PAPER

Synthesis of biodiesel from *Jatropha curcas* oil using waste eggshell and study of its fuel properties

Supriya B. Chavan,[a] Rajendra R. Kumbhar,[b] D. Madhu,[c] Bhaskar Singh[d] and Yogesh C. Sharma*[c]

High purity calcium oxide (CaO) was prepared from eggshell and used as a catalyst for the production of biodiesel. Non-edible oil, *Jatropha curcas* was used as a feedstock for the synthesis of biodiesel. High purity calcium oxide (CaO) was obtained when the eggshell was subjected to calcination at 900 °C for ~2.5 h. Confirmation of the catalyst was carried out by X-ray diffraction, Fourier transform infrared spectrometry (FT-IR), and differential thermal and thermogravimetric analysis (DTA-TGA). The synthesized biodiesel was characterized using ^{1}H NMR. Pure biodiesel was obtained in high yield by taking into account various parameters such as a proper methanol to oil molar ratio, reaction temperature and reaction time. Reusability of the catalyst was observed and the catalyst worked efficiently up to six times without significant loss of activity. Physical and chemical properties of biodiesel such as density, kinematic viscosity, cloud point, *etc.* were studied.

1. Introduction

Dependency on other countries for oil resources, climate change and increase in greenhouse gases compel the search for alternative renewable fuels. Edible and nonedible oils could be alternatives to petroleum oil, but their higher viscosity reduces the fuel atomization and increases the fuel spray penetration leading to high engine deposits and thickening of the lubricating oil. Biodiesel, among renewable resources,[1] can be directly used in a diesel engine as it does not require modification of the injection system or engine or fuel lines. As far as pollution is concerned, the feedstock used for biodiesel synthesis basically contains methyl esters of long chain fatty acids and thus it does not emit any toxic pollutants unlike fossil diesel fuel. Even when they are used in a blended form, a significant decrease in carbon monoxide (CO), hydrocarbon (HC) and particulate matter was observed.[2,3] Moreover, the feedstock for biodiesel synthesis can be easily produced *via* the transesterification of waste oils or vegetable oils if the free fatty acid content is less than 5%.[4] Therefore, in certain cases, when an oil contains more than 5% of free fatty acids, esterification of the oil is needed prior to transesterification. For example, the raw vegetable oils (non-edible oils) like *Pongamia pinnata*, *Jatropha curcus*, *Calophyllumino phylum* and *Citrullus*

colocynthis[4–9] are reported to have higher acid values and prior to transesterification, esterification of such oils has to be carried out. The source of the oil and its composition varies with plant species.[10] Soybean oil in USA, sunflower and rapeseed oils in Europe, palm oil in Malaysia and Thailand and coconut oil in the Philippines are being considered as substitutes for diesel fuel.[11] Climate variations encourage diversity of vegetation and so the study of possible vegetable oils is needed to use biodiesel at an industrial scale for each country. Waste frying oil was also used by several authors to produce biodiesel.[12–15]

Biodiesel can be synthesized either by using heterogeneous or homogeneous solid acid and/or base catalysts. The corrosive nature, increase in pH of the final product and problem of separation are the major issues with the use of a homogenous catalyst during transesterification. To overcome these impediments, a heterogeneous catalyst was explored as an alternative to the conventional homogeneous catalysts.[16] Heterogeneous solid acid and base catalysts include zeolites, metal catalysts,[16–19] *etc.*

Egg consumption is beneficial for health but there are disposal issues associated with eggshells. The eggshell constituents depend on the mechanical as well as biological escape behaviour. The carapace is elastic and ~50 to 89% less mineralized when compared to a finger and claw. The cuticles contain calcium, magnesium, phosphorus, carbon, oxygen and silicon as the main components as well as sodium and chloride in trivial amounts. The most important aspect is that the mineralized part contains calcium carbonate (30–35%) in significant amounts.[20,21] The utilization of the eggshell as a source of a solid heterogeneous catalyst for biodiesel production not only provides a cost effective and eco-friendly way to

[a]*Department of Chemistry, Bhagwant University, Ajmer 305 004, Rajasthan, India*

[b]*Rajashri Chhatrapati Shahu College, Kolhapur 416002, India*

[c]*Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, Varanasi 221005, India. E-mail: ysharma.apc@itbhu.ac.in; Fax: +91 542 6702876; Tel: +91 542 6702865*

[d]*Centre for Environmental Sciences, Central University of Jharkhand, Ranchi 835205, India*

recycle this solid waste but also contributes to a reduction in the cost of biodiesel to make it competitive with diesel fuel.

