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ORIGINAL PAPER

Synthesis of Pure and High-Quality Biodiesel from Waste Frying Oil Using CaO Prepared from Waste Coralline Sand

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Abstract

Biodiesel is projected to replace the conventional diesel which is naturally occurring from a non-renewable resource called petroleum. Biodiesel generally prepared from bioresources and improves rural economy. The present research focuses on synthesis of biodiesel from waste cooking oil using catalyst generated from waste material. Waste coralline sand degraded from parent coral reef rock was used to make high purity and low cost CaO, and used in the production of biodiesel as an effective heterogeneous solid base catalyst. The calcination temperature was held at 800 °C for 3.5 h, yielding a high purity CaO catalyst. Well-known tools namely XRD, FT-IR, and TGA were employed to characterize the catalyst that was obtained. Elemental analysis and surface morphology were observed with SEM–EDX, respectively. To produce biodiesel, each batch went through a succession of transesterification reactions. Each experiment examined how the co-solvent changed the yield of biodiesel. Biodiesel of high grade and purity was produced and analysed using ^{1}H NMR and FT-IR spectra. There are some variables which adversely affected biodiesel yield, like reaction time, temperature, molar ratio, and concentration of the catalyst. The density, kinematic viscosity, cloud point, and other properties of synthesised biodiesel were investigated using ASTM guidelines. It was established that the developed CaO catalyst was reused up to 5 times without substantially degrading its catalytic activity.

Graphical Abstract

Keywords Bioresources · Deep frying oil · Waste coralline sand (WCS) · Heterogeneous catalyst · Biodiesel

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Statement of Novelty

Bidiesel is prepared from waste cooking oil using novel catalyst prepared from a new material, waste coralline sand, which is not explored by other researchers.

- Waste coralline sand derived CaO catalyst is an efficient catalyst for FAME conversion of 98%.
- Designed catalyst was stable and reusable up to five times.
- Basic nature of catalysts CaO is the main driving force in facilitating FAME synthesis.
- Green metrics study reveals that the WCS catalyst is environmental benign and cheaper by nature.

Introduction

Delicious food is prepared through deep oil frying at a high temperature which is a very simple and widespread method. Water content, air and frying at high temperature are the basic sources for which oil got exposed to many chemical process such as oxidation, decomposition, and scission [1, 2]. Previous studies have reported that monoglycerides, diglycerides, and free fatty acids are generated during the de-esterification process when oil is hydrolysed at a higher temperature. Oil frying at a higher temperature not only provides a route to the thermal polymerization of oil but also it facilitates the generation of polar compounds [3–5]. Biodiesel as the renewable energy which can replace the petrodiesel since it succeeds in dealing with many disadvantages of conventional petroleum diesel. Biodiesel produced from frying oil is environmentally friendly and progressively more cost-effective method. Speaking of carbon neutrality, biodiesel is carbon neutral though in a way that the biodiesel release CO_2 when it burnt. Many scientific techniques have been reported but total polar compounds (TPC) are the one of the best indicators to identify the quality of the frying oil that has been used [6]. Raw oil not only can make a major contribution to make high-quality biodiesel but also it to minimize the entire cost of producing biodiesel [7]. Biodiesel from deep frying oil has earlier been reported, however, separation of TPC from fried oil has not been focussed to make high-quality biodiesel. The procedure, which is widely used for producing biodiesel is transesterification. In the transesterification process, catalysts exist in a variety of forms, including homo/heterogeneous, and enzyme-based.

Homogeneous basic catalysts like NaOH, KOH, CH_3ONa, CH_3CH_2ONa and CH_3OK etc. are used because of their faster kinetic reaction rates and high turnover frequency value (TOF). Previous studies explored that homogeneous basic catalysts provides higher conversions, higher yield percentage and insignificant side-reactions. Despite these advantages, there are few drawbacks, like the inability to recover catalyst. It is very essential to neutralise the homogeneous catalyst at the end of reaction where the generation of excess amount of undesired water as well as waste salt. These catalysts require high quality feedstocks which are anhydrous and have free fatty acid (FFA) content < 3% to prevent hydrolysis and saponification side reactions [8]. Enzymatic catalysts can endure FFA and water content, enabling biodiesel/glycerol purification easier. In contrast, they are inapplicable for commercial purposes. Relative to homogeneous catalysts, enzymes are substantially more costly, display unstable activity, and have slower kinetic reaction rates. Now day's continuous process techniques are being used for biodiesel production, but they are not widespread.

Due to these difficulties, development of various heterogeneous catalysts is increasing day by day. Researchers have investigated a variety of heterogeneous catalysts, including zeolites, clays, heterogenized guanidine, and aluminium orthophosphate among others. Heterogeneous catalysts have a few advantages, including easy catalyst recovery, reusability, minimal energy and water usage, and easy glycerol recovery. Realizing that the price of a catalyst makes up a sizable and considerable portion of the total cost of biodiesel, the development of cheap and effective catalysts for transesterification of a wide range of feedstocks is essential for making biodiesel economically feasible. Employing reusable solid catalysts in a fixed-bed continuous reactor could potentially lead to a cheaper cost of production. Dead coral which is occurred through the natural degradation of parent reef rock, contains aragonite (composed of 89–99% calcium carbonate and 1–2% organic matter) which is affluent sources of $CaCO_3$ [9–11].

The present work explained the process of making biodiesel using deep fried oil as raw feedstock. Dead coral was used to make a stable and high-purity CaO catalyst for biodiesel production process since a lot of research has been done on CaO catalyst (heterogeneous) in biodiesel preparation. Hexane was used as a co-solvent to explore biodiesel factors such as temperature, time, catalyst loading, and stirrer speed.

