Sustainable Biodiesel Production from Waste Cooking Oil Using Eggshell-Derived CaO Catalyst

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Abstract

The increasing demand for sustainable energy sources has driven interest in biodiesel production, a renewable alternative to fossil fuels. This paper investigates the production of biodiesel using eggshells as a catalyst in the transesterification of waste cooking oil. Because of their abundance, affordability, and capacity to transform into calcium oxide (CaO), a premium base catalyst, eggshells—which are abundant in calcium carbonate—are an important catalyst. They are therefore a more environmentally responsible and sustainable substitute for conventional catalysts made from non-renewable materials. The catalyst was prepared by three methods: dried at 105°C, calcinated at 900°C, and refluxed at 600°C. The results revealed that the highest yield of produced biodiesel from waste cooking oil was 81.42% when refluxed eggshell was used. The first case of optimization was done on dried eggshell at 105°C; the obtained yield was 76.92% and 80.55% for reaction times of 1 hr and 2 hr, respectively. While the second case was done on dried eggshell at 105°C and calcined at 900°C, the obtained yield was 84.16% for the lowest catalyst (calcined at 900°C) ratio. The final case was recycled calcined eggshell, which gives a good yield. The costs of producing one ton of biodiesel from eggshell and sodium hydroxide (NaOH) catalysts are $1,560 and $1,566, respectively. The used oil, eggshell catalyst, and produced biodiesel were characterized.

Keywords: biodiesel, eggshell catalyst, waste cooking oil, calcium oxide, transesterification

Introduction

Energy is fundamental to life and various processes on Earth. The sun serves as the primary energy source, harnessed directly through photosynthesis or indirectly through fossil fuels, and global energy consumption reached 622,156,806 TJ in 2022, with oil contributing approximately 41% [2]. The global population has rapidly increased, leading to higher energy demands. By 2040, energy consumption is expected to rise by 20-30% due to population growth and economic development [3]. Energy sources are classified into renewable and non-renewable resources. Renewable energy, such as solar and wind, offers a sustainable alternative with lower emissions compared to fossil fuels [4].

Bioenergy, derived from organic materials, has gained attention due to its carbon-neutral qualities [5]. This includes biofuels like biodiesel from waste cooking oil (WCO), which contributes to sustainability [6]. Biodiesel is a diesel substitute made from oils and fats. It is appealing for its potential to reduce greenhouse gas emissions [7].

Biodiesel can be produced through methods like transesterification, which reduces oil viscosity and results in fatty acid methyl esters (biodiesel). This biodiesel production method offers several advantages compared to alternative processes: the reaction conditions are straightforward, the production method is environmentally friendly, and a diverse range of feedstocks can be utilized with this technique. Chemically, biodiesel is a mixture of fatty acid alkyl esters obtained by a transesterification reaction, where triglycerides from vegetable oils or animal fat react with alcohols, usually methanol or ethanol, to form esters (biodiesel) and glycerin [8].

Rashid (et al.) [1] studied the process of biodiesel production from waste cooking oil using calcium oxide catalyst extracted from discarded eggshells. They also optimized both the catalyst preparation and the esterification reaction conditions, which resulted in a high biodiesel conversion rate of 96.11%. They found that the ideal parameters for synthesizing the CaO catalyst from eggshells involved a calcination temperature of 900°C maintained for 3 hours. This process yielded a catalyst characterized by excellent crystallinity, surface area, and a well-distributed active CaO component.

For the transesterification reaction aimed at biodiesel production, the optimal conditions included a methanol-to-oil ratio of 30:1, a reaction temperature of 65°C, a catalyst loading of 3 wt.%, and a reaction duration of 3 hours, achieving a biodiesel conversion rate of 96.11%. Additionally, the treatment of the CaO catalyst with n-hexane enhanced both its activity and longevity.

The main objective of this project is to produce biodiesel from waste cooking oil by using eggshells as a catalyst.
concentration, on the production of biodiesel, and characterize the produced biodiesel against industry standards.

