



## Transesterification of Jatropha and Karanja oils by using waste egg shell derived calcium based mixed metal oxides



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### ABSTRACT

Solid base heterogeneous catalysts are one of the promising materials for the transesterification of vegetable oils because these catalysts are generally more reactive than solid acid catalysts which require very severe operating conditions. Calcium oxide has shown good catalytic activity due to its high basicity which is required for transesterification of triacylglycerides (TAGs). In the present study, the transesterification of non-edible, high free fatty acid containing Jatropha and Karanja oils was studied by using waste chicken egg shell derived calcium (i.e. CaO(cesp)) based mixed metal oxides (M-CaO; M = ZnO, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) as heterogeneous catalyst. A comparison was also made on the catalytic performance of these prepared catalysts. The catalyst characterizations were done by XRD, SEM, TGA, FT-IR and BET techniques. The effectiveness of the catalysts was highly influenced by the calcination temperature. ZnO-CaO(cesp) catalyst was found to be the most efficient catalyst among all. The maximum conversion for the transesterification of Jatropha and Karanja oils were achieved using 5 wt% catalyst, 65 °C temperature and 12:1 methanol/oil ratio. The catalyst could be re-used effectively during four cycles. Use of the CaO(cesp) based mixed oxides made the process more environmental benign and economical. The biodiesel prepared has shown good fuel characteristics as per EN, ASTM and IS standards.

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## 1. Introduction

Increasing industrialization, depleting fossil fuel resources, environmental pollution and global warming, continuously growing energy demand are some of the major concerns to find viable resources of alternative and renewable energy. Biodiesel (fatty acid methyl ester, FAME), which is renewable, biodegradable and non-toxic fuel, produced from the transesterification of vegetable oils, has been globally accepted as a viable alternative to fossil-based diesel fuel [1–4]. Besides, an alternative to diesel fuel, biodiesel could be employed as a precursor for the preparation of diesel fuel additives like lubricity and cetane number improvers, and also considered a cleaner burning fuel due to essentially free of sulphur [5,6].

Usually, both homogeneous and heterogeneous catalysts are being used for the biodiesel production from vegetable oils and animal fat. In homogeneous catalysis, both strong acid and strong base can be used as catalysts for transesterification of triglycerides with short chain alcohols like methanol and ethanol. Due to low

corrosive nature, liquid bases are generally preferred over liquid acid catalysts like sulfuric and sulfonic acids, etc. [5]. Hydroxides and methoxides of sodium and potassium are the frequently used homogenous base catalysts for transesterification reactions [7]. Although, homogeneous catalysis provides high reaction rate under mild reaction conditions, yet these catalysts have several drawbacks such as corrosive nature, non-recyclable, non-eco-friendly and formation of sodium or potassium ion contaminated biodiesel and glycerol. Homogeneous catalysts also produce large amount of waste water [7,8]; which reduces their attractiveness. Therefore, the use of homogeneous catalyst requires more refined feedstocks for biodiesel production which makes the process uneconomical. However, heterogeneous catalysts have the potential to overcome the problems associated with the homogeneous catalysts, specially used for transesterification of triglycerides to produce biodiesel. Heterogeneous catalysts provide easier separation, catalyst free product formation and no requirement of product neutralization and purification steps [9–11]. Moreover, less consumption, and reusability of heterogeneous catalysts makes the biodiesel production much economical in comparison to homogeneous catalyzed processes [12–14]. A large number of heterogeneous solid acid and solid base catalysts have been investigated for

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transesterification of vegetable oils which include ion exchange resins [15], heteropolyacids [16,17], sodium aluminate [18], zeolites and metal catalysts [19–22], alkali earth metal oxides [23–26], alkali-impregnated alumina [27–29], hydrotalcites [30,31], Al<sub>2</sub>O<sub>3</sub>-supported alkali metal oxide catalysts [32,33], K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [34], KF/γ-Al<sub>2</sub>O<sub>3</sub> [35], and magnetic composites such as Ca/Al/Fe<sub>3</sub>O<sub>4</sub> [36], etc. Among all heterogeneous catalysts used for biodiesel production, calcium oxide based catalysts have received much interest and have been extensively studied in recent time [5,37–41]. This is because of the benefits associated with the calcium oxide based catalysts such as mild reaction condition, non-toxicity, high basicity, relatively economical [11], less impact on environment, excellent yield of biodiesel produced and its lower solubility in biodiesel [42–47].

More recently, research interest has been grown towards the production of biodiesel using economic and natural calcium carbonate sources such as waste shells of egg [4,22,48,49], golden apple snail and Meretrix venus [22], oyster shell [50], and mud crab [51], etc. However, the high moisture sensitivity and lesser reactivity towards transesterification reaction is the major problem associated with calcium oxide derived from natural sources. The catalytic property of pure CaO could be improved by preparation of its mixed oxides with active metal oxides [5,25,52]. Chicken egg shell is a rich source of calcium carbonate. It is composed of 85–95% calcium carbonate, 1.4% magnesium carbonate, 0.76% phosphate, 4% organic matter and trace amount of sodium, potassium, zinc, manganese, iron and copper [53,54]. Calcination of chicken egg shell at 600–900 °C produces basic calcium oxide which can be used as basic catalyst for production of biodiesel [37–47].

Eggs are consumed worldwide as a multi nutrition source, due to their huge consumption the waste eggshells generated, pose a solid waste disposal problem, particularly in an over populated country like China and India. Several methods have been identified to use the waste eggshells in various applications like for removal of dyes and metal contaminants from industrial waste water, etc. [53,55–59]. Mostly, the biodiesel production using egg shell derived CaO based catalysts was achieved with edible oils (palm oil and soybean oil). However, in Indian perspective, it is quite difficult to produce biodiesel from the edible oil sources because of the non-availability of adequate feedstock. Thus the use of non-edible oils (Jatropha, Karanja, etc.) could be more economic and viable for biodiesel production in Indian perspective. Such feedstocks are less expensive and thus have a potential to reduce the overall cost of biodiesel production. However, during literature survey it was found that very few reports are available for transesterification of high acid value feeds such as Jatropha and Karanja oils employing waste egg shell derived calcium oxide based heterogeneous catalysts.

Therefore, the present study explores the preparation of waste egg shell derived Ca based mixed metal oxides of Zn, Fe, Mn and Al, and their effectiveness for transesterification of non-edible oils (Jatropha and Karanja) of Indian origin. The prepared catalysts were characterized by X-ray diffraction (XRD), surface area (BET), N<sub>2</sub> adsorption–desorption, TGA, SEM and FT-IR. The fatty acid composition of produced biodiesel was characterized by GC and the basic fuel characteristics of biodiesels were investigated as per ASTM and EN standards.