Methodology

Materials

Sunflower oil was purchased from the neighbourhood market in Varanasi, India. Coralline sand was purchased from Umino Aquarium and Pet, Chennai, India. Chemicals such

as sodium sulphate, methanol and deuterated chloroform were of AR (analytical reagent) grade acquired from Merck.

Synthesis of Catalyst

Collected coralline sand was systematically cleaned with distilled water to get rid of dust particles allied with the sand. After washing, that sand was kept at 110 °C for 2 h to evaporate water content remaining in the coralline sand. Then, coralline sand was converted into powder form with the support of ball mill apparatus. $CaCO_3$ present in the coralline was transformed into CaO when the temperature of the calcination rises to 766 °C in a tubular furnace for 3.5 h. Thereafter, the calcined substance was crushed to fine powder and preserve in nitrogen filled desiccators to keep away from moisture and atmospheric air. The fine powder was used as a solid base heterogeneous catalyst in transesterification reactions for the biodiesel production from deep fried oil.

Catalyst Characterization

The catalyst that was obtained was examined by DTA/TGS, XRD, SEM/SEM–EDX, and FT-IR.

Frying Process

Wheat based snack was prepared from refined wheat flour using sunflower oil. Three litter of sunflower oil was kept in benchtop deep fryer (capacity of 5.0 L) and the temperature of oil was maintained at 190 °C. 100 g of smooth dough (water and 1% (weight of the wheat flour) of salt was added to wheat flour to make smooth dough and the overall hydration level was 50%) was taken and converted into flatten sheets by using rolling pin. The sheets were cut into preferred shapes and were undergone to frying in sunflower oil at 190 °C. The frying process involved in 3 batches. At the end of each cycle (3 batches (each batch takes 3 min) the temperature was lowered to 60 °C and collected the samples to make biodiesel. 20 cycles were carried out and in each cycle, the Testo 270 calculated the TPC% created as a result of oil being used for frying. Further, collected cycle 20 sample was allowed to convert into polar and non-polar fractions to make pure and high quality biodiesel.

Pre-treatment of Deep Frying Oil

After frying, filtration of the collected fried oil was done to get the oil's suspended solid particles. The water content was taken out of fried oil by passing through sodium sulphate and evaporation by rotavapour. Then physical/chemical properties of oil were determined using different testing methods (Table 1).

Quantification of Polar and Non-polar Fractions in Deep Frying Oil

After pre-treatment of deep frying oil, the polar/non-polar fractions in cycle 20 were separated according to well-known methods of AOCS Cd 20-91 and ISO 8420. The cycle 20 oil sample was weighed precisely up to 2.5 g and added to a 50 mL of measuring flask in which petroleum ether & diethyl ether were added in the ratio of 87:13 to make 50 mL solution. 20 mL solution was taken out from 50 mL and poured out into a silica gel-filled column (particle size, 70–230 meshes). Elution-solvent (150 mL) was used to separate the non-polar fraction of cycle 20 oil sample and flow rate was constant at 2 mL/min. Another 150 mL of elution solvent was used to get polar fraction of the cycle 20 oil sample. Each fraction was collected separately in 250 mL flask whose weight already known. Separation

Table 1 Physical and chemical properties of deep-fried oil

Property	Unit	ASTM standards	Value
Color	–		Yellowish red
Acid value	mg KOH/g	ASTM D 664	0.8
Unsaponifiable matter	% w/w		2.5
Density	g/cm^3	ASTM D 1298	0.914
Polar compound		AOCS Cd 20–91	31
Saponification value	mg KOH/g		188
Triglycerides content	wt%	EN 14,105 or ASTM D6584	78
Diglycerides content	wt%	EN 14,105 or ASTM D6584	1.86
Monoglycerides content	wt%	EN 14,105 or ASTM D6584	NA
Ash content		ASTM D5347	0.07
Water content	in %	ASTM D 2709	0.02%

process was monitor with TLC using hexane/diethyl ether (80:20, v/v). The collected polar and non-polar fractions were concentrated in rotary evaporator to remove elute from each fraction. The non-polar fraction was utilized in the making of biodiesel using prepared calcium oxide (CaO) catalyst. Further, the total content of polar and non-polar fractions was measured using the following Eq. (1).

$$\text{Polar compound } = m - \left(m_2 - m_1\right)/m. \quad (1)$$

m = Weight of oil sample, m_1 = Weight of flask, m_2 = Total weight of flask and non-polar fraction.

Acid Value

The practice of oil frying will result in an increase in the amount of free fatty acids, which will be the main constraint. All of the oil samples' acid contents were evaluated by standard test method (ASTM D6751). Most research has recommended minimizing the acid value (< 4 mg KOH/g) for the transesterification reactions. After completion of frying process, the acid value was calculated for all the collected samples and observed within the limits (0.3 ± 0.1 mg KOH/g to 0.4 ± 0.1 mg KOH/g). So, the transesterification reactions for the synthesis of biodiesel have been carried out.

