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Effect of lithium ions in catalytic efficiency of calcium oxide as nanocatalyst for transesterification of lard oil

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Abstract

The present work encompasses the effect of Li^+ ions to CaO nanoparticles for the transesterification of lard oil. The modification of CaO nanoparticles was achieved by impregnation of the different molar ratio of lithium hydroxide. Later, each catalyst was screened for catalytic conversion of lard oil to fatty acid methyl ester (FAME). The nanocatalyst CaO-0.5 LiOH (1:0.5 molar ratio) showed the best conversion rate for biodiesel. Synthesized nanocatalyst was conducted using Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), X-ray diffraction (XRD), Transmission electron microscopy (TEM) and Brunauer-Emmett-Teller (BET), and Hammett indicator for basicity test. The obtained biodiesel was analyzed by gas chromatography with mass spectrometry (GC-MS), ^1H and ^{13}C nuclear magnetic resonance (NMR). The effect of optimum reaction parameters such as catalyst weight percentage, oil to methanol ratio, reaction time, reaction temperature and reusability of catalyst on transesterification reaction was analyzed by ^1H (NMR). The maximum biodiesel yield of 97.33% was obtained at 4 wt% catalyst amount, 1:6 oil to methanol ratio at 65 °C in 120 minutes. The physical properties of synthesized biodiesel were also determined.

Key words: Biodiesel, lard oil, transesterification, nanocatalyst

1. Introduction

Biodiesel is esters of fatty acids obtained by transesterification of fats/ oils with methanol in the presence of various kinds of the catalyst. It can act as a substitute for conventional fuels due to its remarkable features such as readily accessible, technically possible, renewable and has sustainable nature ^[1-3]. Moreover, biodiesel is a renewable fuel that can be produced from the various sources such as vegetable oils, algal oils and animal fat/oils ^[1-6].

Usually, the vegetable oil such as rapeseed, sunflower, soybean was used as feedstock for biodiesel production. The feedstock used in the present work was lard oil due to less expensive and does not compete with food production ^[2,7,8]. Moreover, the biodiesel synthesized from animal fat has higher calorific value and cetane number in comparison with biodiesel from vegetable oil ^[9].

Currently, nanocatalysts play a significant role in biodiesel production from different feedstock due to their higher catalytic activity, increased surface area, reusability, easy operational procedures and reduced mass transfer resistant ^[1,3,10]. CaO based nanocatalyst is recommended for biodiesel production due to its cost-effective nature, eco-friendly material and higher basicity^[11, 12].

The present work is to enable the production of biodiesel from lard oil using lithium-ion doped CaO as a nanocatalyst. One way to reduce the biodiesel production costs is to use the less expensive feedstock. So, Lard oil was selected as a feedstock for biodiesel production. The selection of CaO as nanocatalyst for transesterification of lard oil is due to the positive response of CaO when compared to other commercially available nanocatalysts such as MgO, TiO₂ and ZnO. Later, various concentration of lithium ions was impregnated to CaO nanoparticles using lithium hydroxide as a precursor determine the doping effect of lithium ions on catalytic

activity. Moreover, to the best of our knowledge, the transesterification of lard oil using a lithium doped CaO not been investigated. FTIR, SEM, XRD, TEM, BET and Hammett indicator for basicity test were performed for the characterization of the synthesized catalyst. Moreover, the synthesized catalyst was subjected to transesterification of lard oil where the reaction parameters such as molar ratio of oil and methanol, temperature, catalyst amount and time of transesterification were optimized. The biodiesel was analyzed by GC-MS), ^1H and ^{13}C NMR techniques to investigate the various important characteristics of biodiesel.

2. Experimental

2.1 Chemicals

Lard oil (FFA%= 0.423, average molecular weight=866.82), Calcium oxide nanopowder (CaO), Magnesium oxide nanopowder (MgO), Titanium oxide nanopowder (TiO_2), Zinc oxide (ZnO) nanopowder and methanol ($\geq 99.8\%$), lithium hydroxide were purchased from Sigma-Aldrich. All the chemicals were of analytical grade.

2.2 Catalyst synthesis and selection

The conversion of lard oil using a different catalyst (MgO, TiO_2 , ZnO, and CaO) was conducted by mixing oil to methanol in 1:6 molar ratio with 4wt % of each commercial catalyst at 65 °C for 2 h. After investigation of the primary result of transesterification, CaO was selected for Li^+ ion impregnation and for further use for Lard oil transesterification. Later on, CaO nanoparticles modification by Li^+ ion impregnation was carried out by incipient wetness impregnation method.

The catalysts were prepared by blending CaO/LiOH in different molar ratios of 1:0.15, 1:0.25, 1:0.5 and 1:0.75. The reason behind the selection of LiOH instead of lithium carbonate or lithium nitrate was to avoid nitrate and carbonate ions residue over nanocatalyst. As the leftover residual concentration of anion can affect the surface property of catalyst and hence biodiesel synthesis from lard oil. The CaO–LiOH solutions were stirred continuously for 7 h and later dried at 50 °C. The dried samples were calcined at 400 °C in a muffle furnace (Naberthermb180) for 4 h. As prepared Li⁺ ion impregnated CaO nanocatalyst (Li–CaO) with a different molar ratio of viz. 1:0.15, 1:0.25, 1:0.5 and 1:0.75 were screened for fatty acid methyl ester (FAME) production. Moreover, the effect of lithium ion on the enhancement of CaO catalytic activity in the transesterification of lard oil was examined with a set of lithium impregnated CaO catalysts.

2.3 Catalyst characterization

XRD patterns of bare and modified nanocatalyst were collected by PANalytical – Empyrean X-ray diffractometer with an X-ray source Co-K α of 0.178 nm at 40 mA and 40 kV over a 2 θ range of 10-120°. FTIR of synthesized nanocatalyst was examined with Vertex 70 Bruker FTIR instrument. SEM images of catalysts were scanned by SEM, Hitachi SU3500 with 5 kV accelerating voltage. TEM images of the samples were recorded using HT7700 (Hitachi) TEM by dissolving sample in ethanol. The catalyst samples were degassed at 40 °C for overnight to remove the moisture then followed by BET analysis (BET, Micromeritics Tristar II plus) to determine the surface area of nanocatalyst.

The Hammett indicator such as bromothymol blue ($H_{7.2}$), phenolphthalein ($H_{9.8}$), 2, 4 - dinitroaniline (H_{15}) and 4-nitroaniline ($H_{18.4}$) was used to determine the basic strength of synthesized nanocatalyst with different molar ratio of CaO: LiOH and also for TiO₂, MgO, ZnO and CaO. During this process, 1 ml of Hammett indicator were diluted in 10 ml of methanol and mixed with 300mg of each catalyst. Later, all the samples were kept for 3h to settle [3,13, 14].

