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Application of an Efficient Nonconventional Heterogeneous Catalyst for Biodiesel Synthesis from *Pongamia pinnata* Oil

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Recycled chicken eggshells after calcination have been used as a nonconventional heterogeneous catalyst for biodiesel synthesis from karanja oil from the pongam tree (*Pongamia pinnata*). The catalyst was characterized on X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and differential thermal analysis/thermogravimetric analysis (DTA/TGA). The formation of the calcium oxide phase was confirmed at 900 °C after calcination. A high biodiesel yield of 95.0% and conversion of 97.4% was obtained at an 8:1 (alcohol/oil) molar ratio, 2.5 wt % catalyst, and 2.5 h reaction time at 65 ± 0.5 °C. The biodiesel conversion was determined by Fourier transform nuclear magnetic resonance (FTNMR) spectroscopy.

1. Introduction

Biodiesel has attracted attention in recent years as a renewable fuel with less pollutant emissions compared to mineral diesel on its combustion.[1,2] Biodiesel fuel is made from vegetable oils, animal fats, and microbial oil (algae, yeast, bacteria, and fungi).[3] The most common method of biodiesel preparation is the transesterification reaction, where the triglycerides present in oil react with monohydric alcohol in the presence of a catalyst, such as sodium hydroxide, sodium methoxide, potassium hydroxide, and potassium methoxide.[4] Biodiesel synthesis necessarily needs a catalyst to attain the equilibrium in a practical manner. Homogeneous acid catalysts, such as sulphuric and hydrochloric acids, and homogeneous alkaline catalysts, such as sodium hydroxide, potassium hydroxide, and sodium methoxide, cater to the present need for biodiesel synthesis.[5] However, there are problems associated with both types of catalysts. Acid catalysts take more time for biodiesel synthesis and are also corrosive in nature. Although alkaline catalysts take less time, they increase the pH of the biodiesel, which thus requires thorough rinsing with water to remove the leftover catalyst, resulting in wastewater generation and loss of methyl esters (MEs), and consequently resulting in the loss of yield. To overcome these constraints, research has focused on finding a suitable heterogeneous catalyst that can be easily separated and gives a high yield and conversion without compromise.[6] Heterogeneous solid acid and solid base catalysts presently used include zeolites, metal catalysts,[7,8] Mg/Al hydrotalcite,[9,10] KF/hydrotalcite,[11] KF/Ca−Mg−Al hydrotalcite,[12] KF/Al_2O_3,[13] KF/Eu_2O_3,[14] MgO-supported KOH,[15] alumina-loaded compounds,[16,17] γ-Al_2O_3,[18] SO_4^{2-}/ZrO_2,[19]

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ion-exchange resins,[20] vanadyl phosphate,[21] heteropolyacids,[22,23] dolomites,[24] double-layered hydroxide,[25] sodium aluminate,[26] $SnCl_2$,[27] calcium oxide,[28−32] and calcium ethoxide.[33] However, all of these catalysts, excluding calcium oxide, need a lengthy process for synthesis. The process of their formation is also complex and requires expertise. Recently, calcium oxide has been obtained from chicken eggshells,[34] waste mud crab shell,[35] and mollusk.[36]

Chicken eggshells typically weigh 5−6 g, approximately 10% of the total egg mass, with calcium carbonate constituting 85−95% of the dry eggshell. Other components include 1.4% magnesium carbonate, 0.76% phosphate, 4% organic matter, and trace amounts of sodium, potassium, zinc, manganese, iron, and copper.[37,38] Eggs are consumed worldwide because they contain all essential amino acids, vitamins, and minerals. In India, the consumption of eggs is common, and waste eggshells pose a solid waste disposal problem. Methods are being adopted to use the waste eggshells in various applications, including biosorption of Cr^{III} ions,[37] recovery of gold ions from electroplating wastes,[39] coating pigments for inkjet printing paper,[40] heavy metal removal,[41] adsorbent for removal of dyes,[42] adsorption of iron,[43] removal and recovery of copper,[44] and as a catalyst for isomerization of lactose to lactulose.[45]

Biodiesel has recently gained popularity because it is a renewable and environmentally friendly fuel. A common raw material used in biodiesel synthesis is vegetable oil from terrestrial plants and trees. Because the feedstock is basically MEs of long-chain fatty acids, they do not emit the toxic pollutants that are present in fossil-fuel-derived diesel. Even when they are used in blended form, a significant decrease in carbon monoxide, hydrocarbons, and particulate matter is observed.[46]

Eggshells have been used as catalyst for the transesterification reaction.[34,35] However, in these cases, the feedstock used was edible oil, such as soybean and palm oils. However, with heterogeneous catalysts, not much data are available to judge whether the eggshell catalyst will be effective as a catalyst with high acid value feedstock, such as karanja oil (19.88 mg of KOH/g). Transesterification has been known to be successful when the free fatty acid (FFA) content is low. Parameters that influence the transesterification reaction are the molar ratio, catalyst amount, temperature, and rate of stirring.[2] There is no report on the use of this catalyst on non-edible feedstock. This paper explores the use of recycled eggshells as catalyst source for biodiesel production from karanja oil, a non-edible feedstock possessing a high FFA value.

2. Experimental Section

2.1. Materials. Eggshells were collected from a local student's dining hall kitchen. To remove the edible portion attached to the eggshells and other impurities, eggshells were rinsed thoroughly with tap water until the organic matter, which adheres on the inner surface of the eggshells, was removed, followed by double rinsing with distilled water. The washed eggshells were dried in a hot air oven at 105 °C for 24 h. The dried eggshells were ground in an agate mortar until they became a powder form. Thereafter, the ground eggshells were calcined in an open furnace at 900 °C

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for 2 h. Karanja oil was purchased from a local market in Jharkhand, India. Chemicals used were synthesis-grade methanol (≥99% assay and ≤0.2% water content), *ortho*-phosphoric acid (85% pure), dry purified sodium sulfate, sulphuric acid (98% GR), and deuterated chloroform ($CDCl_3$). All of the chemicals were procured from Merck Limited, Mumbai, India. Standards of fatty acids were obtained from Sigma−Aldrich. Doubly distilled water was prepared in the laboratory.

