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

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Abstract: High purity calcium oxide (CaO) was prepared from egg shell and was 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 egg shell was subjected to calcination at 900 °C for ~ 2.5 h. Confirmation of the catalyst was arried out by X-Ray diffraction, Fourier transform infrared spectrometer (FT-IR), and Differential thermal and thermo-gravimetric (DTA-TGA) analysis. Synthesized biodiesel was characterized with 1H NMR. High yield and pure biodiesel was obtained by taking various parameters such as a proper methanol to oil molar ratio, reaction temperature and reaction time. Reusability of 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 for oil resource over other countries, climate change and increase in greenhouse gases compel for search of alternative renewable fuels. Edible and nonedible oils could be alternate to petroleum oil, but the higher viscosity reduces the fuel atomization and increases the fuel spray penetration leading to high engine deposits and thickening of lubricating oil. Biodiesel, among renewable resource[1] can be directly used in diesel engine as it does not require modification in 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 as in fossil diesel fuel. Even when they are used in blended form, a significant decrease in carbon monoxide (CO), hydrocarbon (HC) and particulate matter was observed[2, 3]. Moreover, it can be easily produced via transesterification of waste oils or vegetable oils if the free fatty acid is less than 5%[4]. Therefore, in certain cases, when the oil containing free fatty acid more than 5%, esterification of oil is needed prior to transesterification. For example, the raw vegetables oils (non-edible oil) like *Pongamia pinnata*, *Jatropha curcus*, *Calophyllumino phylum* and *Citrullus colocynthis* [4-9] are reported to have higher acid value and prior to transesterification, esterification of such oils has to be carried out.The source of oil and its composition varies with plant species[10]. The soybean oil in USA, sunflower and rapeseed oil in Europe, palm oil in Malaysia, Thailand and coconut oil. Philippines are being considered as a substitute for diesel fuel seed oil[11]. Variations of climate encourage the vegetation diversity and so, the study over possible vegetation oil is needed to use biodiesel at industrial scale for each country. Waste frying oil was also used by several authors to produce biodiesel [12-15].

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

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

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provides a cost effective and eco-friendly recycling way of this solid waste but also contributes reduction in biodiesel cost to make it competitive with diesel fuel.

Most of the work reported on transesterification using CaO as a catalyst, the catalyst is derived from egg shells[22, 23]. Edible palm oil has been used for production of biodiesel using egg shell derived CaO as a catalyst [24-27]. The substantial amount of saturated fats is present in palm and therefore, the biodiesel obtained has low temperature properties[11]. Moreover, no work is available to evaluate egg shell catalyst as an effective heterogeneous catalyst option with high free fatty acid containing feedstock and this was motivation that the recycled egg shells as catalyst source were used for biodiesel production with jatropha oil. Karanja oil as a feedstock was used for biodiesel production with calcined egg shell powder as CaO catalyst [28]. The physicochemical properties[3, 29], oil content [30] and energy values of Jatropha have already been explored [31, 32]. Jatropha contains toxic substances due to which it is considered as non-edible [33-35]. Effect of reaction parameters such as molar ratio, catalyst percentage, reaction time, temperature, and stirring speed on synthesis of biodiesel have been studied [4, 36]. The synthesized methyl ester was found with gas chromatogram mass spectra to analyze 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 ASTM-6751 standard.

2. Experimental

2.1. Materials

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

2.2. Catalyst preparation

The egg shells were washed with hot water to eliminate the contaminants present on the shells. Then it was dried in hot air oven at 110 °Cfor 24 h**.** The dried egg shells were ground into powder using a ball mill. The obtained powder was calcined in a muffle furnace under the various temperature ranges starting from 25 °C to 900 °C for 2.5 h to obtain CaO from calcium containing precursor. Granados et.al [37] reported that catalytic poisoning will occur when it is placed in contact with air because of 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 anticipate the poisoning of the catalyst.