The following equation (2) was used to get each sample's acid value.

$$\text{Acid value in mg KOH/g} = \frac{V_{\text{KOH}} \times 56.1 \times C_{\text{KOH}}}{Sample} \times 100. \quad (2)$$

Transesterification

All the reactions were performed using prepared CaO obtained from waste coralline sand. Transesterification reaction was carried out at oil to methanol molar ratio of 1:6 with 1% CaO catalyst at 65 °C for 110 min at 650 rpm [8]. The effect of each reaction parameter such as catalyst concentration (1–3%), stirring speed (450–650 rpm), temperature (35–85 °C) & methanol:oil ratio (6:1 to 14:1) on biodiesel yield was studied. The reaction mixture was removed once the transesterification reaction was finished and poured out in separating funnel to separate the glycerol as by-product, further washed with water followed by rotavapour to remove unreacted methanol. The catalyst was extracted out of the reaction-mixture washed with acetone and re-used. Purified biodiesel characterized by Proton NMR, GC, FT-IR spectroscopy to check the conversion and purity of biodiesel. The following equation (3) was used to compute yield after purifying the product of transesterification reaction.

$$\text{Biodiesel-yield (\%)} = \frac{\text{Weight of FAME produced}}{\text{Weight of fried oil used}} \times 100. \quad (3)$$

GC Analysis of Biodiesel

Synthesized biodiesel from deep fried oil was analysed by using Gas-Chromatography (Agilent-6890 N). The RT (retention time) of each fatty acid was evaluated by matching with those of FAME (Fatty Acid Methyl Ester) standards. Table 2 represents the fatty acid composition of synthesized biodiesel from deep fried oil and their specific chemical formula with RT.

Table 2 Fatty acid composition (%) of synthesized biodiesel from deep fried oil

Sr.	Retention time	Compound name	Composition (%)	Corresponding fatty acid	Corresponding fatty acid chemical formula
1	4.968	Myristic acid methyl ester	0.261	Myristic acid	$CH_3(CH_2)_{12}COOH$
2	19.32	Palmitoleic acid methyl ester	9.70	Palmitoleic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
3	19.55	Palmitic acid methyl ester	14.09	Palmitic acid	$CH_3(CH_2)_{14}COOH$
4	21.06	Arachidonic acid methyl ester	3.21	Arachidonic acid	$CH_3(CH_2)_{10}(CH{=}CH)_4COOH$
5	21.25	Oleic acid methyl ester	11.03	Oleic acid	$CH_3(CH_2)_{14}CH{=}CHCOOH$
6	21.29	Linoleic acid methyl ester	3.45	Linoleic acid	$CH_3(CH_2)_{12}(CH{=}CH)_2COOH$
7	21.46	Stearic acid methyl ester	4.05	Stearic acid	$CH_3(CH_2)_{16}COOH$
8	22.77	Eicosapentaenoic acid methyl ester (EPA)	19.96	Eicosapentaenoic acid	$CH_3(CH_2)_8(CH{=}CH)_5COOH$
9	24.33	Docosahexaenoic acid methyl ester (DHA)	13.93	Docosahexaenoic acid	$CH_3(CH_2)_8(CH{=}CH)_6COOH$
10	24.66	Erucic acid methyl ester	1.08	Erucic acid	$CH_3(CH_2)_{18}(CH{=}CH)COOH$