2.2. Characterizations. X-ray diffraction (XRD), differential thermal analysis/thermogravimetric analysis (DTA/TGA), and Fourier transform infrared (FTIR) spectroscopy experiments were conducted to study the characteristics of the raw and calcined eggshells. DTA/TGA experiments were conducted with a structured text analyzer (DTA/TGA), model STA 409, Netzsch-Gerätebau GmbH (Germany), under nitrogen flow. The XRD pattern was studied on an X-ray diffractometer (Scifert and Co., model 3000). FTIR spectroscopy was performed on 1000 FTIR (Varian). The conversion of oil to fatty acid methyl esters was determined on a JEOL AL300 ^{1}H Fourier transform nuclear magnetic resonance (FTNMR) instrument. $CDCl_3$ was used as the solvent at 300.40 MHz. The elemental analysis of the product was performed with a universal CHNOS elemental analyzer vario EL III. The FFA of karanja oil was determined by the standard American Society for Testing and Materials (ASTM) D664-07 method with alcoholic potassium hydroxide as the titrant and monitoring the color change with a potentiometer. The fatty acid profile of karanja oil was identified on a gas chromatograph (GC) for determination of their fatty acid profile. The instrument GC (Perkin-Elmer XL Autosystem GC) was equipped with a flame ionization detector (FID) with a 14 mL carrier packed column. The temperature was raised from 60 to 240 °C with a 4 °C/min rise in the temperature and then held for 5 min.

2.3. Experimental Procedure. The reactions were performed in an indigenous batch reactor comprised of a three-necked round-bottom flask of 1 L capacity. The middle neck was used to insert a mechanical stirrer; one of the side necks was fitted with a condenser; and the other neck was fitted with a thermometer for regular temperature measurement. A total of 100 mL of the oil was dried in a hot air oven (105 °C for 2 h) and used for each set of experiments. Acid esterification was performed with 1.5% (v/v) H_2SO_4 (i.e., 1.5 mL) as a catalyst with 27.4 mL of methanol, i.e., 6:1 (methanol/oil) to reduce the acid value of the feedstock for 1 h. Agitation was performed by a mechanical stirrer (BioLab BL 232 D). The speed of the mechanical stirrer was monitored by a digital tachometer (Lutron DT-2234C). The rate of stirring was maintained at 600 rpm to overcome the mass-transfer limitation. After acid esterification, water that formed in the product was removed by keeping it in a separating funnel. Thereafter, eggshells were used as the solid catalyst for the transesterification reaction. The reaction conditions taken were a 6:1 (alcohol/oil) molar ratio with 2.5 wt % catalyst at 65 ± 5 °C for 2 h of reaction time. After completion of the transesterification reaction, glycerol was settled at the bottom of the separating funnel because of its higher density compared to MEs. Glycerol was removed from the product, and the fatty acid methyl esters that formed by the conversion of fatty acids to their respective esters were stored as biodiesel. Important parameters that affect the reaction were later optimized to obtain a maximum yield and conversion.

3. Results and Discussion

The FFA was found to be 19.88 mg of KOH/g. Figure 1 depicts the GC analysis of karanja oil. The peaks were identified using the standards of the fatty acids. Table 1 depicts the fatty acid composition of the *Pongamia pinnata* obtained from GC analysis. The molecular weight of karanja (*P. pinnata*) oil was calculated as per the equation given by Komers et al.[47] and found to be 886.61

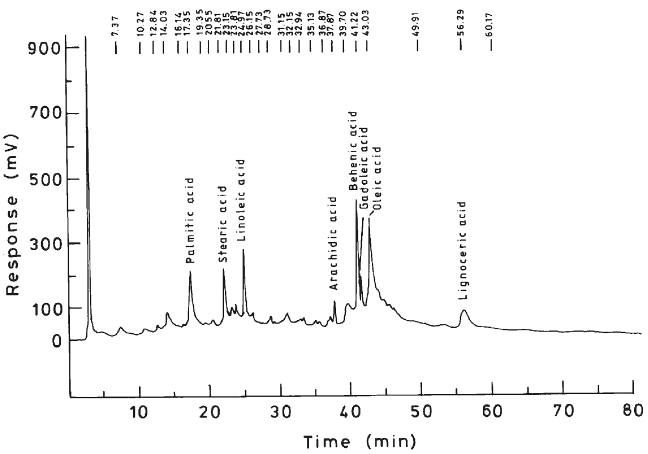

Figure 1. GC analysis of karanja oil.

Table 1. Fatty Acid Composition of Karanja (*P. pinnata*) Oil

fatty acid	systematic name	formula	structure	wt %
palmitic	hexadecanoic	$C_{16}H_{32}O_2$	16:0	8.9
stearic	octadecanoic	$C_{18}H_{36}O_2$	18:0	8.2
oleic	*cis*-9-octadecenoic	$C_{18}H_{34}O_2$	18:1	65.8
linoleic	*cis*-9,*cis*-12-octadecadienoic	$C_{18}H_{32}O_2$	18:2	12.1
arachidic	eicosanoic	$C_{20}H_{40}O_2$	20:0	0.9
gadoleic	11-eicosenoic	$C_{20}H_{38}O_2$	20:1	0.9
behenic	docosanoic	$C_{22}H_{44}O_2$	22:0	2.8
lignoceric	tetracosanoic	$C_{24}H_{48}O_2$	24:0	0.4
saturated fatty acid				21.1
unsaturated fatty acid				78.8
total (identified)				99.9

$$M(\mathrm{TG}) = 92.09 - 3 + 3[M(\mathrm{HA}) - 17] \qquad (1)$$

where M(TG) is the average molecular weight of the triglycerides (karanja oil), 92.09 is the molecular weight of glycerol, 3 is the number of hydrogens to be replaced from glycerol for mono-, di-, and triglycerides, and M(HA) is calculated as the average molecular weight of individual fatty acids.

