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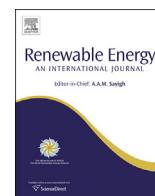


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## Technical note

## 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<sup>-1</sup> and 70.0 kJ mol<sup>-1</sup>, 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.

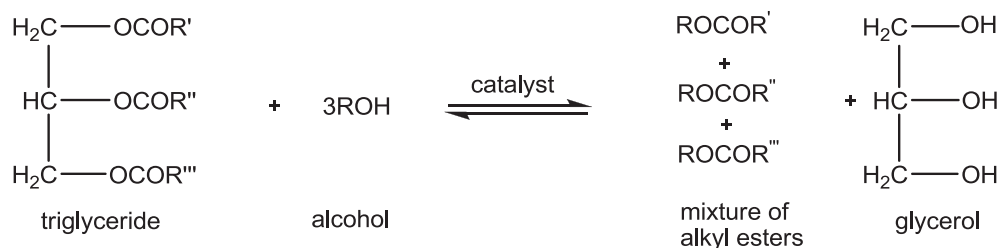
Industrial scale biodiesel production plant utilizes methanol for the transesterification reaction. Methanol is not only toxic but also a refinery product, and hence biodiesel thus produced would not be 100% carbon neutral. On the other hand ethanol is being originated from the agriculture resources (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 ethanolsis. 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 ethanolsis of the waste cottonseed oil. The parameters for ethanolsis have been optimized to obtain the complete transesterification of oil in minimum possible time to reduce the energy demand for FAEs 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 $\alpha$  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 FAEs produced in transesterification reactions were analyzed by  $^1\text{H}$  NMR technique using Bruker-Avance II, (400 MHz) nuclear magnetic resonance (NMR) instrument. All spectra were recorded in  $\text{CDCl}_3$  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, FAE was diluted with methanol to obtain a final concentration of  $1 \text{ mg L}^{-1}$  and one  $\mu\text{L}$  of this sample was injected into the GC for analysis. The FAEs were separated on a 30 m long stabilwax capillary column (Carbowax 20 M, 0.25 mm;

Restek, USA) at  $280^\circ\text{C}$  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  $\text{Li}_2\text{CO}_3$  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 ( $30^\circ\text{C}$ ), and finally dried at  $120^\circ\text{C}$  in oven for 24 h. The prepared catalysts were designated as x-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  $^1\text{H}$  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 FAEs or FAMES (fatty acid methyl esters) layer. The excess alcohol from the upper layer was recovered with the help of rotary evaporator. FAMES or FAEs, thus obtained, were further characterized and quantified by  $^1\text{H}$  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 ( $\text{g kg}^{-1}$ )	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

**Table 2**  
Comparison of BET surface area and basic strength of CaO with 3-Li/CaO catalyst.

S. No.	Catalyst type	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Basic strength (H <sub>+</sub> )	Crystallite size (nm)
1.	CaO	8.1	9.8 < H <sub>+</sub> < 10.1	80
2.	3-Li/CaO	1.3	15 < H <sub>+</sub> < 18.4	60

commercial CaO was found to be in the range of 9.8–10 and the same was found to increase up to 15–18.4 when 3 wt% Li was impregnation in CaO as given in Table 2. The increase in basic strength could be attributed to the formation of strong basic site in CaO upon Li impregnation.

Lithium impregnation in CaO was found to reduce from the surface area from 8.1 to 1.3 m<sup>2</sup> g<sup>-1</sup>, may be due to the pore plugging of CaO upon lithium impregnation.

The powder X-ray diffraction patterns of CaO, and Li<sup>+</sup> impregnated (0.5–5 wt%) CaO have been compared in Fig. 1. The XRD patterns of the commercial CaO show reflections corresponding to the CaO in cubic phase (JCPDS-84-1276), and Ca(OH)<sub>2</sub> (as impurity) in hexagonal phase (JCPDS-82-1690). The XRD pattern of the Li/CaO shows peaks at 2θ = 20.94°, 37.25°, 48.99°, 53.70°, 64.40° and 72.2°, due to the conversion of CaO into Ca(OH)<sub>2</sub> hexagonal phase during wet impregnation of lithium. The absence of XRD patterns corresponding to lithium carbonate in Li/CaO confirms the high degree of dispersion of lithium in calcium oxide. The minor peaks of orthorhombic and hexagonal calcium carbonate were also observed at 2θ = 21.46°, 36.3°, 43.3°, 48.8° (JCPDS-01-0628) and 32.2° (JCPDS-01-1033), respectively. The crystallite size of the 3-Li/CaO catalyst was determined by the Debye–Scherrer method [20] using the peak width of the reflection plane at 34.41° and found to be ~60 nm.