2.4 Biodiesel production

The biodiesel production from lard oil via transesterification process using different catalyst was done by blending oil to methanol in 1:6 molar ratio with 4wt % of each nanocatalyst. The reactions were carried out in triplicates in a 250 ml three-neck round bottom flask with mechanical stirrer and reflux condenser at 65 °C for 120 min in order to select the best catalyst among all synthesized nanocatalyst for biodiesel production. The centrifugation of samples followed by reaction to obtain fatty acid methyl ester. The excess methanol in ester phase was recovered by rotary evaporator. The biodiesel was analyzed by GC-MS (Agilent-GC6890N, MS 5975) with Agilent DB-wax FAME analysis GC column dimensions 30 m, 0.25 mm, 0.25 μ m. The inlet temperature was 250 °C and the oven temperature was programmed at 50 °C for 1 min and it raised at the rate of 25 °C/min to 200 °C and 3 °C /min to 230 °C and then it was held for 23 min. Moreover, esters of lard oil after transesterification reaction was analyzed by ¹H and ¹³C NMR (Bruker). For NMR analysis, fatty acid methyl esters were analyzed by ¹H NMR and ¹³C NMR at 400 MHz with CDCl₃ as a solvent. The conversion percentage of lard oil to fatty acid methyl esters (C %) and percentage of biodiesel yield are estimated by the equation (1) and equation (2) correspondingly [2,3].

134
$$C(\%) = \frac{2 \times \text{Intergration value of protons of methyl ester}}{3 \times \text{Intergraton value of methyl protons}} \times 100 \text{ (Eq. 1)}$$

135
$$\text{Biodiesel yield (\%)} = \frac{\text{mass of biodiesel}}{\text{mass of oil}} \times 100 \text{ (Eq. 2)}$$

136
137
138 Furthermore, in the current study optimization has been done using the best catalyst obtained
139 after screening process. It was conducted with varying oil to methanol molar ratio, catalyst
140 amount, reaction time and reaction temperature.

141
142 **3. Result and discussion**

143
144 *3.1. Screening and selection of nanocatalyst for biodiesel production from lard oil*

145 The transesterification of lard oil using a series of catalysts such as MgO, ZnO, TiO₂, CaO,
146 and CaO/LiOH (1:0.15, 1:0.25, 1:0.5, and 1:0.75 molar ratios) was performed using oil to
147 methanol in 1:6 molar ratio with 4wt % of each nanocatalyst at 65 °C for 120 min in order to
148 select the best catalyst. The catalytic performance of each catalyst is shown in Table 1.
149 Moreover, reaction parameters for the chosen catalyst were optimized to obtain a high yield of
150 fatty acid methyl esters (FAME).

151
152 **Table 1.**

153 The efficiency of various catalyst for transesterification of lard oil

No.	Catalyst	Molar ratio	Catalyst basic strength	Biodiesel yield %
1	MgO	-	H ₊ <7.2	No reaction
2	ZnO	-	H ₊ <7.2	No reaction
3	TiO ₂	-	H ₊ <7.2	No reaction
2	CaO	-	7.2<H ₊ <9.8	66.55
3	CaO:LiOH	1:0.15	9.8<H ₊ <15	71.25
4	CaO:LiOH	1:0.25	9.8<H ₊ <15	83.30
5	CaO:LiOH	1:0.5	15<H ₊ <18.4	97.33
6	CaO:LiOH	1:0.75	15<H ₊ <18.4	85.09

154

155 Based on Table 1, the CaO showed a positive reaction in the conversion of lard oil to
 156 biodiesel compared to other catalysts such as MgO, TiO₂, and ZnO. This is probably due to
 157 two factors, one is that the activity of catalyst depends on the chemical composition of
 158 feedstock and another one is the basicity of catalyst. Therefore the transesterification ability of
 159 CaO catalyst was improved with impregnation of the different molar ratio of LiOH exhibited
 160 relatively high conversion of feedstock into biodiesel and CaO: LiOH with 1:0.5 ratio showing
 161 the best conversion of lard oil to biodiesel. This is due to the optimum loading of lithium ions
 162 to CaO, which offers sufficient active sites for the fatty acids to bind with the catalyst as well
 163 as the basic nature of the catalyst. On the basis of preliminary examination on conversion lard
 164 oil to biodiesel, CaO: LiOH with 1:0.5 ratio (named as CaO-0.5 LiOH) was selected for the
 165 optimization of other reaction parameters for biodiesel production.