Methodology

The flowchart for producing biodiesel from fresh oil, as shown in Figure 1, illustrates all the

The Sub Objectives: to prepare different types of eggshell catalysts, characterize the produced eggshell catalysts, evaluate the catalytic potential of processed eggshells in the transesterification of vegetable oils and compare their effectiveness with traditional methods, investigate the impact of reaction conditions, specifically time and catalyst
steps for the process, from sample selection, analysis, and verification of FFA value, then performing the esterification process, if necessary, transesterification, separation, and washing of the sample, and finally characterization analysis of the properties of the resulting biodiesel.

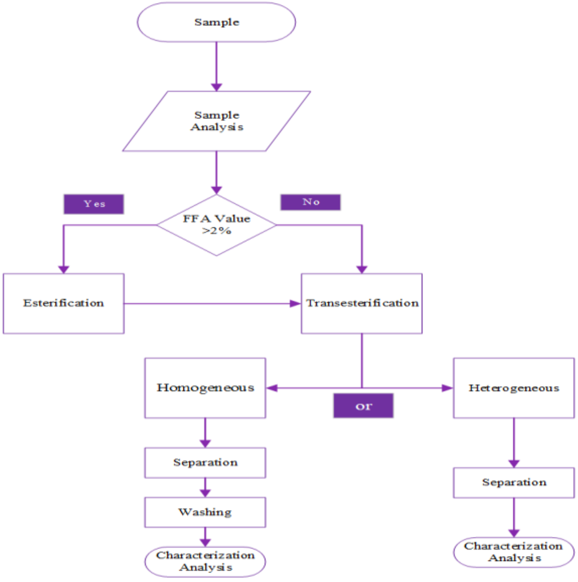


Figure 1: Flowchart for the production of biodiesel from fresh oil

1. Traditional Method (Homogeneous catalyst) of Biodiesel

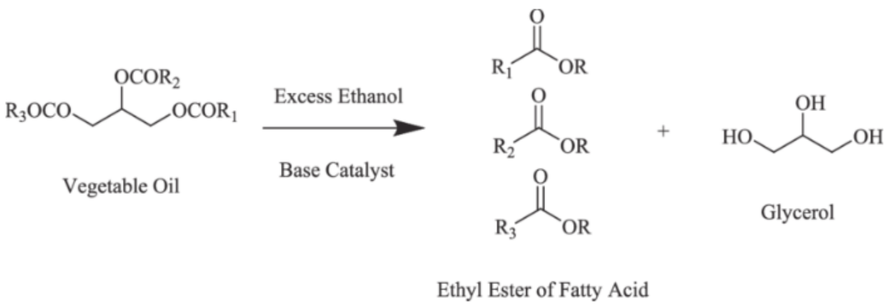
Sample collection and analysis: a sample of oil was collected and standardized to evaluate its properties before use in biodiesel production, which are density, viscosity (measured using a viscometer BRV3000 model device),
flask using a reflux condenser, stirrer, and thermometer. Fresh oil will be preheated, the H_2SO_4 catalyst and alcohol added, and samples suspended for 8 hours.

Transesterification (FFA < 2%): A 200 mL oil sample will be heated at a low temperature

saponification, moisture content was measured using a BOECO Moisture Analyzer device), acid value, and free fatty acid (FFA).

Esterification (FFA>2%): The esterification reaction will be conducted in a 1000 mL glass

to 60-70°C. It will be prepared with a 6:1 methanol-to-oil ratio. NaOH catalyst will be added at a rate of 0.5% by weight of oil to the methanol, which will then be added to the oil. The flask will be covered with a piece of aluminum foil and placed in a water bath for 1 hour.



Separation: At this stage the transesterification product will be transferred to a separating funnel and left for 24 hours at room temperature to separate glycerin (bottom layer) and biodiesel (top layer).

Washing: In this step the biodiesel will be washed after separating it from the glycerin with a sufficient amount of distilled water at 90 °C to remove the remaining catalysts and traces of soap.

Characterization Analysis: A sample of the product will undergo tests to determine its physical properties, including density, viscosity, and heating value, which will be measured using Calorimeter IKA Germany 36561.

