



Technical note

Ethanolysis of waste cottonseed oil over lithium impregnated calcium oxide: Kinetics and reusability studies



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ABSTRACT

A series of Li/CaO catalysts has been prepared by impregnating 0.5–5.0 wt% Li in CaO by wet chemical method. Prepared Li/CaO catalysts have been characterized by powder X-ray diffraction, scanning electron and transmission electron microscopy and Brunauer–Emmett–Teller (BET) surface area studies, in order to establish the structure and surface morphology of the catalyst. Hammett indicator test study was performed to determine the basic strength of the Li/CaO catalysts. The prepared Li/CaO catalysts have been employed as a heterogeneous catalyst for the transesterification of waste cottonseed oil (having 2.8 wt% free fatty acid contents) with ethanol. Under optimal reaction conditions *viz.*, ethanol/oil molar ratio of 12:1, catalyst to oil weight fraction of 5% and 65 °C reaction temperature, 98% fatty acid ethyl ester yield was obtained in 2.5 h of reaction duration. Under the optimized reaction conditions, the pseudo first order constant and Arrhenius activation energy were found to be 0.03 min⁻¹ and 70.0 kJ mol⁻¹, respectively. Further Li/CaO catalyst was also found to be effective for the ethanolysis and methanolysis of vegetable oils having up to 3.4 wt% free fatty acids. The use of 3-Li/CaO catalyst is advantageous considering that it not only utilizes waste cottonseed oil as a feedstock, but also renewable and nontoxic alcohol, ethanol, for the biodiesel production.

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1. Introduction

The spiraling crude oil price, increasing energy demand due to industrialization and environmental pollution caused by the fossil fuel burning are the diverse reasons for the search of eco-friendly and renewable fuel. In recent past biodiesel (BD) has emerged as a greener and renewable substitute to the conventional diesel fuel as BD is nontoxic, almost carbon neutral and free from sulfur and aromatic compound [1,2]. Biodiesel, chemically fatty acid alkyl esters, is frequently produced *via* transesterification of naturally occurring triglycerides (vegetable oils and animal fats) with short carbon chain alcohols in presence of homogeneous acid or base catalysts [3] as shown in Scheme 1.

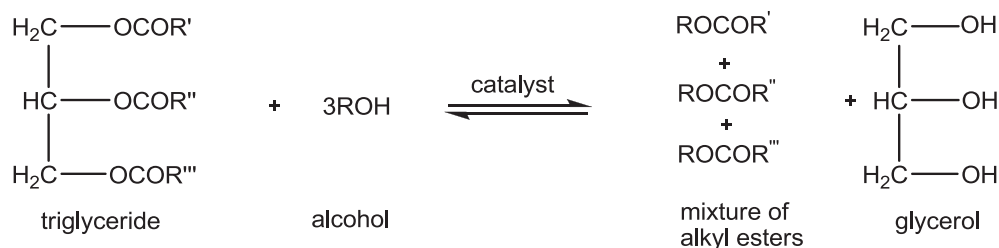
Industrial scale biodiesel production plant utilizes methanol for the transesterification reaction. Methanol is not only toxic but also a refinery product, and hence biodiesel thus produced would not be 100% carbon neutral. On the other hand ethanol is being originated from the agriculture resources (e.g., sugars and starch), could yield

the biodiesel consisting of all renewable carbon atoms. Thus, fatty acid ethyl esters (FAEEs), produced during the ethanolysis, are expected to be more eco-friendly than their methyl ester counter parts [4]. The literature reports regarding the ethanolysis of triglycerides are fewer in comparison to methanolysis [5–7] owing to the lesser reactivity of ethanol than methanol.

Industrial scale transesterification reactions mainly utilize basic homogeneous catalysts such as sodium or potassium hydroxides [8–10]. Although such catalysts show excellent activity even under mild reaction conditions, however they suffer several drawbacks *viz.*, non-reusability, formation of the catalyst contaminated biodiesel and glycerol, deactivation by free fatty acid (FFA) and moisture content [11]. To overcome the problems associated with homogeneous catalysts efforts were made in recent past to develop heterogeneous catalysts for the ethanolysis of vegetable oils. Some catalyst includes mixed metal oxides [12], ion exchange resins [13], sulfonated carbohydrates and heteropolyacids [14,15]. Due to the phase difference, such catalyst often required high reaction temperature (up to 200 °C) and pressure (up to 25 atm), higher catalyst amount (20 mol% to oil) and higher ethanol to oil molar ratio (>30:1) to achieve satisfactory (>96.5%) FAEEs yield [16]. Such reaction conditions lead to increase the overall biodiesel production cost, although, the same need to be *at par* with convention diesel fuel.

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Scheme 1. Transesterification reaction of triglyceride (vegetable oil or fat) with alcohol in presence of catalyst.

