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ORIGINAL ARTICLE

Modification of egg shell and its application in biodiesel production



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Abstract Egg shells were subjected to calcination–hydration–dehydration treatment to obtain CaO with high activity. The performance of CaO obtained from the calcination–hydration–dehydration treatment of egg shell and commercial CaO was tested for its catalytic activity via transesterification of waste frying oil (WFO). The results showed that the methyl ester conversion was 67.57% for commercial CaO and it was 94.52% for CaO obtained from the calcination–hydration–dehydration treatment of egg shell at a 5 wt% catalyst (based on oil weight), a methanol to oil ratio of 12:1, a reaction temperature of 65 °C and a reaction time of 1 h. The biodiesel conversion was determined by ¹H Nuclear Magnetic Resonance Spectroscopy (¹H NMR).

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1. Introduction

Increase in demand for energy and more consciousness about the environment have led to search for an alternative fuel which can supplement or replace fossil fuel. Biodiesel is considered as one of the most alternative fuel for diesel engines and it is nontoxic, renewable and biodegradable [25,15]. The price of edible plant and vegetable oils is usually higher than the conventional diesel [3]. An effective way to reduce the cost of biodiesel production is to use non-edible oils [10,23,14], animal

fats [9], fish oil [8] and waste frying oil [29,3,16] as raw materials. Huge quantity of waste frying oil is available all over the world. Some part of this waste frying oil is used for soap preparation and fodder making, but major quantities of waste frying oil are illegally dumped into landfills and rivers causing environmental pollution [16]. Several studies have reported the feasibility of making biodiesel from this feed stock [29,3,16]. Feedstock constitutes approximately 70–95% of the overall cost of biodiesel production [4]. Transesterification is the most commonly employed method for the production of biodiesel using acidic or alkaline catalysts. Transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. Transesterification process using homogeneous alkali catalyst provides high yield and conversion of biodiesel at a mild temperature, atmospheric pressure and shorter reaction time but these catalysts have some problems such as separation of the catalyst after reaction, generation of excess wastewater, emulsification and more consumption of energy [17,6]. To address these issues, heterogeneous catalysts have been developed. Mathiarasi et al. [14] utilized boiler ash as a solid catalyst for transesterification of soap nut oil.

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Several advantages of heterogeneous catalysts are simple catalyst recovery, catalyst reusability, simple product purification and less energy and water consumption [1]. Heterogeneous catalytic reactions are usually time consuming due to diffusion problems owing to the formation of three phases of the reactants (methanol/oil/solid catalyst) [28]. Therefore, it is a great challenge to identify a solid base catalyst for transesterification process under mild reaction conditions in a shorter reaction time. Alkaline earth metal oxides with high basicity are suitable for biodiesel production and among the alkaline earth metal oxides, calcium oxide is one of the most promising heterogeneous base catalysts for biodiesel production [2]. Waste shells of oyster [19], egg and mollusks [24,20,11], capiz [22], mussel [21] and white bivalve clam [5] were calcined to obtain calcium oxide and used effectively as a heterogeneous catalyst in biodiesel production. Nakatani et al. [19] utilized oyster shells for the transesterification of soybean oil and obtained a biodiesel yield of 73.8% using 25 wt% catalyst for a reaction time of 5 h. Viriya-empikul et al. [24] utilized waste shells of egg, golden apple snail and meretrix venus for the transesterification of palm oil. A high biodiesel yield of above 90% was obtained using 10 wt% catalyst for a reaction time of 2 h. Navajas et al. [20] utilized waste shells of egg for the transesterification of used cooking oil and obtained a biodiesel yield of 100% using 4 wt% catalyst for a reaction time of 5 h. Khemthong et al. [11] utilized industrial egg shell wastes as the heterogeneous catalysts for microwave-assisted biodiesel production. Suryaputra et al. [22] utilized waste capiz shells for the transesterification of palm oil and achieved a maximum biodiesel yield of 93% by employing 3 wt% catalyst for a reaction time of 6 h. Rezaei et al. [21] utilized waste mussel shells for the transesterification of soybean oil and reported 12 wt% catalyst and a reaction time of 8 h is required to obtain a biodiesel yield of 94.1%. In our previous work [5], recently we utilized white bivalve clam shell for the transesterification of waste frying oil. A biodiesel yield of 95.84% was obtained using 8 wt% catalyst for a reaction time of 3 h. All these studies on waste materials revealed that a higher catalyst wt% and longer reaction time are needed to achieve a high biodiesel yield.