2. Production of Biodiesel from Fresh Oil Using Eggshell Catalysts (Heterogeneous Catalyst)

Sample collection and analysis: a sample of oil will be collected and standardized to evaluate its properties before use in biodiesel production, which are density, viscosity, saponification, moisture, acid value, and free fatty acid (FFA).

Catalyst Preparation: The highly active CaO catalyst will be prepared by calcinating, hydrating, and dehydrating eggshell. The eggshell is washed, rinsed, dried at 105°C overnight, and reduced into small pieces. The CaO is calcined at 900°C for 2.5 hours, then refluxed in water for 6 hours. The solid product is dried and dehydrated at 600°C for 3 hours, resulting in a highly active CaO (Eggshell-CaO900-600). The highly active CaO catalyst will be prepared by calcinating, hydrating, and dehydrating eggshell. The eggshell is washed, rinsed, dried, and reduced into small pieces. The CaO is calcined at 900°C for 2.5 hours, then refluxed in water for 6 hours. The solid product is dried and dehydrated at 600°C for 3 hours, resulting in a highly active CaO (Eggshell-CaO900-600).

Characterization of CaO (eggshell) catalyst: The resulting calcium oxide catalyst will be characterized using thermogravimetric analysis (TGA) using a Thermogravimetric Analysis device and Fourier Transform Infrared Spectroscopy test (FTIR) using Thermo Scientific iDS ZnS 14866.

Reaction Test: A mixture of oil, eggshell catalyst, and methanol will be mixed in a flask, stirred for 1 hour, and maintained at 60-70°C. After filtering, the mixture will be separated for 24 hours, and the resulting biodiesel will be collected and separated from the glycerol layer. The reaction will be done by using all the eggshell stages (dried, calcinated, and refluxed).

To produce biodiesel from Waste Cooking Oil (WCO), the oil used is falafel frying oil. The oil will undergo pretreatment, either in the traditional way or using eggshells as a catalyst for the reaction.

In order to determine the optimum operating conditions of the transesterification, the previous steps will be repeated at different times (1 and 2 hours) and catalyst ratios (1, 5, and 10 wt.%). To determine the yield (%) of produced biodiesel, this equation will be used.

$$\boldsymbol{Yield}(\%)\,\boldsymbol{of\ Biodiesel} = \frac{\boldsymbol{Mass\ of\ biodiesel\ obtained}}{\boldsymbol{Mass\ of\ oil\ used}} \times \mathbf{100}\%$$

Results & Discussions

1. Eggshell Catalyst Preparation

The process of eggshell catalyst preparation started from collecting the eggshell, washing, drying, and sieving. Then prepare it in four forms: dried at room temperature, oven-dried at 105°C for 24 hours, calcinated at 900°C in the oven for 2.5 hours, and refluxed at 600°C for 6 hours. As shown in figure 2.

Figure 2: Eggshell catalyst preparation steps.

2. Characterization of eggshell catalyst

1. Fourier Transform Infrared Spectroscopy (FTIR) Test.

The FTIR test was measured by using Thermo Scientific iDS ZnS 14866. The details concerning the stretching and bending vibrations of the functional groups in the dried, calcinated, and refluxed eggshells, which are responsible for the adsorption of adsorbate molecules, are illustrated in Figure 3.