On the basis of the molecular weight of karanja oil (i.e., 886.61 g/mol), the methanol quantity was taken at a 6:1 (methanol/oil) molar ratio for initial experiments for acid esterification and alkaline transesterification, respectively.

3.1. Characterization of the Eggshell Catalyst. *3.1.1. DTA/TGA.* The sample weight used was 23.0 mg for uncalcined catalyst and 23.7 mg for calcined catalyst. The temperature ranged from 28.73 to 897.0 °C. Figure 2 depicts the decomposition temperature of the uncalcined eggshell catalyst. The weight loss observed from TGA occurred from 700 to 850 °C. This indicated that, although decomposition of calcium carbonate started at 700 °C, complete decomposition occurred at 850 °C. At 850 °C, the calcium carbonate of eggshell decomposed to calcium oxide and carbon dioxide. This is given by the reaction[48]

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (2)$$

Release of CO_2 confirms the formation of calcium oxide, which acts as a catalyst in biodiesel synthesis. The decomposition as

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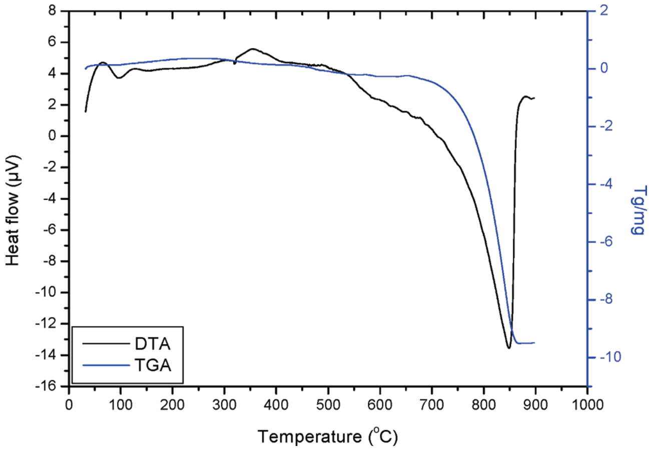

Figure 2. Uncalcined eggshell catalyst.

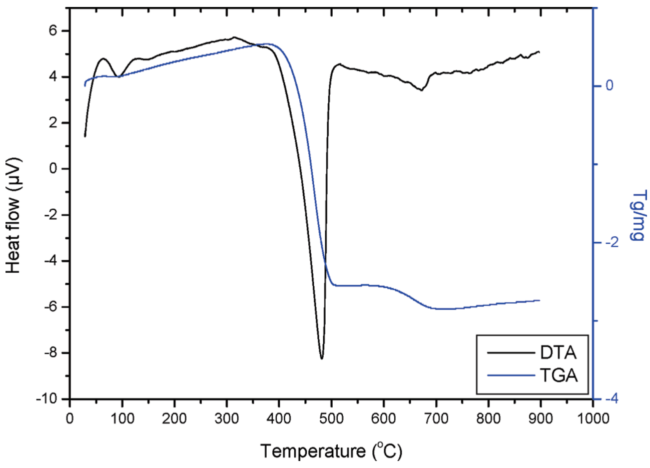

Figure 3. Calcined eggshell catalyst.

observed from DTA of the uncalcined eggshells started at 530 °C, and complete decomposition at 850 °C was observed from DTA.

According to the TGA of the calcined catalyst, weight loss was observed when the temperature exceeded 400 °C, which continued until 480 °C. The weight loss in this temperature range has been attributed to the decomposition of $Ca(OH)_2$. This was an indication that CaO reacted with atmospheric moisture to form $Ca(OH)_2$. The first derivative, DTA at 480 °C, also confirms decomposition of $Ca(OH)_2$. Another weight loss occurred at 700 °C, which attributes to the remaining $CaCO_3$ decomposition and loss of inorganic impurities (Figure 3). Granados et al.[28] reported that $Ca(OH)_2$ can be decomposed to CaO by treating it at 500 °C. However, a very little increment in the yield of biodiesel was observed on such a treatment, which confirmed that the formation of $Ca(OH)_2$ is not detrimental for CaO as a catalyst. Granados et al.[28] also report that it is not possible to prevent the complete removal of the surface OH group after calcination of the catalyst because, after cooling the calcined catalyst to room temperature, surface moisture is enough to cover the surface of the catalyst by layers of $Ca(OH)_2$. CaO is soluble to some extent in methanol (0.035 wt %), and the dissolution reaction in given as[28]

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^- \tag{3}$$

$$CaO \leftrightarrow Ca^{2+} + O^{2-} \tag{4}$$

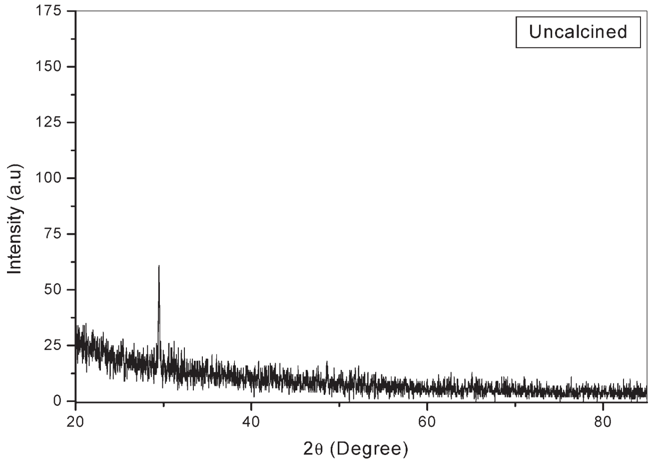

Figure 4. XRD of the uncalcined egg shell catalyst.