The present study focused toward the development of a highly active CaO catalyst obtained from egg shells on calcination–hydration–dehydration treatment. The newly obtained CaO was characterized by Hammett indicators, Brunauer–Emmett–Teller (BET) and Scanning Electron Microscopy (SEM). The performance of the newly obtained CaO from the calcination–hydration–dehydration treatment of egg shell was compared with the commercial CaO for the transesterification of waste frying oil.

2. Experimental

2.1. Materials

Egg shells were collected from a nearby bakery Tiruchirapalli, Tamil Nadu, India. Waste frying oil was procured from the canteen, National Institute of Technology, Tiruchirappalli, Tamilnadu, India and its physicochemical properties were measured and presented in Table 1. Anhydrous methanol of analytical grade and commercial CaO purchased from Merck Limited, Mumbai, India were used in the transesterification

Table 1 Physicochemical properties of waste frying oil used in the present study.

Properties	Measured values
Density at 25 °C (kg/m ³)	914
Kinematic viscosity at 40 °C (mm ² /s)	28.93
Acid value (mg of KOH/gm of oil)	2.14

reaction. Commercial CaO was treated in the muffle furnace at 600 °C for 3 h before use.

2.2. Catalyst preparation

Highly active CaO catalyst was prepared by the calcination–hydration–dehydration treatment of egg shells. Egg shells were washed thoroughly in tap water to remove any unwanted material adhered on its surface, and rinsed twice with distilled water. The washed egg shells were then dried in hot air oven at 105 °C for 24 h. The dried egg shells were reduced to small pieces and calcined in a muffle furnace under static air conditions at 900 °C for 2.5 h to transform the calcium species in the shell into CaO particle (denoted as Egg shell–CaO-900). Then the CaO derived from the egg shell was refluxed in water at 60 °C for 6 h and the solid particle was filtered and dried in hot air oven at 120 °C overnight [27]. The solid product was dehydrated by performing calcination at 600 °C for 3 h to change the hydroxide form to oxide form. Thus the egg shells subjected to the calcination–hydration–dehydration treatment generate a highly active CaO (denoted as Egg shell–CaO-900-600).

2.3. Catalyst characterization

Scanning Electron Microscopy (SEM) analysis was performed to confirm the morphology of the catalyst using a High Resolution Scanning Electron Microscope (Model: F E I Quanta FEG 200). The surface areas of Egg shell–CaO-900, Egg shell–CaO-900-600 and commercial CaO were determined by BET analysis using an ASAP 2020 surface area analyzer (Micromeritics). Basic strength of the catalyst was measured using the Hammett Indicator Titration.

2.4. Transesterification process

The transesterification reactions were carried out in a 250 ml 3-necked round bottomed flask. The middle neck was used to insert a mechanical stirrer (BioLab BL 232 D), one of the side necks was fitted with a water-cooled condenser, and the other neck was fitted with a temperature indicator. The speed of the mechanical stirrer was monitored by using an analog tachometer (Fuji Kogyo Co. Ltd., Kyoto). The desired amount of catalysts, methanol and waste frying oil was introduced into the round bottomed flask and the reactions were carried out at 65 °C for 1 h. After the reaction is completed, the catalyst was separated by filtration and the transesterification products were allowed to settle overnight for the clear separation of biodiesel and glycerol. The conversion of oil to fatty acid methyl esters was analyzed by ¹H Nuclear Magnetic Resonance Spectroscopy (¹H NMR) using a Bruker Avance III 500 MHz (AV

