

Utilization of Waste Chicken Eggshell as Heterogeneous CaO Nanoparticle for Biodiesel Production

Kumar Gaurav*, Soni Kumari, Joydeep Dutta

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Abstract

Calcium oxide (CaO) is a widely used solid catalyst for biodiesel production due to its cheap and easy availability. Chicken eggshell, which is otherwise a waste, is a valuable source material of CaO which can be utilized as an environment-friendly catalyst for biodiesel production. The present research work deals with the preparation and characterization of CaO nanoparticles from the waste chicken eggshell. The performance of CaO nanocatalyst was tested for its catalytic activity via transesterification of jatropha oil into biodiesel. To get a better biodiesel yield, different physicochemical parameters affecting the transesterification process such as methanol to oil molar ratio, catalyst loading, reaction temperature, reaction time, and agitation speed were optimized. The recorded optimum conditions were found to be 9:1 methanol to oil molar ratio with 5% catalyst loading, at a reaction temperature of 65°C, 3 h of reaction time, and 240 rpm. The maximum biodiesel yield obtained under these optimum conditions was 80.64%. The key fuel properties such as kinematic viscosity (5.2 mm²/s), flash point (99°C), calorific value (40.3 MJ/Kg) and density (0.86 g/cm³) resulted in good quality of biodiesel. The results obtained showed good fuel properties in the range as prescribed by ASTM for diesel.

Keywords: Nanocatalyst, Biodiesel, Chicken eggshell, Jatropha oil, Transesterification

Introduction

Overconsumption of fossil fuels leads to the energy crisis, global warming, and environmental pollution which are the major issues of this century that the world is going through (Vasudevan & Briggs, 2008; Gaurav *et al.*, 2013). The efforts in the search for sustainable and green energy lead to biodiesel as one of the most promising renewable, eco-friendly forms of energy (Janaun & Ellis, 2010; Liu *et al.*, 2012; Gaurav *et al.*, 2016). Biodiesel is a

fuel that can be a solution to these issues as it is renewable, biodegradable, non-toxic, and leads to lesser emission of CO₂, SO_x, NO_x, and hydrocarbon. It is a mixture of methyl esters which is prepared by biomass oil or fats by transesterification with alcohol (usually methanol due to low cost) in the presence of a catalyst and it can be used in diesel engines directly or with little modification. It can be produced by pyrolysis, emulsification, cracking and transesterification (Shuit *et al.*, 2012; Avhad & Marchetti, 2015) but among these methods transesterification is the most preferred method because it requires mild conditions. Based on the catalyst used, transesterification reactions are homogeneously and heterogeneously catalyzed. These catalysts may be acidic, basic, or enzymatic.

Base catalyzed transesterification reactions are faster than acid-catalyzed (Liu *et al.*, 2008; Tan *et al.*, 2015) whereas, enzyme-catalyzed transesterification is not of much interest in research due to the high cost of enzymes. However, heterogeneously catalyzed transesterification is more advantageous over homogeneously catalyzed because of easy product separation with less water requirement for washing, avoids soap formation due to presence of free fatty acids in the oil, less catalyst requirement, and catalyst reusability (Joshi *et al.*, 2015). The commonly used heterogeneous catalysts are CaO (Farooq *et al.*, 2015; Widiarti *et al.*, 2019), MgO (Mutreja *et al.*, 2011), ZnO (Gurunathan & Ravi, 2015), TiO₂ (Feyzi & Shahbazi, 2015), BaO, SrO₂, and zeolites (Sun *et al.*, 2015; Chua *et al.*, 2020). Nanocatalysts have a smaller particle size, larger surface area, and a large number of active sites and these sites of nanocatalyst facilitate the ionization of alcohol into alkoxide and hydrogen ion in the process of transesterification. The alkoxide ion potentially attacks the electron-deficient carbonyl groups of triglyceride molecules and gives methyl ester and glycerol (Kouzu *et al.*, 2008). So, the nanocatalyst gives high biodiesel yield in less reaction time (Wen *et al.*, 2010; Gupta & Agarwal, 2016). CaO nanoparticles are the most widely studied nanocatalyst due to their high basicity, high catalytic activity, and easy availability at low cost (Kawashima *et al.*, 2009; El-Gendy *et al.*, 2014; Bet-Moushoul *et al.*, 2016). In this study, the eggshell-derived CaO nanocatalyst is prepared and characterized by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), and Thermogravimetric analysis (TGA). Further their application in transesterification of jatropha oil for biodiesel production was evaluated. Biodiesel yield is investigated by optimizing different parameters such as catalyst loading, methanol to oil ratio, reaction temperature, reaction time,

Kumar Gaurav*

Amity Institute of Biotechnology, Amity University Haryana, India.

Soni Kumari, Joydeep Dutta

Amity School of Applied Sciences, Amity University Haryana, India.

*E-mail: gauravbiotech@rediffmail.com



and agitation speed. To determine the quality of produced biodiesel, the sample was analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS).

Materials and Methods

The waste chicken eggshells were collected from the university canteen for CaO nanocatalyst preparation. Methanol (99% pure) and non-edible jatropha oil were purchased from the market and used as such. The physicochemical properties of oil were analyzed Density (at 10°C) was found to be 0.920 g/cm³ and kinematic viscosity (at 40°C) was found 35.6 mm²/s. Free fatty acid content was 3.925% w/w and acid value 7.85 mg KOH/g. Saponification value of oil was 185 with flash point and fire point as 235 °C and 275 °C respectively. Calorific value was found to be 35.6 MJ/Kg.