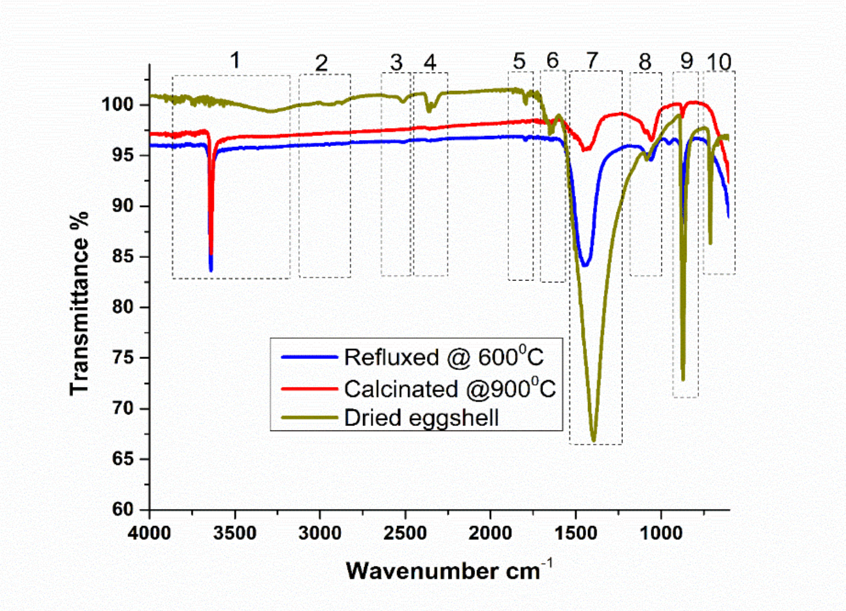


Figure 3: FTIR spectra of eggshell catalysts.

An intense peak at 1391 cm⁻¹ is noted for the eggshell particles, which can be closely linked to the presence of carbonate minerals in the eggshell matrix. A strong peak for eggshell particles was observed at 1426 cm⁻¹, which can be closely linked to the presence of carbonate minerals within the eggshell matrix. The peaks observed at 3298 and 2515 cm⁻¹ can be attributed to the stretching of the alcohol hydroxyl group (-OH) and the hydrogen group, respectively. Two peaks were also observed at 709 and 876 cm⁻¹, associated with in-plane and out-of-plane distortion, respectively, indicating the presence of calcium carbonate ($CaCO_3$).

The bands at 2940 and 2870 cm^{-1} represent calcium hydroxide vibration, indicating the presence of organic layers, composed of amino acids, in the eggshell. The bands at 1790 and 1644 cm^{-1} correspond to the stretching of the carbonyl (amide) and carbonyl (amide) groups, respectively.

The results are consistent with the results of a study entitled "Efficiency of calcium carbonate from eggshells as an adsorbent for cadmium removal in aqueous solution" [9].

2. Thermogravimetric Analysis (TGA).

Figure 4 shows a TGA analysis of three eggshell samples, measuring mass change with temperature, to understand thermal stability and decomposition stages.

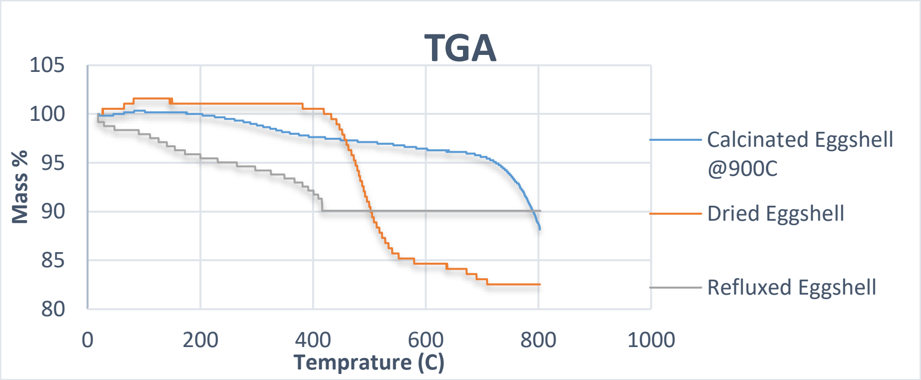


Figure 4: TGA test for eggshell catalysts.

1. Dried eggshell: From 0 to 400°C the weight loss was slight and not obvious because the sample was dried for 24 hours at 105°C. After 400°C calcination began, converting calcium carbonate ($CaCO_3$) to calcium oxide (CaO). The sharp weight loss, attributed to the loss of carbon dioxide (CO_2), continued from 750 to 800°C.

$$CaCO_3 \Rightarrow CaO + CO_2$$

2. Calcinated eggshell: During the calcination process, the eggshell sample lost a significant amount of weight, and it was clear that the weight loss began at a very high temperature, approximately 700°C. Although the process was carried out at 900°C, the apparent result indicates that the process was incomplete and required a higher temperature.