In most of the work reported on transesterification using CaO as a catalyst, many times, the catalyst is derived from eggshells.[22,23] Edible palm oil has been used for the production of biodiesel using eggshell derived CaO as a catalyst.[24–27] A substantial amount of saturated fats are present in palm oil and therefore, the biodiesel obtained has low-temperature properties.[11] Moreover, no work is available to evaluate the eggshell catalyst as an effective heterogeneous catalyst option with a high free fatty acid containing feedstock and this was the motivation to use recycled eggshells as a catalyst source for biodiesel production with *Jatropha* oil. Karanja oil as a feedstock was used for biodiesel production with calcined eggshell powder as the catalyst.[28] The physicochemical properties,[3,29] oil content[30] and energy values of *Jatropha* oil have already been explored.[31,32] *Jatropha* oil contains toxic substances due to which it is considered as non-edible.[33–35] The effect of reaction parameters such as the molar ratio, catalyst percentage, reaction time, temperature, and stirring speed on the synthesis of biodiesel have been studied.[4,36] The synthesized methyl ester was analyzed using gas chromatography-mass spectrometry (GC-MS) to evaluate the yield and purification. Important parameters like density, viscosity, flash point, fire point, cetane number, calorific value, cloud point and moisture content have been analyzed as per the ASTM-6751 standard.

2. Experimental

2.1. Materials

Raw eggshells were collected from the waste of the Institute's hostel canteen, IIT BHU Varanasi, India. Crude *Jatropha* oil was extracted from seeds purchased from the Indian Biodiesel Corporation, Baramati, Maharashtra, India. Chemicals such as sulphuric acid, methyl alcohol, *ortho*-phosphoric acid and sodium sulphate were purchased from Merck Ltd. Mumbai, Maharashtra.

2.2. Catalyst preparation

The eggshells were washed with hot water to eliminate contaminants present on the shells. Then they were dried in a hot air oven at 110 °C for 24 h. The dried eggshells were ground into powder using a ball mill. The obtained powder was calcined in a muffle furnace under various temperature ranges from 25 °C to 900 °C for 2.5 h to obtain CaO from a calcium containing precursor. Granados *et al.*[37] reported that catalytic poisoning will occur when the catalyst is placed in contact with air because of the presence of moisture and carbon dioxide. Though, the catalytic poisoning was less because of water and carbon dioxide, the poisoning was found to be consequential. Therefore, the catalyst was placed in a plastic bottle container and then in desiccators to avoid poisoning of the catalyst.

2.3. Characterization of the catalyst

Differential thermal analysis/thermogravimetric analysis (DTA/TGA), X-ray diffraction (XRD), scanning electron microscopy

(SEM) and Fourier transform infrared (FT-IR) spectroscopy were used to study the characteristics of calcined eggshells. DTA/TGA experiments were performed under nitrogen flow with a structured text analyzer (DTA/TGA), model STA 409, Netzsch-Gerätebau GmbH (Germany). FT-IR spectroscopy was performed on a BRUKER ALPHA Eco ATR in the wavelength range from 4000–500 cm^{-1}. The XRD patterns were studied on an X-ray diffractometer (Scifert and Co., model 3000). The fatty acid profile of *Jatropha* was performed using gas chromatography-mass spectrometry (GC-MS).

2.4. Oil extraction

As the seeds often possess a hard outermost shell which bears no oil, it was essential to de-husk the hard and woody part of the seeds before carrying out the estimation of oil content. Then the seeds were dried at 105 °C for 30 min in an oven. The dried seeds were taken for further oil extraction by solvent extraction.[6]

The extractability of oil was examined with three different solvents *viz.* petroleum ether (40–60 °C), *n*-hexane and diethyl ether. The optimum time required for maximum extractability was also examined.[4,5,9] The extraction result is mentioned in Table 1. It was observed that petroleum ether and *n*-hexane, were both equally good for the extraction of oil. The optimum time required for maximum extractability of oil was 3 h.

The extracted *Jatropha* oil was filtered and used to investigate its physico-chemical properties as well as its fatty acids content using gas chromatography-mass spectrometry. The peaks were identified using fatty acid standards and the identified fatty acids are listed in Table 2. The physico-chemical parameters are illustrated in Table 3.

Jatropha oil consists of both saturated and unsaturated fatty acids. Among these, oleic acid was found to be in the highest proportion (37.279%) followed by linoleic acid (35.00%), palmitic acid (14.240%), and stearic acid (6.585%). The presence of stearic acid is responsible for the high cloud point of biodiesel.

2.5. Esterification and transesterification reactions

Esterification and transesterification reactions were performed in a three-necked batch reactor of 2 L capacity. First of all, 1000 mL *Jatropha* oil was dehydrated in an oven at 107 °C for 2.5 h. To perform the acid esterification, 100 mL *Jatropha* oil was used with 1.7% (v/v) sulphuric acid (as a catalyst). The molar ratio of oil and methanol was taken as 1 : 8. The reaction was performed for 1.3 h at 60 ± 0.5 °C. The speed of the mechanical stirrer was kept constant at 600 rpm to overcome limitations due to mass transfer. After completion of the reaction, the reaction mixture was transferred to a separating funnel for 4 h. The water formed was dehydrated using a Rotavapor. Esterified *Jatropha* oil was used for further transesterification and the calcined eggshell powder was used as a heterogeneous catalyst. The optimum reaction conditions were obtained at 1 : 8 (oil/methanol) molar ratio with 2.0 wt% of CaO catalyst at 65 ± 0.5 °C for 2.5 h of reaction time. The factors affecting the conversion were studied separately.