Preparation of CaO Nanocatalyst

First of all, the inner membrane of eggshells was removed. After that, the shells were washed several times with warm tap water to remove organic matter and any unwanted material adhered to the surface and finally rinsed with distilled water. Washed eggshells were then kept to dry in a hot air oven at 120°C for 12 h. Later the dried shells were grinded using mortar pestle until a fine powder was obtained. The powdered eggshells were then calcinated at 850°C (in a Muffle furnace) for 4 h to obtain a nanoparticle of CaO.

Characterization of CaO Nanocatalyst

FT-IR spectra of powder sample CaO were obtained to determine the structure and functional groups present in the catalyst by using an FTIR spectrometer (Thermo Scientific Nicolet 380) in the range of 4000-400 cm⁻¹. KBr (AR, Sigma USA) powder was used for sample preparation. The surface morphology and particle size of nanocatalyst were investigated by Hitachi (3400 N) SEM and micrographs were recorded at a high magnification of 5µm.

To determine the crystalline nature of the CaO nanoparticles, a powder- XRD pattern was obtained using Bruker, D8 advance with Cu K α radiation ($k = 1.5418 \text{ \AA}$) at 40 KV and 30 mA. The scanning range 2θ was set between 20-80° with a step of 0.02° at the scan rate of 6 °min⁻¹. The Crystallite size of samples was calculated by XRD data and was measured by TEM analysis. For TEM analysis, the grid was prepared by diluting CaO with distilled water and sonicated at 34°C for 20 minutes and then the drop was placed in a membrane coated Cu grid provided by Sophisticated Analytical Instrument Facility (SAIF), All India Institute of Medical Science (AIIMS), NewDelhi.

TGA was performed on the catalyst sample for the characterization of thermal stability of calcined CaO nanocatalyst by using Perkin Elmer (4000 TGA analyzer). The changes in physicochemical properties were measured concerning temperature with a heating rate of 10°C min⁻¹.

Two Steps Method for Biodiesel Production

Two-step transesterification was used to produce biodiesel. The esterification was used because of the high acid value of jatropha oil which caused soap formation and reduced the yield of biodiesel during the alkali-catalyzed transesterification process. The soap formation hinders the separation of the biodiesel layer from glycerol. The esterification reaction was used to reduce the acid-value, and then alkali-catalyzed transesterification was carried out to obtain biodiesel.

Esterification Reaction of Jatropha Oil

The free fatty acid (FFA) content of oil was determined by the chemical titration method and was found to be 7.85 mg KOH/g that corresponds to an FFA content of 3.925 % which should ideally be below 1%. The acid-catalyzed esterification was carried out to reduce the acid value (FFA content) of oil by using para-toluene sulphonic acid (p-TSA) with catalyst loading 0.5%, 6:1 molar ratio of methanol to oil. The oil (100ml) was pre-heated at 60°C in a reactor. The catalyst (0.5g) was dissolved in methanol (600 ml) and then added into the reactor. The reaction temperature, agitation speed, and reaction time were 60°C, 200 rpm, and 2 hr respectively. After this time, the reaction mixture was allowed to settle for several hours to produce distinct liquid phases. The top phase (esterified oil of 98.2 ml) was separated from the bottom phase which consisted of; methanol and water (597.3 ml) and fatty acid methyl ester (5.0 ml) by decantation. After esterification, the acid value of oil was 1.683 mg KOH/g that corresponds to 0.8415% of FFA. The esterified oil was used for the further transesterification process.

Transesterification of Jatropha Oil

This is a two steps process viz. activation of catalyst followed by transesterification. CaO nanocatalyst (1.5 g) and methanol (300 ml) were added in a round bottom flask with an attached condenser and refluxed at 60°C for 1-2 h. The esterified oil (50 ml) was preheated at 60°C using a heating mantle and added to the activated catalyst-methanol mixture and stirred continuously with heating at different temperatures for 1-4 h for reaction to reach completion. The biodiesel (25 ml) was obtained in the upper phase; while the glycerol (7.5 ml), as a by-product, in the middle phase, and a mixture of catalyst and methanol (319 ml) were in the lower phase. After the completion of the reaction, biodiesel and catalyst were recovered using centrifugation at 5000 rpm for 10 minutes. The biodiesel was separated from glycerol by washing with distilled water. The yield of biodiesel was calculated by the equation;

$$\text{Biodiesel yield (\%)} = \frac{\text{volume of biodiesel obtained}}{\text{volume of oil used}} \times 100 \quad (1)$$

The transesterification reaction was carried out with a 6:1 molar ratio of methanol to oil, 3% wt of oil at 55°C for 2 h. The reaction conditions were optimized by varying: catalyst loading (1 to 6 % wt), methanol to oil ratio (3:1 to 15:1), agitation speed (60- 300 rpm), reaction temperature (35 to 75 °C), and reaction time (1 to 5 h).

Biodiesel Characterization

To determine the quality of produced biodiesel, Gas-Chromatography Mass Spectrometry (GC-MS) analysis was carried out using a Shimadzu GCMS- QP-2010 plus system. RTX-5 Sil MS column (30 m×0.25 mm id×0.25 film thickness) was used for the analysis. Oven temperature program from 100°C to 235 °C at 3°C/min and the final temperature was kept for 20 min. The injector temperature was maintained at 240°C. Helium was used as a carrier gas. The sample was characterized by using ASTM (American Society for Testing Materials) standard methods for diesel properties and compared with standards values.

Results and Discussion

Characterization of CaO Nanocatalyst

CaO nanoparticle was characterized by FTIR, SEM, XRD, TEM, and TGA analysis.