3. Refluxed eggshell: Due to the use of water in the refluxed process, the sample began to lose water from 0 to 4000°C, but after this stage, and because the sample had previously undergone a calcination process at a temperature of 900, it didn't have any weight loss.

3. Characterization of Fresh Oil and Waste Cooking Oil.

One of the most important tests that identified the mechanism of action was the free fatty acid test, which showed values below 2% for both types of oil, indicating no need for the esterification process.

The results are consistent with the results of a study entitled "Biodiesel production from cotton oil using heterogeneous CaO catalysts from eggshells prepared at different calcination temperatures" [10].

Table 1 shows the characterized properties of fresh and waste cooking oil for biodiesel production.

Table 1: Characterization of Fresh Oil and Waste Cooking Oil.

Test Name	Fresh Oil	Standard value for fresh oil	WCO	Standard value for WCO oil
Free Fatty Acid (%)	1.38	-	1.38	-
Acid Value (mg KOH/g)	2.76	0.16-1.94	2.76	1-2
Density (g/mL)	0.91	0.92	0.91	0.91-0.93
Moisture (%)	0.59	< 0.2	0.41	0.5%-1%

Saponification Value (mg KOH/g)	216	188-194	165	180-200

4. Biodiesel Production

Biodiesel production stages: the raw material (fresh and waste cooking oil, NaOH catalyst, eggshell catalyst, methanol, and magnetic stirrer) was prepared. Biodiesel reaction for 1 hour at 60°C. Vacuum filtration. Then separation of the produced biodiesel. As shown in figure 5.

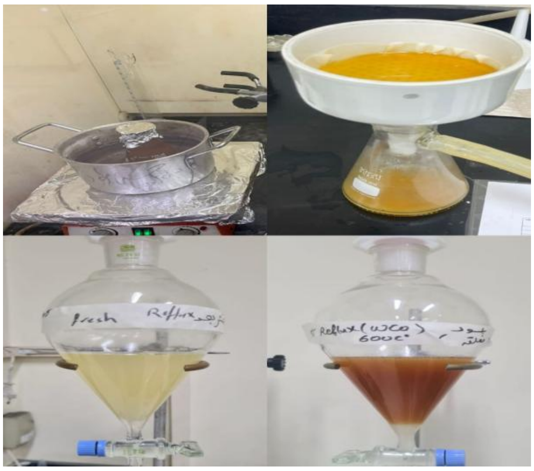


Figure 5: Biodiesel production steps

5. Biodiesel conversion from fresh and waste cooking oil.

The comparison between the biodiesel production yield obtained from fresh oil and waste cooking oil (WCO) using different catalysts, including NaOH and eggshell catalysts under various treatment conditions. The results indicate that NaOH achieved the highest biodiesel yield for both types of oils, as shown in Figure 6.

Overall, fresh oil consistently produced slightly higher yields than WCO, though the difference was not significant when using eggshell-derived catalysts under various treatment conditions. These findings support the potential use of thermally treated eggshells as sustainable and effective alternatives to conventional catalysts in biodiesel production.

Based on FTIR analysis of the eggshells, dried eggshells at 105°C and refluxed at 600°C contained $CaCO_3$ in both the in and out planes (at wavelengths between 800 and 700 cm^{-1}), increasing the likelihood of eggshells acting as a catalyst. This is due to the higher yield of oxygen groups in dried eggshells at 105°C than in refluxed eggshells at 600°C. Fresh oil is poor in oxygen groups, while dried eggshells at 105°C are rich in oxygen groups. This attracts the oil with dried eggshell, while refluxed eggshells at 600°C are poor in oxygen groups.

Since calcined eggshells contain only an in-plane of calcium carbonate and are poor in oxygen groups, this explains why the catalyst yield for biodiesel is lower than for dried and refluxed.