The SEM study gives the morphological characteristics of 3-Li/CaO, which supports the formation of clusters of oval and irregular shaped particles as shown in Fig. 2a. The cluster formation is due to the agglomeration of the catalyst particles during their preparation by wet chemical method. The average size of the

catalyst particles by SEM studies was found to be ~1 μm. The crystalline size and shape of the agglomerated particles were further analyzed by the TEM analysis. The TEM image (Fig. 2b) confirms that catalyst particles are either in spherical or oval shape. The average size of these particles by TEM study was found to be ~13 nm.

### 3.2. FAME and FAEF characterization by <sup>1</sup>H NMR

The efficiency of the selected catalyst, 3-Li/CaO, has been evaluated for the transesterification of a variety of feedstocks, viz., WO, FO, SO and KO. However, WO was selected as a feedstock for optimizing the reaction parameters to achieve the complete conversion (>98% FAEFs yield) in minimum possible time. The FAMES and FAEFs were characterized and quantified by proton NMR technique, as this technique is not only quick, simple, and non-destructive but also not required any derivatization of the products.

The <sup>1</sup>H NMR spectrum of waste cottonseed oil shows a multiplet at 4.15–4.34 ppm due to the presence of glyceridic protons. The peaks appearing at 0.8–2.8 ppm in the proton NMR spectra of biodiesel as well as WO (Fig. 3a) are due to the presence of saturated hydrocarbon protons of fatty acids. The unsaturated protons of fatty acid carbon chain in WO as well as FAMES/FAEFs appear at 5.25 ppm. In proton NMR spectrum of FAMES (Fig. 3b) a new peak appears at 3.6 ppm due to –OCH<sub>3</sub> protons, and peaks corresponding to the glyceridic protons were no longer found, to support the formation of fatty acid methyl ester upon methanolysis of oil. FAMES produced during the methanolysis of WO were quantified [17,22] following equation (1):

$$\%C_{ME} = 100 [2I_{ME}/3I_{\alpha CH_2}] \quad (1)$$

where,  $I_{ME}$  and  $I_{\alpha CH_2}$  are the integration of peaks corresponding to –OCH<sub>3</sub> protons (3.6 ppm), and α-methylene protons (2.3 ppm), respectively in the <sup>1</sup>H NMR of FAMES.

In proton NMR spectrum of FAEFs (Fig. 3c) appearance of a quartet at 4.09–4.16 ppm due to the methylenic protons (–OCH<sub>2</sub>–) of ester group, supports the formation of fatty acid ethyl esters. FAEFs produced during the ethanolysis of triglycerides were calculated [19] following equation (2):

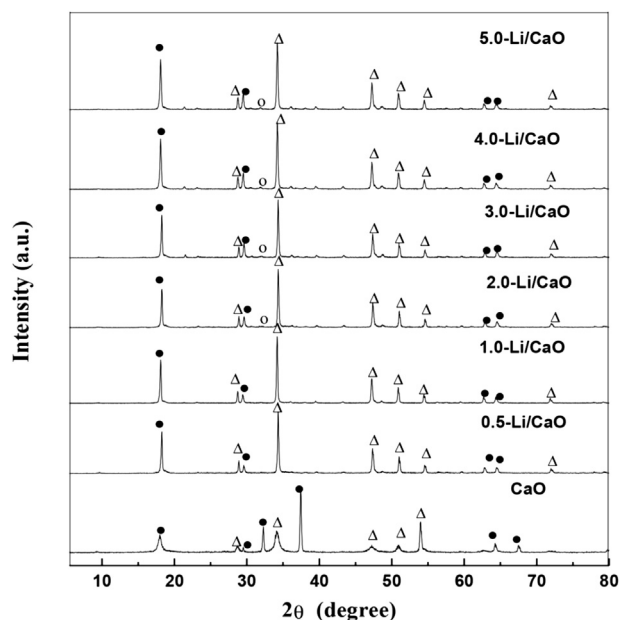
$$\%C_{ME} = 100 [(I_{TAG+EE} - I_{TAG})/I_{\alpha CH_2}] \quad (2)$$

where,  $I_{TAG+EE}$  is the integration of peak corresponding to the glyceryl methylenic and –OCH<sub>2</sub>– of ethoxy protons superimposed at 4.09–4.16 ppm,  $I_{\alpha CH_2}$  is the integration of peak corresponding to the α-methylene protons (2.3 ppm), and  $I_{TAG}$  is the integration of peak corresponding to the glyceryl methylenic protons (4.27–4.33 ppm) in the <sup>1</sup>H NMR of FAEFs.

The quantification of the completely transesterified product and ester profile of prepared FAEFs was also determined by GC-MS technique [21] and the relative percentage of each ester in the mixture is given below in Table 3.

### 3.3. Catalytic activity

Transesterification reactions of ethanol with WO (12:1 molar ratio) were performed in the presence of prepared catalysts in order to optimize the reaction conditions to achieve the complete conversion of oil into corresponding fatty acid ethyl esters in minimum possible time. During the course of study, the following parameters have been varied (i) impregnated lithium ion concentration in CaO support, (ii) catalyst amount, (iii) reaction temperature, and (iv) ethanol/oil molar ratio.