FTIR Analysis

The FTIR analysis result for calcined (850°C) eggshell derived CaO nanoparticle is shown in **Figure 1**. According to the spectra, the major absorption bands can be observed at 3668.6, 3438.4, 1633.1, 1064.7, and 445.0 cm⁻¹. The sharp absorption band at 3668.6 corresponds to stretching vibration of hydroxyl (O-H) groups which resulted due to the presence of Ca(OH)₂ formed by the hydration of CaO (El-Gendy *et al.*, 2014; Bet-Moushoul *et al.*, 2016; Gupta & Agarwal, 2016; Sumathi, 2017). The broad peak at 3438.4 cm⁻¹ indicates absorbance due to -OH stretching vibration of physically adsorbed water molecule attached to nanoparticles (Safaei-Ghomi *et al.*, 2013; Joshi *et al.*, 2015) whereas absorption bands at 1633.1 and 1064.7 cm⁻¹ corresponds to CO₂ adsorbed on the surface of nanoparticles (Sadeghi & Husseini, 2013) and Ca-OH stretching vibration respectively (Sumathi, 2017) The strongest peak observed at 445 cm⁻¹ is assigned to Ca-O vibration modes of pure CaO (Sadeghi & Husseini, 2013).

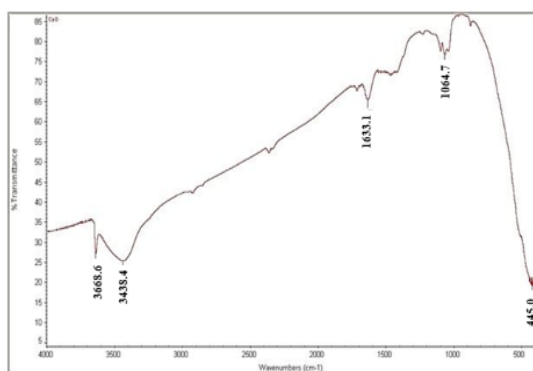


Figure 1. FTIR of CaO Nanocatalyst

SEM Analysis

To determine the surface morphology of eggshell derived CaO calcined at 850°C, SEM was done using a high magnification of

9000× with 5µm. The obtained SEM image of CaO nanoparticles is shown in **Figure 2**, which is giving a clear picture of the shape and size of particles. It seems that particle shapes and surfaces are irregular with a large number of cavities like a porous material which corresponds to the increase in basic sites of the catalyst. According to the report of El-Gendy *et al.* (2014), this porosity comes due to the escape of a large number of gaseous water molecules upon decomposition of CaCO₃.H₂O. The SEM photograph also shows that the particle size is from 25 to 55 nm which leads to a large surface area. Both these factors are the most appropriate characteristics of a catalyst for high catalytic activity.

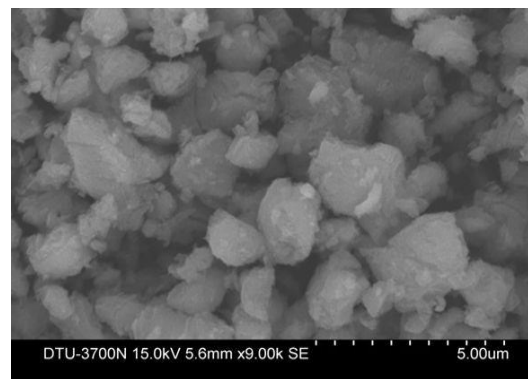


Figure 2. SEM of CaO Nanocatalyst

XRD Analysis

The XRD pattern of CaO nanoparticles is shown in **Figure 3**. The result shows that the structure of CaO nanoparticles is a face-centered cubic phase. The XRD results obtained were matched with the JCPDF card number 37-1497, the peaks were observed at $2\theta = 33.67^\circ, 39.07^\circ, 52.22^\circ$ and 67.03° with corresponding (h k l) values (1 1 1), (2 0 0), (2 2 0) and (2 2 2) respectively. Some peaks of Ca(OH)₂ at $2\theta = 55.90, 59.37, 69.03$ and 77.00 were also observed with corresponding (h k l) values (0 0 3), (2 0 0), (2 0 2) and (0 0 4) respectively (Tangboriboon *et al.*, 2012). The average crystallite size (D) of CaO nanoparticle was calculated by Debye-Scherrer equation which is given as;

$$D = K\lambda/\beta \cos \theta \quad (2)$$

where, β = full-width at half-maximum (in radian) and θ = is the position of the maximum of the diffraction peak. K is defined as the so-called shape factor, which usually has a value of about 0.9

$$\lambda = \text{the X-ray wavelength (1.5406 \AA for Cu K}\alpha\text{)}. \quad (3)$$

The average crystallite size of CaO nanoparticles obtained from the above formula was about 43.26 nm. In the XRD pattern, it was confirmed that there is a formation of calcium oxide with cubic phase (Almutairi, 2019; Bahshwan, *et al.*, 2019; Mozayyeni, *et al.*, 2019; Babaei *et al.*, 2020). The obtained results were similar to those obtained by Gupta and Agarwal (2016) and Moushoul (2016).

