triglycerides to produce fatty acids [3]. The utilization of glycerol contributes to biodiesel production economics [4]. There is a global need for technologies that efficiently convert glycerol into various value-added products. Kapicak and Schreck [5] have reported synthesis of an anhydrous basic metal salt of glycerol and used as catalysts for biodiesel production. They reported 90–98% conversion of TG to biodiesel using glycerol metal salts. Reaney and Westcott [6] have produced alkoxide catalysts by reacting aqueous metal hydroxide solutions (40–50% w/v) with polyether alcohols (polyethylene glycol and polypropylene glycol). The resulting alkoxide compounds were effective in isomerization of linoleic and linolenic acid alkyl esters to fatty esters with conjugated double bonds. This process was used for commercial synthesis of conjugated linoleic acid [7]. Reaney et al. [8] have synthesized different metal alkoxide catalysts from a series of non-toxic and non-volatile polyols. Production of potassium alkoxide catalyst from KOH solution and glycerol is not reported. The present study describes potassium glyceroxide catalyst production from low cost starting materials, i.e. 50% KOH solution and glycerol mixed at different mole ratios under different vacuum pressures and temperatures. A statistical experimental design was used to optimize reaction parameters [9,10]. In this study, reaction parameters were optimized using response surface methodology (RSM). The RSM approach was selected as it is effective for designing statistically valid experiments, building models and investigating complex processes and optimization of target values [11–13]. The objective of this study was to optimize potassium alkoxide base catalysts production from low cost starting materials including potassium hydroxide and glycerol so that optimum conditions could be used to prepare these alkoxide catalysts in biodiesel production facilities. Potassium glyceroxide catalysts were then used for fatty acid methyl ester production. It was found that the transesterification reaction rate using this catalyst was high in comparison to other base catalysts [14].

Materials and methods

Catalyst production

Alkoxide catalysts were synthesized using KOH solution and glycerol by a two-stage vacuum dehydration process. KOH solution (50 wt.%) was prepared by dissolving 2 g (0.0357 mol) of potassium hydroxide pellets (EMD Chemicals, Gibbstown, NJ, USA) in distilled water (2 g). Glycerol (EMD Chemicals) which was mixed in three different mole ratios of glycerol to produce KOH to glycerol at 1:1, 2:1 and 3:1 mole ratios. Moles of KOH were held constant (2 g or 0.0357 mol) while glycerol was added at different mole amounts of 0.0357 mol (3.287 g), 0.01785 mol (1.6438 g) and 0.0119 mol (1.0965 g) to create the desired mole ratios 1:1, 2:1 and 3:1, respectively.

Mixtures were added to a round bottom flask and the reaction was conducted in a Kugelrohr short path distillation apparatus (GKR-50, Büchi®, Flawil, Switzerland) fitted to a vacuum pump (Model V-700; Büchi) for 2 h. The reaction was carried out at different vacuum pressures (200, 113, 50 and 25 mbar) and temperatures (120, 130 and 140 °C) for 2 h to evaporate free water added in the reaction mixture with the KOH as well as water released during the formation of alkoxide catalyst. The reaction temperatures used were above the boiling point of water but below than that of glycerol. After 2 h of reaction the flask was weighed to calculate the loss of weight, which is due to water loss during the reaction of KOH and glycerol and free water added to KOH. The % of free water loss was calculated as follows:

$$\textit{free water loss}\ (\%) = \frac{\textit{Total water released}}{\textit{Free water added to}\ \mathrm{KOH}} \times 100 \quad (1)$$

Solids obtained after 2 h reaction time were further dried in a vacuum oven (Model 280A; Fischer Scientific, St. Louis, MO) at 120 °C under vacuum gauge pressure of 94.8 kPa for an additional 24 h.

Experimental design and statistical analysis

Response surface methodology (RSM) was employed to evaluate the effects of various parameters on free water mass loss during the reaction of glycerol and KOH to prepare potassium glycerolate catalyst. The experimental design for this reaction was conducted utilizing a central composite design. The total experiment number was 20 ($=2^n+2n+6$) where n is the number of independent variables. Six axial and eight factorial experimental runs were conducted with six replications at the center point to evaluate the error. The three independent variables were KOH to glycerol mole ratio (1:1–3:1) (*A*), temperature (120–140 °C) (*B*) and vacuum pressure (200–25 mbar) (*C*). All variables at zero level constitute the center point. Therefore, the lowest and the highest levels are assigned to be −1 and +1 respectively.

A second-order polynomial equation (Eq. (2)) was fitted to the experimental data using RSM (Design Expert 8.0.6) to determine the relationship between response variable (free water mass) and independent variables.

$$Y = b_{o'} + \sum_{i=1}^{n} bi \times Xi + \sum_{i=1}^{n} bii \times Xi^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} bij \times XiXj \quad (2)$$

where Y is the free water mass loss; b_o, b_i, b_{ii}, b_{ij} are intercept, linear, quadratic and interaction constant coefficients, respectively; n is the number of variable factors studied and optimized in the experiment; X_i, X_j are the encoded independent variables. The Design Expert version 8.0.6 software was used for regression and graphical analysis of the experimental data. Response surfaces and contour plots were developed using fitted quadratic polynomial equations obtained from regression analysis, holding one independent variable at a constant value corresponding to the stationary point and changing the other two variables.

Catalyst characterization by powder X-ray diffraction

Dried products obtained after two-stage vacuum dehydration were analyzed by X-ray powder diffraction (XRD) [15] using a Bruker-D8 Advance, II series®, Germany equipment having a vertical diffractometer (Cu Kα radiation λ = 0.154 nm) equipped with a PW Bragg–Brentano (BB) goniometer ($\theta/2\theta$), operated at 45 kV and 40 mA. The X-ray diffractometer control stage enabled both atmosphere and temperature control, where all samples were scanned with Bragg angles between 10° and 90° using a step size (θ) of 0.046° per step having scan step time 177 s and the goniometer at a radius of 240 mm. Data were collected at ambient temperature using a Lynxeye® detector. The sample was placed in a sample holder of 2.5 cm diameter and 0.5 cm depth. The total run time for each sample was 1 h. XRD JCPDS® software was used for identifying peaks with its corresponding phases. The powder diffraction patterns of potassium glyceroxide catalysts obtained from KOH solution and glycerol were compared with those of dried powders of KOH obtained by KOH solution dehydration without glycerol. Microsoft Office Excel 2007 and Systat software Sigma Plot Version 11.2 were used to generate these diffraction patterns.

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