500) spectrometer. CDCl_3 was used as solvent. An equation has been given by Knothe [12] to calculate the percentage conversion of methyl esters

$$C = 100 \times \frac{2A_{\text{ME}}}{3A_{\alpha\text{CH}_2}} \quad (1)$$

where C = percentage conversion of triglycerides to methyl esters, A_{ME} = integration value of the methoxy protons of the methyl esters and $A_{\alpha\text{CH}_2}$ = integration value of the α -methylene protons.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. SEM analysis

Fig. 1 shows the SEM image of the CaO catalyst obtained from the calcination–hydration–dehydration treatment of egg shells (i.e.) Egg shell-CaO-900-600. It indicates a honey comb like porous surface as observed by Hu et al. [7] for the treated mussel shell. However in the case of the Egg shell-CaO-900, regular micro morphology of rod like particles with size ranging from 1.29 to 2.0 μm of width was observed (Fig. 2).

3.1.2. BET analysis

BET analysis was performed on Egg shell-CaO-900, Egg shell-CaO-900-600 and commercial CaO to determine the specific surface area. The surface area of a solid catalyst has direct impact on its catalytic activity, and hence the higher surface area catalyst is expected to have higher catalytic activity [13]. Hydration and dehydration treatments play a vital role in improving the surface area of a catalyst [27]. As shown in Table 2, the surface area of the commercial CaO and Egg shell-CaO-900 was found to be 3.0022 m^2/g and 3.7262 m^2/g , respectively. However the surface area of CaO obtained from the calcination–hydration–dehydration treatment of egg shell (Egg shell-CaO-900-600) was determined as 8.6401 m^2/g . These results are in accordance with the findings of Yoosuk et al.

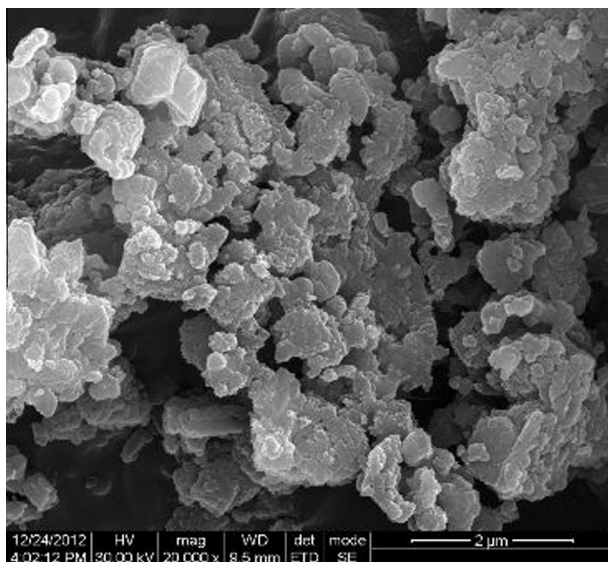


Figure 1 SEM image of the Egg shell-CaO-900-600.

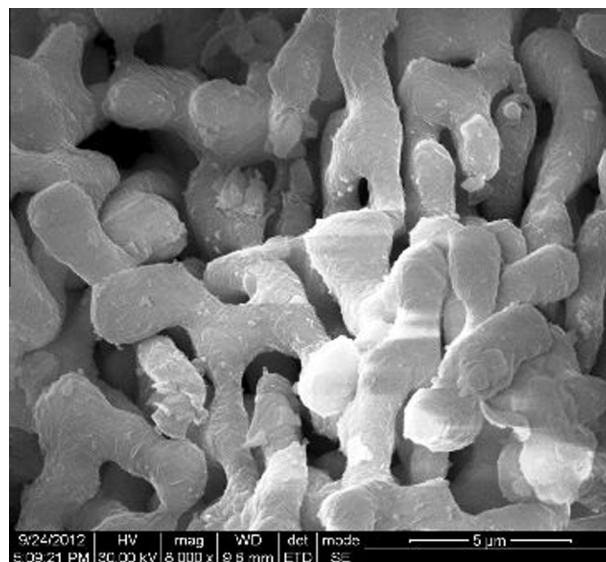


Figure 2 SEM image of the Egg shell-CaO-900.

Table 2 Specific surface area and basic strength of catalysts.