**Fig. 1.** Comparison of the powder XRD patterns of commercially available CaO and Li/CaO (● = cubic calcium oxide; Δ = hexagonal calcium hydroxide; □ = orthorhombic calcium carbonate; and ○ = hexagonal calcium carbonate).

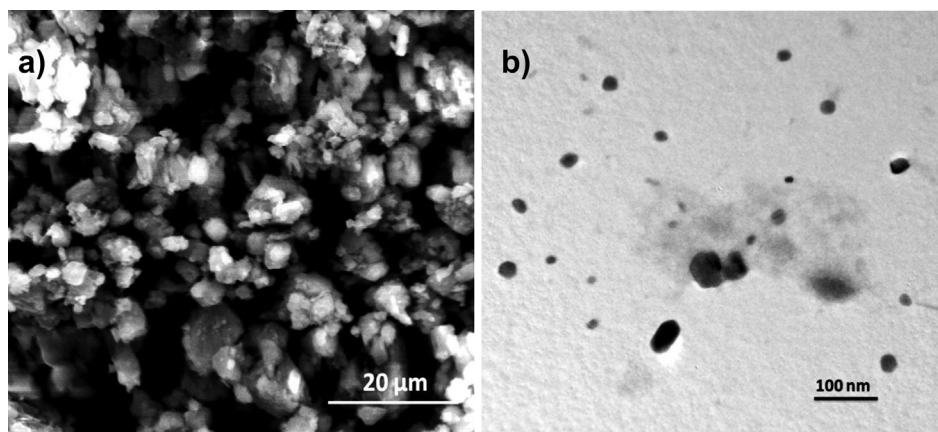


Fig. 2. a) SEM and b) TEM image of 3-Li/CaO catalyst.

### 3.3.1. Effect of impregnated lithium ion concentration

To determine the optimum lithium concentration in Li/CaO catalyst for better catalytic activity, a series of catalyst was prepared by varying the lithium amount (0.5–5 wt%) in Li/CaO. Transesterification of WO was performed with ethanol (1:12 molar ratio) at 65 °C in the presence of 5 wt% Li/CaO (oil/catalyst). The reaction time required for the complete transesterification (>98% FAEs yield) was found to decrease from 5 h to 2.5 h as the Li amount in CaO was increased from 0.5 to 3 wt% as shown in Fig. 4. Hence, Li/CaO catalyst having 3 wt% Li has been selected for optimizing other reaction parameters.

### 3.3.2. Effect of catalyst concentration

In order to find the optimum catalyst concentration, a series of transesterification reactions of WO with ethanol (1:12 molar ratio) at 65 °C were performed in the presence of 3-Li/CaO catalyst by varying its concentration in the range of 1–8 wt% (catalyst/oil). The reaction rate was found to increase as the catalyst amount was

increased from 1 to 5 wt%, and complete conversion of WO to FAEs was achieved in 2.5 h in presence of 5 wt% catalyst. A further increase in catalyst concentration (>5 wt%) doesn't reduce the reaction time significantly as shown in Fig. 5, and hence, the transesterification reactions of WO were studied in presence of 5 wt% catalyst concentration.

### 3.3.3. Effect of reaction temperature

To determine the optimum reaction temperature for the transesterification of WO, a series of reactions have been performed using 12:1 molar ratio of ethanol to oil in the presence of 5 wt% 3-Li/CaO catalyst, and varying the reaction temperature 35–75 °C. The rate of ethanolysis of WO was found to increase with increase in temperature and complete conversion of WO to FAEs required 2.5 h at 65 °C. A further increase in the reaction temperature does not reduce the reaction time significantly as shown in Fig. 6, and hence all transesterification reactions were performed at 65 °C.