## 2. Methods

### 2.1. Materials

Chicken eggshell were collected from university (UPES) student's dining hall kitchen to prepare the CaO(cesp). Nitrates of Zn, Fe, Mn and Al were used as metal precursors. The analytical

grade metal precursors were purchased from Sigma Aldrich India, and Methyl alcohol (99.8% purity) was purchased from S.D. Fine Chemicals Ltd. Non-edible feedstocks (Jatropha and Karanja oils) were purchased from local market. The main physical properties, including the free fatty acid content of crude Jatropha and Karanja oils are listed in Table 1. All the chemicals were used as received without further purification.

### 2.2. Preparation of catalyst

The collected chicken eggshells were rinsed thoroughly with tap water until the organic matter was removed. The washed eggshells were again rinsed twice with distilled water and were dried in hot air oven at 100–120 °C for 24 h. The dried eggshells were powdered in an agate mortar and the powder form was calcined at three different temperatures 500, 700 to 900 °C in muffle furnace for 4 h (heating rate 2° min<sup>-1</sup>) and then stored in a desiccator. Material thus obtained was the CaO(cesp) and used for transesterification and preparation of metal impregnated CaO(cesp) based catalysts. The incorporation of metals was carried out by impregnation of the metal oxide on CaO support by using wet-incipient method with aqueous solutions of their metal nitrates. 5 gm of CaO(cesp) was suspended in 30 mL of deionized water. To this 5 mL of aqueous solution of 3 wt% of metal nitrate was added. The reaction mixture thus obtained was stirred for 4 h at room temperature. The reaction mixture was filtered and the solid material was dried in air, then in oven at 120 °C for 4 h and finally calcined in a muffle furnace at three different temperatures 500, 700 to 900 °C in muffle furnace for 4 h (heating rate 2° min<sup>-1</sup>). The catalysts thus prepared were characterized by powder XRD, BET surface area measurement, SEM and FT-IR techniques.

### 2.3. Characterization of catalyst prepared

The X-ray diffraction patterns of CaO(cesp) and metal impregnated CaO(cesp) based catalysts prepared were recorded on X'pert PRO Multi-Purpose X-ray diffractometer, PANalytica) with monochromated Cu K $\alpha$  radiation ( $\lambda$ -1.54 Å). The scanning range of 2 $\theta$  was set between 2° and 70°. N<sub>2</sub> adsorption–desorption using a Belsorp instrument of samples evacuated at 350 °C for 3 h before exposure to nitrogen gas at 77 K. The Brunauer–Emmett–Teller (BET) equation was used to determine specific BET surface area and pore-volume. Pore size was calculated from desorption isotherms by using Barrett–Joyner–Halenda (BJH) method. The FT-IR spectra were recorded in KBr (0.3% w/w) disks in the wavelength region of 4000–400 cm<sup>-1</sup> with a Perkin Elmer 1760 X FT-IR

**Table 1**  
Physical Properties of Jatropha and Karanja crude oil [54–56].

S. No	Properties	Jatropha Oil	Karanja Oil
1	Density (g/cm <sup>3</sup> ) at 15 °C	0.91	0.94
2	Viscosity (mm <sup>2</sup> /s) at 40 °C	24.5	38.7
3	Calorific value (MJ/kg)	35.6	29.5
4	Acid value (mg of KOH/g)	12.5	17.5
5	Moisture content (mg/kg)	0.059%	0.063%
6	Flash point (°C)	176	198
7	Free Fatty acid composition		
	Palmitic (C16:0)	17.6	2.2
	Palmitoleic (16:1)	0.7	–
	Stearic (C18:0)	8.1	4.8
	Oleic (C18:1)	41.8	61.2
	Linoleic (C18:2)	31.5	25.2
	Arachidic (C20:0)	–	0.9
	Elcosenoic (C20:1)	–	1.3
	Behenic (C22:0)	–	2.8
	Lignoceric (C24:0)	–	1.4
	Others	0.3	0.2

spectrometer. The surface morphology of the prepared catalysts was analyzed by SEM using scanning electron microscope Quanta 200F (30 kv) instrument. Basic strength of the CaO(cesp) and other metal impregnated CaO(cesp) catalysts was determined by using Hammett indicators. To optimize the calcination temperature range TG analysis of the waste eggshell powder was done by using NETZSCH TG 209F1 Libra TGA209F1D-0105-L Thermal analysis machine under a flow of nitrogen. The sample weight used was about 20 mg, and the temperature ranged from 35 °C to 950 °C with a ramping rate of 10.0 (°C/min).

#### 2.4. Transesterification of *Jatropha* and *Karanja* oils with methanol

Transesterification of *Jatropha* and *Karanja* oils with methanol were carried out in a transesterification reactor with 250 mL three-neck round bottom flask fitted with an overhead stirrer and water-cooled reflux condenser. The reactor was also equipped with an oil bath with digital temperature controller for heating purpose. Optimized amount of catalyst (see Section 3.1.6) was suspended in required volume of methanol and heated under a control temperature of 65 °C ( $\pm 2$  °C) for 5 min, and then the desired amount of oil was added to the reaction mixture. The reaction mixture was stirred at 500 rpm for required time duration (1 h for *Jatropha* and 1.5 h for *Karanja*). After the completion of the reaction the catalyst was separated by filtration and the excess methanol was recovered by evaporation at reduced pressure. The mixture was then washed three to four times with lukewarm distilled water to remove the glycerol formed. The mass thus obtained was dried with anhydrous sodium sulphate. The transesterification of oil was carried out under different reaction conditions in order to optimize the best condition, such as catalysts loading from 1 to 10 wt%, reaction time from 0.5 to 2 h, reaction temperature from 50 °C to 70 °C and methanol to oil ratio from 5:1 to 18:1. The reaction condition for maximum conversion of oil into biodiesel was optimized by analyzing the reaction mixture by GC–MS. The detailed conditions of GC–MS were described in our previous reports [60–62].

### 3. Results and discussion

#### 3.1. Characterization of the catalysts

##### 3.1.1. XRD analysis

The XRD patterns of CaO(cesp) calcined at 900 °C was investigated and it showed the complete transformation of CaCO<sub>3</sub> to CaO(cesp) (Fig. 1a). The intense and sharp peaks at  $2\theta$  (°): 31.35, 36.58, 52.96, 61.64 and 66.27 were observed, which can be indexed in the cubic structure of CaO(cesp) (JCPDS 00-001-1160). The XRD patterns of Zn/CaO(cesp) which was calcined at three different temperatures 500, 700 and 900 °C showed the combined diffraction pattern along with the formation of ZnO in hexagonal phase (JCPDS 00-003-0888) with low intensity peaks at  $2\theta$  (°): 31.84, 32.33, 34.51, 37.37, 38.55, 40.82, 41.31, 43.39, 47.62, 48.71, 52.17, 55.81, 56.60 and 62.39. Better hexagonal phase formation was observed for ZnO calcined at 900 °C. The XRD pattern with important peaks and their corresponding planes are presented in Fig. 2a. Similarly, the XRD patterns of MnO<sub>2</sub>/CaO(cesp) (JCPDS 00-005-0600), Fe<sub>2</sub>O<sub>3</sub>/CaO(cesp) (JCPDS 00-002-0272) and Al<sub>2</sub>O<sub>3</sub>/CaO(cesp) (JCPDS 00-002-1124) were also recorded for the catalysts calcined at 500, 700 and 900 °C; and the important peaks along with their corresponding planes are presented in Fig. 2b–d respectively. Calcination of the Mn/CaO(cesp), Fe/CaO(cesp) and Al/CaO(cesp) at 900 °C exhibited better diffraction patterns in comparison to the samples calcined at lower temperatures i.e. 500 and 700 °C. Peaks observed at  $2\theta$  (°): 39.5, 43.5, 47.7 and 48.8 indicate