Name of the catalyst	Surface area (m^2/g)	Basic strength (H_+)
Commercial CaO	3.0022	$9.8 < \text{H}_+ < 12.2$
Egg shell-CaO-900	3.7262	$9.8 < \text{H}_+ < 12.2$
Egg shell-CaO-900-600	8.6401	$12.2 < \text{H}_+ < 15.0$

[27]. The surface area of the CaO obtained from the calcinations of calcium carbonate subjected to hydration–dehydration treatment was twice that of CaO obtained from the calcination of calcium carbonate [27].

3.1.3. Hammett indicator titration

Hammett indicator experiments were conducted to determine the H range of basic sites in each catalyst. 25 mg of sample was shaken with 4 ml of a solution of Hammett indicator diluted in methanol and left to equilibrate for 2 h. The Hammett indicators used are phenolphthalein ($\text{pK}_a = 9.8$), indigo carmine ($\text{pK}_a = 12.2$) and 2, 4-dinitroaniline ($\text{pK}_a = 15$). The basic strength of the catalyst was taken to be higher than the weakest indicator that underwent a color change and lower than the strongest indicator that underwent no color change [26]. Among the catalysts tested, Egg shell-CaO-900-600 had the strongest basic strength and the results obtained are presented in Table 2.

3.2. Comparison of the biodiesel production activity for CaO based catalysts

Egg shell-CaO-900-600, Egg shell-CaO-900 and commercial CaO were employed for biodiesel production via transesterification of waste frying oil. The reaction was performed with a 5 wt% catalyst (based on oil weight), methanol/oil ratio of 12:1, a reaction temperature of 65 $^\circ\text{C}$ and a reaction time of 1 h. Commercial CaO produced a biodiesel conversion of 67.57% and Egg shell-CaO-900 produced a biodiesel conversion of 79.62%. However under these conditions, Egg

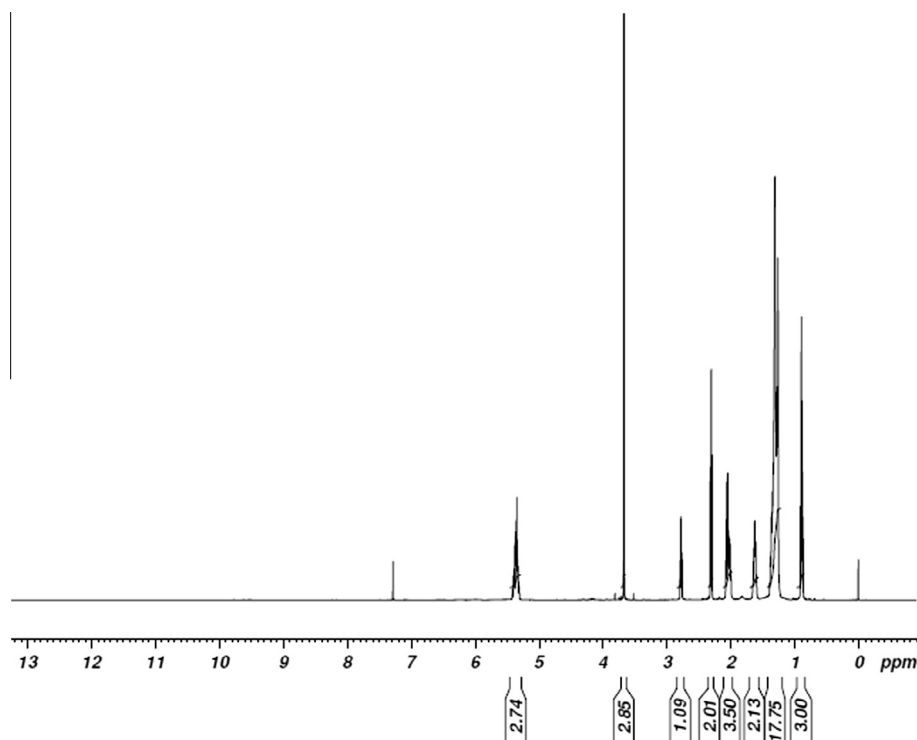


Figure 3 ^1H NMR spectrum of the synthesized biodiesel catalyzed by Egg shell-CaO-900-600.