Table 1 The extractability of *Jatropha curcas* seed oil with different solvents

Solvent (10 mL g^{-1} of seed)	Weight of seed (g)	Stirring time (h)	Weight of crude oil (g)	Yield of oil (%)
Hexane	10.078	2	2.436	24.17
	10.045	3	2.553	25.41
	10.072	4	2.492	24.74
Petroleum ether	10.06	2	2.313	22.99
	10.001	3	2.569	25.68
	10.003	4	2.489	24.88
Diethyl ether	10.003	2	2.307	23.06
	10.06	3	2.363	23.48
	10.09	4	2.371	23.49

Table 2 Fatty acid constituents and their composition (%) in *Jatropha* oil

Sr. no.	Fatty acid name	Formula	Composition (%)
1	Caprylic acid	C8:0	0.036
2	Myristic acid	C14:0	0.066
3	Pentadecanoic acid	C15:0	0.009
4	Palmitic acid	C16:0	14.240
5	Heptadecanoic acid	C17:0	0.085
6	Stearic acid	C18:0	6.585
7	Palmitoleic acid	C16:1	0.796
8	*cis*-10-Heptadeconic acid	C17:1	0.038
9	Oleic acid	C18:1	37.279
10	*cis*-11-Eicosenoic acid	C20:1	0.230
11	Linoleic acid	C18:2n6c	35.00
12	Alpha-linolenic acid	C18:3n3	0.086
13	Gamma-linolenic acid	C18:3n6	0.238
14	Eicosadienoic acid	C20:2	0.0
15	*cis*-11,14,17-Eicosatrienoic acid	C20:3n3	0.086
16	Arachidonic acid	C20:4n6	0.153
17	*cis*-13′,16-Docosadienoic acid	C22:2	0.202

Table 3 Physico-chemical properties of *Jatropha* oil

Sr. no.	Parameter	*Jatropha curcas* oil
1	Density (g cm^{-3}), 30 °C	0.94
2	Kinematic viscosity (mm^2 s^{-1}), 30 °C	55
3	Flash point (°C)	265
4	Fire point (°C)	277
5	Cloud point (°C)	5
6	Pour point (°C)	−1
7	Cloud filter plugging point (°C)	5
8	Saponification value	187
9	Acid value (mg KOH per g)	17.88
10	Cetane value	51
11	Calorific value kcal kg^{-1}	8908
12	Sulphur (%) by wt	0.0.13
13	Oxygen (%, w/w)	11.06
14	Carbon (%, w/w)	76.11
15	Hydrogen (%, w/w)	10.52
16	Ash content (%, w/w)	0.03 ± 0.0

The conversion of an ester from Free Fatty Acids (FFA) has been estimated by the equation,

$$\text{Conversion} = \text{acid value (initial)} - \text{acid value (final)}/ \\ \text{acid value (initial)} \times 100$$

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. DTA/TGA. For calcination, 24.6 mg of sample was used within the temperature range from 27 to 899 °C. Weight loss was observed in the temperature range from 700 °C to 850 °C (Fig. 1). This implies that decomposition of calcium carbonate into its respective oxide started at 700 °C.

The decomposition was completed at 850 °C to form calcium oxide with the release of carbon dioxide.[26] This is shown by the following reaction:

$$CaO_3 \xrightarrow{\Delta} CaO + CO_2 \tag{1}$$
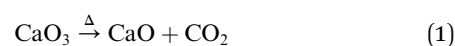
Release of CO_2 ratifies the formation of calcium oxide, which is used as a heterogeneous catalyst in the present work.

3.1.2. XRD analysis. Fig. 2 represents the X-ray diffraction pattern of the calcined eggshell catalyst. After calcination, the appearance of the eggshells became white which indicates the conversion of calcium carbonate into calcium oxide with the loss of carbon dioxide.[15] The peaks were matched with the Joint Committee on Powder Diffraction Standards (JCPDS) files. The X-ray diffraction (Fig. 2) peaks at *ca.* 32, 37, 53, 64 and 67 (JCPDS 48-1467) show the presence of calcium oxide. So, the prepared catalyst has a cubic system with a face-centered lattice.

3.1.3. SEM analysis. The SEM image of the catalyst is given in Fig. 3. It is clear from this figure that irregular but near-spherical particles are present in the catalyst. The particles agglomerated which might have occurred due to the high temperature calcination of the precursor. The plot of the 'frequency of the particle *vs.* size' revealed that the size of these particles varied between 1.0–3.2 μm but the majority of particles were in the 1.5–2 μm range.