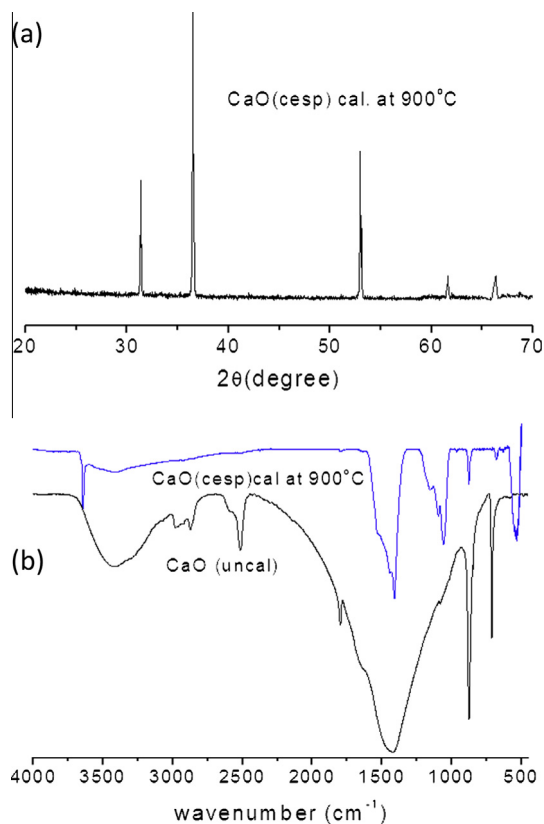


Fig. 1. (a) X-ray diffraction spectrogram of CaO(cesp); (b) FTIR spectra of CaO(cesp).

the presence of Mn (Fig. 2b); peaks at  $2\theta$  (°): 26.0, 35.9, 40.1, 43.1, 47.7, 48.3 and 57.5 show the presence of Fe (Fig. 2c); whereas peaks at  $2\theta$  (°): 33.0, 35.0, and 43.0 due to presence of Al (Fig. 2d). The occurrence of peaks for the catalysts calcined at 900 °C reveals their crystalline structures and also indicates that the catalysts should be thermally activated before being used for transesterification reactions [51].

##### 3.1.2. FT-IR analysis

The FT-IR spectra for un-calcined and calcined CaO(cesp) are shown in (Fig. 1b). Un-calcined CaO(cesp) exhibited the sharp absorption bands for CO<sub>3</sub><sup>2-</sup> at 1422 (asymmetric stretching), 875 (out of plane bending) and 707 cm<sup>-1</sup> (for in plane bending) respectively. However, a shift to higher energy of absorption bands for CO<sub>3</sub><sup>2-</sup> was observed at 1450, 1050, 875 and 525 cm<sup>-1</sup> respectively, due to decrease in reduced mass of the group CO<sub>3</sub><sup>2-</sup> upon calcination at 900 °C. The moderate to weak absorption bands at 2980, 2875 and 2515 cm<sup>-1</sup> correspond to organic matters, were observed for un-calcined CaO(cesp), which disappeared completely when the catalysts was calcined at 900 °C. A broad absorption band around 3432 cm<sup>-1</sup> was observed due to the stretching vibration mode of associated water molecule. However, absorption band for associated water molecule was disappeared when the catalyst was calcined at 900 °C and a sharp absorption band for OH stretching was appeared at 3640 cm<sup>-1</sup>. The IR absorption band pattern for uncalcined and calcined eggshells agrees with the reported literature [49]. The FT-IR was also recorded for all the metal impregnated catalysts calcined at 500, 700 and 900 °C, and are presented in Fig. 3a–d respectively. For Zn impregnated CaO(cesp) catalyst moderate to sharp absorption bands at 678, 612, 597, 528, 510 and 483 cm<sup>-1</sup> correspond to the stretching vibrations for Zn–O bond (Fig. 3a). The less intense band at 3642 correspond to OH stretching of CaO(cesp), while the absorption bands at 1534,