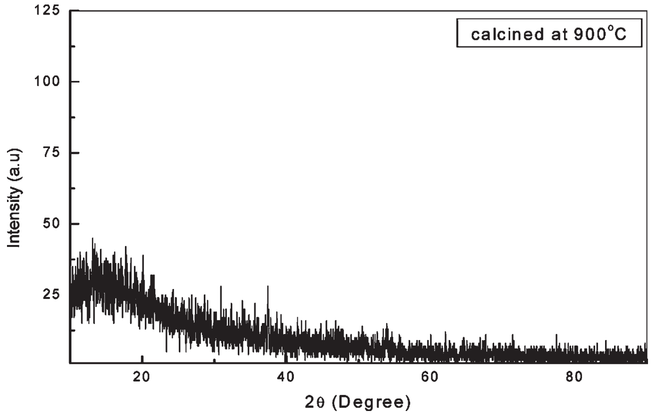

Figure 5. XRD of the calcined egg shell catalyst.

Equations 3 and 4 are responsible for the formation of the methoxide anion from the O^{2-} and OH^- species, which acts as the catalyst for the transesterification reaction of oil to MEs. This is given by the equations[28]

$$O^{2-} + CH_3OH \leftrightarrow OH^- + CH_3O^- \tag{5}$$

$$OH^- + CH_3OH \leftrightarrow H_2O + CH_3O^- \tag{6}$$

3.1.2. XRD Analysis. Figures 4 and 5 depict the XRD of uncalcined and calcined catalysts, respectively. Upon calcination, the eggshells turned completely white in appearance, which indicates that the calcium carbonate escaped and the product constitutes only calcium oxide.[48] The peaks were compared to the Joint Committee on Powder Diffraction Standards (JCPDS) file. XRD spectra of natural and calcined eggshell samples were obtained with Cu Kα radiation ($\lambda = 0.154\,06$ nm) at 40 kV, 30 mA, a scan speed of 1.0°/min, and a scan range of 10−90°. For the uncalcined catalyst, the main peak was observed at $2\theta = 29.478°$ and other peaks were observed at $2\theta = 48.601°$, 51.825°, 57.579°, and 65.158° (Figure 4). These peaks were characteristics of calcium carbonate.

The peaks for the calcined catalyst appeared at $2\theta = 32.318°$, 37.455°, and 53.930°, which were characteristics of calcium oxide. Calcium hydroxide was also observed at $2\theta = 14.772°$ and 17.8690° (Figure 5).

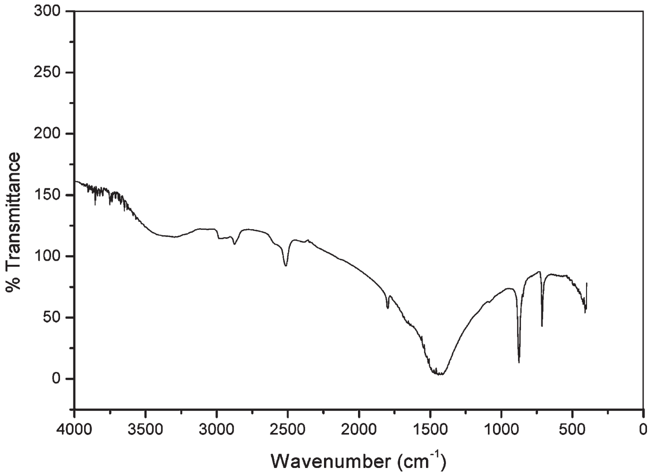

Figure 6. FTIR of uncalcined eggshell.

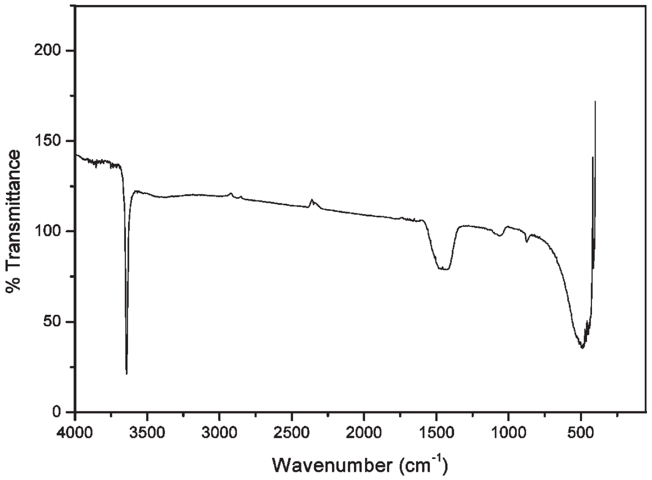

Figure 7. FTIR of calcined eggshell.

The crystalline size of the catalyst was also calculated from the XRD data using Scherrer's formula, given by Qin et al.[49]

$$D \approx 0.89\lambda/\beta \cos\theta \tag{7}$$

The particle size of the uncalcined catalyst was calculated and was found to be 29.7 nm, whereas the particle size of the catalyst upon calcination reduced to 0.952 nm. This shows that crystallinity of the eggshell decreased on calcination. Yoosuk et al.[50] also observed that calcination of CaO decreased its crystallinity. This has been attributed to the presence of water in CaO. This is in compliance with our study, where calcium hydroxide was formed upon instant exposure to atmospheric air.

3.1.3. FTIR Analysis. FTIR analysis of eggshell (uncalcined and calcined) was performed and is shown in Figures 6 and 7, respectively. A thorough study on FTIR spectra is reported by Engin et al.,[48] where in the uncalcined catalyst the major absorption bands occurred at 1415, 879, and 700 cm^{-1}, which are attributed to asymmetric stretch, out-of plane bend and in-plane bend vibration modes, respectively, for CO_3^{2-} molecules. Upon calcination, eggshell starts to lose carbonate and absorption bands of CO_3^{2-} molecules shift to higher energy (i.e., 1470, 1040, and 820 cm^{-1}). This has been attributed to the decrease of the reduced mass of the functional group attached to the CO_3^{2-} ions. A sharp OH^- stretching band is observed at 3625 cm^{-1} at the catalyst calcined at 900 °C. The finding in our study on uncalcined and calcined eggshells agrees with that observed by Engin et al.[48]

3.2. Esterification and Transesterification Reactions of Karanja Oil over the Eggshell Catalyst.

3.2.1. Esterification Reaction. The acid value of karanja oil after acid esterification reduced to 1.86 from 19.88 mg of KOH/g. The conversion of FFA to ester has been calculated by the equation

$$\text{conversion} = \frac{\{\text{acid value(initial)} - \text{acid value(final)}\}}{\text{acid value(initial)}} \times 100 \tag{8}$$

The conversion was calculated to be 90.64%.