3.1.4. FT-IR analysis. The FT-IR spectrum of the calcined eggshell (Fig. 4) shows important information regarding the
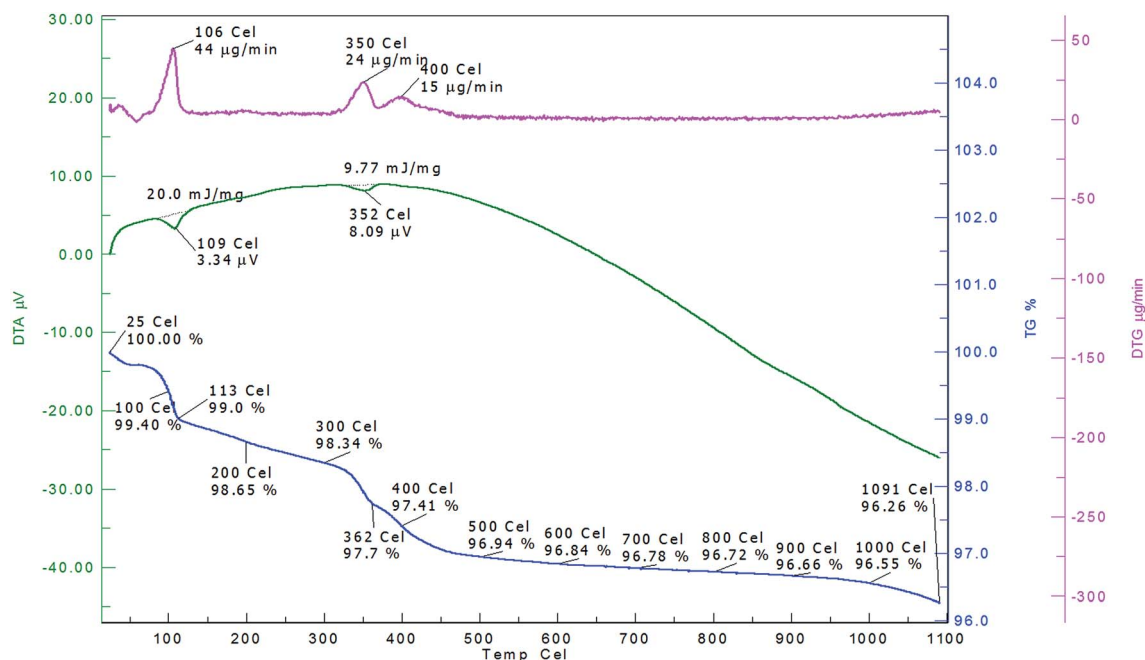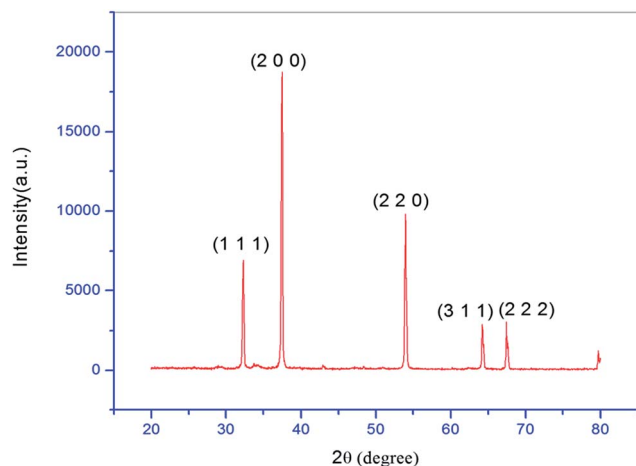
Fig. 1 DTA/TGA of uncalcined eggshell.

Fig. 2 The XRD pattern of the calcined eggshell catalyst.

Fig. 3 SEM of the calcined eggshell catalyst.

catalyst. The study of unannealed eggshell IR spectra was described by Engin et al.[38] The infrared band at 700 cm^{-1} indicates its characteristic Ca–O stretching vibration mode. The broad band that occurs at ~3620 cm^{-1} represents the –OH stretching vibration because of water content present in CaO since CaO absorbs water from atmospheric air. The broad and wide band at nearly 500 cm^{-1} is attributed to the Ca–O. A sharp stretching vibration band at 1700 cm^{-1} is due to the presence of C=O because of the small amount of carbonate present in calcined eggshell.