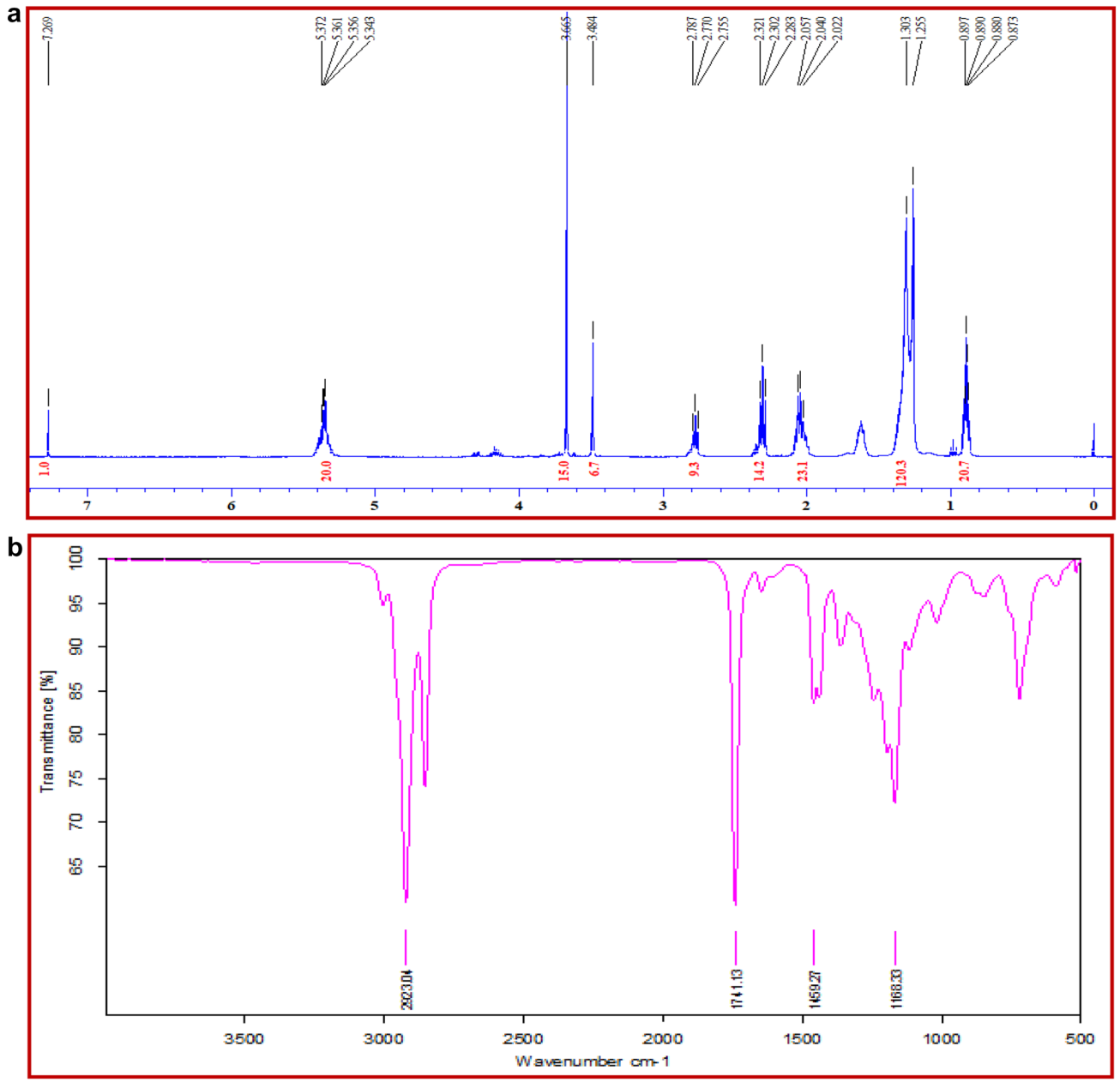

Fig. 1 **a** ^{1}H NMR spectra of synthesized biodiesel. **b** FT-IR spectrum of synthesized biodiesel

Proton NMR of Biodiesel

NMR analysis was done on prepared biodiesel since proton NMR spectroscopy is more sensitive and accurate to analyze the biodiesel as shown in Fig. 1a. ^{1}H NMR analysis was done by using Bruker SFO1 500 MHz. Each and every ^{1}H NMR spectra was observed when the 180 µL biodiesel dissolved in 0.8 mL of deuterated $CDCl_3$ chloroform. Horst et al. studies shown that the methyl esters consist of methoxy proton provide a singlet at around 3.66 ppm and methylene group of methyl esters provide a triplet at around 2.3 ppm. The conversion of biodiesel from NMR data is calculated using well known equation (4).

$$C = 100\left(2 \times A_{CH3}\right)/\left(3 \times A_{CH2}\right), \tag{4}$$

where A_{CH3}= Area of methxy group and A_{CH2}= Area of methylene group.

FT-IR Analysis of Biodiesel

FT-IR spectroscopy is another analytical mode to conclude the functional groups, which are present in the synthesized material. Stretching band at 1741 cm^{-1} is associated with the C=O and C–H stretching frequency was spotted at 2923 cm^{-1}. Absorption band at 1459 cm^{-1} is related to CH_2 and another band at 1168 cm^{-1} is ascribed to C–O functional group present in the FAME as shown in Fig. 1b.