3.2.2. Transesterification Reaction. The transesterification reaction has been carried out with calcined eggshell as the catalyst with karanja oil feedstock. The reaction was carried out with karanja oil without lowering its acid value. However, no conversion of triglycerides to their respective esters was observed. Thereafter, the transesterification reaction was carried out after lowering the acid value of karanja oil (by acid esterification), which resulted in a high conversion and high yield of biodiesel. Parameters that influenced the transesterification reaction are the molar ratio, catalyst amount, temperature, and rate of stirring. Each of these parameters was studied separately after optimizing each parameter to obtain a high product yield.

3.2.3. Optimization of Reaction Variables. The DTA/TGA of the uncalcined catalyst gave a clear indication of the decomposition of calcium carbonate at 850 °C. Wei et al.[34] and Engin et al.[48] also found that the calcination temperature at 900 °C results in the formation of the calcium oxide phase from eggshell. Hence, on the basis of DTA/TGA, waste eggshell was calcined for 2 h at a little higher temperature, i.e., at 900 °C, for the formation of calcium oxide. Granados et al.[28] report poisoning of the catalyst when kept in contact with air because of moisture and carbon dioxide. Although poisoning of the catalyst was less relevant with water, carbon dioxide poisoning was found to be significant.[18] The catalyst was thus stored in a plastic bottle and kept in a desiccator to prevent the poisoning of the catalyst. The reaction was carried out by taking 100 mL of karanja oil and 2.5 wt % catalyst with a 6:1 (methanol/oil) molar ratio. No conversion of oil to MEs was observed. This can be attributed to the effect of FFA playing a vital role in inhibiting the transesterification reaction. The acid value of karanja oil was reduced by acid esterification and then tried for its conversion to MEs by the transesterification reaction. The sole objective during acid esterification is to reduce the acid value of the catalyst. It was observed that a 6:1 molar ratio (alcohol/oil) with 1.5% (v/v) H_2SO_4 for 1 h of reaction time at 60 ± 0.5 °C resulted in a reduction of the FFA value from 19.88 to 1.86 mg of KOH/g by acid esterification, whereby the FFA present in the oil was converted to fatty acid methyl ester and water was formed. The transesterification reaction was then performed with waste eggshell as the catalyst with a reduced acid value. Experiments were performed by taking 2.5 wt % of catalyst with a 6:1 (alcohol/oil) molar ratio at 65 ± 0.5 °C. The yield was optimum with a molar ratio of 8:1 (alcohol/oil). Further addition of

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(49) Qin, C.; Li, C.; Hu, Y.; Shen, J.; Ye, M. Facile synthesis of magnetite iron oxide nanoparticles using 1-methyl-2-pyrrolidone as a functional solvent. *Colloids Surf., A* **2009**, *336*, 130–134.

(50) Yoosuk, B.; Udomsap, P.; Puttasawat, B.; Krasae, P. Improving transesterification activity of CaO with hydration technique. *Bioresour. Technol.* **2010**, *101*, 3784–3786.

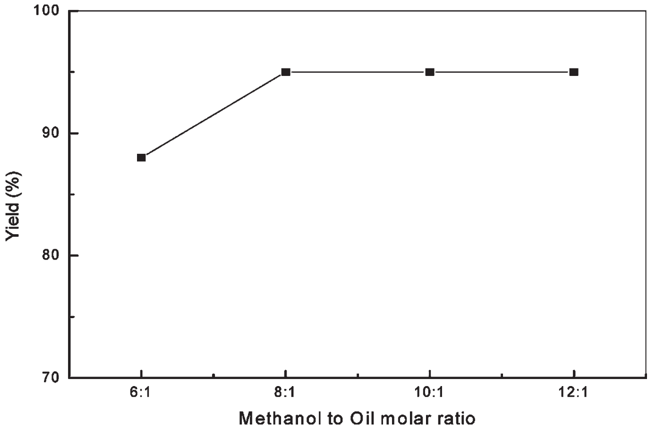

Figure 8. Effect of the molar ratio on the yield of biodiesel.

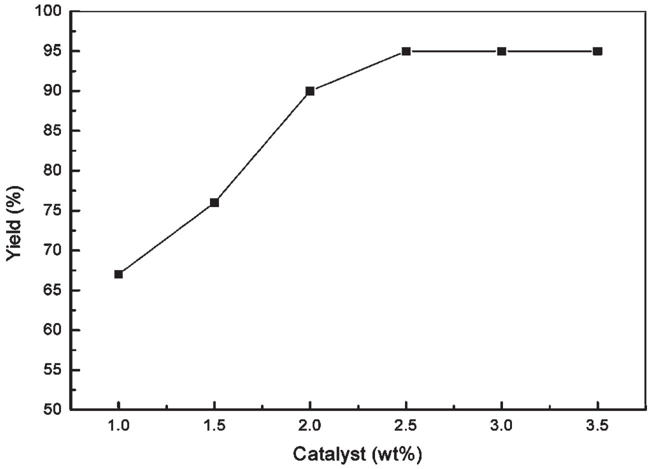

Figure 9. Effect of the catalyst amount on the yield of biodiesel.

methanol did not increase the yield (Figure 8). The catalyst (calcined eggshell) amount of 2.5 wt % was found to be optimum. With 1.0 wt % of catalyst, only a 67% yield was obtained, which increased to 90% with a 2.0 wt % catalyst. The catalyst amount beyond 2.5 wt % did not show any increase in the yield of biodiesel (Figure 9).