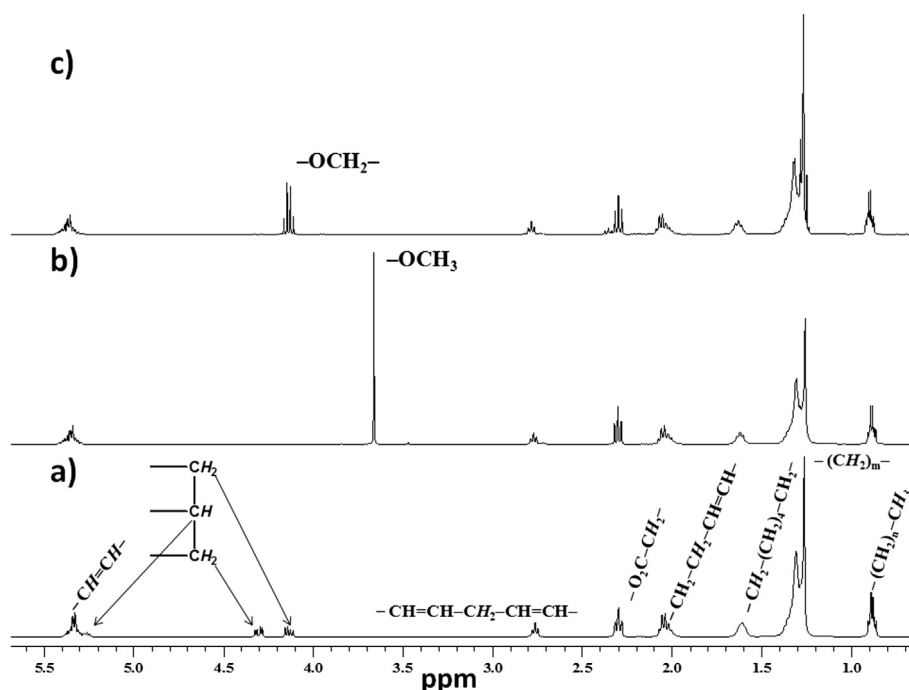


Fig. 3. Comparison of the  $^1\text{H}$  NMR spectra of a) waste cottonseed oil, b) FAMES and c) FAEs.



**Table 3**

Composition of waste cottonseed oil derived FAEs by GC-MS technique.

S. No.	Compound <sup>a</sup>	wt%
1.	Ethyl palmitate (C16:0)	34.13
2.	Ethyl stearate (C18:0)	3.99
3.	Ethyl oleate (C18:1)	21.68
4.	Ethyl linoleate (C18:2)	40.20

<sup>a</sup> In C<sub>n</sub>:x, n indicates the number of carbons and x number of –C=C– bonds in the FAEs.

### 3.3.4. Effect of ethanol/oil molar ratio

The effect of ethanol/oil molar ratio on transesterification reaction is one of the important parameter which affects the ester yield as well as cost of the biodiesel production. Theoretical minimum alcohol to oil molar ratio should be 3:1 for the complete conversion of vegetable oil to corresponding mono alkyl esters. However, transesterification being a reversible reaction, usually such reactions were performed with excess of alcohol to shift the equilibrium in forward direction and to achieve the maximum ester yield. Heterogeneous catalysts, due to phase difference, usually catalyze the transesterification reaction at slower rate and required more time for the completion of the reaction. The efficacy of the same catalysts has been reported to improve when higher alcohol to oil molar ratios was used [22].

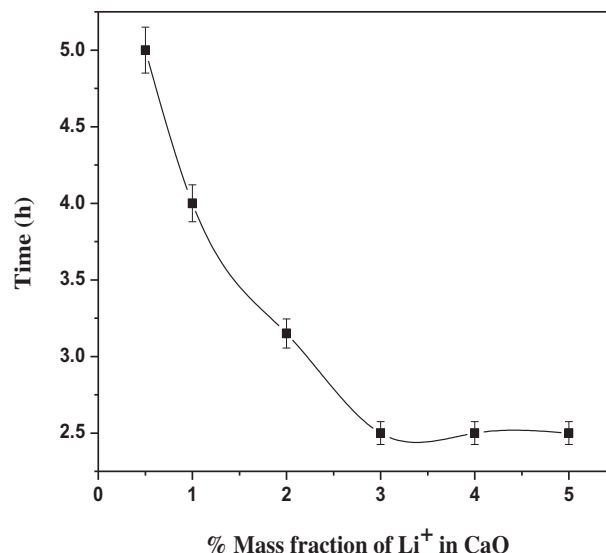
To determine the optimum ethanol/oil molar ratios for the better catalytic activity, a series of reactions were performed in presence of 5 wt% catalyst, 3-Li/CaO, at 65 °C employing 3:1 to 18:1 ethanol to oil molar ratio. The rate of transesterification reaction increases as ethanol/oil molar ratio was increased from 3:1 to 12:1 and reaction was found to be completed in 2.5 h when 12:1 ratio was employed. A further increase in ethanol/oil ratio was not found to increase the percentage conversion to the significant extent as shown in Fig. 7.

Hence, on the basis of above mentioned experiments under optimized reaction conditions, viz., a 12:1 ethanol to oil molar ratio, 5 wt% of 3-Li/CaO catalyst and at 65 °C reaction temperature, maximum fatty acid ethyl ester yield (98%) was achieved in 2.5 h of reaction duration.

### 3.3.5. Effect of the FFA on catalytic activity

In order to test the efficacy of the prepared 3-Li/CaO catalyst towards the transesterification of various commonly available vegetable oils (having various amount of FFA) in the vicinity, it has also been employed for the ethanolysis and methanolysis of WO, FO, KO and SO. All reactions were performed in presence of 5 wt% of catalyst at 65 °C using ethanol or methanol with oil in 12:1 molar ratio. The time required for conversion of various feedstocks to fatty acid methyl/ethyl esters is shown in Fig. 8. Catalyst required longer reaction duration for the ethanolysis than the corresponding methanolysis reaction and the activity of catalyst was found to be adversely affected by the FFA present in the feedstock. The catalyst took minimum time (1.5 h) for the ethanolysis of FO (0.23% FFA).