2.3. Characterization of catalyst

Differential thermal analysis/thermos gravimetric 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 egg shells. DTA/TGA experiments were performed under nitrogen flow with a structured text analyzer (DTA/TGA), model STA 409, Netzsch-Gerratebau GmbH (Germany). The FT-IR spectroscopy was performed on BRUKER ALPHA Eco ATR in the wavelength ranges from 4000-500 cm-1. The XRD patterns were studied on X-ray diffractometer (Scifert and Co., model 3000). The fatty acid profile of jatropha was performed on gas chromatogram mass spectra (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 seeds before carrying out the estimation of oil content. Then seeds were dried at 105 °C for 30 min in oven. 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. Optimum time required for maximum extractability was also examined [4,5,9]. The extraction result has been mentioned in Table 1. It was observed that petroleum ether and n-hexane, both were equally good for extraction of oil. The optimum time required for maximum extractability of oil was 3 h.

Table 1

The extracted jatropha oil was filtered and used to perform its physico-chemical properties as well as fatty acids content by Gas chromatography mass spectra. The peaks were identified using standards of fatty acids and the identified fatty acids were listed in Table 2. The physico-chemical parameters were illustrated in Table 3.

Table 2

The jatropha oil consists of both saturated and unsaturated fatty acids. Among these Oleic acid was found to be in highest proportion (37.279%) after that Linoleic acid (35.00%), Palmitic acid (14.240%) and Stearic acid (6.585%) were assessed. Presence of stearic acid is responsible for high cloud point of biodiesel.

Table 3

2.5. Esterification and transesterification reactions

Esterification and Transesterification reactions were performed in necked batch reactor of 2 L capacity. First of all 1000ml Jatropha oil was dehydrated in an oven at 107 °C for 2.5 h. To perform the acid esterification, 100ml 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 mechanical stirrer was kept constant at 600 rpm to overcome limitations due to mass transfer. After completion of reaction,

the reaction mixture was transferred to separating funnel for 4h. Water formed was dehydrated using rotavapor. Esterified jatropha oil was used for further transesterification and calcined egg shell powder used as a heterogeneous catalyst. The optimum reaction conditions 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 on the conversion were studied separately.
The conversion of ester from FFA has been estimated by the equation,
Conversion = Acid value (initial)-Acid Value(final)/Acid value (initial) x 100

3. Result and discussion

3.1 Characterizations 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 temperature range 700 °C to 850 °C (Fig. 1). This implies that decomposition of calcium carbonate to its respective oxide started at 700 °C.

Figure 1

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

$$CaO_3 \xrightarrow{\Delta} CaO + CO_2 \qquad (1)$$

Release of CO_2 ratifies the calcium oxide formation, which is used as heterogeneous catalyst in present work.

3.1.2. XRD Analysis

Figure 2 Represents the X-ray diffraction pattern of claimedegg shell catalyst. After calcination, the appearance of egg shells became white which indicates 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. X ray diffraction (Fig. 2) peaks at c.a. 32, 37, 53, 64, 67 (JCPDS 48-1467) shows the presence of calcium oxide. So, the prepared catalyst has cubic system with face-center lattice.

Figure 2

3.1.3. SEM Analysis

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

Figure 3

3.1.4. FT-IR Analysis

FT-IR spectra of calcined egg shell (Fig. 4) shows important information regarding the catalyst. The study of unannealed egg shell IR spectra was described by Engin et.al [38]. Infrared band at 700 cm^{-1} indicates its characteristic of Ca-O stretching vibration mode. The broad band occurs at ~ 3620 cm^{-1} represents -OH stretching vibration because of water content present in CaO since CaO absorbs water from atmospheric air. The broad and wide band indicates at nearly 500^{-1}is attributed to Ca-O band. Sharp stretching vibration band at 1700cm^{-1} is due to presence of C=O because of little amount of carbonate present in calcined egg shell.