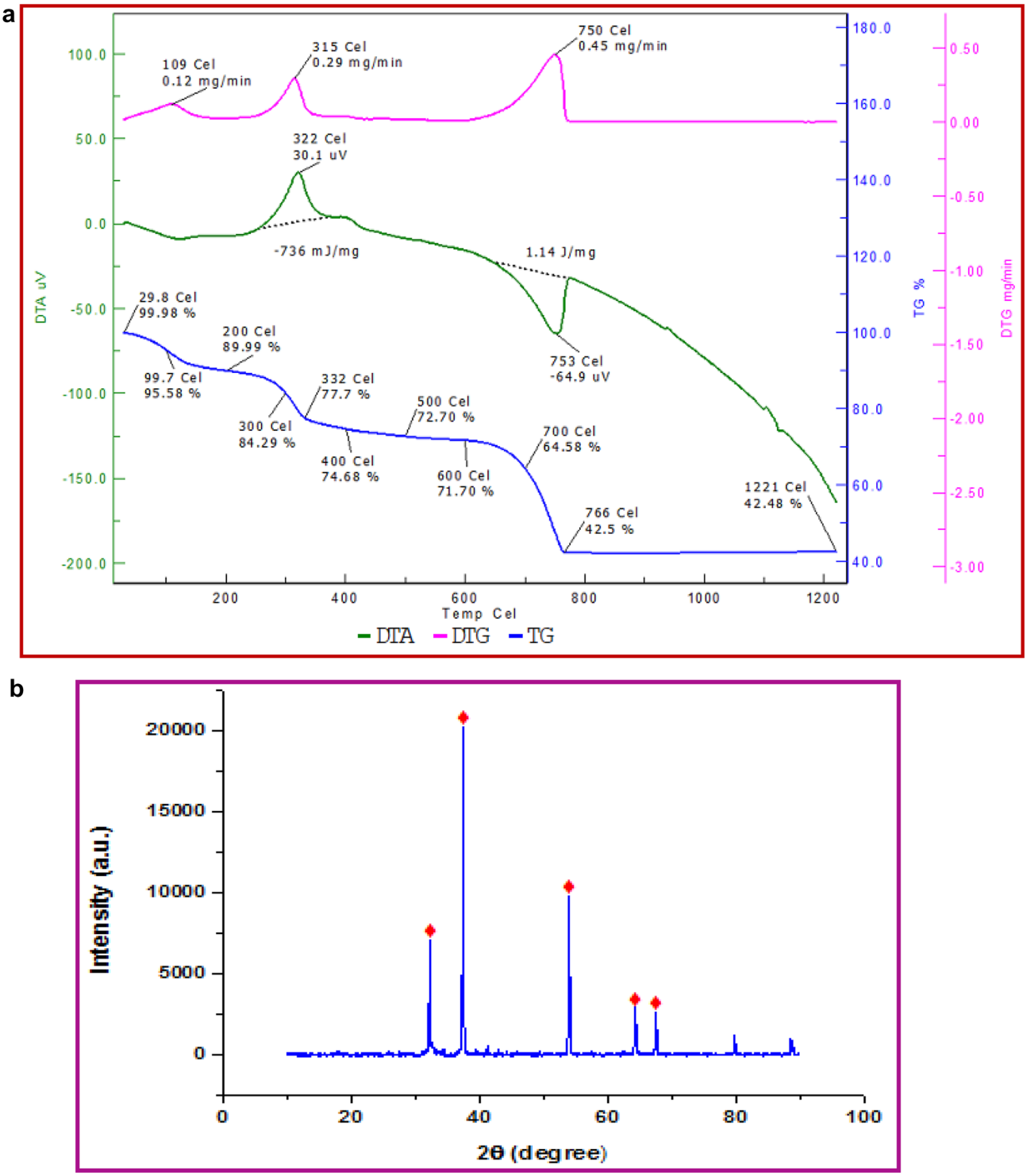

Fig. 2 **a** TGA/DTA of uncalcined waste coral sand. **b** XRD patterns of calcium oxide derived from waste coral sand

Result and Discussion

Characterization of Prepared Catalyst

TGA/DTA Analysis

Collected waste coral sand was subjected to thermal gravimetric analysis to quantify the sample's mass loss in proportion to the decomposition temperature. 10.32 mg of waste coral sand was weighed out and used for TGA/DTA analysis. The first weight loss was observed (10.01%) between the temperature from 27 °C near to 200 °C was mainly for the reason that the vaporization of physically absorbed H_2O (water) molecule associated with waste coral sand. There was a noticeable drop of weight (29.2%) from 600 to 766 °C was because of formation of calcium oxide from the calcium carbonate by the decomposition process in which carbon dioxide was released as shown in Fig. 2a [12–14]. A constant weight was observed as temperature raised from 766 to 1200 °C which shown that pure and stable CaO (calcium oxide) was made since the entire $CaCO_3$ converted into CaO.

XRD Analysis

Figure 2b represents the XRD analysis of calcined calcium oxide prepared from waste coral sand. The XRD pattern was observed by using Shimadzu diffractometer model XRD 6000. Each peak was compiled with JCPDS files. The diffraction patterns were identified at 32.2°, 37.4°, 53.9°, 64.2°, 67.4° and 79.7° (JCPDS 82-1690). In XRD, it is clearly shown that the complete conversion of calcium carbonate into calcium oxide when the calcination temperature raised up to 800 °C for 4 h [15]. The data obtained in XRD analysis is also matching with other researchers, who have prepared biodiesel from waste cooking oil and microalgal oil using CaO nanoparticle [16, 17]. The particle size of synthesized CaO catalyst is 38 nm, which is calculated using Scherrer Equation. According to JCPDS file 82-1690, the obtained XRD pattern indicated that the existence of calcium oxide has a face-centred lattice.

SEM–EDS Analysis

Figure 3a represents the SEM (Scanning Electron Microscopy) image of calcium oxide prepared from waste coral sand. The surface morphology was observed at different magnifications at a preset voltage (20 kV). The calcium oxide molecules were assemble with irregular structure but no overlapping of calcium oxide particles was seen in the Fig. 3a. The frequency vs. size of particle graph gave the size range from 1.50 to 2.61 µm but the greater number of particles acquires the average size range from 1.7 to 2.2 µm [18–20].

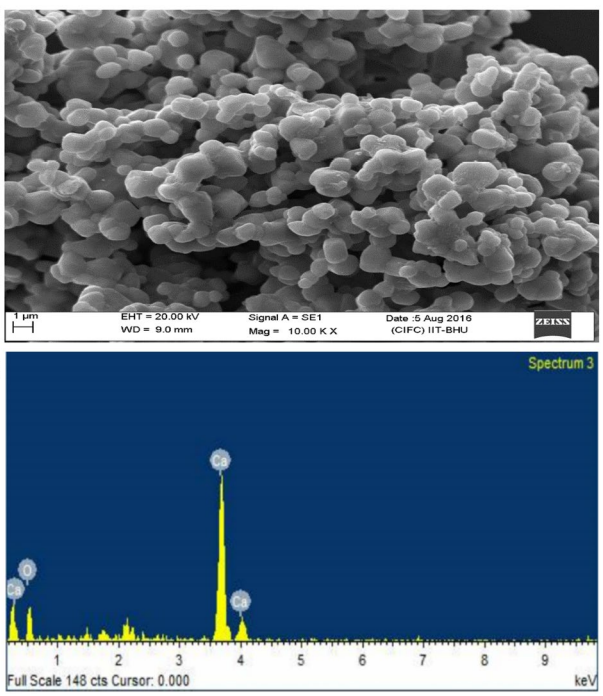

Fig. 3 **a** SEM micrograph of calcium oxide prepared from waste coral sand. **b** EDS spectrum of calcium oxide prepared from waste coral sand

EDS was used to understand the composition (elemental) of obtained CaO. Prepared CaO precise the existence of calcium (weight% was 53.21 and atomic weight% was 31.22) and oxygen (wt% was 46.79 and at.% was 68.78) respectively as shown in Fig. 3b.

In the EDS spectrum, it is openly displayed that the absence of other elements than the calcium and oxygen.

Surface area Analysis

Surface area (Brunauer–Emmett–Teller (BET)) analysis of catalyst developed from waste coral sand by the process called adsorption-desorption at − 193 °C. A plot was drawn in between the adsorbed nitrogen (cm^3/g STP) vs. pressure (P/Po) to estimate surface area of the prepared catalyst as shown in Fig. 4a. Pore volume, surface area were 0.3712 cm^2/g and 17.231 m^2/g, respectively.