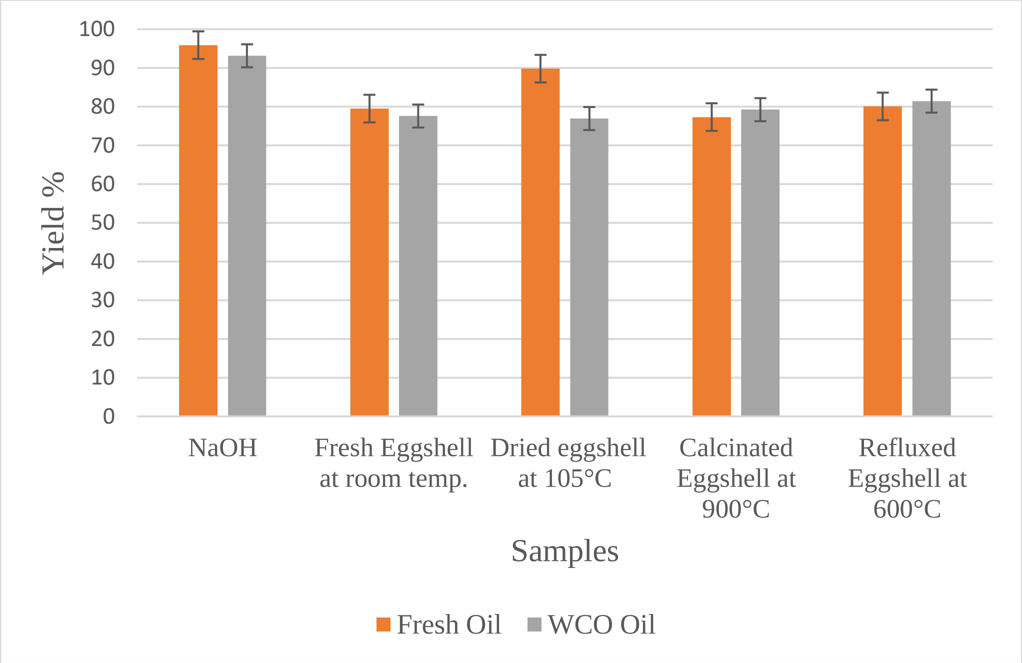


Figure 6: *Comparison of biodiesel yields from fresh oil and waste cooking oil (WCO) using NaOH and eggshell-derived CaO catalysts prepared via drying at 105°C, calcination at 900°C, and reflux at 600°C. Error bars indicate variation from replicate experiments*

6. Optimization

Case 1: *Change the reaction time.*
In case 1, the change in time was studied by increasing it from 1 to 2 hr and by keeping the other parameter constant. As shown in Figure 7, the results show a decrease in the yield of fresh oil from 89.81% to 82.97% when increasing the reaction time. While in waste cooking oil, the yield increased with increasing reaction time from 76.92% to 80.55%.

Case 2: *Change the catalyst ratio.*

The effect of using different catalyst ratios (2 g, 10 g, 18.18 g) in producing biodiesel from fresh and WCO. The result shows that decreasing the catalyst ratio to 2 g gives the highest yield. As illustrated in figure 7.