Figure 4

3.2 Optimization of reaction parameters

Optimization of parameters was done both for esterification and transesterification reactions. Before preceding to esterification, transesterification was executed with jatropha oil, the feedstock. No conversion of respective ester from triglycerides was observed. This shows that the presence of FFA plays constitutive role in prohibiting transesterification reaction. To overcome this aspect, transesterification reaction has been conducted after lowering its acid value (i.e. after acid esterification), which contributes to high conversion of biodiesel. It has been observed that at 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 17.88mg to 1.78 mg of KOH/g by acid esterification. During this reaction, the FFA present in the oil was transformed to fatty acid methyl ester and moisture. The transesterification reaction was then carried out with egg shell catalyst.
To optimize the loading of catalyst and molar ratio of oil and methanol, experiment was carried out varying the molar ratio of methanol to oil from 4 to 12 for each wt% loading of catalyst (0.5-2.5 wt%) considering the weight of oil in grams. The other variable parametersnamely temperature (65 ± 0.5 °C) and time of reaction (2.5 h) were kept constant. From figure4 it is clear that except 2wt% and 2.5 wt% loading of catalyst, methyl ester yield is increasing constantly with increase in molar ratio of oil and methanol. But it gave maximum upto 80% yield at methanol to oil ratio 1:12. It indicates that less conversion is obtained with more consumption of methanol in this case. In case of 2.0 wt% loading of catalyst, highest yield (90%) is obtained at molar ratio of 8. Further increase in molar ratio of methanol and oil has negative effect on the yield of methyl ester. Yield of methyl ester with 2.5 wt% catalyst also shows activity near to 2wt% catalyst but the maximum yield is obtained with 2wt%

catalyst at molar ratio 8:1(methanol: oil). It proves that 2wt% of catalyst and methnol to oil molar ratio 8 is an optimum parameter for this reaction.

Figure 5

Figure 6

However, Sharma et.al.[28] have reported the optimum yield with 2.5wt% of catalyst with the Pongamia oil and Weietal.[23] have reported the maximum yield with 3.0wt% of catalyst by using soybean oil as a feedstock. An optimum yield of 90% was achieved at the reaction temperature 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 rising in the temperature. Due to higher temperature (i.e.70±0.5 °C) yield will be decreased since loss of some amount of methanol at high temperature may occur (Figure 6). In 30 min. of reaction time, 55% conversion of biodiesel was obtained, which rises gradually with an increment in time. A reaction time of 2.5 h was optimum condition to obtain yield up to 90% of biodiesel (Figure 7).

Figure 7

Figure 8

Further increase in time could not raise the yield of biodiesel. It is because of maximum triglyceride getting converted into its corresponding ester. Hence 2.5 h is the optimum reaction time for the reaction. The rate of stirring was studied from 200 rpm to 1000 rpm. The maximum yield was obtained with the agitation to 600rpm. As the agitation speed was lowered than 600 rpm, yield was decreased and with increase in an agitation higher than 600 rpm, no further increment in yield was observed (Figure 8).

3.2.4 Study of Jatropha oil methyl ester properties

Table 4

Fuel properties as well as other parameters of biodiesel were characterized by ASTM D6751 method (Table 4). Acid value of Jatropha oil methyl ester was found to be 1.78 mg of KOH/g which was within the ASTM standard for carrying out esterification. Density of the feedstock obtained was 0.872 gm/cc and kinematic viscosity 4.9 Cst at 40 °C, which were as per ASTM range. The cloud point and pour points were dependent on presence of stearic acid in biodiesel. Cloud point as well as pour point were also within standards as 4 and -1 respectively. The density of raw oil was 0.940gm/cc while that of its methyl ester was 0.872gm/cc. As viscosity is directly proportional to density, viscosity was reduced by simply transesterification reaction, automatically density was reduced and shows 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 ASTM limit. But both of these parameters were considered as a safe parameter for storage and transport of biodiesel. The cetane number of biodiesel was 51 which crossed the limit of ASTM. It indicates ignition delay time of the fuel upon injection into the combustion chamber. The calorific or heating value of biodiesel was found to be 37.5 which matched diesel fuel up to 90%. The moisture was found 0.02% which was in the ASTM limits. The elemental composition of jatropha biodiesel shows 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 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 comprises around 1% and 4% respectively [39]. Apart from calcium carbonate (85-95%), eggshell from various birds also contains calcium phosphate, magnesium carbonate, sodium, potassium, zinc, manganese, iron, copper, and protein. The chicken eggshell is reported to contain high amount of calcium carbonate that results in the formation of CaO content as high as 97.4% [40]. The eggshell could be converted to hydroxyapatite by sol-gel method which possessed 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 fatty acid methyl ester content of >90% obtained in 2 h at 60^{o} C, methanol to oil molar ratio of 18:1, and catalyst amount of 10 wt%. It is reported that the chicken eggshell contains highest amount of calcium (99.21%) as compared to other similar material {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 eggshell derived catalyst. Chakraborty et al., 2010 [41] has reported preparation of eggshell by wet-impregnation method supported over fly ash. The synthesized catalyst possessed surface area of 0.701 m^2/g, pore volume of 0.0044 cc/g, pore diameter of 5.2 nm, and basicity of1.6 mmol HCl/g. The FAME yield obtained was 96.97% using CaO (1.0 wt.%) and 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 to be reusable for about 16 times, thereafter it loses it activity.