166

167 3.2. Characterization of nanocatalyst

168

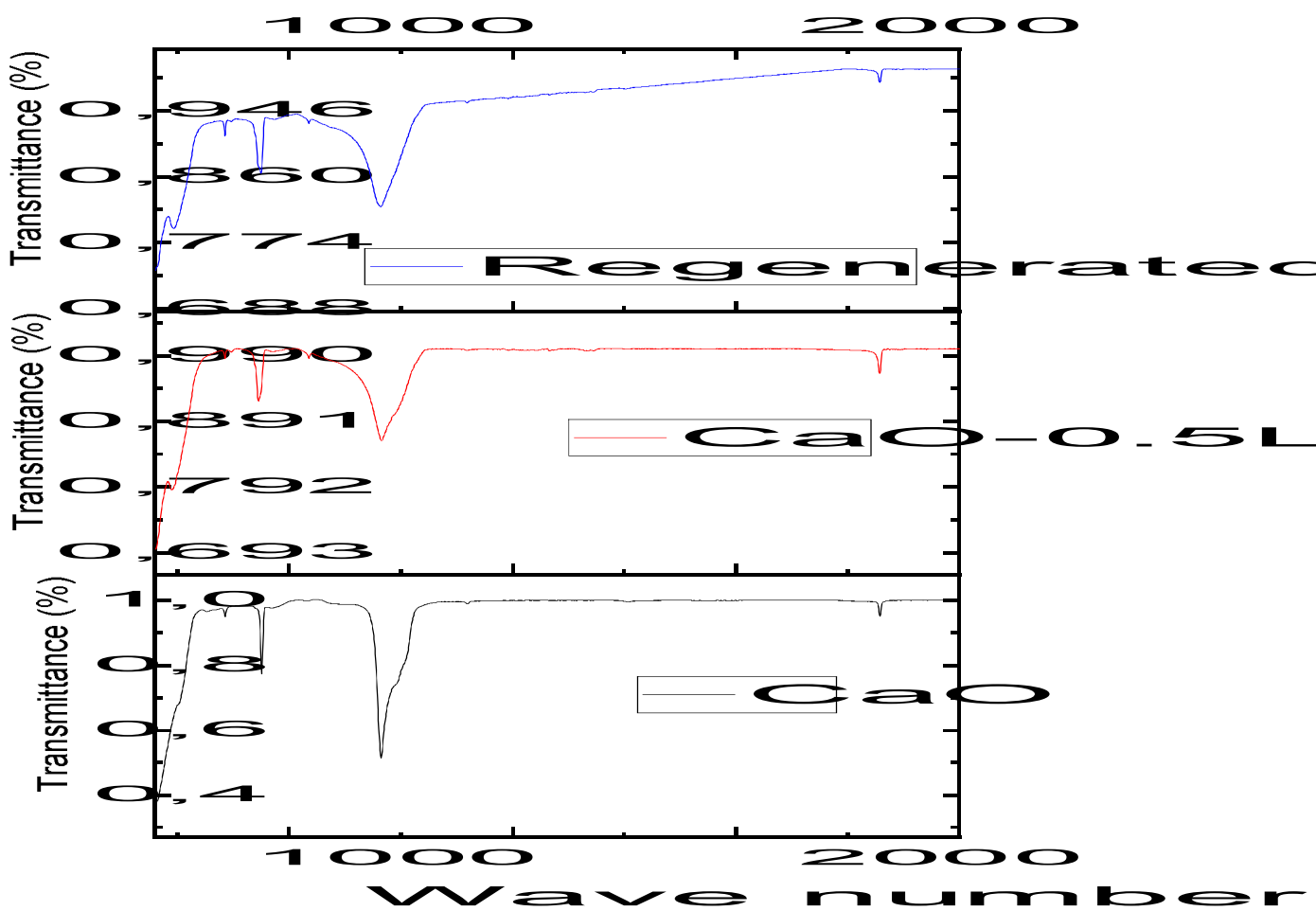
169 The FTIR peaks of CaO, CaO-0.5 LiOH, and regenerated CaO-0.5LiOH are shown in Fig.1.

170 The FTIR spectrum observed in the region 3600 and 1350 cm^{-1} is due to OH stretching and

171 bending respectively. The FTIR band at 489.85 cm^{-1} , 713.57 cm^{-1} , 1087.71 cm^{-1} are possibly

172 due to Li-O stretching ^[15]. Furthermore, the non-regenerated and regenerated CaO-0.5LiOH

173 shows similar FTIR spectra.



174

175 **Fig. 1.** FTIR spectra of CaO, CaO-0.5 LiOH, and regenerated CaO-0.5LiOH

176

The Fig. 2 shows the XRD pattern of bare CaO, Lithium-ion impregnated CaO-0.5 LiOH and regenerated CaO-0.5LiOH nanocatalyst. The X-ray diffraction patterns of unmodified CaO shows a good match to standard reference code ICDD: 98-002-8905. Concisely, the diffractogram lithium ion impregnated CaO-0.5 LiOH provides a consistent harmony to reference standard code ICDD: 98-041-3207. Moreover, lithium ions impregnated peaks are also visible in regenerated CaO-0.5LiOH. Thus, both XRD and FTIR analysis results support the impregnation of lithium ions to CaO nanostructure [15-17].