In India due to the shortage of edible oils, application of non-edible and waste cooking oils is encouraged for biodiesel product in order to avoid food vs fuel situation. However, such oils usually possess high FFA (1–10%) and moisture (0.5–5%) content [17], and hence, homogeneous base catalysts could not be directly employed for their ethanolysis. In order to utilize the waste cooking oil for biodiesel production, present work demonstrates the preparation of Li impregnated CaO by wet chemical method and its application for the ethanolysis of the waste cottonseed oil. The parameters for ethanolysis have been optimized to obtain the complete transesterification of oil in minimum possible time to reduce the energy demand for FAEEs production. The reusability of the catalysts and kinetics of the reaction were also studied under optimized reaction conditions.

2. Materials and methods

2.1. Materials

Karanja (KO) was obtained from Medors Biotech Pvt. Ltd., New Delhi (India). Waste cottonseed oil (WO) has been procured from the restaurants located in Patiala, while fresh cottonseed oil (FO) and soybean oil (SO) were purchased from the local shops. Ethanol (99%) and methanol (99.8%) used in present study were obtained from Merck, India and used as such without any purification.

The free fatty acid (FFA) value, saponification, and the iodine value of the vegetable oils employed as a feedstock in present work were determined by following the methods as reported in literature [18] and given in Table 1.

X-Ray diffraction (XRD) data for powder samples were collected on Panalytical's X'Pert Pro with Cu K α radiation. The samples were scanned in the range of $2\theta = 5-80^\circ$ at the scanning speed of $2^\circ/\text{min}$. The surface area pore size and pore volume of the catalyst were determined by using the adsorption/desorption method at 77 K by the standard Brunauer–Emmett–Teller (BET) method using Micromeritics Tristar 3000 equipment. Prior to the analysis samples were degassed at 473 K for 90 min under nitrogen atmosphere to remove the physisorbed moisture from the catalysts. Scanning electron microscopy (SEM) was performed on TECNAI G220 S-TWIN to collect the SEM images of the catalysts, and transmission electron microscopy (TEM) was performed on QUANTA 200 FEG to record TEM images. The FAEEs produced in transesterification reactions were analyzed by ^1H NMR technique using Bruker-Avance II, (400 MHz) nuclear magnetic resonance (NMR) instrument. All spectra were recorded in CDCl_3 solvent and chemical shifts were expressed in parts per million (ppm) using tetra methyl silane (TMS) as an internal standard. The gas chromatography-mass spectrometry (GC-MS) was performed on Shimadzu, QP-2010S instrument. For GC-MS analysis, FAEE was diluted with methanol to obtain a final concentration of 1 mg L^{-1} and one μL of this sample was injected into the GC for analysis. The FAEEs were separated on a 30 m long stabilwax capillary column (Carbowax 20 M, 0.25 mm;

Restek, USA) at 280°C column temperature and using helium as a carrier gas.

2.2. Catalyst preparation

A series of lithium ion impregnated CaO (Li/CaO) catalysts was prepared by following the earlier reported [22] wet chemical method. In a typical preparation 10 g of calcium oxide was mixed with 40 mL of deionized water to form a slurry and to this 10 mL aqueous solution of Li_2CO_3 of desired concentration was added to obtain 0.5–5 wt% Li in CaO. The resulted slurry was stirred for 2 h at room temperature (30°C), and finally dried at 120°C in oven for 24 h. The prepared catalysts were designated as $x\text{-Li/CaO}$, where x being the wt% of lithium in CaO.

2.3. Transesterification of waste cottonseed oil

All transesterification reactions were carried out in 250 mL, three necked round bottom flask equipped with a water cooled reflux condenser, thermometer, oil bath and a magnetic stirrer. In a typical run, the flask was charged with 10 g vegetable oil, desired amount of ethanol and catalyst and heated at required temperature ($35-75^\circ\text{C}$). To monitor the progress of the reaction, the aliquots were collected from the reaction mixture after every 15 min with the help of glass capillary and subjected to the ^1H NMR studies. After the completion of the reaction, the solid catalyst was removed from the reaction mixture by filtration. The liquid phase was kept in separating funnel for 24 h to separate the lower glycerol layer from the upper FAEEs or FAMES (fatty acid methyl esters) layer. The excess alcohol from the upper layer was recovered with the help of rotary evaporator. FAMES or FAEEs, thus obtained, were further characterized and quantified by ^1H NMR [17,19] technique and an error of $\pm 2\%$ was observed in this method.

3. Results and discussions

3.1. Catalyst characterization

In present work, CaO being non-toxic and inexpensive has been preferred as a support over other corresponding alkaline earth metal oxides. Additionally, the basic strength of CaO could be tuned by impregnating it with alkali metal ions. The basic strength of

Table 1
The chemical analysis of the vegetable oils employed as a feedstock in present study.

S. No.	Feedstock	Free fatty acid (wt%)	Saponification KOH value (g kg^{-1})	Iodine value
1.	FO	0.23	206.3	118
2.	SO	0.31	212.1	116
3.	WO	2.8	193.2	94.7
4.	KO	3.4	189.1	96.8

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