Cho and Seo, 2010 [42] reported treatment of 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 enhanced catalytic activity for quail eggshell during transesterification that was comparable to potassium methoxide. Though, the constituent of quail and chicken eggshell comprises of the same material, calcium carbonate, calcination resulted in a higher catalytic activity in quail eggshell than the chicken eggshell. This has been attributed to larger number of strong basic sites in the quail eggshell derived catalyst as compared to chicken eggshell. The acid treatment was reported to have negligible effect on the catalytic activity of chicken eggshell. A high conversion of >98% has been reported with the quail eggshell for five repeated times at 65^{o} C, with a methanol to oil molar ratio of 12:1 and catalyst amount of 1.5 wt.% with respect to oil. Mosaddegh 2013 [43] has reported synthesis of nano eggshell powder upon mixing with dichloromethane for the synthesis of 2-aminochromenes. The synthesis of the catalyst was reported to be done by ultrasonication at a frequency of 60 Hz at 50 ^{o}C for 1 h. The average size of the catalyst using Transmission Electron Microscope and Field Emission Scanning Electron Microscope was reported to be 50 nm. Chen et al., 2014 [44] has reported the ostrich eggshell derived catalyst to be cost effective for 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 ultrasonic power of 60%, methanol to oil molar ratio of 9:1, and 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 $CaO\text{-}SiO_2$ catalyst for the synthesis of biodiesel from palm oil. The catalyst, $CaO\text{-}SiO_2$ was reported to exhibit decreased catalytic activity. However, the reusability of the catalyst was reported to increase with increased proportion of silica.

An excellent review by Tan et al., 2015 [40] on the review of calcium carbonate derived from eggshells derived from various birds. The temperature at which it is obtained is 700 to 1000^{o} 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 eggshell is removal of impurities and its calcination at 800-1000 ^{o}C for a few hours (usually around 2 h). Thus the major cost incurred in the production of CaO from alkaline catalyst will be the energy required to attain the temperature of around 1000 ^{o}C for 2 h.

The homogeneous catalyst requires a lesser time for the synthesis of biodiesel as compared to 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 not to overlook. 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. Apart from this, the trace elements present in the eggshell may leach and contaminate the environment. Another major and important advantage from the utilization of heterogeneous catalyst is (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 the biodiesel. This results to generation of minimal or nil amount of wastewater using heterogeneous catalyst which otherwise will be required using a homogeneous catalyst in the synthesis of wastewater. 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 synthesis of biodiesel which include extraction of feedstock oil, synthesis and characterization of catalyst from egg shell, synthesis and characterization of biodiesel through transesterification, and test of reusability of catalyst is the fourth step. Calcium oxide used as a heterogeneous catalyst has been derived from waste material, has been found to be 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 commercial scale. Reaction temperature used during transesterification in the present work gave high yield at 65 °C which is not highly energy intensive.