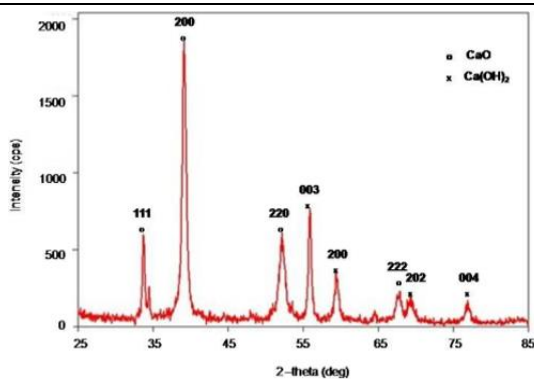


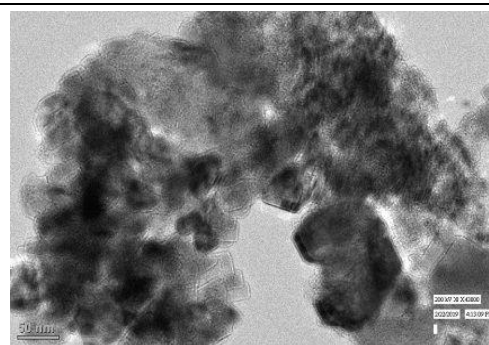
Figure 3. XRD of CaO Nanocatalyst

TEM Analysis

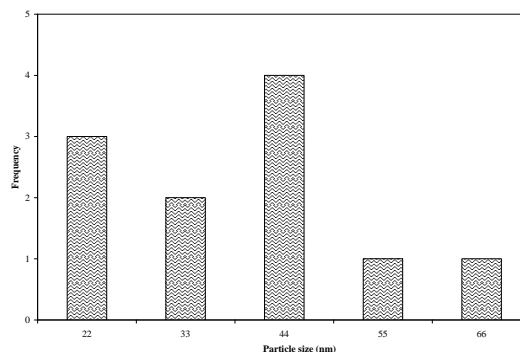
The TEM micrograph of prepared CaO nanocatalyst is shown in **Figure 4a**. The particle size distribution of CaO nanoparticles is shown in **Figure 4b** by counting nearly 11 particles from the TEM image. From the TEM micrograph, it was found that the CaO nanoparticles were bonded together to form aggregates. The smaller size and aggregation is directly proportional to the higher specific surface area. The average particle size was 43 nm with a cubical shape.

Thermal Analysis

The prepared CaO nanocatalyst was analyzed to know the effect of high temperature on its thermal stability and to determine the thermal transition that occurred during the calcination by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA/DTA curves of CaO nanoparticles are shown in **Figure 5** and TGA curve shows that during calcination of eggshells first weight loss (0.6% weight) occurred between 100 and 300°C due to the removal of water molecules and some organic impurity. After that weight loss of 0.4% was observed at 340-390°C due to removal of water from Ca(OH)₂ and decomposition of CaCO₃ (Roschat *et al.*, 2016). The final weight loss of 0.6 % was monitored in the temperature range of 550-620°C. These results were also supported by the DTA curve which showed a weak broad exothermic peak at 150-300°C that might have been caused by evaporation of water, crystallization, decomposition of organic impurities, or change in the structural arrangement of compound (Yan *et al.*, 2010). DTA curve also showed two sharp endothermic peaks at 320-400°C and 550-620°C which can be attributed to decomposition reaction and formation of the new compound. Therefore, TGA/DTA results confirmed that a high temperature (above 700°C) is required for the calcination of CaO nanoparticles.



a)



b)

Figure 4. (a) TEM image of CaO nanocatalyst, (b) Particle size distribution of CaO nanocatalyst

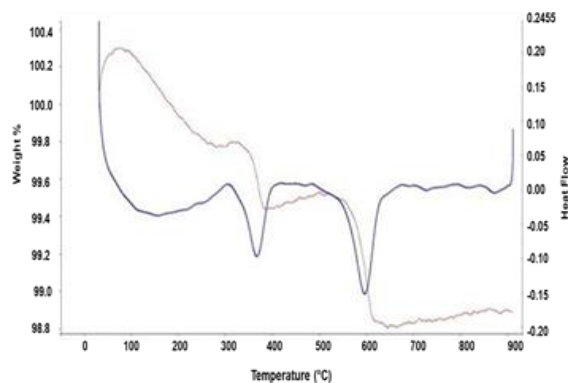


Figure 5. TGA curve of CaO Nanocatalyst

Factors Affecting Biodiesel Yield

There are various factors affecting biodiesel yields such as catalyst loading, methanol to oil ratio, reaction temperature, reaction time, and agitation speed. The prepared catalyst was tested for its effect on the transesterification of jatropha oil for biodiesel production. All the experiments were performed in triplicate and the results reported are average of all the three experiments.

Effect of Catalyst Loading

Catalyst loading is an important parameter that is required to be optimized to get a higher yield of -biodiesel (Fatty acid methyl ester, FAME). Generally, the FAME yield increases with an

increase in the amount of catalyst, as basic sites of CaO abstracts methoxide anion from methanol which attacks the electrophilic carbonyl carbon of triglyceride as a good nucleophile to form biodiesel (Wen *et al.*, 2010). In the present investigation, the optimum concentration of catalyst was determined by varying the mass ratio of catalyst from 1 to 6 wt% with 6: 1 molar ratio of methanol to oil at 55°C for 2 h and shown in **Figure 6a**. It was found that yield of biodiesel increased when loading concentration was increased from 1 wt% to 5 wt%. Beyond the optimum concentration of catalyst, that is 5 wt%, loading did not give higher biodiesel yield because of the mass transfer limitations. A higher amount of catalyst also increases the viscosity of the system to the point that adequate mixing is not reached (Wen *et al.*, 2010; Sumathi, 2017) thus resulting in the decline of biodiesel yield. Hence, the optimal catalyst loading was 5 wt% for the production of biodiesel from the jatropha oil.