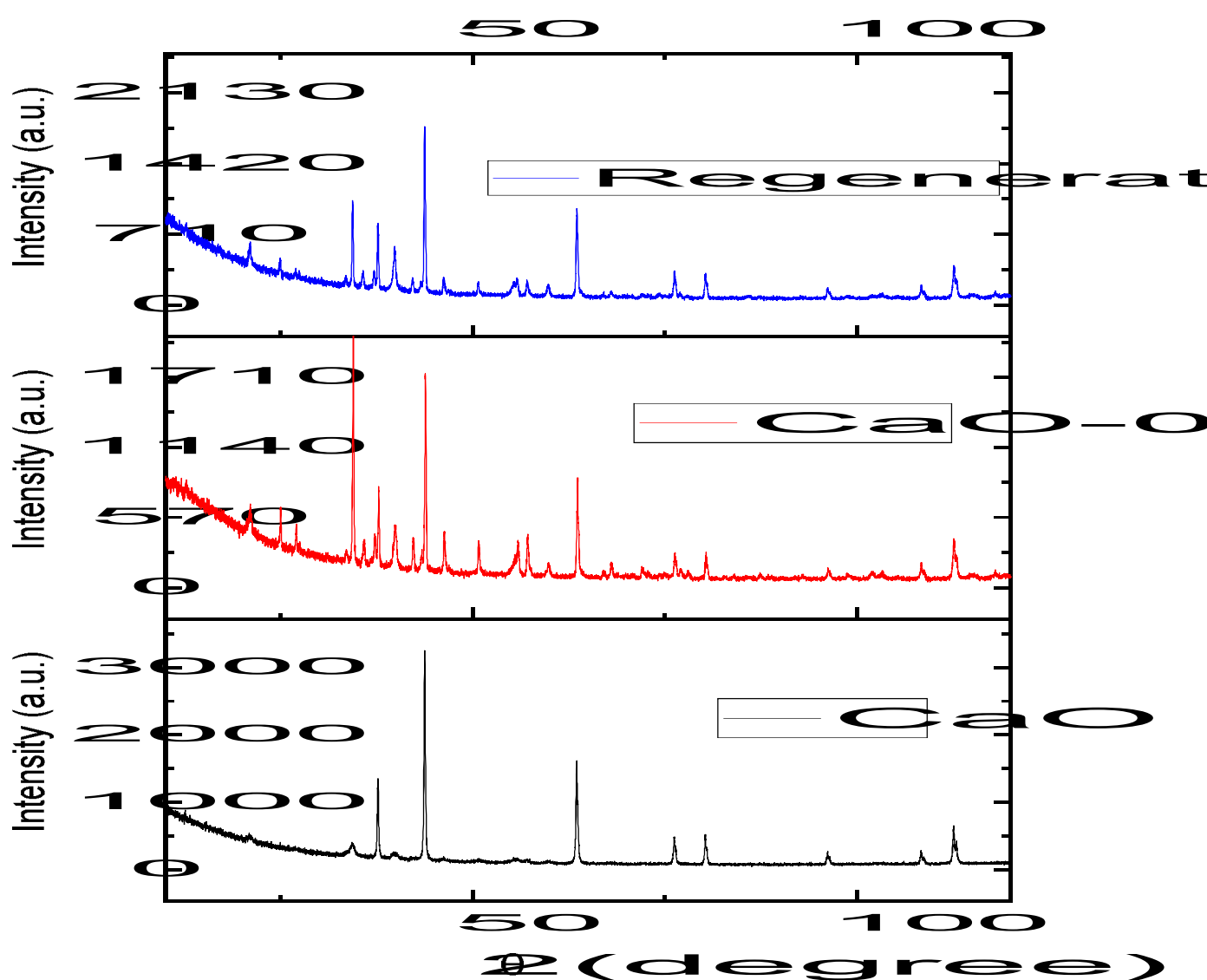


Fig. 2. XRD pattern of CaO, CaO-0.5 LiOH, and regenerated CaO-0.5LiOH

Surface structure and composition of nanocatalyst were studied by SEM. Fig. 3 a and 3 b depict the SEM images of unmodified CaO and CaO-0.5 LiOH respectively. From SEM images it is clear that there was a significant difference in the structure of CaO-0.5 LiOH (1:0.5 molar ratio) due to the impregnation of lithium. The flat surface is possibly due to impregnation of lithium particles on the surface of CaO (Fig. 3 b).

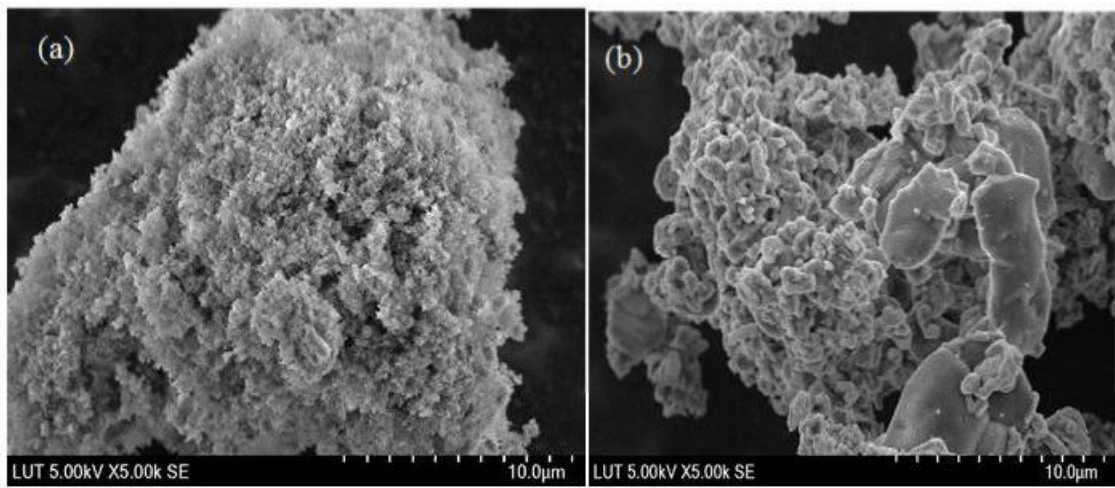
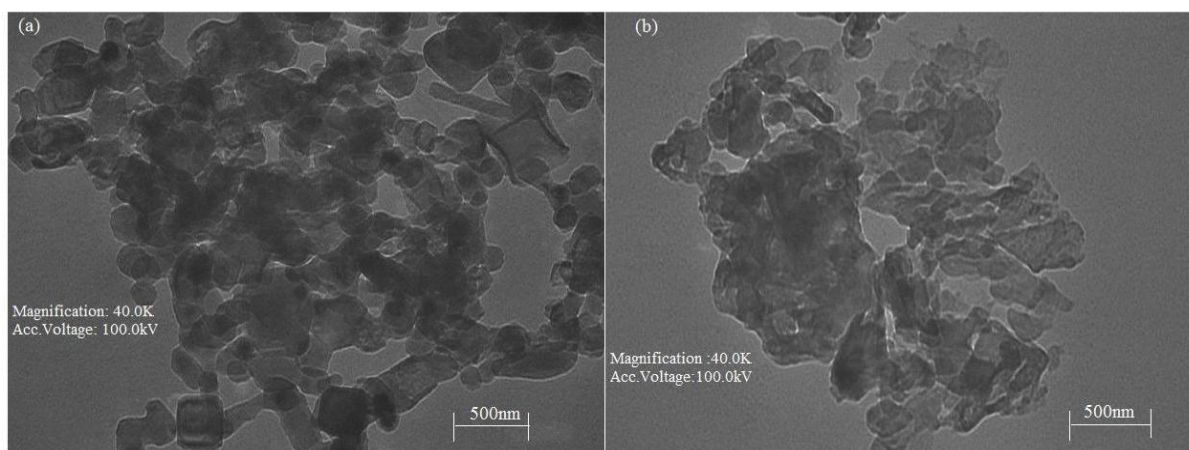


Fig 3. SEM images of (a) CaO (b) CaO-0.5 LiOH

The TEM image of CaO (unmodified) and CaO-0.5 LiOH were depicted in Fig. 4a and 4b respectively. The CaO (unmodified) and CaO-0.5 LiOH catalyst have a particle size of 54.5-127 nm. The TEM results confirmed the size of the particle in the catalyst. Further, after Li-ion impregnation agglomeration of particles was also observed (Fig. 4b).



The nitrogen adsorption/desorption measurements were performed to determine the surface area, pore volume and pore size of the catalyst. The surface area analysis of CaO and CaO-0.5 LiOH using BET is shown in Table 2. The decrease in porosity of CaO-0.5 LiOH was probably due to the insertion of lithium ions in pores. Even though there is a decrease in porosity and surface area, but there is an increase in catalytic activity for transesterification, which is depicted in Table 1. It may be due action of the strength of basic sites in the catalyst which enhance transesterification of oil ^[14-15]. The BET adsorption-desorption isotherm plot for CaO and CaO-0.5 LiOH are given in Fig. 5. The nature of isotherm specifies the presence of mesoporous materials.

Table 2.