As evident from Fig. 8, under optimized reaction conditions 3-Li/CaO catalyst required more time for the ethanolysis than methanolysis for the all vegetable oils. The difference in activity may be due to the fact that methanol is more reactive than ethanol due to high mobility of methoxy group than ethoxy group [25]. Hence, more time requirement for the completion of the ethanolysis would also increase the energy consumption during the reaction which in turn may increase the FAEs production cost. Although FAEs produced during the reaction expected to be more eco-friendly fuel than FAMES, however, lesser reactivity of ethanol is major hurdle for the commercialization of this reaction.



**Fig. 4.** Effect of lithium ion concentration on the activity of 3-Li/CaO catalyst for the complete transesterification of waste cottonseed oil to FAEs (Reaction conditions: EtOH/oil molar ratio = 12:1; catalyst amount = 5 wt%; temperature = 65 °C).

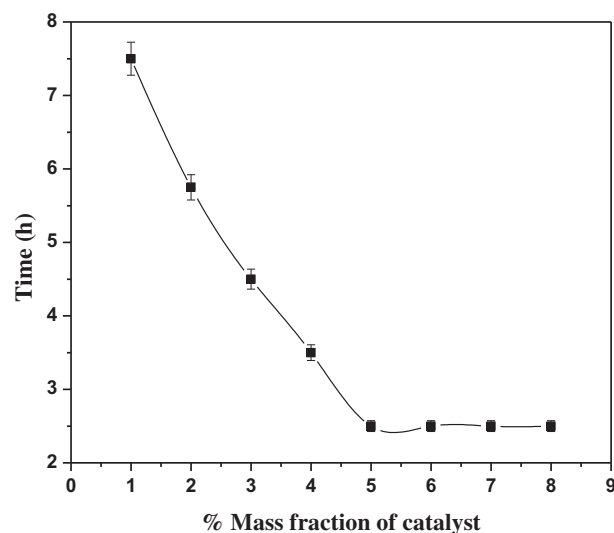
### 3.3.6. Kinetics of 3-Li/CaO catalyzed transesterification

In order to study the kinetics of the ethanolysis of WO in presence of 3-Li/CaO catalyst, reaction has been performed under optimized reaction conditions. Since one mole of oil required 3 mol of ethanol for the complete transesterification, the reaction should follow 4th order kinetic model. However, usually such reactions were performed in presence of excess of alcohol and hence found to follow the pseudo first order kinetics [23] as given in equation (3).

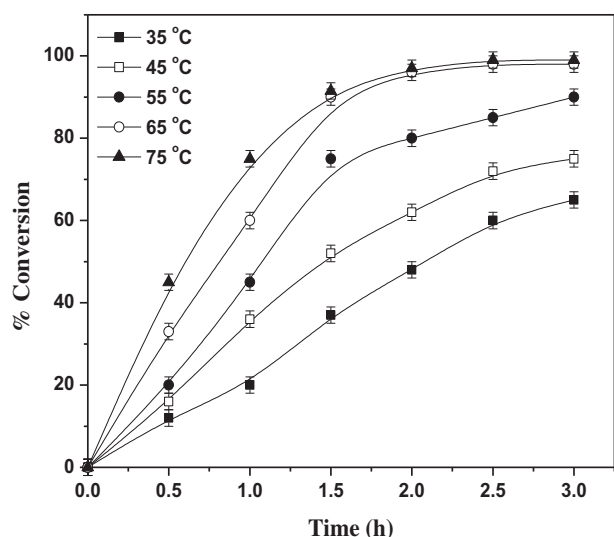
$$-\ln(1 - X_{ee}) = kt \quad (3)$$

where,  $X_{ee}$  is the FAE yield at time 't'.

Plots between  $-\ln(1 - X_{ee})$  and 't' for the WO ethanolysis reactions performed in the temperature range of 35–65 °C, are given Fig. 9. Linear nature of these plots supports that 3-Li/CaO catalyzed



**Fig. 5.** Effect of catalyst concentration on the time required for complete transesterification of waste cottonseed oil to FAEs (Reaction conditions: EtOH/oil molar ratio = 12:1; temperature = 65 °C).



**Fig. 6.** Effect of reaction temperature on the catalytic activity of 3-Li/CaO catalyst for the complete transesterification of waste cottonseed oil to FAEs (Reaction conditions: EtOH/oil = 12:1; catalyst amount = 5 wt%).