Effect of Methanol/ Oil Ratio

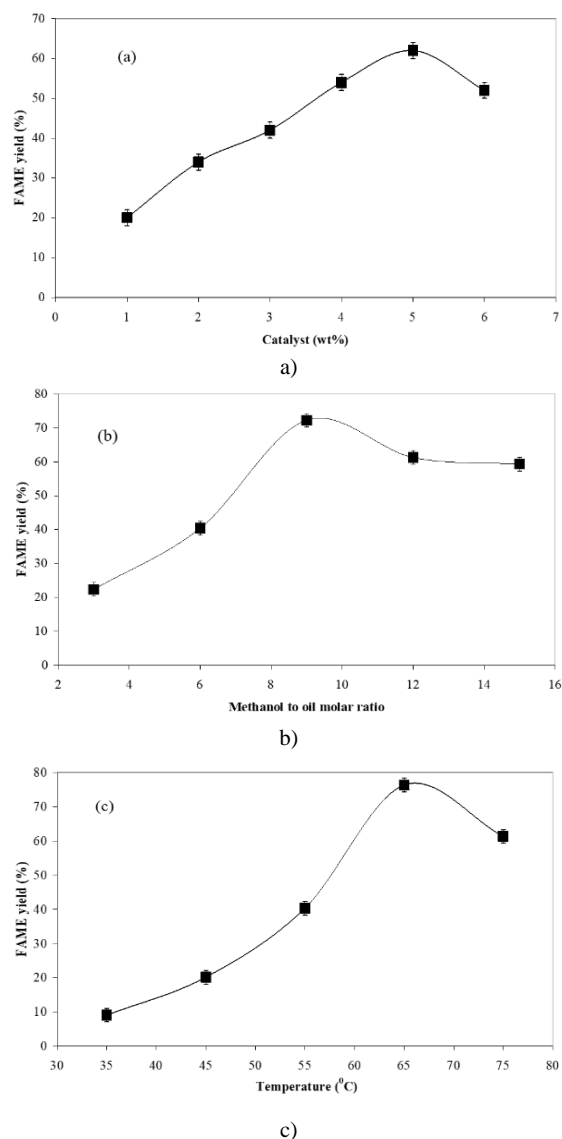
The molar ratio of methanol to oil is also one of the most important parameters that directly affect the FAME yield. The FAME yield % concerning the different molar ratio of methanol to oil is shown in **Figure 6b**. The stoichiometric ratio between alcohol and triglycerides is 3:1, but the transesterification is commonly carried out with an excess amount of alcohol to shift the equilibrium towards the forward direction and higher yield of FAME. The effect of the molar ratio of methanol to oil (in range of 3:1 to 15:1) on the transformation was examined with 5 wt% catalysts at 55°C for 2 h. It was observed that when the ratio was 3: 1 the yield of FAME was 22.35% and when the molar ratio was increased from 3:1 to 9:1, biodiesel yield was increased up to 72.3 %. The molar ratio 9: 1 was sufficient to complete the reaction, beyond 9:1, the FAME yield did not change due to the dilution effect (Sadeghi & Hussein, 2013). But, a high molar ratio can also lead to difficulty in biodiesel isolation from the glycerol phase which decreases biodiesel yield (Janaun & Ellis, 2010). Thus the maximum FAME yield was achieved at a 9:1 methanol to oil ratio.

Effect of Reaction Temperature

The effect of reaction temperature on FAME yield was investigated by varying the temperature from 35°C to 75°C with methanol to oil ratio 9:1 in presence of 5% wt catalyst at constant stirring for 2h. FAME yield increase from 9.04% to 75.32% when the reaction temperature was increased from 35°C to 75°C as presented in **Figure 6c**. It is clear that the reaction temperature directly affects the transesterification reaction. At higher temperatures, faster reaction equilibrium is reached as compared to the lower temperature. Above the optimum temperature (65°C), the reduction in FAME yield was observed which was most probably due to vaporization of methanol causing lack of methanol for transesterification (Janaun & Ellis, 2010; Sadeghi & Hussein, 2013; Gurunathan & Ravi, 2015). Thus, in the present study, 65°C was found to be the optimum temperature for the transesterification of triglycerides.

Effect of reaction time

Reaction time is another important parameter that highly affects the FAME yield therefore, it should be optimized to obtain high FAME yield. The effect of reaction time on FAME yield was studied by varying time from 1 to 5 h with methanol to oil ratio 9:1 in presence of 5% wt catalyst at 65°C and shown in **Figure 6d**. In the first 1 h, the reaction was slow with a yield of 45% and then increased gradually after 1 h of reaction and increased up to 52% after the second hour. The maximum yield obtained was 78.23% after 3 h of reaction and beyond this, the yield of biodiesel started decreasing. Since the FAME yield is directly proportional to methanol to oil ratio and as the reaction proceeds, this ratio also decreases i.e. reaction rate slows down with an increase in reaction time, and finally at equilibrium reaction rate becomes zero and negative beyond the equilibrium. Thus, the decrease in biodiesel yield after a specific reaction time was due to the backward reaction of transesterification as transesterification is a reversible process (Janaun & Ellis, 2010; Sadeghi & Hussein, 2013). The optimum reaction time observed in this study was 3 h.