The results of Brunauer-Emmett-Teller surface area analysis

	Parameters	Unmodified CaO	CaO-0.5LiOH nanocatalyst
Surface area	BET surface area (m ² /g)	22.09	2.41
	BJH adsorption cumulative	19.14	2.03
	surface area of pores (m ² /g)		

	BJH desorption cumulative surface area of pores (m ² /g)	19.00	2.83
Pore volume	Single point adsorption total pore volume of pores (cm ³ /g)	0.04	0.006
	BJH adsorption cumulative volume of pores (cm ³ /g)	0.08	0.023
	BJH desorption cumulative volume of pores (cm ³ /g)	0.09	0.028
Pore size	Adsorption average pore width	70.60	103.26
	BJH adsorption average pore diameter(A°)	177.30	455.41
	BJH desorption average pore diameter (A°)	189.23	389.56

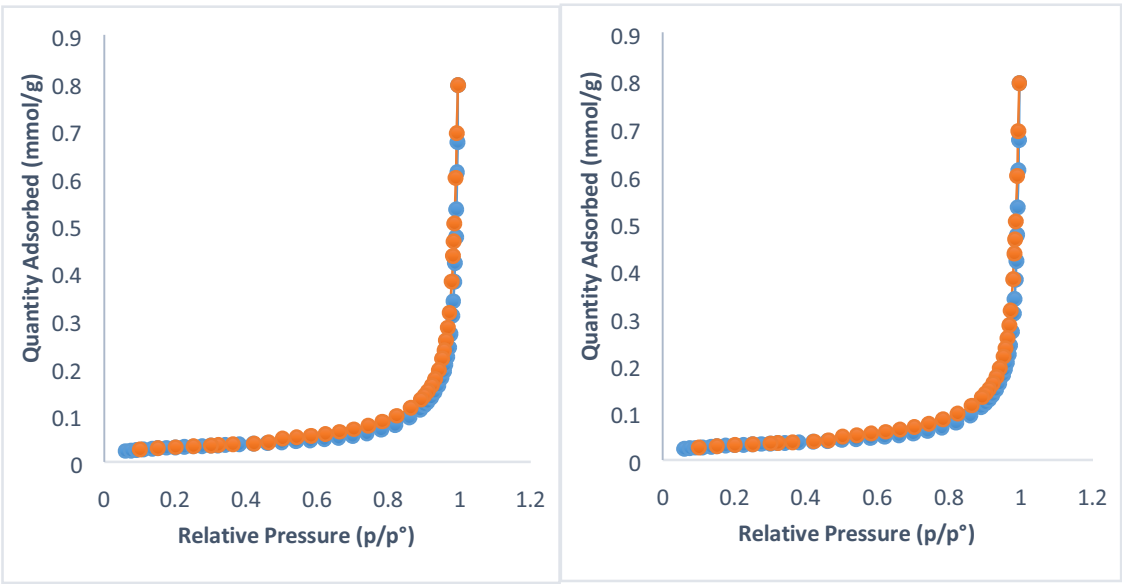
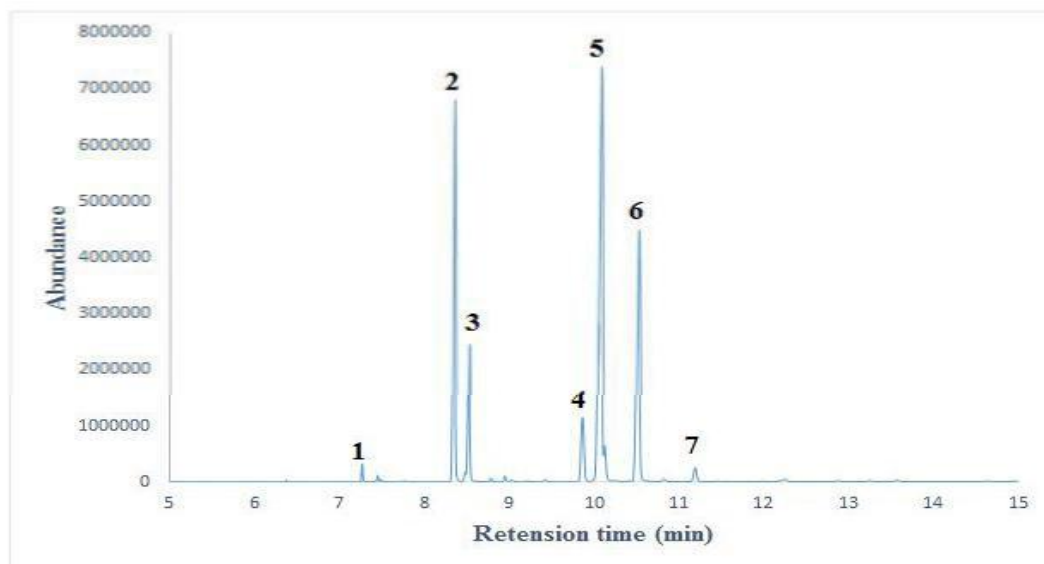


Fig. 5. BET adsorption-desorption isotherm plot of (a) CaO (b) CaO-0.5 LiOH

3.3. Characterization of biodiesel synthesized for Lard oil

223 The biodiesel obtained after transesterification of lard oil with CaO-0.5 LiOH showed in Fig
 224 6. Each peak corresponds to fatty acid methyl esters present in the sample was recognized with
 225 the support of National Institute of Standards and Technology (NIST) 2014 MS library and
 226 depicted in Table 3.



227

228 **Fig. 6.** Illustrates GC-MS spectrum of biodiesel obtained after transesterification with CaO-
 229 0.5 LiOH

230

231 **Table 3.**

232 The composition of biodiesel attained after transesterification with CaO-0.5LiOH

Peak	Retention (min)	time	Library (%)	match	Compound details
1	7.26		91.7		Tridecanoic acid, 12 methyl-methyl ester
2	8.35		91.5		Hexadecenoic acid , methyl ester
3	8.52		94.35		9-Hexadecenoic acid , methyl ester
4	9.87		93.51		Methyl stearate

5	10.08	96.01	13-Octadecenoic acid, methyl ester
6	10.52	96.53	11, 14 - Octadecadienoic acid, methyl
7	11.21	89.09	9,12,12- Octadecatrienoic acid, methyl

233

234

235

236 FAME characterization and percentage conversion of lard oil to FAME was estimated using
237 ¹³C and ¹H NMR spectroscopic analysis respectively. The ¹H NMR and ¹³ C spectrum of fatty
238 acid methyl esters sample attained after transesterification of lard oil using CaO-0.5 LiOH
239 catalyst depicted in Fig. 7a and 7b respectively. It provides sufficient information for FAME
240 characterization and also conforms the presence of fatty acid methyl esters. The 97.33%
241 conversion of lard oil to fatty acid methyl esters was calculated with the equation 1 using the
242 results from ¹H NMR analysis.