Conclusions

The catalyst CaO, obtained by calcination (900 °C for 2.5 h) of egg shell had better activity in transesterification of Jatropha oil for biodiesel production. 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. Acid value of crude Jatropha was 17.88 mg KOH/g which was lowered through acid esterification to 1.78 mg KOH/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 temperature 60± 0.5 °C for 1.3 h. The optimized parameters for transesterification also showed oil methanol in similar proportion with 2 wt% and 2.5 h time of reaction at 65± 0.5 °C. Yield of synthesized biodiesel obtained was 90%. The parameters of the bioiesel like 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 a superior quality.

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Table 1 Extractability of *Jatropha curcus* seed oil with different solvents

Solvent (10mL/g of seed)	Weight of seed (g)	Stirring time (hr)	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(%) of Jatropha oil.

Sr.	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 Heptodeconic 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	
15	Cis- 11,14,17Eicosatrienoc 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	JatrophaCurcas Oil
1	Density (gm/cc),30 °C	0.94
2	Kinematic viscosity (mm^2/s), 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/g)	17.88
10	Cetane value	51
11	Calorific value Kcal/Kg	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

Table 4 Properties of Jatropha methyl ester

Parameters	ASTM- 6751 test method [30]	Jatropha methyl ester
Acid value (mg KOH/g)	D664-07	1.78
Density (gm/cc)	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

Figure 1DTA/TGA of uncalcined egg shell.

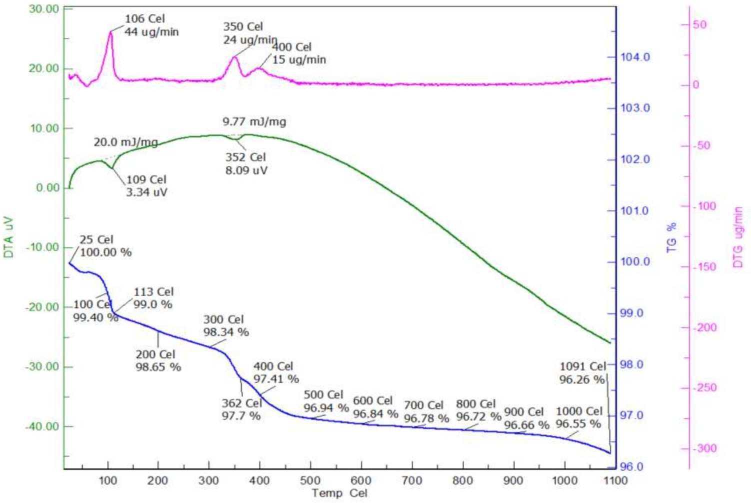


Figure 2 XRD patterns of calcined egg shell catalyst.

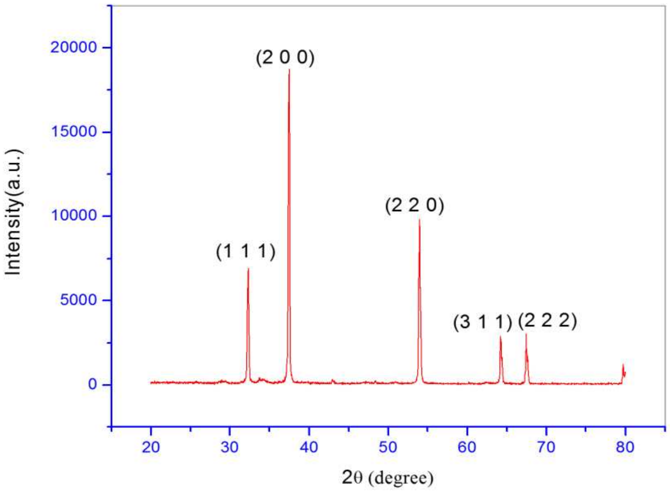


Figure 3 SEM of calcined egg shell catalyst.