Impact of Co-solvent

The synthesis of biodiesel required an unusually high molar ratio of methanol to oil. So to lower the quantity of methanol and improving solubility of oil in methanol, co-solvent was provided to the reaction mixture. Oil is less soluble

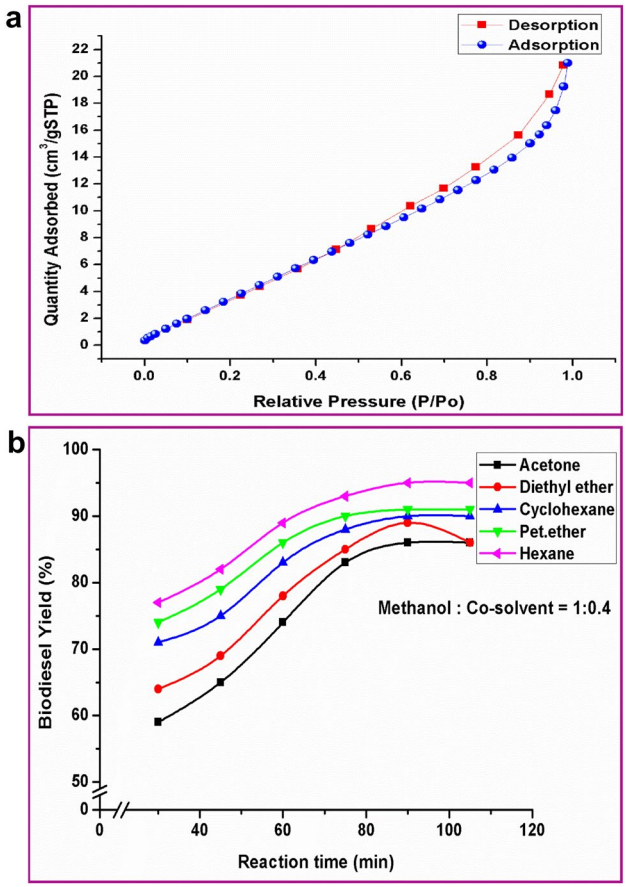

Fig. 4 **a** BET-surface area of calcium oxide (CaO) derived from waste coral sand. **b** Effect of different co-solvent on biodiesel yield

in methanol and adding co-solvent during transesterification increases the solubility of oil, which reduces the mass transfer limitation during trasesterfication and increases the homogenity of the reaction and easy separation of product after transesterification [21]. Acetone, cyclohexane, pet-ether, and hexane, diethyl ether were used as co-solvent to investigate the improvement on FAME yield. Reaction factors for instance CaO loading (2.5 wt%), temperature (65 °C), methanol:oil molar ratio (10:1), speed of stirrer (650 rpm), were kept as constant while reaction increased from 30 to 110 min as shown in Fig. 4b. The purpose of adding co-solvent to the reaction mixture is to reduce the reaction time, reaction temperature, and stirring speed since co-solvent makes reaction mixture into more homogeneous [22–24]. From the results, it is clearly observed that the hexane as co-solvent gave high biodiesel yield (95%) whereas, acetone gave low (77%) biodiesel yield. The rate of evaporation was high in the case of acetone but not in the case of hexane due to the fact that its boiling point is close to methanol. As a result, hexane was chosen as co-solvent to produce biodiesel from deep frying oil.

The co-solvent was optimized by taking different ratios of co-solvent: methanol starting from 0.1:1 to 0.6:1 but high yield was found at 0.4:1 and shown in Fig. 5a.

Effect of CaO Concentration

Concentration of catalyst is extremely vital to the biodiesel yield. Catalyst influence on yield was observed by conducting different experiments with changing the catalyst concentration from 1% (w/w of oil) to 3% but the other parameters such as the temperature at 65 °C, reaction time 110 min, stirrer speed at 650 rpm were taken as constant. As concentration of catalyst increases from 1 to 3%, the yield was significantly increased up to 2.5% and then it became constant (Fig. 5b). As CaO concentration increases, chances of interaction of reactants with catalyst increases which will increase the biodiesel yield but after 2.5% catalyst concentration doesn't render any increase in biodiesel yield. Once the catalyst was added after 2.5% the viscosity of the reaction mass increased [25–27] hence, making mixing more difficult. The yield was improved from 77 to 1% catalyst (10:1 methanol to oil ratio) to 93 with 2.5% catalyst. The gap between the layers of alcohol and oil that are immiscible is minimized through co-solvent. Using co-solvent (0.4:1 hexane to methanol ratio), the yield was enriched from 77 to 81% (1% catalyst) and from 93 to 97% (2.5% catalyst) respectively.

Effect of Temperature

Temperature significantly effects on biodiesel yield therefore, the reaction carried out at varied temperature from 35 to 85 °C by retaining other components constant(oil:methanol ratio(1:10) which was found to be optimum earlier, time (110 min) and stirrer speed with 650 rpm). The CaO catalyst concentration was taken to be 2.5%. We noticed as given below in Fig. 5c, the yield was increased as temperature raised up to 65 °C with and without co-solvent mixture. In all instances, biodiesel yield was higher with the addition of co-solvent which was taken to be in the ratio 0.4:1. We observed the highest yield (97% with co-solvent) at 65 °C, which is the boiling point of methanol since methanolysis reaction decreases the viscosity of the mixture and increases the reactivity of mixture due to increase in mass transfer [28–30]. This effect was drenched after 65 °C and the evaporation of methanol caused a minor drop in the biodiesel yield since its interaction with reactants decreases. Thus we observe that biodiesel output is substantially enhanced by temperature and also increased with the addition of co-solvent as clearly perceived in Fig. 5c.