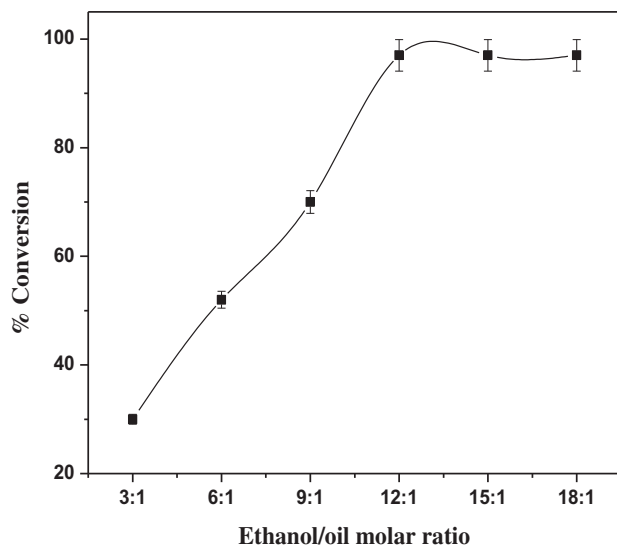
ethanolysis of WO has followed the pseudo first order kinetic model.

The activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) for the ethanolysis of WO were estimated by following the Arrhenius model as given in equation (4).

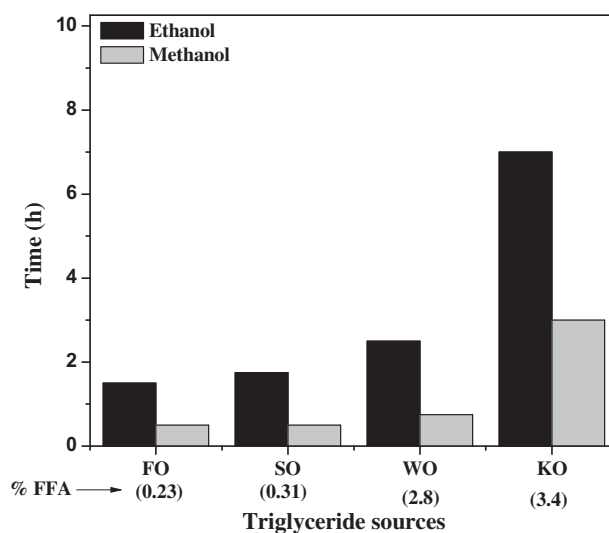
$$\ln k = -E_a/RT + \ln A \quad (4)$$

where,  $R$  is the gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $T$  is the reaction temperature in K.

A plot of  $\ln k$  vs  $1/T$ , as shown in Fig. 10, was found to give the straight line with a slope equals to  $-E_a/2.303R$ . The values of  $E_a$  and  $A$  from this plot were found to be  $70.0 \text{ kJ mol}^{-1}$  and  $1.6 \times 10^9 \text{ min}^{-1}$ , respectively. The calculated activation energy was found pretty close to the reported value of  $70.6 \text{ kJ mol}^{-1}$  for the ethanolysis of castor oil in presence of homogeneous catalyst [24].



**Fig. 7.** Effect of ethanol/oil molar ratio on the catalytic activity 3-Li/CaO catalyst for the complete transesterification of waste cottonseed oil to FAEs (Reaction conditions: catalyst amount = 5 wt%; temperature =  $65^\circ\text{C}$  and reaction duration = 2.5 h).

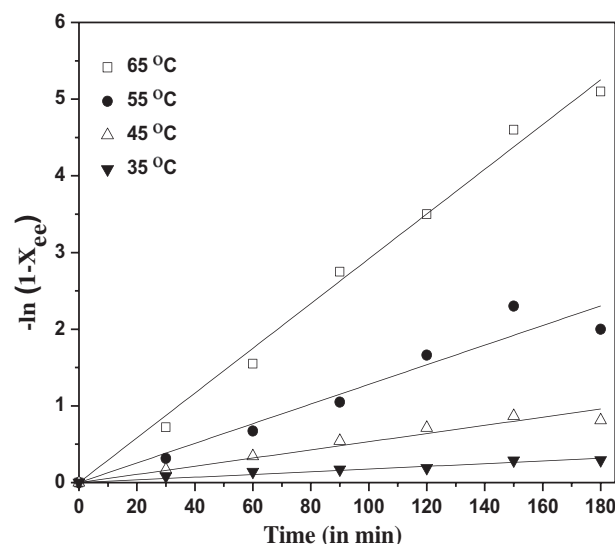


**Fig. 8.** Effect of FFAs on the Li/CaO catalyst catalyzed ethanolysis and methanolysis of various triglycerides.

### 3.3.7. Catalyst reusability and homogeneous contribution

To test the reusability of 3-Li/CaO catalyst, the ethanolysis of WO has been performed under the optimized reaction condition. Catalyst was recovered from the reaction mixture through filtration after the first catalytic run. Recovered catalyst was washed with hexane in order to remove the adsorbed organic molecules from its surface and finally dried at  $120^\circ\text{C}$ . The catalyst thus recovered and regenerated was used for three more successive runs under the same experimental condition and regeneration method, respectively. Reused catalyst was able to yield 98, 90 and 84% conversion of WO into corresponding FAEs in first, second, and third catalytic run, respectively as shown in Fig. 11. Thus regenerated catalyst could catalyze the transesterification of WO, but with the partial loss of activity in every successive run.