243 The signals at 3.64 ppm and at 2.27 ppm in ¹H NMR spectra defines methoxy group (A_{ME}) of
244 FAME and the methylene group (A_{CH2}) respectively. The existence of methyl ester in biodiesel
245 sample obtained via transesterification was confirmed by these two peaks. Other
246 comprehensible peaks such as a signal at 0.93 to 0.97 ppm for the latter methyl group. The
247 presence of olefinic groups confirmed by signal at range of 5.3 ppm whereas peaks in the range
248 of 1.23 to 2.3 represent methylene group^[3,18]. The ¹³C NMR spectra indicates signals at the
249 range of 174 ppm and 51 ppm indicates the existence of ester carbonyl –COO- and C-O
250 respectively. The signals at 132.11 ppm and 126.89 ppm shows unsaturation in synthesized
251 biodiesel. The signals in the region of 22-34ppm supports the presence of -CH₂ group. The
252 existence of methyl ester in biodiesel sample obtained via transesterification was confirmed by
253 the signal at 3.64 ppm and signal at 2.27 ppm in ¹H NMR spectra^[2,3,18].

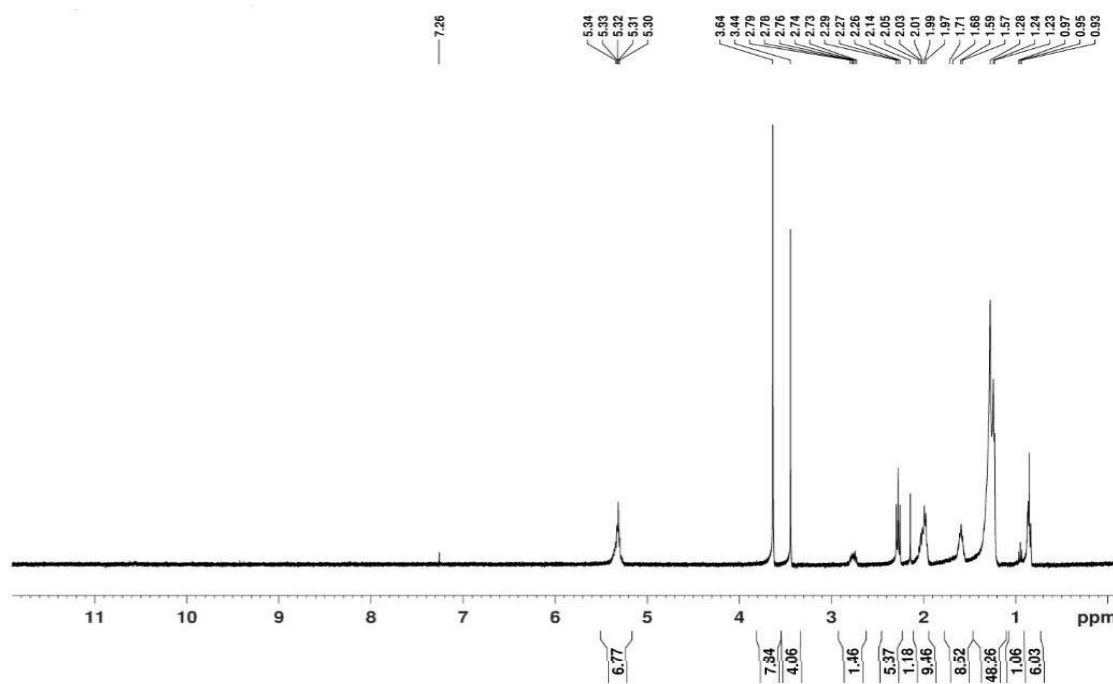


Fig. 7a. The ^1H NMR for the biodiesel sample obtained with CaO- 0.5LiOH

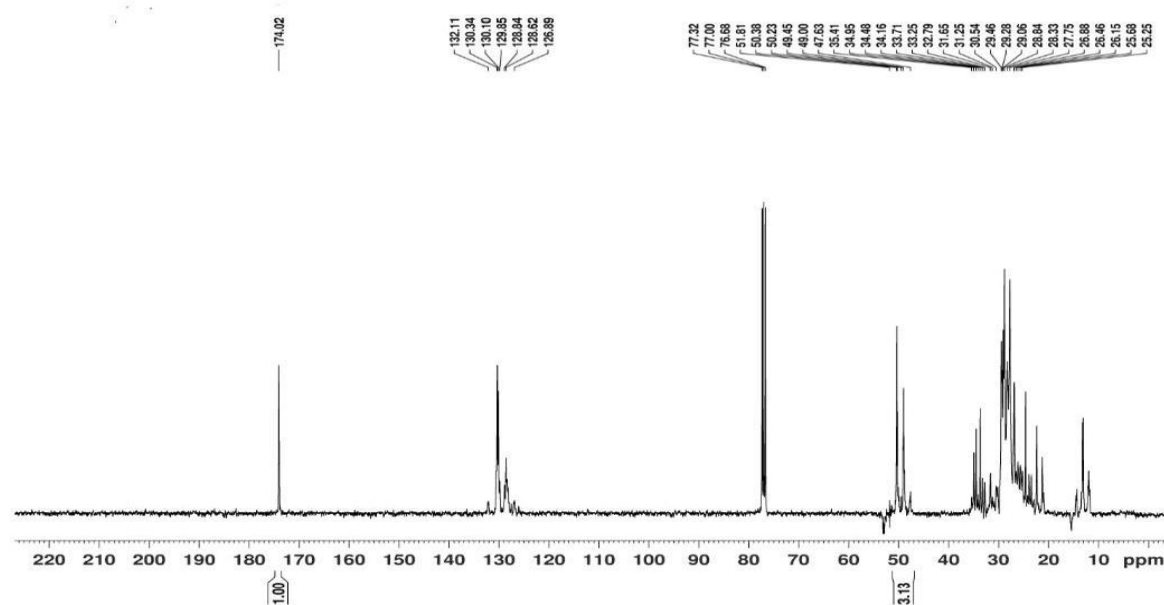


Fig. 7b. The ^{13}C NMR for the biodiesel sample obtained with CaO- 0.5LiOH

3.4. *Influence of various parameters on transesterification*

The Li-CaO nanocatalyst with 1:0.5molar ratio of CaO: LiOH, was found to be the most efficient catalyst for the conversion of lard oil to biodiesel as a result of the initial screening process. In the present work, optimization has been done using the best catalyst (CaO-0.5 LiOH) under different reaction conditions such as varying oil to methanol molar ratio, catalyst amount, reaction time and reaction temperature.