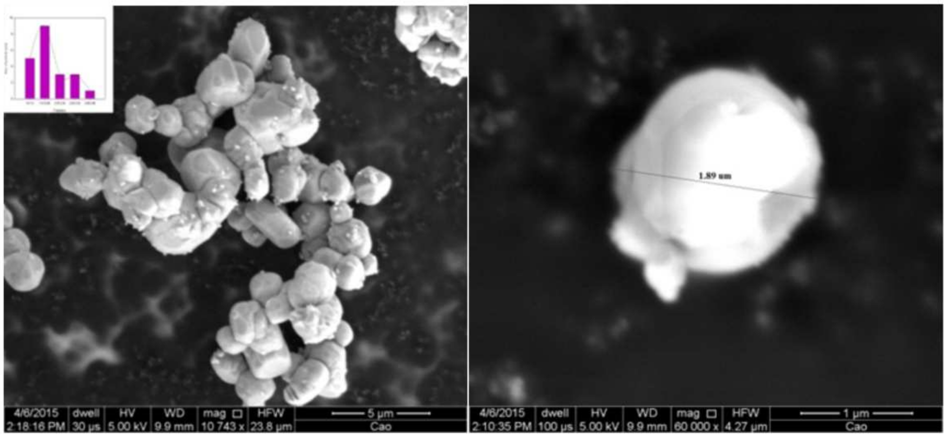


Figure 4 FT-IR of calcined egg shell catalyst.

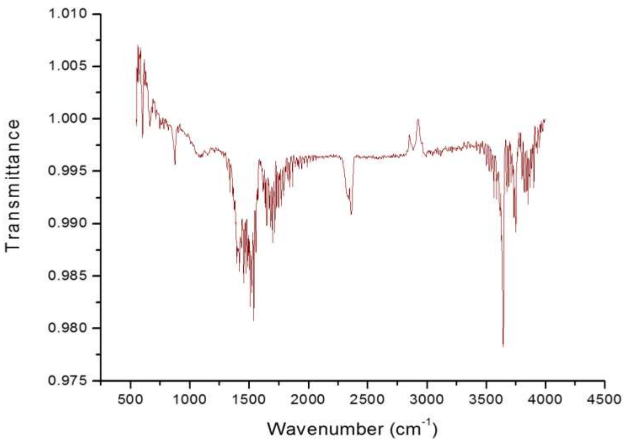


Figure 5 Effect of molar ratio (oil to methanol) on the yield of methyl ester.

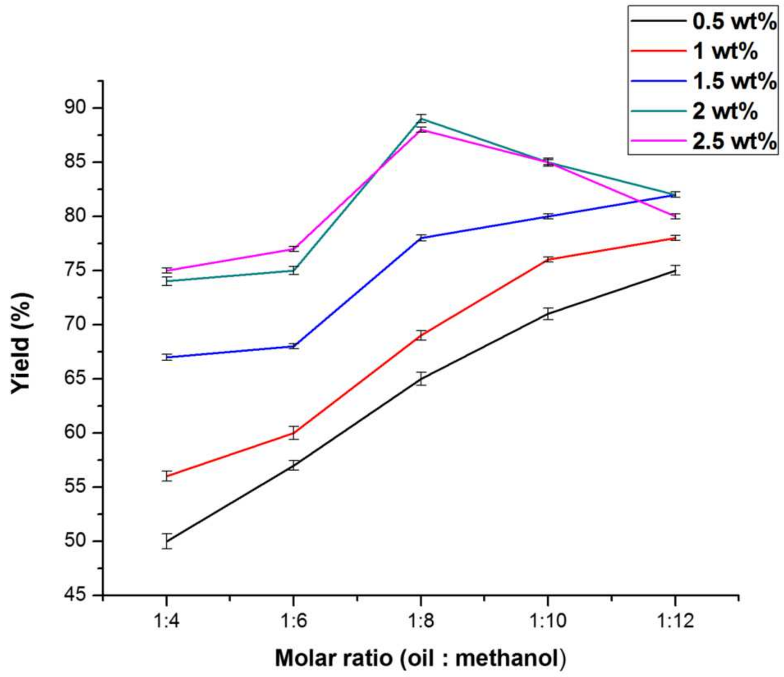


Figure **6** Effect of reaction temperature on the yield of methyl ester.