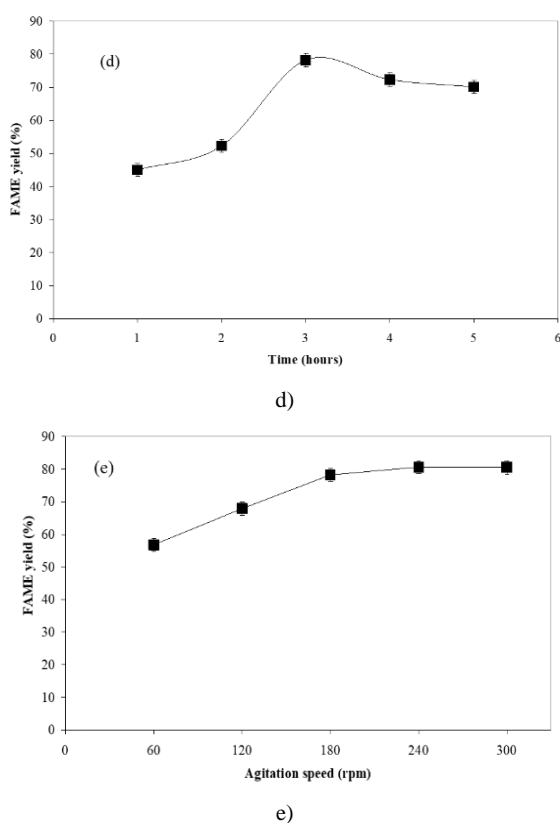


Figure 6. a) Effect of catalyst loading on the percentage of FAME yield using methanol to oil molar ratio of 6:1, reaction temperature of 55°C, the reaction time of 2 h and agitation speed of 120 rpm, b) Effect of methanol to oil molar ratio on the percentage of FAME yield using catalyst loading of 5 wt%, reaction temperature of 55°C, reaction time of 2 h and agitation speed of 120 rpm, c) Effect of reaction temperature on the percentage of FAME yield using methanol to oil molar ratio of 9:1, catalyst loading of 5 wt%, the reaction time of 2 h and agitation speed of 120 rpm, d) Effect of reaction time on the percentage of FAME yield using methanol to oil molar ratio of 9:1, catalyst loading of 5 wt%, reaction temperature of 65°C and agitation speed of 120 rpm, e) Effect of agitation speed on the percentage of FAME yield using methanol to oil molar ratio of 9:1, catalyst loading of 5 wt%, reaction temperature of 65°C and reaction time of 3 h.

Effect of Agitation Speed

The mixing of reactants is very important for the completion of any reaction and increase in the product yield. During transesterification, a two-phase liquid system (immiscible) is formed where one phase has the catalyst and the other phase has the oil or fat. The contact between catalyst and oil should be maximum for the most effective reaction to take place. Vigorous mixing or agitation is required to increase the contact area between two phases resulting in the mixing of the catalyst with the reactant and affecting the FAME yield. The present work was carried out in a biodiesel reactor with an inbuilt agitator where agitation speed can be varied from 30 to 300 rpm. The increase in

the agitation speed increases the collision between the particles. The optimization of stirring speed was carried out from 60 to 300 rpm by keeping the other parameters constant. The results, shown in **Figure 6e**, clearly indicate that the biodiesel yield increases with the increase in the agitation speed, and a maximum of 80.64% yields was obtained at 240 rpm. It can also be concluded from the figure that no appreciable change was observed in FAME yield on increasing the agitation speed from 240 to 300 rpm. Hence, 240 rpm is considered to be the optimum speed for the reaction in the present study.

Reusability of Catalyst

The reusability of catalyst is a significant characteristic of the heterogeneous catalyst and advantageous over a homogeneous catalyst in the transesterification reaction. After the completion of the reaction, the catalyst was separated by filtration and washed three times with hexane, and dried overnight at 100°C. The catalyst was subjected to transesterification reaction under the optimum conditions (9:1 methanol/ to oil ratio, 5 wt% catalysts, 65°C reaction temperature, 3 h reaction time, and 240 rpm agitation speed). **Figure 7** shows the FAME yield gradually decreases with increasing the number of reuse. The FAME yield did not show significant changes in the first cycle where the activity and stability of catalyst were maintained. The yield was decreased from 73.21% to 62.31% from the second to fourth cycle and further decreased to 42.32% in eight cycles. The decrease in catalytic activity was attributed to a reduction in the amount and strength of basic sites of the catalyst during regeneration.

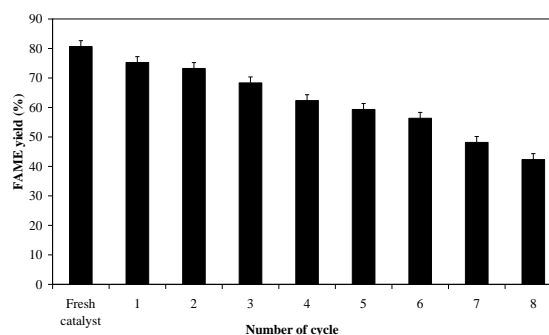


Figure 7. Reusability of catalyst

Biodiesel Characterization

Several physicochemical and fuel properties of resulting biodiesel, such as oxidative stability, calorific value, flash point, fire point, etc depend on its fatty acids composition (Knothe, 2009). Therefore, determination and analysis of the fatty acid composition of biodiesel have become an important quality parameter. Hence GC-MS of obtained biodiesel was carried out in the present work to determine its methyl ester profile. The results obtained showed that the fatty acid profile consisted of mainly five fatty acids, palmitic acid (C16:0, 20.08%), oleic acid

(C18:1, 28.94%), linoleic acid (C18:2, 37.87%), palmitoleic acid (C16:1, 1.09%), and linolenic acid (C18:3, 5.17%)