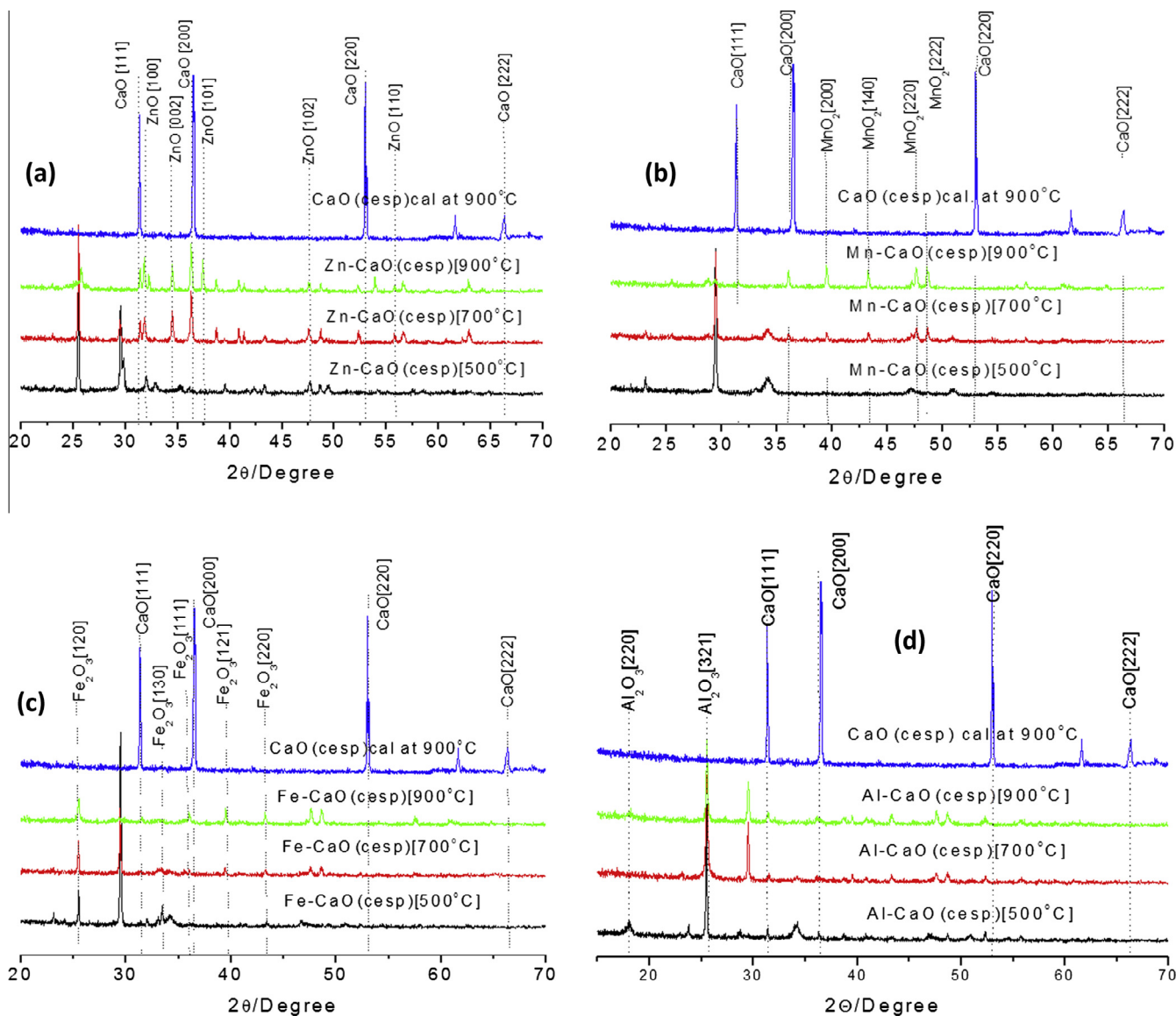


Fig. 2. X-ray diffraction spectrogram of Zn-CaO(cesp) (a), Mn-CaO(cesp) (b), Fe-CaO(cesp) (c) and Al-CaO(cesp) (d).

1408, 1155 and 873  $\text{cm}^{-1}$  corresponds to bending vibration modes of CaO(cesp). Similarly, the FT-IR of  $\text{MnO}_2/\text{CaO(cesp)}$ ,  $\text{Fe}_2\text{O}_3/\text{CaO(cesp)}$  and  $\text{Al}_2\text{O}_3/\text{CaO(cesp)}$ , calcined at 500, 700 and 900  $^\circ\text{C}$  respectively, were also recorded (Fig. 3b-d, respectively). Calcination of the  $\text{MnO}_2/\text{CaO(cesp)}$ ,  $\text{Fe}_2\text{O}_3/\text{CaO(cesp)}$  and  $\text{Al}_2\text{O}_3/\text{CaO(cesp)}$  at 900  $^\circ\text{C}$  exhibited better absorption bands in comparison to the samples calcined at lower temperatures. Besides, the characteristic bands of CaO(cesp), absorption bands at 677, 613, 594 and 519  $\text{cm}^{-1}$  for Fe impregnated CaO(cesp); absorption bands at 737, 679, 613, 595 and 526  $\text{cm}^{-1}$  for Mn impregnated CaO(cesp); absorption bands at 2137, 674, 647, 613, 595 for Al impregnated CaO(cesp) were observed. These absorption bands correspond to respective metal-oxygen stretching vibration modes.

### 3.1.3. BET surface area determination

The specific surface areas of prepared catalysts were determined by BET surface area measurement. The surface areas of CaO(cesp) and M-CaO(cesp) (M: ZnO,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ) were determined. The results are summarized in Table 2.

The results from Table 2 clearly indicate that the specific surface area of metal impregnated CaO(cesp) catalysts is higher than neat

CaO(cesp). It was also observed that the surface areas of the catalysts were increased with the calcination temperature. This may be because of the maximum conversion of  $\text{CaCO}_3$  to CaO at 900  $^\circ\text{C}$ . ZnO impregnated CaO(cesp) has the maximum surface area and pore volume. Whereas the surface area and pore volume of other metal impregnated CaO(cesp) catalysts were comparatively less than that of Zn impregnated CaO(cesp). This may be because of the higher dispersion ability of Zn metal in comparison to rest of the metals used [52]. The differences in surface areas of M-CaO(cesp) and CaO(cesp) indicate that the metal impregnated catalysts should have greater activity than neat CaO(cesp).

### 3.1.4. Basicity determination of prepared catalysts

Basicity of the catalysts was measured conducting Hammett indicator experiments. The experiments were conducted to determine the H range of basic sites in each catalyst. 20 mg of sample was shaken with 5 ml of moisture free ethanolic solution of Hammett indicator and left to attain equilibrium for 2 h. Bromothymol blue,  $\text{pK}_a = 7.2$ ; phenolphthalein,  $\text{pK}_a = 9.8$ ; 2,4,6-Trinitrobenzene amine,  $\text{pK}_a = 12.2$ ; 2,4-dinitroaniline,  $\text{pK}_a = 15.0$ ; 4-chloride-2-nitroaniline,  $\text{pK}_a = 17.2$  and nitroaniline  $\text{pK}_a = 18.4$