3.4.1 Influence of nanocatalyst amount (weight %) on biodiesel production

The catalyst concentration from 2 wt% to 8 wt% of oil were used to examine the effect of nanocatalyst concentration on biodiesel production. Fig. 8a shows that conversion of lard oil to biodiesel increased with catalyst concentration and highest conversion (97.33%) was achieved at 4 wt% concentration within 2h using 1:6 oil to methanol molar ratio at 65 °C. The rise in catalyst amount above the optimum concentration (4 wt%) showed reduction in biodiesel production due to decrease in the availability of active sites. The extra amount of catalyst leads to saponification of oil which will finally inhibits the reaction ^[2,3]. Based on comparison with reported research studies the present catalyst (CaO-0.5 LiOH) showed better production of biodiesel ^[15,19,20].

3.4.2 Influence of Methanol to oil molar ratio on biodiesel production

The effect of oil to methanol molar ratios in biodiesel production was investigated by increasing oil to methanol ratio from 1:3 to 1:12 using 4 wt% catalyst at 65 °C for 2 h of reaction time. Fig. 8b, shows that FAME conversion increases with increase in methanol concentration up to optimum value (1:6) thereafter it was adversely effected. The reduction in FAME conversion beyond optimum value favors reverse reaction due to increased solubility

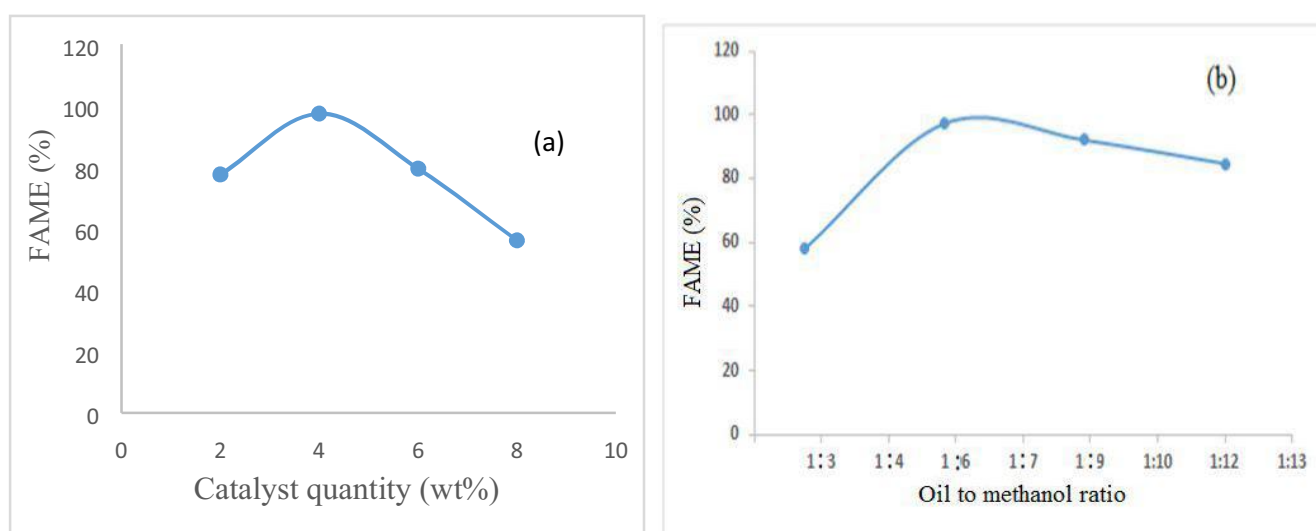
of glycerol to FAME phase^[3,6,21,22]. Therefore 1:6 oil to methanol ratio was used for rest of the optimization studies.

3.4.3 Influence of reaction temperature on biodiesel production

A series of transesterification reactions using 4 wt% catalyst, 1:6 oil to methanol molar ratio for 2 h reaction time were performed at various temperatures to determine the effect of temperature on biodiesel production. The yield of biodiesel increased progressively up to 65 °C beyond that elevated temperature supports saponification reaction and methanol vaporization. The maximum yield of lard oil to fatty acid methyl esters observed at 65 °C shown in Fig 8c^[3, 23,24].

3.4.4 Influence of reaction time on biodiesel production

Fig. 8 d represents a set of reactions conducted for different time intervals using 4 wt% catalyst, 1:6 oil to methanol molar ratio at 65°C. The maximum percentage conversion of FAME obtained at 120 min and after that FAME content remains almost constant.



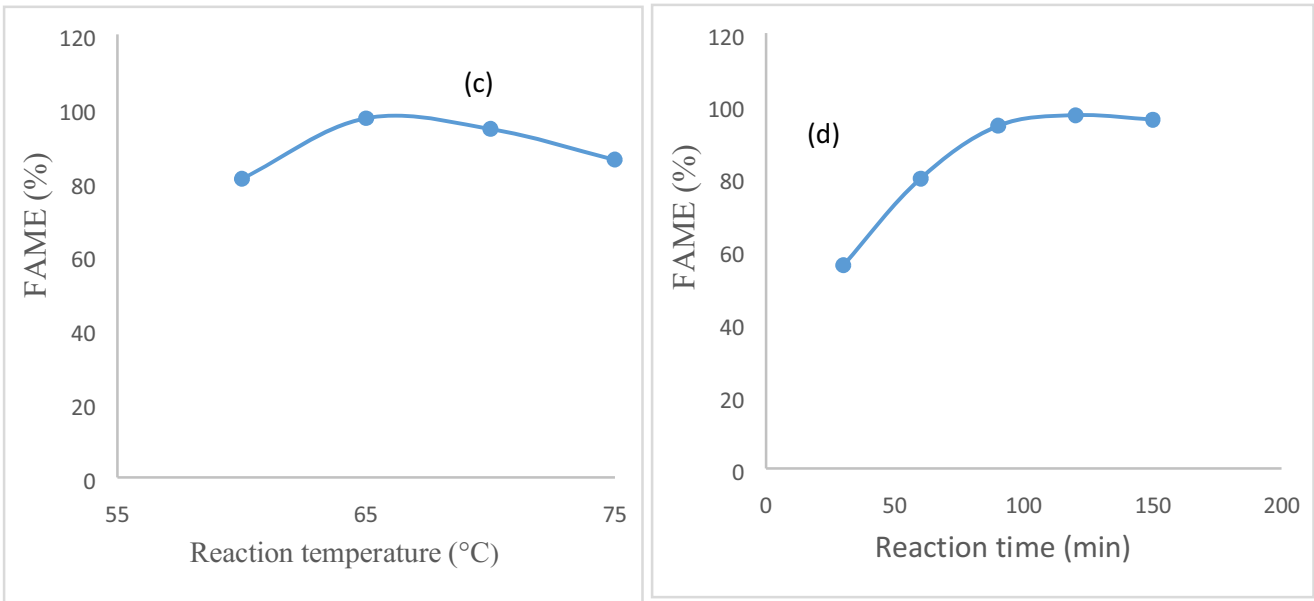


Fig 8. (a). Influence of catalyst amount (weight %) on biodiesel yield (b). Influence of oil to methanol molar ratio on biodiesel yield (c). Influence of reaction temperature on biodiesel yield (d). Influence of reaction time on biodiesel yield.