Table 3 Comparison of properties of the synthesized biodiesel with the ASTM standards of biodiesel.

Properties	Standard values of biodiesel (as per ASTM D6751)	Values obtained for synthesized biodiesel
Density (kg/m^3) at 25 °C	860–900	881.1
Kinematic viscosity (mm^2/s) at 40 °C	1.9–6.0	4.79
Flash point (°C)	100–170	154
Cloud point (°C)	(–3)–15	4.0

shell-CaO-900-600 exhibited the greatest catalytic activity and produced a high biodiesel conversion of 94.52%. The conversion of triglycerides to fatty acid methyl esters catalyzed by Egg shell-CaO-900-600 was analyzed using ^1H NMR and it is shown in Fig. 3. The characteristic peaks of methoxy protons as a singlet at 3.672 ppm and α -methylene protons as a triplet at 2.31 ppm were observed. These two peaks are the distinct peaks for the confirmation of methyl esters [12]. The other peaks observed were at 0.876 ppm, due to terminal methyl protons, a strong signal at 1.312 ppm arises from the methylene proton of carbon chain, a multiplet at 1.6 ppm related to β carbonyl methylene protons, and a signal at 5.352 ppm due to olefinic hydrogen [18]. The percentage conversion of triglycerides to methyl esters using Eq. (1) was found to be 94.52%.

3.3. Determination of the properties of synthesized biodiesel

The properties density, kinematic viscosity, flash point and cloud point of the synthesized biodiesel catalyzed by Egg

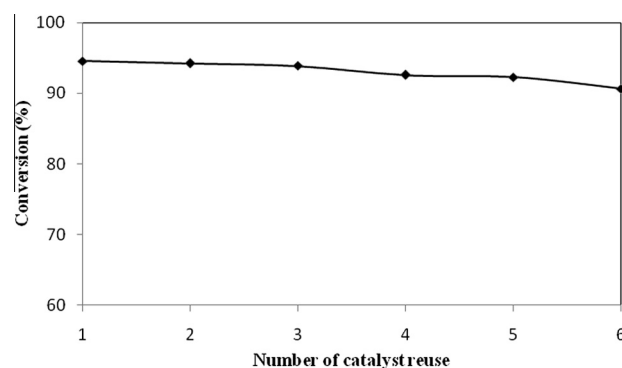


Figure 4 Effect of repeated use of Egg shell-CaO-900-600 on biodiesel conversion.

shell-CaO-900-600 were measured and compared with the ASTM standards of biodiesel and presented in Table 3.

3.4. Reusability of the Egg shell-CaO-900-600

One of the most important features for a heterogeneous catalyst is the ability to be recycled. Reusability of the Egg shell-CaO-900-600 catalyst obtained by the calcination–hydration–dehydration treatment of egg shells was examined for 6 cycles with 5 wt% catalyst (based on oil weight), a methanol to oil ratio of 12:1, a reaction temperature of 65 °C and a reaction time of 1 h and it is shown in Fig. 4. After each cycle, the solid catalyst was separated from the reaction mixture by filtration and washed with methanol to remove the adsorbed stains and recalined at 600 °C for further use. The results indicate that a high biodiesel conversion of above 90% was achieved for all the 6 tested runs.

4. Conclusion

The present study revealed that the calcination–hydration–dehydration treatment is a sufficient method to increase the catalytic activity of waste shells possessing calcium carbonate as their main constituent. The experimental results showed that the methyl ester conversion for commercial CaO was 67.57% whereas it was found to be 94.52% for the CaO obtained from the calcination–hydration–dehydration treatment of egg shell at a 5 wt% catalyst (based on oil weight), a methanol to oil ratio of 12:1, a reaction temperature of 65 °C and a reaction time of 1 h. The synthesized biodiesel was compared with the ASTM standards of biodiesel and the properties density, kinematic viscosity, flash point and cloud point conformed to the ASTM D6751 specifications.

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