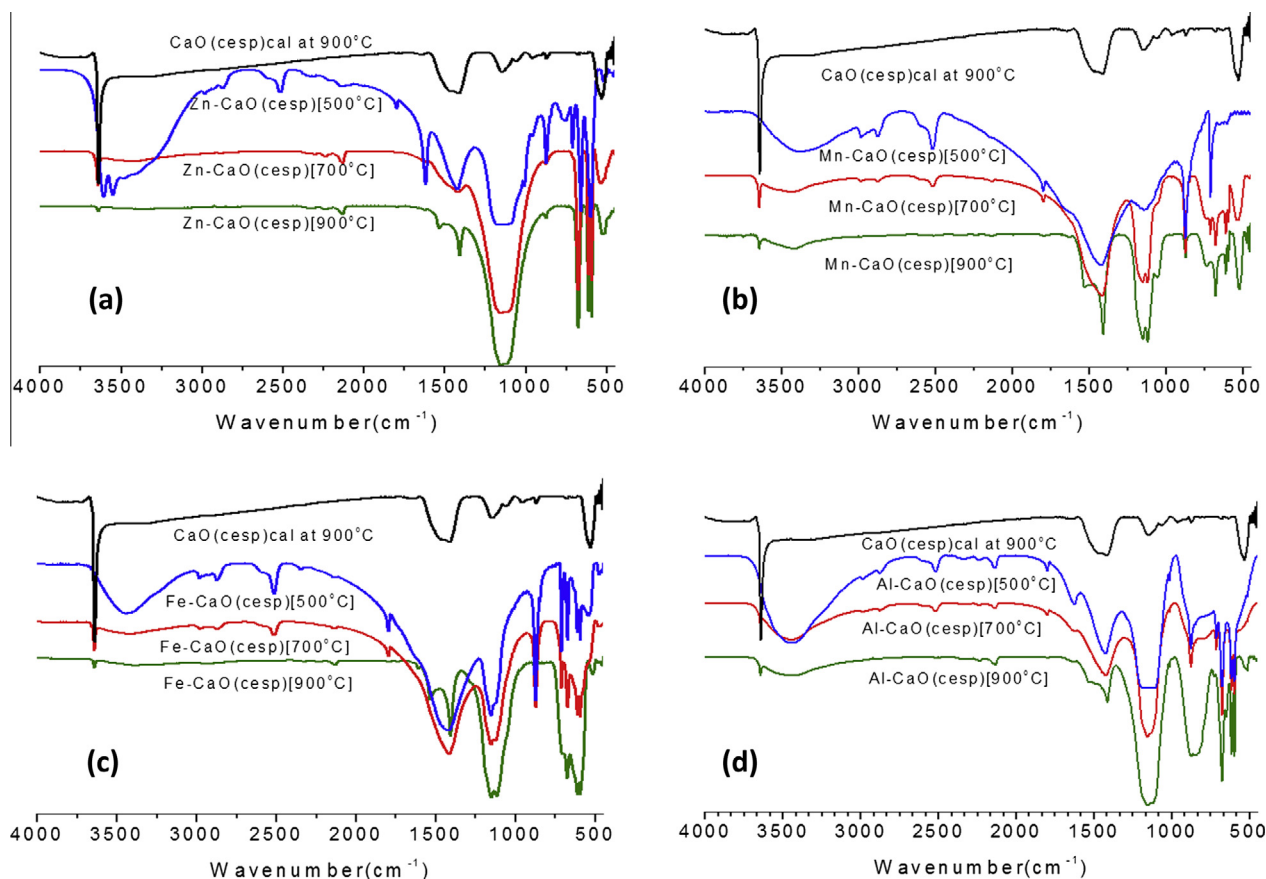


Fig. 3. FTIR spectra of Zn–CaO(cesp) (a), Mn–CaO(cesp) (b), Fe–CaO(cesp) (c) and Al–CaO(cesp) (d).

**Table 2**  
BET surface areas, pore volume, pore diameter and basicity of catalysts.

S. No	Catalyst	Cal. temp. (°C)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore diameter (Å)	Basic strength (H <sub>L</sub> )
1	CaO (cesp)	<b>900</b>	<b>1.4</b>	0.01732	nd	7.2 < H <sub>L</sub> < 9.8
		700	1.3	0.01462	nd	nd
		500	1.1	0.01202	nd	nd
2	ZnO–CaO (cesp)	<b>900</b>	<b>12.1</b>	0.16671	116.4	15.0 < H <sub>L</sub> < 18.4
		700	11.6	0.14712	nd	15.0 < H <sub>L</sub> < 17.2
		500	10.7	0.11671	nd	15.0 < H <sub>L</sub> < 17.2
3	MnO <sub>2</sub> –CaO (cesp)	<b>900</b>	<b>9.5</b>	0.10844	232.4	15.0 < H <sub>L</sub> < 17.2
		700	8.4	0.07542	nd	12.2 < H <sub>L</sub> < 15.0
		500	6.9	0.06104	nd	12.2 < H <sub>L</sub> < 15.0
4	Fe <sub>2</sub> O <sub>3</sub> –CaO (cesp)	<b>900</b>	<b>7.3</b>	0.08816	268.1	15.0 < H <sub>L</sub> < 17.2
		700	6.8	0.05987	nd	15.0 < H <sub>L</sub> < 17.2
		500	6.1	0.05313	nd	10.0 < H <sub>L</sub> < 12.2
5	Al <sub>2</sub> O <sub>3</sub> –CaO (cesp)	<b>900</b>	<b>3.1</b>	0.03314	271.0	10.0 < H <sub>L</sub> < 12.2
		700	2.9	0.02342	nd	10.0 < H <sub>L</sub> < 12.2
		500	2.4	0.01932	nd	9.8 < H <sub>L</sub> < 10.2
6.	ZnO–CaO (cesp) after 4th cycle	<b>900</b>	<b>9.8</b>	0.10057	nd	12.2 < H <sub>L</sub> < 15.0

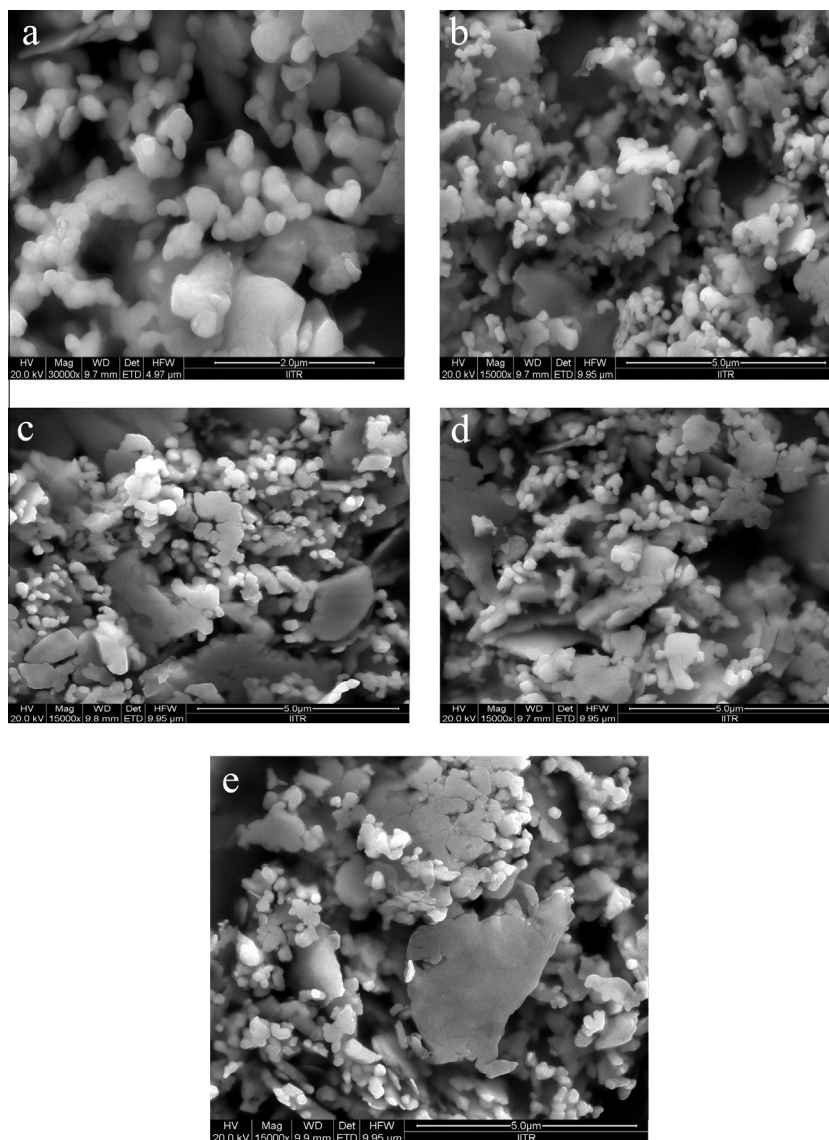
Values given in bold types represent optimized parameters.