However, Wei et al.[34] have reported the optimum yield with 3.0 wt % of catalyst with soybean oil as the feedstock. An optimum yield of 95% was achieved when the reaction temperature was 65 ± 0.5 °C, which is just above the reflux temperature of methanol. The yield was less than 80% when the temperature was lowered to 50 ± 0.5 °C, which increased with an increase in the temperature. A higher temperature (i.e., 70 ± 0.5 °C) resulted in a decreased yield, which can be attributed to the loss of some methanol at high temperature (Figure 10). The rate of stirring was varied from 150 to 1200 rpm. The yield was optimum with 600 rpm of agitation. With agitation lower than 600 rpm, a lesser yield was obtained. With an agitation rate higher than 600 rpm, no increase in either yield or conversion was observed (Figure 11). In 30 min of reaction time, 64% conversion of biodiesel was obtained, which increased gradually with an increase in time. A reaction time of 2.5 h was found to give a conversion (97.43%) and yield (95%) of biodiesel (Figures 12 and 13). A further increase in time could not increase the yield of biodiesel. However, a conversion further increased to 99.17% in 3.5 h of reaction time (Figure 14). As per the specification by EN 14103, at least 96.5% mass conversion is needed for the product to be termed as a biodiesel.[51] Hence, 2.5 h is the optimum reaction time for the reaction.

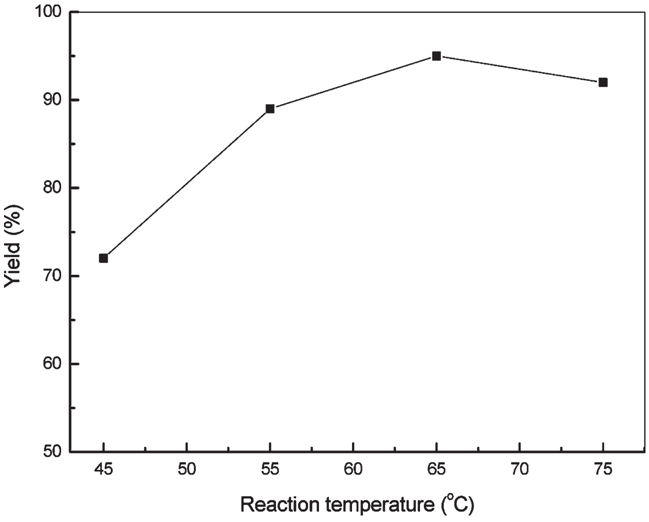

Figure 10. Effect of the temperature on the yield of biodiesel.

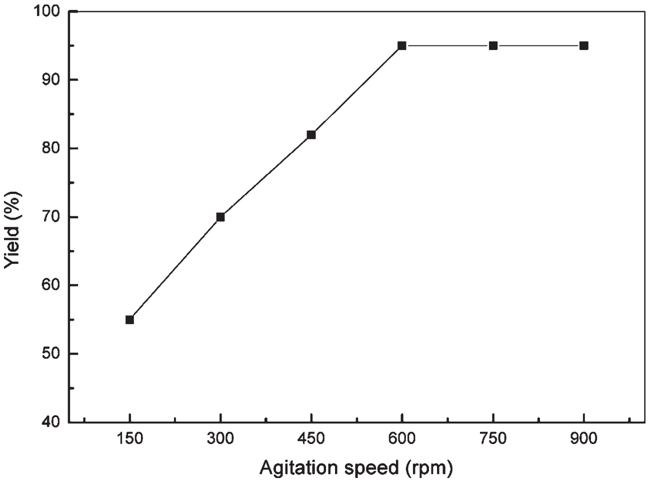

Figure 11. Effect of the agitation on the yield of biodiesel.

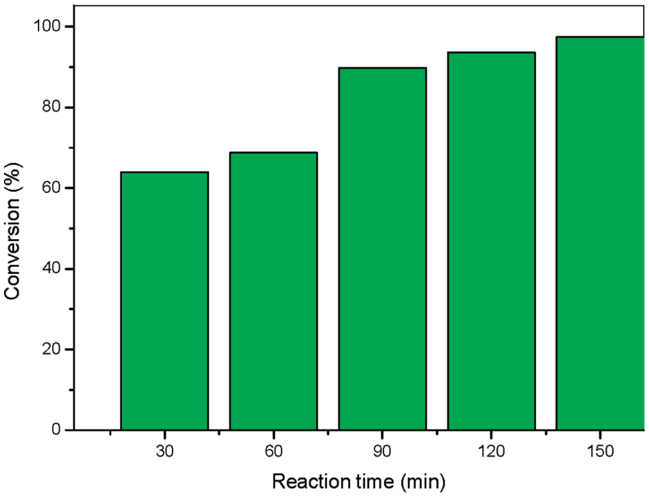

Figure 12. Effect of the reaction time on the conversion of biodiesel.

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(51) Sarin, R.; Kumar, R.; Srivastav, B.; Puri, S. K.; Tuli, D. K.; Malhotra, R. K.; Kumar, A. Biodiesel surrogates: Achieving performance demands. *Bioresour. Technol.* **2009**, *100*, 3022–3028.

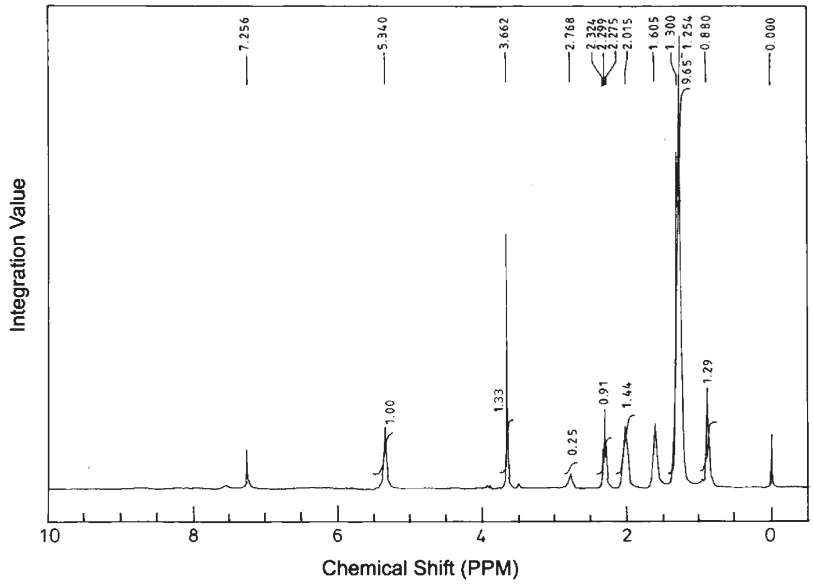

Figure 13. ^{1}H FTNMR of karanja oil with 2.5 wt % catalyst in 2.5 h (C = 97.43%).