3.2. Optimization of the reaction parameters

Optimization of parameters was done both for esterification and transesterification reactions. Before proceeding to
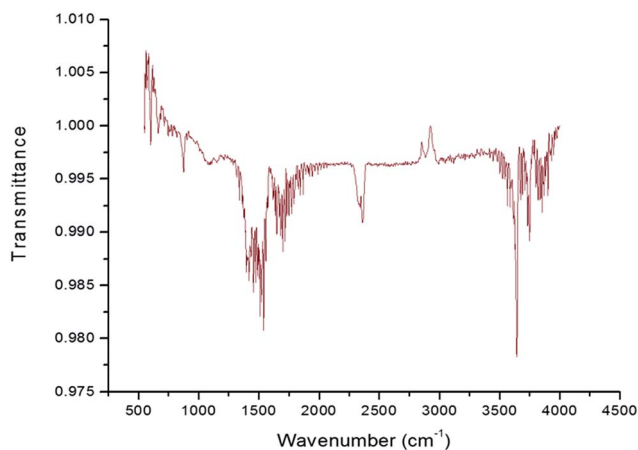

Fig. 4 The FT-IR spectrum of the calcined eggshell catalyst.

esterification, transesterification was executed with *Jatropha* oil, the feedstock. No conversion of the respective ester from triglycerides was observed. This shows that the presence of FFA plays a constitutive role in prohibiting the transesterification reaction. To overcome this aspect, the transesterification reaction has been conducted after lowering its acid value (*i.e.* after acid esterification), which contributes to the high conversion of biodiesel. It has been observed that a 1 : 8 molar ratio (oil/methanol) with 1.7% (v/v) sulphuric acid (H_2SO_4) for 1.3 h of reaction time at 60 ± 0.5 °C resulted in diminishing of the FFA value from 17.88 mg to 1.78 mg of KOH per g by acid esterification. During this reaction, the FFA present in the oil was transformed to a fatty acid methyl ester and moisture. The transesterification reaction was then carried out with the eggshell catalyst.

To optimize the loading of the catalyst and molar ratio of oil and methanol, the experiment was carried out by varying the molar ratio of methanol to oil from 4 to 12 for each wt% loading of the catalyst (0.5–2.5 wt%) considering the weight of oil in grams. The other variable parameters, namely temperature (65 ± 0.5 °C) and time of the reaction (2.5 h) were kept constant. From Fig. 5 it is clear that except for 2 wt% and 2.5 wt% loadings of the catalyst, the methyl ester yield increases constantly with the increasing molar ratio of oil and methanol. But a maximum of up to 80% yield was reached at a methanol to oil ratio of 1 : 12. It indicates that less conversion is obtained with more consumption of methanol in this case. In the case of 2.0 wt% loading of the catalyst, the highest yield (90%) is obtained at a molar ratio of 8. Further increase in the molar ratio of methanol and oil has a negative effect on the yield of the methyl ester. The yield of the methyl ester with 2.5 wt% of the catalyst also shows activity near to the 2 wt% catalyst but the maximum yield is obtained with the 2 wt% catalyst at a molar ratio of 8 : 1 (methanol : oil). It proves that 2 wt% of the catalyst and the methanol to oil molar ratio of 8 are optimum parameters for this reaction (Fig. 5).

However, Sharma *et al.*[28] have reported an optimum yield with 2.5 wt% of catalyst with *Pongamia* oil and Wei *et al.*[23] have reported a maximum yield with 3.0 wt% of catalyst by using soybean oil as a feedstock. An optimum yield of 90% was achieved at a reaction temperature of 65 ± 0.5 °C, just above the reflux temperature of methanol. The yield obtained was below 80% when the temperature was decreased to 50 ± 0.5 °C, which rises with a rise in temperature. At a higher temperature (*i.e.* 70 ± 0.5 °C) the yield will decrease since the loss of some amount of methanol at a high temperature may occur (Fig. 6). In 30 min of reaction time, 55% conversion of biodiesel was obtained, which rises gradually with an increase in time. A reaction time of 2.5 h was optimum to obtain a yield of up to 90% of biodiesel (Fig. 7).

Further increase in time could not raise the yield of biodiesel, because the maximum amount of triglyceride was converted into its corresponding ester. Hence 2.5 h is the optimum time for the reaction. The rate of stirring was studied from 200 rpm to 1000 rpm. The maximum yield was obtained with agitation at 600 rpm. As the agitation speed was lowered below 600 rpm, the yield decreased and with an increase in agitation
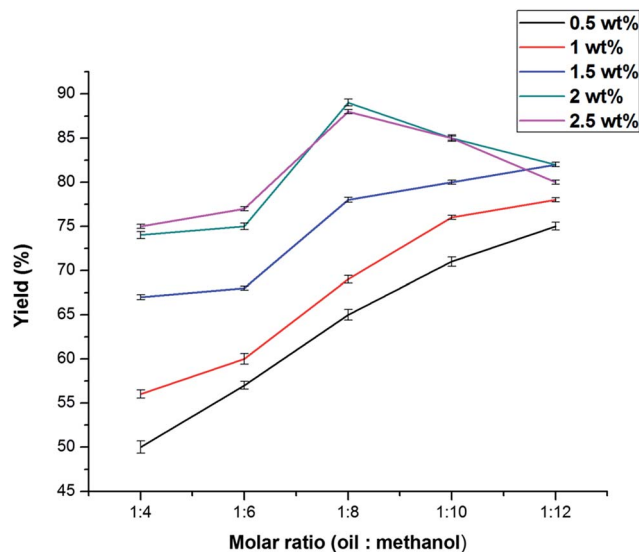

Fig. 5 The effect of molar ratio (oil to methanol) on the yield of the methyl ester.

higher than 600 rpm, no further increment in yield was observed (Fig. 8).