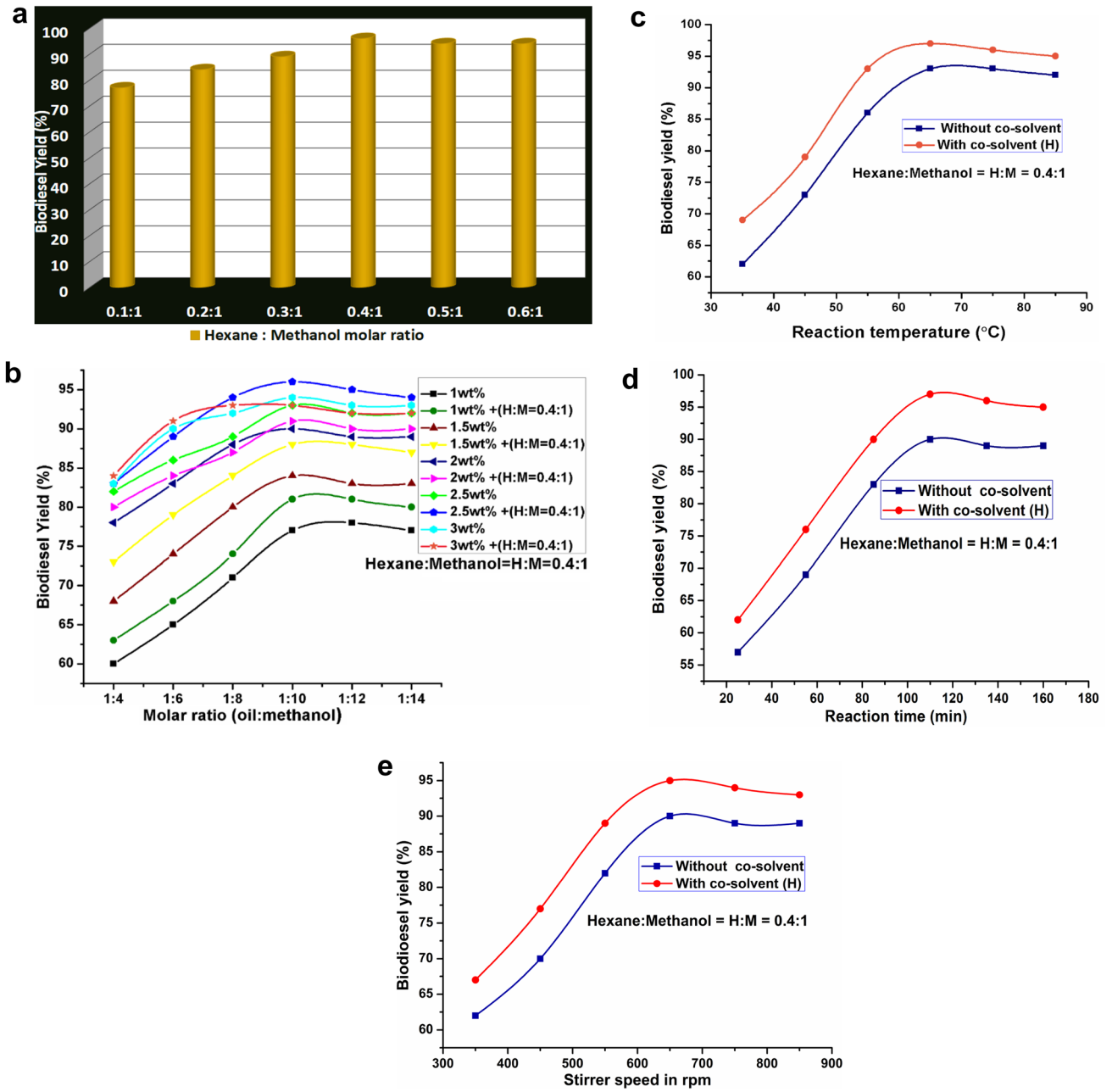

Fig. 5 **a** Optimization of hexane (cosolvent) with methanol (solvent). **b** Effect of catalyst loading on biodiesel yield. **c** Effect of reaction temperature on biodiesel yield. **d** Effect of reaction time on biodiesel yield. **e** Effect of agitation speed on biodiesel yield

Effect of Reaction time

While other variables like methanol-to-oil molar ratios etc. were held constant, the impact of time on obiodiesel yield was examined. The stirring speed was maintained at 650 rpm. The experiment was undertaken with and without co-solvent for reaction time from 25 to 110 min. As the time prolonged from 25 to 110 min, output yield also increased, further no discernible growth in biodiesel yield as revealed in Fig. 5d. Highest biodiesel yield (97%) was observed at 110 min with co-solvent.

Effect of Stirrer Speed

The effect of stirring speed from 350 to 850 rpm was studied on biodiesel yield. Stirrer speed is crucial in every transesterification reaction. The yield was better with rise in stirrer speed till 650 rpm with the highest yield being 97% along

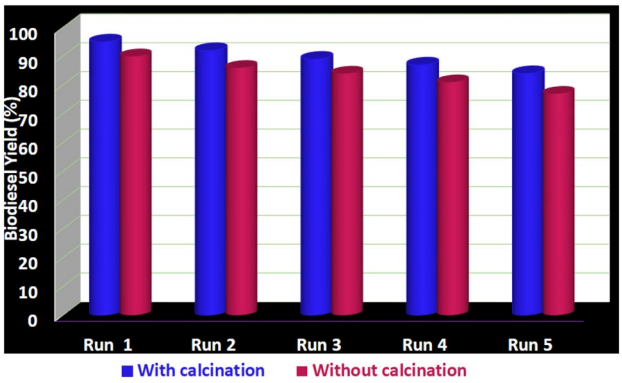

Fig. 6 Reusability of prepared catalyst with and without calcination

with co-solvent (Fig. 5e). Further escalation in stirrer speed reduced the yield by a small amount which can be assumed due to vaporization of methanol [30–33].