are the Hammett indicators used for this experiments. The basicity of the catalyst was determined by titrating with 0.02 mol/L anhydrous ethanolic solution of benzoic acid using Hammett indicator. The color change of the solution was observed. When the solution

exhibits a color change, this indicates that the basic strength of the catalyst is stronger than the indicator used. However, when the solution produces no color change, the basic strength of the catalyst is weaker than that of the indicator used [63,64]. The results obtained for basicity of the catalysts are shown in Table 2. The data reveals that the Zn–CaO(cesp) catalyst have shown better basic strength in comparison to neat CaO(cesp) and other metal impregnated catalysts. The basicity of transition metal impregnated CaO(cesp) is comparatively greater than that of neat CaO(cesp) may be because of the synergistic relation between multi-metal ions which generally enhances the basicity on active site of the catalyst [63,64]. The synergistic effect of multi-metal ions may also be explained as the basicity of an metal oxide surface is closely related to the electron donating property of oxygen anion which increases with the increase in electropositive character of combined metal ion which will probably form more Lewis base sites (–O–) on CaO(cesp) surface [65].

### 3.1.5. SEM analysis

The surface morphology of the calcined catalysts was studied by scanning electron microscopy (SEM) and the images obtained are shown in Fig. 4a–e, respectively. The calcined eggshell surface contained irregular shapes of particle such as rod, dumbbells etc., thus they constructed a net like porous structure. However, the surfaces of metal impregnated catalysts generally comprise the formation of smaller aggregates of variable morphologies. The irregularities in the morphologies of metal impregnated catalysts may be due to the formation of clusters of M–CaO(cesp) particles during their preparation and calcination. The smaller size of aggregates could provide the higher specific surface areas. The fact can also be

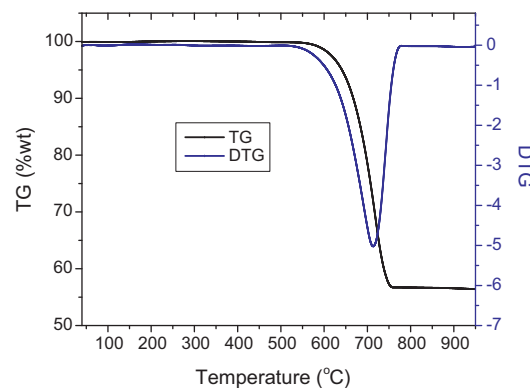


**Fig. 4.** SEM images of CaO (a), Zn/CaO (b), Mn/CaO (c), Fe/CaO (d) and Al/CaO (e) calcined at 900 °C.

supported by the XRD pattern and surface area analysis obtained for those M-CaO(cesp) catalysts.

### 3.1.6. TGA analysis

In order to explain the effect of calcination temperature, we have investigated the calcination process of waste eggshell powder with Thermogravimetric analysis (TGA). The results are shown in Fig. 5. TGA results showed that the temperature at which the waste eggshell powder decomposed when heated in a controlled environment. Water and other organics were removed up to 500 °C, whereas carbon dioxide CO<sub>2</sub> was lost 600–800 °C. Only one dominant step of weight loss was found over a temperature range of 600–800 °C. Above 850 °C, the weight of the sample kept almost constant. Since, the chicken eggshell generally contains CaCO<sub>3</sub> as main calcium based component. Thus it is clear from the TG analysis that the high temperature >800 °C is required for the transformation of the CaCO<sub>3</sub> to CaO(cesp) which could be confirmed by Tg and DTG analysis. Therefore, in perspective of preparation temperature and time, and energy consumption, the temperature of 900 °C was selected as a suitable calcination temperature to



**Fig. 5.** TGA analysis of egg shell powder.

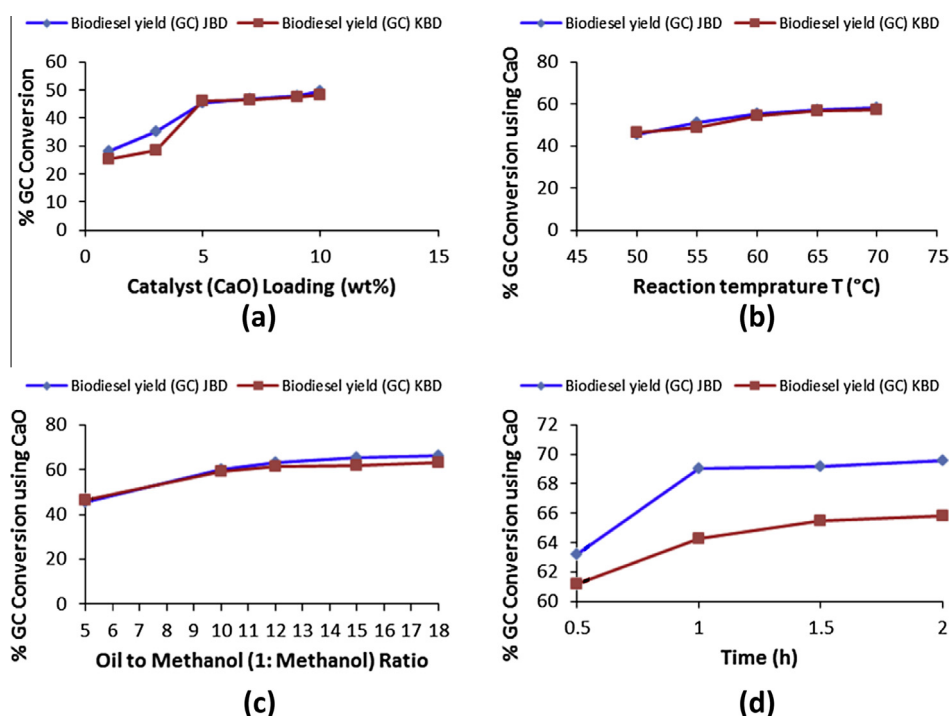
produce the CaO(cesp) catalyst from the waste chicken egg shell. Similar observations were also reported for the material derived from waste shells [48–50].

**Table 3**

The effect of catalysts loading, reaction time, temperature and methanol-to-oil ratio on transesterification reactions.