3.2.1. The study of *Jatropha* oil methyl ester properties. Fuel properties as well as other parameters of biodiesel were characterized using the ASTM D6751 method (Table 4). The acid value of the *Jatropha* oil methyl ester was found to be 1.78 mg of KOH per g which was within the ASTM standard for carrying out esterification. The density of the feedstock obtained was 0.872 g cm^{-3} and the kinematic viscosity was 4.9 cSt at 40 °C, which were as per the ASTM range. The cloud point and pour point were dependent on the presence of stearic acid in biodiesel. The cloud point as well as the pour point were also within the standards as 4 and −1 respectively. The density of the raw oil was 0.940 g cm^{-3} while that of its methyl ester was 0.872 g cm^{-3}.
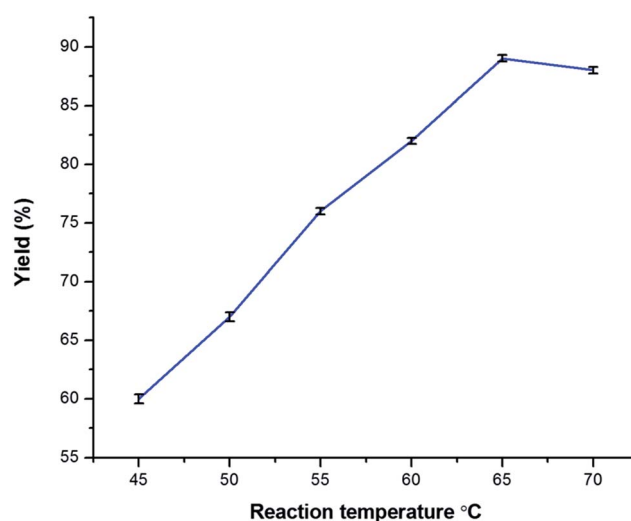

Fig. 6 The effect of reaction temperature on the yield of the methyl ester.
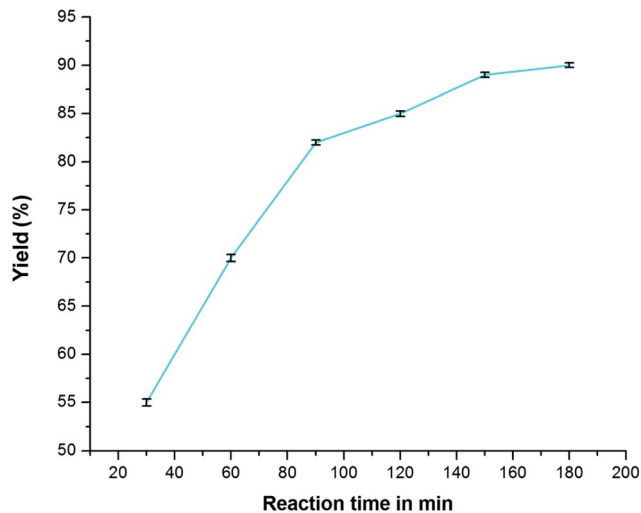
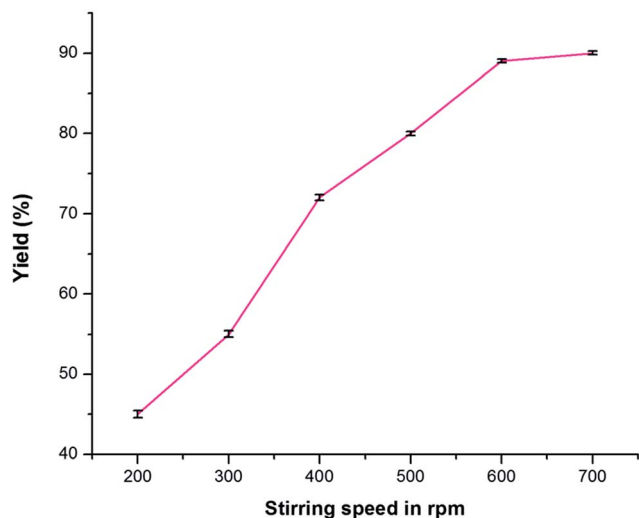Fig. 7   The effect of reaction time on the yield of the methyl ester.