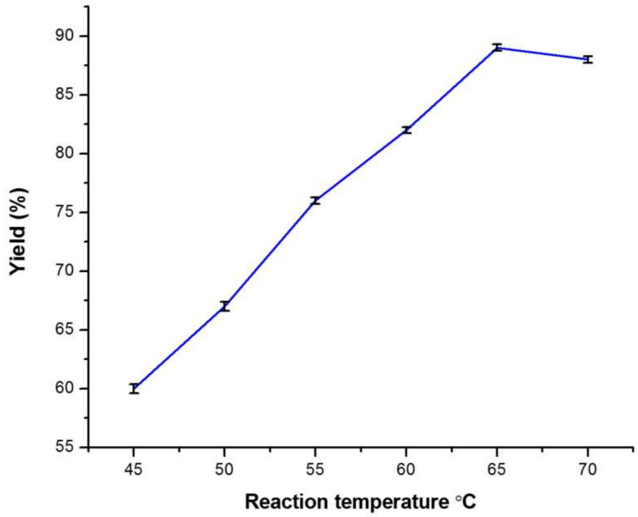


Figure **7** Effect of reaction time on the yield of methyl ester.

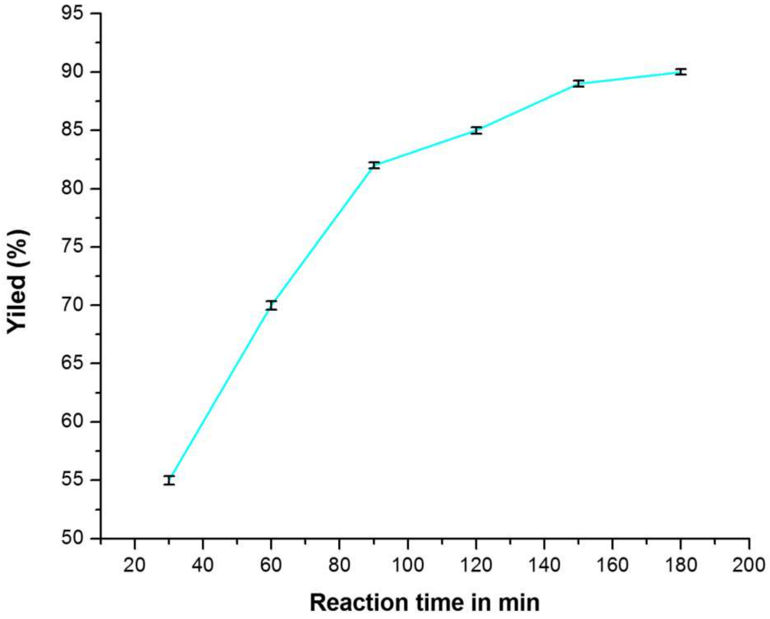
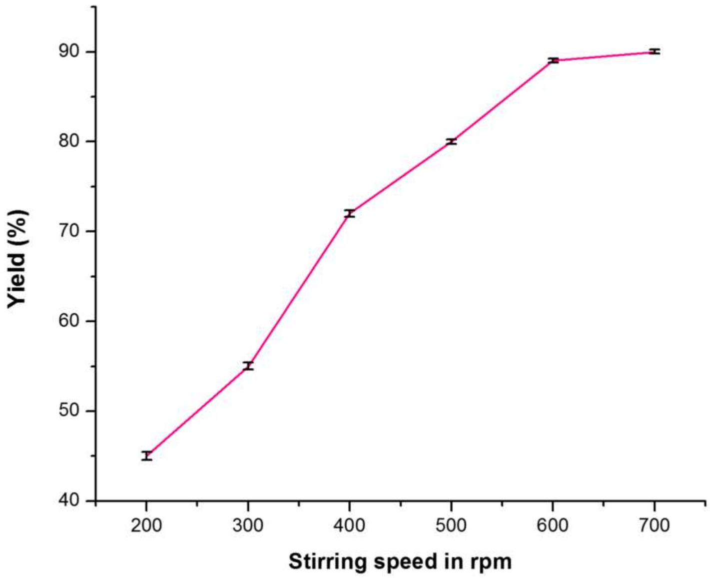


Figure **8** Effect of stirring speed on the yield of methyl ester.



Graphical abstract