S. no	Catalysts	Catalysts amount (wt%)	Reaction temperature (°C)	Methanol/oil ratio	Reaction time (h)	Biodiesel yield (GC)	
						JBD	KBD
1	<b>CaO</b> (cesp)	1	50	5:1	0.5	28.2	25.4
2		3	50	5:1	0.5	35.2	28.3
3		<b>5</b>	50	5:1	0.5	<b>45.6</b>	<b>46.2</b>
4		7	50	5:1	0.5	46.7	46.4
5		9	50	5:1	0.5	47.8	47.4
6		10	50	5:1	0.5	49.8	48.3
7	<b>CaO</b> (cesp)	5	55	5:1	0.5	48.9	51.2
8		5	60	5:1	0.5	55.6	54.3
9		5	<b>65</b>	5:1	0.5	<b>57.4</b>	<b>56.7</b>
10		5	70	5:1	0.5	58.1	57.1
11	<b>CaO</b> (cesp)	5	65	10:1	0.5	60.0	59.1
12		5	65	<b>12:1</b>	0.5	<b>63.2</b>	<b>61.2</b>
13		5	65	15:1	0.5	65.3	62.0
14		5	65	18:1	0.5	66.1	63.1
15	<b>CaO</b> (cesp)	5	65	12:1	<b>1</b>	<b>69.0</b>	<b>64.3</b>
16		5	65	12:1	<b>1.5</b>	<b>69.2</b>	<b>65.5</b>
17		5	65	12:1	2	69.6	65.8
18	<b>ZnO</b> / <b>CaO</b> (cesp)	<b>5</b>	<b>65</b>	<b>12:1</b>	<b>1</b>	<b>98.2</b>	
19	<b>ZnO</b> / <b>CaO</b> (cesp)	<b>5</b>	<b>65</b>	<b>12:1</b>	<b>1.5</b>		<b>95.8</b>
20	MnO <sub>2</sub> /CaO(cesp)	5	65	12:1	1	95.1	
21	MnO <sub>2</sub> /CaO(cesp)	5	65	12:1	1.5		93.6
22	Fe <sub>2</sub> O <sub>3</sub> /CaO(cesp)	5	65	12:1	1	96.6	
23	Fe <sub>2</sub> O <sub>3</sub> /CaO(cesp)	5	65	12:1	1.5		94.1
24	Al <sub>2</sub> O <sub>3</sub> /CaO(cesp)	5	65	12:1	1	76.2	
25	Al <sub>2</sub> O <sub>3</sub> /CaO(cesp)	5	65	12:1	1.5		71.3

Values given in bold types represent optimized parameters.

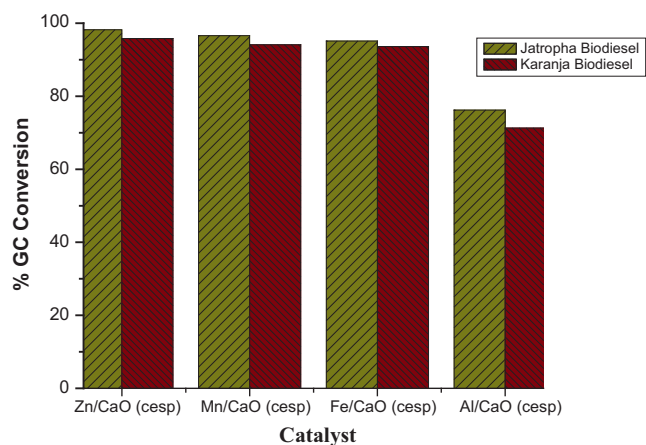


**Fig. 6.** The effect of catalysts loading, methanol-to-oil ratio, reaction time and reaction temperature on transesterification reactions of Jatropha and Karanja Oil: (a) Optimization of catalyst loading at temp 50 °C, oil/methanol ratio (1:5) and reaction time 0.5 h; (b) Optimization of temperature for catalyst loading of 5 wt%, oil/methanol ratio (1:5) and reaction time 0.5 h; (c) Optimization of oil:methanol ratio for catalyst loading of 5 wt%, T = 65 °C and reaction time 0.5 h; (d) Optimization of time for catalyst loading of 5 wt%, T = 65 °C and oil:methanol ratio (1:12).

### 3.1.7. Transesterification of Jatropha and Karanja oils with methanol by using prepared catalysts

The activity of prepared catalysts including the CaO(cesp) was established by performing transesterification reactions of

Jatropha and Karanja oils according to the procedure described in Section 2.4. The effect of catalysts loading, methanol-to-oil ratio, and reaction time and reaction temperature on transesterification reactions was also studied. The optimization results are shown in



**Fig. 7.** The effectiveness of catalysts (M–CaO) for transesterification of Jatropha and Karanja Oils.

**Table 3** and **Fig. 6**. **Table 3** represents the optimization of reaction conditions (catalyst loading, methanol-to-oil ratio reaction time and reaction temperature) for transesterification of Jatropha and Karanja oils. The transesterification of Jatropha and Karanja oil was started using 1 wt% of catalysts loading at 50 °C using 5:1 methanol-to-oil ratio for 0.5 h; a GC conversions of 28.2% for Jatropha and 25.4% for Karanja biodiesel were obtained (entry 1 **Table 3**). It is clear from the **Table 3** that maximum GC conversions of 69.0% (reaction time, 1 h) for Jatropha and 65.5% (reaction time, 1.5 h) for Karanja biodiesels were obtained using 5 wt% of CaO(cesp) catalyst at 65 °C with 12:1 M ratio of methanol-to-oil (entries 15 and 16, **Table 3**). Karanja oil has high acid value in comparison to Jatropha oil [52], because of that it may react with base catalysts to form soap or insoluble scum and water during reaction. The formation of such insoluble scum may decrease both the biodiesel yield and the CaO catalytic activity [66].

The optimized reaction conditions (5 wt% catalyst, 65 °C temperature and 12:1 methanol/oil ratio) used for CaO(cesp) were extended to carry out the transesterification reactions for both Jatropha and Karanja oils using the prepared metal impregnated catalysts. It was found that all the metal impregnated CaO(cesp) shown better activity for transesterification in comparison to neat

CaO(cesp). Zn impregnated CaO(cesp) has shown maximum activity among all metal impregnated catalysts for transesterification of both Jatropha and Karanja oils (**Fig. 7**).

This may be because of the greater surface area and more basic strength of the ZnO–CaO mixed oxide in comparison to others. Also it is well accepted that higher basic strength of the solid base catalysts is directly related to their effectiveness towards the transesterification reactions [52]. Therefore, based on the results of BET surface area and basicity determination of the prepared catalysts it is clear that why the ZnO–CaO(cesp) has shown maximum activity towards the transesterification reactions of Jatropha and Karanja oils. The maximum conversion of 98.2% for Jatropha and 95.8% of Karanja biodiesels were obtained with Zn impregnated CaO(cesp) under the optimized reaction conditions (entries 18 and 19, **Table 3**).

The main fuel properties of the prepared Jatropha and Karanja biodiesels were determined as per ASTM and/or EN standards and listed in **Table 4** along with their fatty acid composition determined by GC–MS analysis. The fuel properties of prepared biodiesels using these eggshell based catalysts were in good agreement with the limits prescribed in fuel standards, whereas the fatty acid composition of biodiesels were supported by the previous reports [60–62].