Reusability of Catalyst

The catalyst capacity to be reused was tested using two different processes (Fig. 6). In the first process, used catalyst was cleaned by using acetone and reused in transesterification reactions whereas in the second process, used catalyst was washed with acetone furthermore calcined at 700 °C for 2 h and reused in the transesterification reactions. The reused catalyst delivered 95% yield in Run 1 in the first process whereas in the second process; the catalyst gave 90% biodiesel yield. The removal of water was primarily responsible for the rise in biodiesel output and other adsorbed matter associated with catalyst since the used catalyst was calcined in the second process. Reusability of prepared catalyst was observed up to Run 5 (with calcination and without calcination) but in both the process, the decrease in biodiesel yield was negligible and shown beyond doubt that the produced catalyst remained stable and had negligible loss of catalytic activity up to the fifth run.

Physico Chemical Properties of FAME of Waste Frying Oil

The physico–chemical properities of synthesized FAME from waste frying oil (WFO) was measured as per the ASTM guidelines and given in Table 3. The results obtained were in agreement with biodiesel standards, meet the specification of petrodiesel and is also comparable with the fuel properties of FAME of waste cooking oil determined by other researchers [16].

Green Metrics Study

Environmental Factor (E-factor)

E-factor being the simple and fast metric frequently used to know the potential environmental acceptability of a chemical process. It is the simple ratio of total amount of waste to the desired product (Eq. 5). Higher value of E-factors indicates excess amount of waste generated and causes negative environmental effect [34–36]. An ideal E-factor implies no waste generation and environmentally friendly nature of the reaction process.

$$\text{E-factor} = (\text{Total waste (kg)})/(\text{Product (kg)}). \quad (5)$$

The E-factor of the biodiesel produced from waste frying oil was calculated by assuming glycerol as waste and found to be 1.06 which is ideal E-factor value and signifies that production of biodiesel using CaO as catalyst is environmental being by nature.

Atom Economy

Molecular weight of biodiesel product, waste cooking oil, catalyst and alcohol used in reaction process and AE for methanol and ethanol were 88% and 86% respectively. Atom economy being one of the most used green metrics and it is based on molecular weight a conclusion cannot be drawn. From the atom efficiency it was observed that methanol is

Table 3 Physico–chemical properties of FAME of waste frying oil

Properties	Method used	ASTM-6751 biodiesel	Diesel	FAME of WFO
Acid value (mg KOH/g)	D664	0.8	–	0.51 ± 0.02
Density (40 °C, g cm^{-3})	D4052	0.86–0.90	0.804	0.89 ± 0.02
Kinematic viscosity (cSt at 40 °C)	D445	1.9 to 6.0	3.9	4.52 ± 0.26
Cetane number	D613	47	49	48 ± 1.53
Calorific value (MJ/Kg)	D240	35	42	41.32 ± 0.75
Flash point (°C)	D93	100 to 170	68	140 ± 2.52
Cloud point (°C)	D2500	− 3 to 12	− 10	4 ± 1.53
Pour point (°C)	D97	− 15 to16	− 15	6 ± 2.08

more efficient than ethanol as ethanol having higher molecular weight and higher boiling point. With increase in reaction time the efficiency of reaction process increased and affects the atom economy of reaction process [37, 38]. Depending upon the solvent molecular weight and temperature range the atom efficiency of the biodiesel production process can be calculated.

Process Mass Intensity

Process mass Intensity being one of the green metrics can be calculated for biodiesel production process from deep frying oil using CaO as the catalyst. It can be calculated simple ratio of total mass used in the reaction process to total mass produced in final product [39–41]. Mass used in this work includes deep frying oil, Methanol as reagent and CaO as catalyst and total biodiesel produced in the transesterification process were taken into calculation and the PMI value for the reaction process was 0.97 g indicating the ideal PMI value for the transesterification reaction. Since the ideal PMI value is 1 and in our work PMI approximately equal to 1 hence the transesterification reaction of deep frying oil using CaO exhibits ideal green metrics and environmental friendly in nature.

$$\mathrm{PMI} = \frac{\text{Total mass used in the process (g)}}{\text{Mass of final product (g)}}. \tag{6}$$

Conclusions

High quality and pure biodiesel were synthesized from deep fried oil using solid base calcium oxide catalyst. Heterogeneous solid base calcium oxide catalyst was prepared by calcinations of coralline sand for synthesis of FAME (biodiesel) of deep-frying oil. The catalyst (CaO) was identified by TG-DTA/DTG, XRD, SEM–EDS, BET, and FT-IR methods. Impact of different reaction parameters such as catalyst concentration, time, methanol to oil reaction temperature and stirrer speed on biodiesel yield with and without co-solvent were optimized. The highest biodiesel yield (97%) was produced by using CaO as a catalyst developed from waste coralline sand at optimized reaction conditions (oil: methanol molar ratio (10:1); speed of the stirrer (650 rpm) reaction time (105 min); catalyst loading (2.5 wt%) at 65 °C). The fuel properties like viscosity, density, and cloud point were measured as per the ASTM biodiesel standards and found to adhere to the specifications. The prepared catalyst is reusable and can be used upto 5th cycle with negligible loss in catalytic activity.

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Data Availability Enquiries about data availability should be directed to the authors.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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