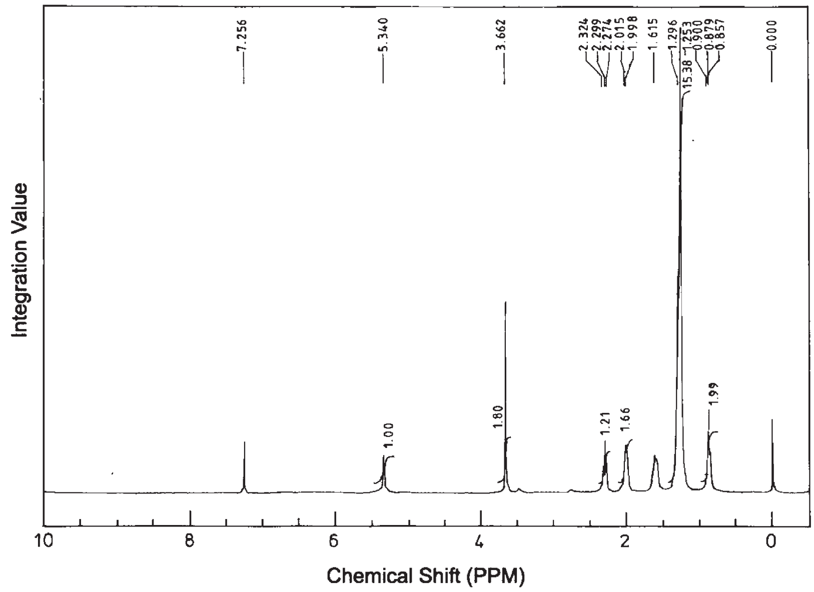

Figure 14. ^{1}H FTNMR of karanja oil with 2.5 wt % catalyst in 3.5 h (C = 99.17%).

3.2.4. Calculation of Conversion and Yield. The conversion of fatty acids present in karanja oil to its esters was determined by ^{1}H FTNMR spectroscopy. Figure 15 depicts ^{1}H FTNMR spectroscopy of karanja oil, whereas Figures 13 and 14 depict the biodiesel developed from karanja oil with eggshell as the catalyst. Knothe[52] reports ME protons to peak at 3.6 ppm and the protons on the carbons next to the glyceryl moiety (α-CH_2) to peak at 2.3 ppm. An equation has been given by Knothe[53] to calculate the percent conversion of MEs as

$$C = 100 \times (2A_{\mathrm{ME}}/3A_{\alpha\text{-}\mathrm{CH}_2}) \qquad (9)$$

where C is the conversion percentage of triglycerides present in the feedstock to their respective MEs, A_{ME} is the integration value of the protons of the MEs, and $A_{\alpha\text{-}\mathrm{CH}_2}$ is the integration value of the methylene protons. A_{ME} appears at 3.7 ppm, while $A_{\alpha\text{-}\mathrm{CH}_2}$ appears at 2.3 ppm. Integrating the areas under these signals in the above equation gives the ME (biodiesel) conversion. Samios et al.[54] studied ^{1}H NMR results in their experiment with sunflower oil. Disappearance of the resonance signal was observed between 4.22 and 4.42 ppm, and the emergence of new signal at 3.67 ppm is an indication of biodiesel formation. A similar result has been observed in our study (Figures 8 and 9). The peak obtained, which is indicative of ME, is obtained at 3.662 ppm with eggshell as the catalyst. The conversion calculated by the above equation was found to be 97−99%.

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(52) Knothe, G. Analytical methods used in the production and fuel quality assessment of biodiesel. *Trans. ASAE* **2001**, *44*, 193–200.

(53) Knothe, G. Analyzing biodiesel: Standards and other methods. *J. Am. Oil Chem. Soc.* **2006**, *83*, 823–833.

(54) Samios, D.; Pedrotti, F.; Nicolau, A.; Reiznautt, Q. B.; Martini, D. D.; Dalcin, F. M. A transesterification double step process−TDSP for biodiesel preparation from fatty acids triglycerides. *Fuel Process. Technol.* **2006**, *90*, 599–605.

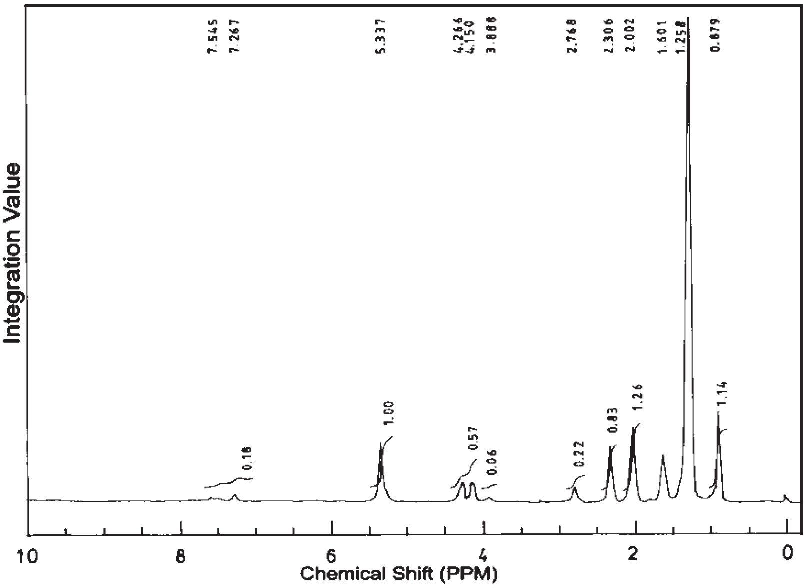

Figure 15. ^{1}H FTNMR of karanja oil.