This gradual loss in catalytic activity, after every successive cycle, could be due to the partial leaching of the active species ( $\text{Li}^+$ ) from the catalyst support. The leached  $\text{Li}^+$  from the catalyst could catalyze the transesterification reaction similar to the homogeneous catalyst. Hence, it is noteworthy to quantify the



**Fig. 9.** A plot of  $-\ln(1 - X_{ee})$  vs reaction time at different temperatures (Reaction conditions: EtOH/oil molar ratio = 12:1; catalyst amount = 5 wt%).

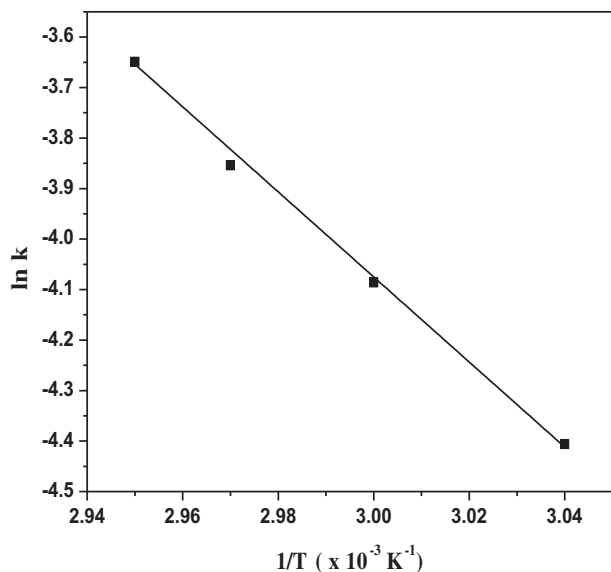


Fig. 10. The Arrhenius plot for the ethanolysis of waste cottonseed oil in presence of 3-Li/CaO catalyst.

homogeneous contribution in catalytic activity. In order to quantify the homogeneous contribution, the catalyst, 3-Li/CaO (500 mg), was refluxed with ethanol (4.8 g) for 2.5 h at 65 °C. After the stipulated time the catalyst was filtered out, and ethanol thus obtained has been employed for the transesterification of WO (EtOH/oil = 12:1, m/m) at 65 °C for 2.5 h. Under these experimental conditions negligible conversion (~5%) of the WO into FAEs was achieved. Thus it is safe to assume that there is no significant homogeneous contribution involved in catalytic activity.

To establish the reason behind the loss in catalytic activity the BET surface, basic strength, crystallite size and XRD patterns of the fresh and reused catalyst were compared. It is evident from Table 4 that surface area as well as basic strength of Li/CaO catalyst decrease upon reuse. On the other hand the crystallite size of the reused catalyst was found to be smaller than the fresh catalyst.

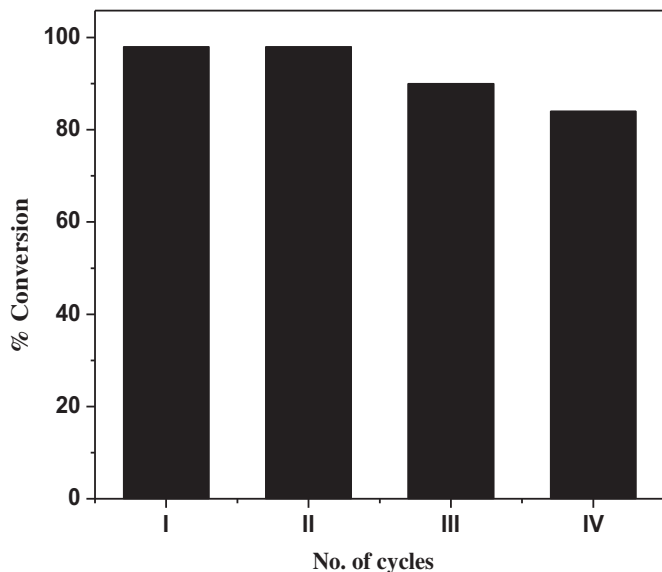


Fig. 11. Reusability studies of the 3-Li/CaO catalyst towards the ethanolysis of waste cottonseed oil.

Table 4

Comparison of BET surface area, basic strength and crystallite size of fresh and reused 3-Li/CaO catalyst.