According to the result obtained, 20.08% corresponded to methyl esters with saturated chains, whereas 73.07% was attributed to unsaturated methyl esters. The results clearly show high unsaturation of the jatropha oil. The high degree of unsaturation, mainly due to the presence of linoleic acid methyl ester, is the reason for the low viscosity of biodiesel produced in the present work. According to the specified standards, the content of linolenic acid methyl ester, a polyunsaturated fatty acid with three double bonds, should be lower than 12% otherwise it can lead to biodiesel rancidity. In the present work, this was found to be 5.17% which is according to the standards (Zuleta *et al.*, 2012). Oxidation stability is another parameter that ensures the stability of biodiesel during long storage hours. The high concentration of palmitic acid, which is responsible for good oxidation stability of biodiesel, in the present work leads to good quality biodiesel. If Biodiesel complies with the standards set by EN (European norms) or ASTM (American Society for Testing and Materials) then only it is considered suitable for use in compression ignition engines. The main fuel properties of jatropha biodiesel such as kinematic viscosity, density, flash point, and calorific value were determined and compared with ASTM biodiesel standards. Jatropha biodiesel shows viscosity value of 5.2 (mm²/s), which is comparably lower than the standard value 1.9-6.0. Low viscosity of fuel will provide easy engine operation and increase the engine life (Kumar & Sharma, 2016) while, high viscosity will result in increased emission, damage to the pump, poor combustion efficiency, and filter blockage (Aytor *et al.*, 2015). The density of fuel affects the fuel injection properties such as spray penetration, injection time, and calorific value which is the important fuel property and shows the energy content of the fuel. The density (0.86 Kg/L) and calorific value of biodiesel (40.3 MJ/kg) are within the range (for density it is 0.860-0.900 Kg/L and calorific value 40-45 MJ/Kg) required by the standard. In other literature, the calorific value of jatropha biodiesel was 41 MJ/Kg (Rahman *et al.*, 2010), so it was similar to the reported result. Acid -the value of biodiesel is 0.46 mg KOH gm⁻¹ and it is within the range of the specified limit of ASTM (0.5). It indicates the chances of corrosion of the parts of the engine. A similar result was reported by Rashid *et al.* (2010). Flashpoint is important to fuel property for storage and safety. The flashpoint of Jatropha biodiesel is 99, which is less than standard, so, it is much safer than fossil fuel diesel because it decreases the chances of fire hazard (Lee & Ha, 2003).

Conclusion

In this study, we examined the catalytic activity of CaO nanocatalyst obtained from chicken eggshell (cheaper source) in the production of biodiesel from jatropha oil. FTIR, SEM, XRD, TEM, and TGA analysis of CaO nanocatalyst showed that the synthesized nanoparticles are highly basic, contain a larger surface area, and are porous *i.e.* possess good catalytic activity. We also optimized the various parameters affecting transesterification and reached the result that 9:1 methanol to oil molar ratio, 5% catalyst loading, 65°C reaction temperature, 3 h

of reaction time, and 240 rpm agitation speed are the optimum conditions for maximum biodiesel production. Thus, the present work results in reducing the cost of catalyst as well as using an environmentally friendly catalyst. This can easily be used for economical industrial production of biodiesel. Hence, we conclude that CaO nanocatalyst is a potential catalyst for high-quality biodiesel production.

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Financial support: None

Ethics statement: None

References

- Almutairi, F. M. (2019). Biopolymer Nanoparticles: A Review of Prospects for Application as Carrier for Therapeutics and Diagnostics. *International Journal of Pharmaceutical Research & Allied Sciences*, 8(1), 25-35
- Avhad, M. R., & Marchetti, J. M. (2015). A review on recent advancement in catalytic materials for biodiesel production. *Renewable and Sustainable Energy Reviews*, 50(c), 696-718.
- Aytor, G. K., Sunnu, A., & Parbey, J. (2015). Effect of biodiesel production parameters on viscosity and yield of methyl esters: *Jatropha curcas*, *Elaeis guineensis* and *Cocos nucifera*. *Alexandria Engineering Journal*, 54(4), 1285-1290.
- Babaei, H., Sepahy, A. A., Amini, K., & Saadatmand, S. (2020). The Effect of Titanium Dioxide Nanoparticles Synthesized by *Bacillus tequilensis* on *clb* Gene Expression of Colorectal Cancer-causing *Escherichia coli*. *Archives of Pharmacy Practice*, 11(1), 22-31.
- Bahshwan, S. M., Rabah, S. O. A., & Turkistani, A. M. (2019). A Comparative Study of the Effect of Crude and Nanoparticles *Costus Speciosus* on Testicular Damage Associated to Experimentally Induced Type 2 Diabetes. *Pharmacophore*, 10(6), 99-106.
- Bet-Moushoul, E., Farhadi, K., Mansourpanah, Y., Nikbakht, A. M., Molaei, R., & Forough, M. (2016). Application of CaO-based/Au nanoparticles as heterogeneous nanocatalysts in biodiesel production. *Fuel*, 164, 119-127.
- Chua, S. Y., Goh, C. M. H., Tan, Y. H., Mubarak, N. M., Kansedo, J., Khalid, M., Walvekar, R. & Abdullah, E. C. (2020). Biodiesel synthesis using natural solid catalyst derived from biomass waste—A review. *Journal of Industrial and Engineering Chemistry*, 81, 41-60.
- El-Gendy, N. S., Hamdy, A., & Abu Amr, S. S. (2014). An investigation of biodiesel production from wastes of