Table 2. Properties of Karanja Oil MEs

parameter	ASTM D-6751 test method	ASTM D6751-08 limits	value	unit
acid value (mg of KOH/g)	ASTM D664-07	maximum at 0.50	0.44	mg of KOH/g
kinematic viscosity (cSt at 40 °C)	ASTM D445-06	1.9−6.0	5.44	cSt
flash point (°C)	ASTM D93-07	minimum at 130	158	°C
cloud point (°C)	ASTM D2500-05	report	5	°C
pour point (°C)	ASTM D97-07		−2	°C
oxidation stability (h)	EN 14112	minimum at 3 h	2.33	h
cetane number	ASTM D613-05	minimum at 47	57	
ester content (minimum %)	^{1}H FTNMR	96.5	97.43−99.17	%
methanol (vol %)	EN14100:2003	maximum at 0.2	0.05	%
free glycerin (mass %)	ASTM D6584-07	maximum at 0.02	0.01	%
total glycerin (mass %)	ASTM D6584-07	maximum at 0.24	0.17	%
water and sediment (vol %)	ASTM D2709-96 (reapproved 2006)	maximum at 0.050	0.02	%
carbon residue (mass %)	ASTM D4530-07	maximum at 0.05	0.005	%
sulfated ash (mass %)	ASTM D874-07	maximum at 0.02	0.005	%
elemental composition (wt %)	elemental analyzer			
carbon			75.04	%
hydrogen			12.76	%
nitrogen			0.10	%
oxygen			11.62	%
sulfur			< 0.005	%
HHV (kJ g^{-1})			41.50	kJ g^{-1}

The yield of biodiesel is determined by the following equation given by Leung and Guo[55]

$$\text{yield } (\%) = \frac{\text{weight of biodiesel}}{\text{weight of raw oil}} \times 100 \qquad (10)$$

3.2.5. Study of Properties of Karanja Oil MEs as Fuel. Biodiesel was characterized for its fuel properties and other parameters by ASTM D6751-08 and EN 14112 methods (Table 2). The tests were performed using the instruments as per the specifications given in ASTM D6751.[56] The acid value of karanja oil biodiesel was determined to be 0.44 mg of KOH/g, which is within the ASTM specification. The kinematic viscosity of biodiesel was 5.44 cSt at 40 °C, which is also within the ASTM specification. The flash point of biodiesel was 158 °C, which was well above the minimum ASTM specification (i.e., 130 °C) and can be considered safe for storage and transportation. The cloud and pour points of biodiesel were 5 and −2 °C, respectively. The cloud point and pour point values indicate that the fuel can be used in moderate cold climates. India, being a tropical country, is suitable for usage of karanja oil biodiesel. However, usage of karanja oil as biodiesel fuel should be restricted in a place where an extreme cold climate persists.

The induction time of the fuel, which is a measure of oxidation stability, was found to be 2.33 h, which is less than the minimum specification (i.e., 3 h) specified by ASTM. A low value of induction time makes the fuel susceptible to oxidation. This, however, could be overcome by the addition of antioxidants. The cetane number, which indicates the ignition delay time of the fuel upon injection into the combustion chamber, was found to be 57, which is above the minimum value of 47 specified by ASTM standards. The EN standard reports the conversion of oil to MEs to be at least 96.5%. The ester content was observed to be between

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(55) Leung, D. Y. C.; Guo, Y. Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Process. Technol.* **2006**, *87*, 883–890.

(56) American Society for Testing and Materials (ASTM) International. An American National Standard. http://www.astm.org (accessed on May 14, 2008).

97.43 and 99.17%, which is an indicative of a very high conversion of karanja oil feedstock to MEs (i.e., biodiesel). Methanol, free glycerine, total glycerine, water, and sediment were also within the specified limits, indicating that the synthesized biodiesel fuel from karanja oil is suitable for usage as fuel. The carbon residue and sulfated ash were determined to be 0.005 (mass %) for each. The elemental composition of the biodiesel showed the presence of carbon (75.04%), hydrogen (12.76%), nitrogen (0.10%), and oxygen (11.62%). Sulfur was found to be less than 0.005%. The oxygen content of biodiesel (i.e., 11.62%) is helpful in its better combustion as compared to mineral diesel. The higher heating value (HHV) was determined from the elemental composition of biodiesel fuel $\{\mathrm{HHV} = 33.5(\mathrm{C}) + 142.3(\mathrm{H}) - 15.4(\mathrm{O})\ (\mathrm{kJ\ g^{-1}})\}$, as given by Demirbas.[57]

4. Conclusion

A high yield and conversion of karanja oil to biodiesel were achieved by optimizing the parameters, such as molar ratio (alcohol/oil), amount of catalyst, reaction time, and temperature. Karanja oil possessing high FFA of 19.88 mg of KOH/g underwent acid esterification with H_2SO_4. The acid value became lowered to 1.86 mg of KOH/g and was followed by transesterification with calcined eggshell as the catalyst. Parameters optimized during acid esterification were a molar ratio of 6:1 (methanol/oil) with 1.5% (v/v) H_2SO_4 at 60 ± 0.5 °C for 1 h. The same parameters were optimized for transesterification with eggshell as the catalyst. The optimized values obtained were a 8:1 (methanol/oil) molar ratio, 2.5 wt % catalyst (eggshell), and 2.5 h reaction time at 65 ± 0.5 °C, which produced a high conversion (97.43%) and yield (95%) of biodiesel. The biodiesel derived from karanja oil fulfilled the minimum ASTM D6751 specifications, such as acid value, viscosity, flash point, cetane number, and ester content, which were well above their minimum specifications. Other parameters, such as methanol content, free glycerin, total glycerin, water, sediment, carbon residue, sulfated ash, and sulfur, were also within the specified limit of ASTM D6751. However, the biodiesel fuel could not fulfill the norm of oxidation stability and is a matter of concern. This demands the addition of antioxidants for its long-term storage. Another precaution that has to be taken into account is that the usage of biodiesel derived from karanja oil is at a moderate temperature considering the fact that the cloud point and pour point values are 5 and −2 °C, respectively.

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