Fig. 8   The effect of stirring speed on the yield of the methyl ester.

As viscosity is directly proportional to density, viscosity was reduced by simply performing the transesterification reaction, automatically the density was reduced and shown as per ASTM limits. The flash point and fire point of *Jatropha* biodiesel were 167 °C and 176 °C, respectively, which were just slightly above that of the ASTM limits. But both of these parameters were considered as safe parameters for storage and transport of biodiesel. The cetane number of the biodiesel was 51 which crossed the limit of ASTM. It indicates the ignition delay time of the fuel upon injection into the combustion chamber. The calorific or heating value of the biodiesel was found to be 37.5 which matched diesel fuel up to 90%. The moisture was found to be 0.02% which was within the ASTM limits. The elemental composition of *Jatropha* biodiesel shows a composition of carbon (75.08%), hydrogen (12.78) and oxygen (11.68%). The presence of oxygen in biodiesel helps in complete combustion as compared to diesel fuel.

3.3.   Comparison of eggshell derived from various sources

Eggshell has been widely used by researchers as a potential and alternative source of catalyst for production of biofuels. It has been reported that million tons of eggshells are generated as waste. The major constituent in the waste eggshell is calcium carbonate, *i.e.* around 94%. Calcium phosphate and organic matter comprise around 1% and 4%, respectively.[39] Apart from calcium carbonate (85–95%), the eggshell from various birds also contains calcium phosphate, magnesium carbonate, sodium, potassium, zinc, manganese, iron, copper, and protein. Chicken eggshell is reported to contain a high amount of calcium carbonate that results in the formation of a CaO content as high as 97.4%.[40] The eggshell could be converted into hydroxyapatite using a sol–gel method which possesses large surface energy with nanocrystalline size (5 to 90 nm).[39]

The efficiency of eggshell derived CaO has shown varying results in the production of biodiesel. Viriya-Empikul *et al.*, 2010 [25] has reported production of biodiesel with a fatty acid methyl ester content of >90% obtained in 2 h at 60 °C with a methanol to oil molar ratio of 18 : 1, and a catalyst amount of 10 wt%. It is reported that chicken eggshell contains the highest amount of calcium (99.21%) as compared to other similar materials {the golden apple snail shell (99.05%) and *Meretrix venus* shell (98.59)}. This resulted in a better catalytic activity of the chicken eggshell in transesterification.[27] However, few researchers have reported a high catalytic yield using an eggshell derived catalyst. Chakraborty *et al.*, 2010 [41] has reported preparation of an eggshell using the wet-impregnation method supported over fly ash. The synthesized catalyst possessed a surface area of 0.701 $m^2 \, g^{-1}$, pore volume of 0.0044 $cm^3 \, g^{-1}$, pore diameter of 5.2 nm, and basicity of 1.6 mmol HCl per g. The FAME yield obtained was 96.97% using CaO (1.0 wt%) and a methanol to oil molar ratio of 6.9 : 1. The modified catalyst thus fulfilled the specification by EN 14214 for the FAME content (minimum value for which should be 96.5 wt%). It has also been reported that CaO derived from eggshell can be reusable for about 16 times, thereafter it loses it activity.

Cho and Seo, 2010 [42] reported the treatment of a quail and chicken eggshell catalyst with 0.005 M hydrochloric acid in the transesterification of palm oil. It was reported that the acid treatment of the solid catalyst led to an enhanced catalytic activity for the quail eggshell during transesterification that was comparable to potassium methoxide. Though the constituents of quail and chicken eggshell are comprised of the same material, calcium carbonate, calcination resulted in a higher catalytic activity for the quail eggshell than the chicken eggshell. This has been attributed to a larger number of strong basic sites in the quail eggshell derived catalyst as compared to that of the chicken eggshell. The acid treatment was reported to have a negligible effect on the catalytic activity of a chicken eggshell. A high conversion of >98% has been reported with the quail eggshell for five repeated times at 65 °C, with a methanol to oil molar ratio of 12 : 1 and a catalyst amount of 1.5 wt% with respect to oil. Mosaddegh 2013 [43] has reported the synthesis of a nano eggshell powder upon mixing with dichloromethane for the synthesis of 2-aminochromenes. The synthesis of the