### 3.1.8. Reusability of the catalyst

Reusability of the heterogeneous catalysts is an important advantage over the homogeneous catalysts. The reusability of the catalyst ZnO–CaO(cesp) was also investigated by performing the transesterification of Jatropha and Karanja oils with methanol under optimized reaction conditions. The ZnO–CaO(cesp) catalyst was recovered after the fresh reaction by filtration and was washed twice with distilled water followed by hexane and dried for overnight at 120 °C. The dried catalysts were calcined at 900 °C for 4 h. The activated recovered catalyst was used for four successive cycles under the same reaction conditions and regeneration method. The results are shown in **Fig. 8**. The reused catalyst gave >95% GC conversions of Jatropha biodiesel and >92% GC conversions of Karanja biodiesel after four successive cycles. The gradual loss in catalytic activity of catalyst may be due to the adsorption of organic matters on the catalyst surface, and/or leaching of active sites during the reaction [52].

**Table 4**  
Fuel properties and fatty acid composition of prepared biodiesels.

S. No	Property (unit)	Jatropha biodiesel	Karanja biodiesel	Std. Limits		Test method
				Jatropha biodiesel	Karanja biodiesel	
1	Flash point (°C)	134.5	143.3	Min 100		ASTM D 93
2	Moisture content (mg/kg)	0.040%	0.042%	Max. 0.05%		ASTM-D 2709
3	Cloud Point (°C)	+6	+5			ASTM–D 2500
4	Pour point (°C)	+1	–3			ASTM–D 97
5	Calorific value (kJ/kg)	39211	36581			
6	Density (g/cm <sup>3</sup> ) at 15 °C	0.8844	0.8916	0.82–0.85	0.88–0.89	ASTM–D 4052
7	Kinematic viscosity (mm <sup>2</sup> /s) at 40 °C	4.6118	4.9221	1.9–6.0		ASTM–D 445
8	Oxidation stability (IP, at 110 °C, h)	4.8	4.1	3 h, min		ASTM–D 7545, prEN16091
<i>GC data for fatty acid composition of biodiesels</i>						
Jatropha biodiesel		GC area%	Karanja biodiesel			GC area%
Octanoic acid, methyl ester ( <b>C 8:0</b> )		0.21	Hexadecanoic acid, methyl ester ( <b>C 16:0</b> )			2.21
9-Hexadecenoic acid, methyl ester ( <b>C 16:1</b> )		0.74	Octadecanoic acid, methyl ester ( <b>C 18:0</b> )			4.81
Hexadecanoic acid, methyl ester ( <b>C 16:0</b> )		17.52	9-Octadecenoic acid, methyl ester ( <b>C 18:1</b> )			56.09
9,12-Octadecadienoic acid (Z,Z)-, methyl ester ( <b>C 18:2</b> )		31.13	Octadecenoic acid, methyl ester ( <b>C 18:1</b> )			3.81
9-Octadecenoic acid (Z)-, methyl ester ( <b>C 18:1</b> )		41.78	9,12-Octadecadienoic acid, methyl ester ( <b>C 18:2</b> )			25.21
Octadecanoic acid, methyl ester ( <b>C 18:0</b> )		8.62	9-Octadecenoic acid (Z)-methyl ester ( <b>C 18:1</b> )			1.34
			11-Eicosenoic acid, methyl ester ( <b>C 20:1</b> )			1.25
			Eicosenoic acid, methyl ester ( <b>C 20:0</b> )			0.89
			Docosanoic acid, methyl ester ( <b>C 22:0</b> )			2.83
			Tetracosanoic acid, methyl ester ( <b>C 24:0</b> )			1.44



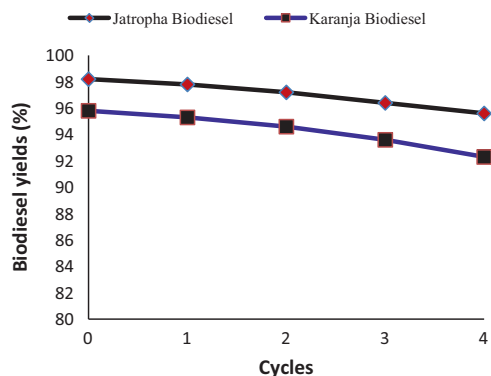


Fig. 8. Reusability of Zn/CaO(cesp) catalyst for transesterification of Jatropha and Karanja oils.

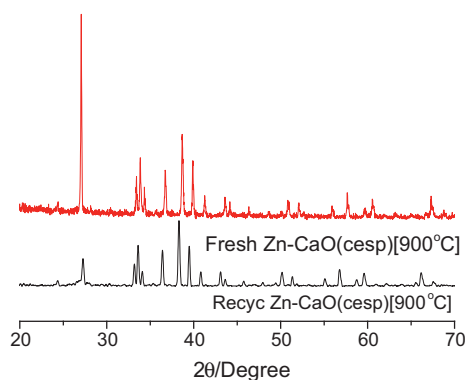


Fig. 9. XRD of Fresh and Recycled Zn–CaO(cesp).

To observe the structural changes that could be occurred in ZnO–CaO(cesp), the X-ray diffraction patterns of fresh and recovered catalysts were compared (Fig. 9). The XRD pattern of the recycled catalyst (after 4 cycles) has shown slight shifting of the peaks, this may be because of the separation of the CaO and ZnO upon repeated use and recalcination, this may also be the reason for significant decrease in basicity of recovered ZnO–CaO(cesp) (cal. at 900 °C) catalyst, consequently catalytic activity was decreased. The surface area and basic strength of recovered ZnO–CaO(cesp) (cal. at 900 °C) catalyst was also determined (entry 6, Table 2), and it was observed that because of the separation of CaO and ZnO the surface area and basicity was also decreased significantly.

#### 4. Conclusions

CaO(cesp) was prepared and modified by metal impregnation. The effectiveness of different Ca based mixed metal oxides (CaO–ZnO, CaO–MnO<sub>2</sub>, CaO–Fe<sub>2</sub>O<sub>3</sub> and CaO–Al<sub>2</sub>O<sub>3</sub>) for methanolysis of Jatropha and Karanja oils, was studied. Higher surface areas of the catalysts were observed when they calcined at 900 °C and therefore have shown the higher catalytic activity. Metal oxide impregnated catalysts have shown better activity in comparison to that of neat CaO(cesp). The ZnO–CaO(cesp) catalyst was found to be the best among all. The biodiesel yield was not much affected by the increase in optimized catalyst loading, reaction temperature and methanol:oil molar ratio. The catalyst has shown good reusability. The biodiesels derived from Jatropha and Karanja oils

have also shown good fuel characteristics which were under the limits prescribed by fuel standards (EN and ASTM). By using CaO(cesp) based mixed oxides reduced the catalyst cost and made the process more economic and also more environmental benign.

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