- seafood restaurants. *International Journal of Biomaterials*, 2014, 1-18.
- Farooq, M., Ramli, A., & Naeem, A. (2015). Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. *Renewable Energy*, 76, 362-368.
- Feyzi, M., & Shahbazi, E. (2015). Catalytic performance and characterization of Cs–Ca/SiO₂–TiO₂ nanocatalysts for biodiesel production. *Journal of Molecular Catalysis A: Chemical*, 404, 131-138.
- Gaurav, K., Srivastava, R., & Singh, R. (2013). Exploring biodiesel: Chemistry, biochemistry, and microalgal source. *International Journal of Green Energy*, 10(8), 775-796.
- Gaurav, K., Srivastava, R., Sharma, J. G., Singh, R., & Singh, V. (2016). Molasses-based growth and lipid production by *Chlorella pyrenoidosa*: a potential feedstock for biodiesel. *International Journal of Green Energy*, 13(3), 320-327.
- Gupta, J., & Agarwal, M. (2016). Preparation and characterization of CaO nanoparticle for biodiesel production. Citation: AIP Conference Proceedings. 1724(1), 020066.
- Gurunathan, B., & Ravi, A. (2015). Biodiesel production from waste cooking oil using copper doped zinc oxide nanocomposite as heterogeneous catalyst. *Bioresource Technology*, 188, 124-127.
- Janaun, J., & Ellis, N. (2010). Perspectives on biodiesel as a sustainable fuel. *Renewable and Sustainable Energy Reviews*, 14(4), 1312-1320.
- Joshi, G., Rawat, D. S., Lamba, B. Y., Bisht, K. K., Kumar, P., Kumar, N., & Kumar, S. (2015). Transesterification of *Jatropha* and *Karanja* oils by using waste egg shell derived calcium based mixed metal oxides. *Energy Conversion and Management*, 96, 258-267.
- Kawashima, A., Matsubara, K., & Honda, K. (2009). Acceleration of catalytic activity of calcium oxide for biodiesel production. *Bioresource Technology*, 100(2), 696-700.
- Knothe, G. (2009). Improving biodiesel fuel properties by modifying fatty ester composition. *Energy & Environmental Science*, 2(7), 759-766.
- Kouzu, M., Kasuno, T., Tajika, M., Sugimoto, Y., Yamanaka, S., & Hidaka, J. (2008). Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel*, 87(12), 2798-2806.
- Kumar, M., & Sharma, M. P. (2016). Optimization of transesterification of *Chlorella protothecoides* oil to biodiesel using box-behnken design method. *Waste and Biomass Valorization*, 7(5), 1105-1114.
- Lee, S., & Ha, D. M. (2003). The lower flash points of binary systems containing non-flammable component. *Korean Journal of Chemical Engineering*, 20(5), 799-802.
- Liu, J., Huang, J., Jiang, Y., & Chen, F. (2012). Molasses-based growth and production of oil and astaxanthin by *Chlorella zofingiensis*. *Bioresource technology*, 107, 393-398.
- Liu, X., He, H., Wang, Y., Zhu, S., & Piao, X. (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*, 87(2), 216-221.
- Mozayyeni, N., Morsali, A., Bozorgmehr, M. R., & Beyramabadi, S. A. (2019). Structural and mechanistic studies of γ -Fe₂O₃ nanoparticle as troxacitabine drug nanocarrier. *Archives of Pharmacy Practice*, 10(1), 31-37.
- Mutreja, V., Singh, S., & Ali, A. (2011). Biodiesel from mutton fat using KOH impregnated MgO as heterogeneous catalysts. *Renewable Energy*, 36(8), 2253-2258.
- Rahman, K. M., Mashud, M., Roknuzzaman, M., & Al Galib, A. (2010). Biodiesel from *Jatropha* oil as an alternative fuel for diesel engine. *International Journal of Mechanical & Mechatronics (IJMME-IJENS)*, 10(3), 1-6.
- Rashid, U., Anwar, F., Jamil, A., & Bhatti, H. N. (2010). *Jatropha curcas* seed oil as a viable source for biodiesel. *Pakistan Journal of Botany*, 42(1), 575-582.
- Roschat, W., Siritanon, T., Yoosuk, B., & Promarak, V. (2016). Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. *Energy Conversion and Management*, 108, 459-467.
- Sadeghi, M., & Hussein, M. H. (2013). A novel method for the synthesis of CaO nanoparticle for the decomposition of sulfurous pollutant. *Journal of Applied Chemical Research*, 7(4), 39-49.
- Safaei-Ghomi, J., Ghasemzadeh, M. A., & Mehrabi, M. (2013). Calcium oxide nanoparticles catalyzed one-step multicomponent synthesis of highly substituted pyridines in aqueous ethanol media. *Scientia Iranica*, 20(3), 549-554.
- Shuit, S. H., Ong, Y. T., Lee, K. T., Subhash, B., & Tan, S. H. (2012). Membrane technology as a promising alternative in biodiesel production: a review. *Biotechnology Advances*, 30(6), 1364-1380.
- Sumathi, N. (2017). Optical characterization of calcium oxide nanoparticles. *International Journal of Advanced Technology in Engineering and Science*, 5(2), 63-67.
- Sun, K., Lu, J., Ma, L., Han, Y., Fu, Z., & Ding, J. (2015). A comparative study on the catalytic performance of different types of zeolites for biodiesel production. *Fuel*, 158, 848-854.
- Tan, Y. H., Abdullah, M. O., Nolasco-Hipolito, C., & Taufiq-Yap, Y. H. (2015). Waste ostrich-and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. *Applied Energy*, 160, 58-70.
- Tangboriboon, N., Kunanurksapong, R., & Sirivat, A. (2012). Preparation and properties of calcium oxide from eggshells via calcination. *Materials Science-Poland*, 30(4), 313-322.
- Vasudevan, P. T., & Briggs, M. (2008). Biodiesel production—current state of the art and challenges. *Journal of Industrial Microbiology and Biotechnology*, 35(5), 421-430.
- Wen, L., Wang, Y., Lu, D., Hu, S., & Han, H. (2010). Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil. *Fuel*, 89(9), 2267-2271.
- Widiarti, N., Ni'mah, Y. L., Bahruji, H., & Prasetyoko, D. (2019). Development of CaO from Natural Calcite as a Heterogeneous Base Catalyst in the Formation of Biodiesel. *Journal of Renewable Materials*, 7(10), 915-940.

- Yan, S., Mohan, S., DiMaggio, C., Kim, M., Ng, K. S., & Salley, S. O. (2010). Long term activity of modified ZnO nanoparticles for transesterification. *Fuel*, *89*(10), 2844-2852.
- Zuleta, E. C., Rios, L. A., & Benjumea, P. N. (2012). Oxidative stability and cold flow behavior of palm, sachainchi, jatropa and castor oil biodiesel blends. *Fuel Processing Technology*, *102*, 96-101.