Table 4 The properties of the *Jatropha* methyl ester

Parameters	ASTM-6751 test method[30]	*Jatropha* methyl ester
Acid value (mg KOH per g)	D664-07	1.78
Density (g cm^{-3})	D1448-1972	0.872
Kinematic viscosity (cSt at 40 °C)	D664-06	4.9
Cloud point	D2500	4
Pour point	D2500	−1
Flash point (°C)	D93	167
Fire point (°C)	D93	176
Cetane number	D613	51
Calorific value	D6751	37.5
Water (%)	D2709	0.02
Carbon (%)	By elemental analysis	75.08
Oxygen (%)	By elemental analysis	11.68
Hydrogen (%)	By elemental analysis	12.78
Nitrogen (%)	By elemental analysis	0.09

catalyst was reported to be done using ultrasonication at a frequency of 60 Hz at 50 °C for 1 h. The average size of the catalyst using Transmission Electron Microscopy and Field Emission Scanning Electron Microscopy was reported to be 50 nm. Chen *et al.*, 2014 [44] has reported an ostrich eggshell derived catalyst to be cost effective for the transesterification of palm oil *via* ultrasound. The conversion reported by the catalyst, CaO derived from ostrich eggshell, was reported to be 92.7% in 1 h, with an ultrasonic power of 60%, a methanol to oil molar ratio of 9 : 1, and a catalyst loading of 8 wt% (with respect to oil). The conversion reported was less than that desired by the EN specifications. Chen *et al.*, 2015 [45] modified the eggshell by loading with Na_2SiO_3 to synthesize a $CaO–SiO_2$ catalyst for the synthesis of biodiesel from palm oil. The catalyst, $CaO–SiO_2$, was reported to exhibit decreased catalytic activity. However, the reusability of the catalyst was reported to increase with increasing proportion of silica.

An excellent review by Tan *et al.*, 2015 [40] on the comparison of calcium carbonate derived from the eggshells of various birds. The temperature at which the calcination is obtained is 700 to 1000 °C. The cost that is incurred in the synthesis of CaO is the energy involved to achieve this calcination temperature. The process involved in the synthesis of CaO from eggshells is the removal of impurities and its calcination at 800–1000 °C for a few hours (usually around 2 h). Thus the major cost incurred in the production of CaO from an alkaline catalyst will be the energy required to attain the temperature of around 1000 °C for 2 h.

The homogeneous catalyst requires a lesser time for the synthesis of biodiesel compared to the heterogeneous catalysts. Usually 30 min to 1 h is required when a homogeneous catalyst is used in the synthesis of biodiesel, whereas, a longer time (around 1–5 h) is usually required using a heterogeneous catalyst.[46,47] The benefits of the eggshell derived catalyst are quite significant and should not be overlooked. This includes utilization of a waste material in the environment that creates a nuisance as solid waste. Its large colossal use involves its dumping at disposal sites that attracts mice and rodents. In addition to this, the trace elements present in the eggshell may

leach and contaminate the environment. Another major and important advantage for the utilization of a heterogeneous catalyst (including eggshell derived CaO) is its reusability.[45] The utilization of a heterogeneous catalyst over a homogeneous catalyst is the easy separation of the former from biodiesel. Using a heterogeneous catalyst results in the generation of a minimal amount or no wastewater which otherwise would occur using a homogeneous catalyst. By loading another compound with CaO, the catalytic activity has been reported to enhance to >96.5% FAME as desired by the EN specifications.

The work carried out in the present study appears to be economically viable. There are four steps involved in the synthesis of biodiesel which include the extraction of the feedstock oil, synthesis and characterization of the catalyst from eggshell, synthesis and characterization of biodiesel through transesterification, and test of reusability of the catalyst as the fourth step. Calcium oxide used as a heterogeneous catalyst has been derived from waste material and has been found to give a high yield of biodiesel. After completion of the transesterification reaction, the unreacted methanol was collected and reused which will further bring down the cost at a commercial scale. The reaction temperature used during the transesterification in the present work gave a high yield at 65 °C which is not highly energy intensive.

4. Conclusions

A CaO catalyst, obtained by calcination (900 °C for 2.5 h) of eggshells had better activity in the transesterification of *Jatropha* oil for biodiesel production. A high yield of *Jatropha* oil methyl ester can be attained by optimization of reaction parameters such as molar ratio (oil/methanol), catalyst concentration, reaction time, reaction temperature and rate of stirring. The acid value of the crude *Jatropha* oil was 17.88 mg KOH per g which was lowered through acid esterification to 1.78 mg KOH per g. The different reaction parameters like methanol to oil molar ratio, catalyst loading, temperature and reaction time were optimized. The optimum oil and methanol molar ratio was 1 : 8 with 1.7% (v/v) H_2SO_4 at a temperature of 60 ±

0.5 °C for 1.3 h. The optimized parameters for the transesterification also showed oil and methanol in similar proportions with 2 wt% of the catalyst and 2.5 h time of reaction at 65 ± 0.5 °C. The yield of the synthesized biodiesel obtained was 90%. The parameters of the biodiesel like the acid value, density, kinematic viscosity, flash point, fire point, cloud point, pour point, cetane number and calorific value were ASTM D6751 standard. Other parameters such as water (%), carbon (%), oxygen (%), hydrogen (%) and nitrogen (%) were also studied and were within the limit of ASTM standard. Thus, the biodiesel obtained was economically viable and possessed superior quality.

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