3.5. Properties of synthesized biodiesel from lard oil

Table 4 illustrates the properties of lard oil methyl esters Li-CaO nanocatalyst with 1:0.5 molar ratio of CaO: LiOH. The properties of synthesized biodiesel were within limits of EN ISO method / ASTM standard methods. Flash point and cetane number of synthesized biodiesel were recorded to be 130 °C and 62.6 respectively. The acid value, density and kinematic viscosity of lard oil methyl ester was found to be 0.282 mg KOH/g, 881.76 kg/m³ and 4.08 mm²/s correspondingly. Besides, all other factors of fuel such as calorific value, cloud point, and pour point are also within EN ISO/ASTM limits. Higher values for features such as acid value, density, viscosity, cetane number, flash point and cloud point leads to corrosion, filter clogging, fuel injection problems, fuel quality, risk in storage and usage of fuel [25-28].

Table 4.

Properties of lard oil methyl esters (CaO-0.5 LiOH catalyst at concentration of 4wt%, 1:6 oil to methanol ratio, reaction temperature 65°C, reaction time 2h)

Property	EN 14214 test method	Limits	Methyl ester from lard oil
Acid value (mg KOH/g)	Pr EN14104	0.5 max	0.282
Density at 15°C (kg/m ³)	EN ISO 12185	860-900	881.76
Kinematic viscosity at 40°C (mm ² /s)	EN ISO 3104	3-5	4.08
Flash point (°C)	EN ISO 2719	-	130
Cloud point (°C)	D2500		7
Pour point (°C)	ISO 3016		5
Cetane point	EN ISO 5165	≥51	62.6
Calorific value (MJ/kg)	D6751		41.23

3.6. Regeneration, reusability and stability of nanocatalyst

Initially the regeneration of catalyst after transesterification reaction was performed by separating it from lard oil methyl esters and glycerol by centrifugation. After centrifugation, the obtained catalyst was washed a few times with heptane to remove impurities. The washed catalyst was dried at 70 °C and calcined at 400 °C for 4 h to reactivate the catalyst [2]. Fig. 9a, indicates that catalyst activity decreased from 97.33 % to 94.4 % in five cycles. However, the decrease in catalytic efficiency might be due to reduction in stability of catalyst. To evaluate

the stability of catalyst by determining the leached metal ion concentration after each run with the help of inductively coupled plasma (ICP, Agilent 5110). The Fig 9b shows Ca ion leaching was null up to 5 cycles where as the Li concentrations in solution are less than 0.32mg/L. Moreover, the synthesized catalyst showed better conversion rate and reusability compared to other reported lithium doped catalyst^[17,19,20].

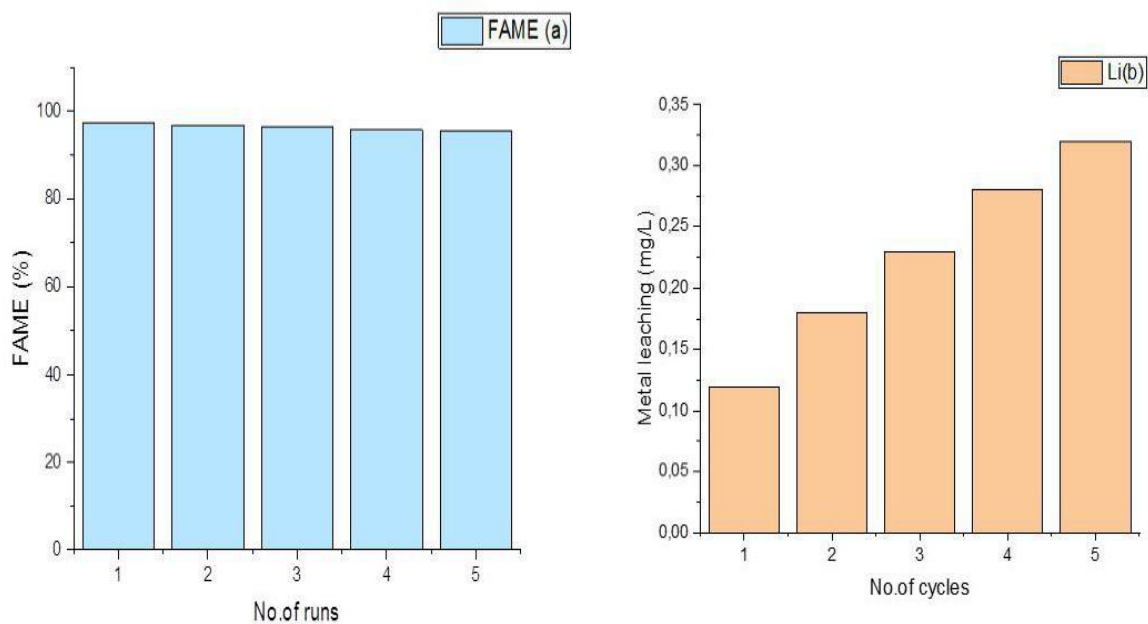


Fig. 9 a. Reusability analysis of CaO-0.5LiOH and (b) stability analysis of CaO-0.5LiOH

4. Conclusion

The conversion of lard oil to biodiesel was successfully conducted with help of CaO-0.5 LiOH (1:0.5 molar ratio). The improved properties of nanocatalyst were obtained due to impregnation of lithium ions to CaO nanostructure and showed better conversion in comparison to unmodified CaO. The impregnation of lithium ions to CaO nanostructure confirmed by FTIR, XRD, SEM, TEM. The best activity was attained at optimum loading of Li ions to CaO in 0.5:1 molar ratio. The nanocatalyst showed 97.33% fatty acid methyl ester content using a 4wt %

catalyst amount, 1:6 oil to methanol ratio at 65 °C with a reaction time of 120 minutes. The properties of biodiesel such as acid value, density, kinematic viscosity and flash point were within the EN 14214 limits. All these results indicate that lithium-ion impregnated CaO nanocatalyst is an efficient catalyst for the production of superior quality biodiesel from lard oil as a feedstock. The reusability of nanocatalyst also exhibited favorable result, which makes it cost effective and eco-friendly.

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