S. No.	3-Li/CaO	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Basic strength (H <sub>+</sub> )	Crystallite size (nm)
1.	Fresh	1.3	15 < H <sub>+</sub> < 18.4	60
2.	Reused	0.88	11.1 < H <sub>+</sub> < 15.0	52

The comparison of the XRD patterns (Fig. 12) of fresh and reused catalyst signifies that some structural changes have occurred in reused catalyst. Appearance of peaks at  $2\theta = 32.3^\circ$  and  $67.6^\circ$  in the diffraction patterns of reused catalyst supported the formation of hexagonal calcium carbonate as one of the major phase. The formation of calcium carbonate may be due to the reaction of calcium hydroxide with atmospheric CO<sub>2</sub> during repeated use of catalyst and drying at 120 °C. Thus, decrease in basic strength and structural changes are primarily responsible for the reduction in Li/CaO catalytic activity upon its repeated use.

### 3.3.8. Physicochemical properties of FAEs

Few important properties of FAEs produced from the ethanolysis of WO in presence of 3-Li/CaO catalyst have been evaluated following the standard test methods as given in Table 5. The observed values of the studied properties of prepared FAEs were found within the limits of the EN 14214 specifications except the kinematic viscosity. The kinematic viscosity at 40 °C of WO derived FAEs was found to be marginally higher (5.47 cSt) than the maximum accepted value of 5.0 cSt.

## 4. Conclusions

The catalyst, 3-Li/CaO, was found an efficient for the ethanolysis of vegetable oils having up to 3.4 wt% FFAs. The catalytic activity was found to be a function of ethanol to oil molar ratio, catalyst amount, reaction temperature and FFA present in the feedstock. Under optimized reaction condition, catalyst was found to follow pseudo first order kinetic model and values of the first order rate

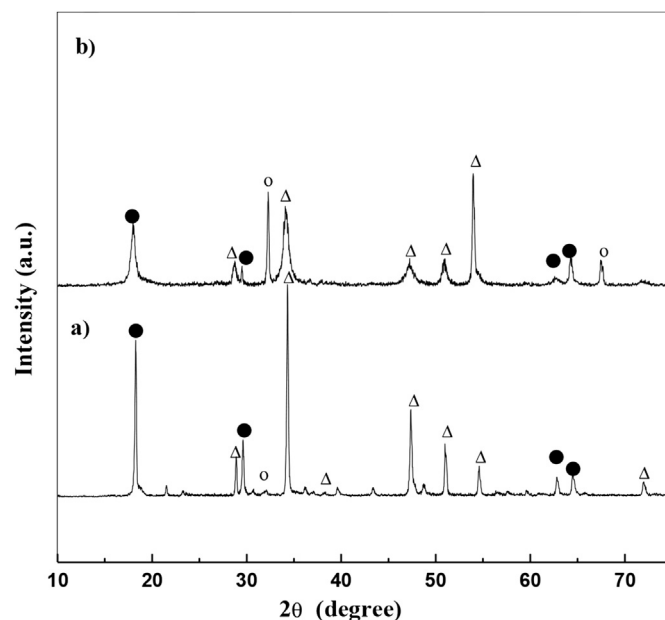


Fig. 12. Comparison of powder XRD patterns of a) fresh 3-Li/CaO, b) reused 3-Li/CaO catalysts. (● = cubic Calcium oxide; Δ = hexagonal calcium hydroxide; □ = orthorhombic calcium carbonate; and ○ = hexagonal calcium carbonate).



**Table 5**  
Physicochemical properties of waste cottonseed oil derived FAEs.

Physicochemical properties	WO derived FAEs	EN 14214 specifications	Test methods
Ester content (%)	98%	96.5	<sup>1</sup> H NMR
Flash point (°C)	120	≥100	ASTM D 93
Pour point (°C)	0	—	ASTM D 2500
Kinematic viscosity at 40 °C (cSt)	5.47	3.5–5.0	ASTM D 445
Calorific value (MJ kg <sup>−1</sup> )	39.44	—	ASTM D 7870
Ash (%)	Nil	0.02	ASTM D 874
Density at 31 °C (g mL <sup>−1</sup> )	0.88	0.86–0.90	EN ISO 3675
Acid KOH value (mg KOH g <sup>−1</sup> )	0.35	0.5	ASTM D 974

EN14214 = European Standard that describes the requirements and test methods for FAMES; ASTM = American Standards for Testing and Materials.

constant and activation energy were found to be 0.03 min<sup>−1</sup> (at 65 °C) and 70.0 kJ mol<sup>−1</sup> (at 35–65 °C), respectively. The lixiviation study suggested negligible homogeneous contribution in catalyst activity. The catalyst was also recovered and reused in four catalytic runs but with partial loss in activity during successive catalytic cycles. Few physicochemical properties of the waste cottonseed oil derived FAEs were also evaluated and observed values, except kinematic viscosity, were found within the limits of EN 14214 specifications.

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