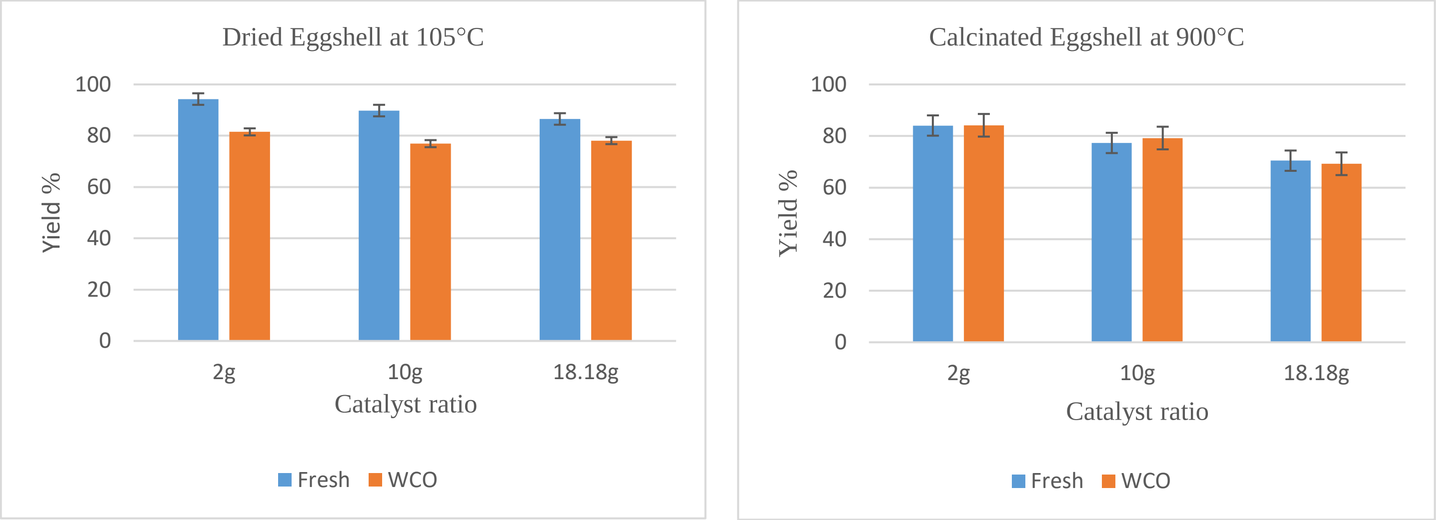


Figure 7: *Effect of catalyst mass (2 g, 10 g, 18.18 g) on biodiesel yield from fresh oil and WCO using dried eggshell catalyst (105°C). Error bars represent standard deviations from duplicate experiments***.**

Case 3: *Use recycled catalyst*

. In this case, the calcinated eggshell at 900°C used in biodiesel production was recycled for the first time. As shown in figure 9, in fresh oil there was an increase in the biodiesel production yield, increasing from 81.13% to 88.75%, while in waste cooking oil there was a decrease in the biodiesel production yield from 80.22% to 73.94%. Recycled, calcinated eggshells exhibit different catalytic activity in fresh versus waste cooking oil due to variations in their composition and the presence of contaminants. Fresh oil, being cleaner, allows the eggshell-derived calcium oxide (CaO) catalyst to efficiently promote transesterification, the process of converting oil into biodiesel. However, in waste cooking oil, the presence of free fatty acids, water, and other impurities can hinder the catalyst's performance by 1) reducing the active CaO sites through reactions with free fatty acids and 2) physically blocking pores and reducing surface area.

The results of biodiesel production from fresh and waste cooking oil based on the catalyst type are shown in Figure 8.

Figure 8: *Biodiesel products obtained under various catalyst types and operating conditions, from left to right:NaOH; dried eggshell (105 °C) at 10 g for 1 and 2 h; dried eggshell (105 °C) at 2 g and 18.18 g; room-temperature eggshell (25 °C); calcined eggshell (900 °C) at 10 g, 2 g, and 18.18 g; refluxed eggshell (600 °C) at 10 g; and recycled calcined eggshell*

Compared to Rashid et al. [8], studies in the same field found that the optimal conditions included a methanol-to-oil ratio of 30:1, a reaction temperature of 65°C, a catalyst loading of 3 wt.%, and a reaction duration of 3 hours, achieving a biodiesel yield of 96.11%. The reaction conditions that were used in this paper are a 60°C reaction temperature, a 1-hour reaction time, a 6:1 methanol-to-oil ratio, and 5.43 wt% (10 grams) eggshell catalyst with an 81.42% biodiesel yield.

7. Estimate the cost of biodiesel production.

The cost of biodiesel production from eggshell catalyst was lower than the cost of biodiesel production from NaOH catalyst, $1560 and $1566, respectively. Although the difference in production price is not big, this result was consistent with the results of other studies. Economically, there is not a significant difference in production costs.

However, both NaOH and eggshell catalysts offer unique sustainability and environmental advantages. NaOH, when produced sustainably (e.g., through green methods), can reduce carbon emissions and electricity costs in industrial processes. Eggshells, on the other hand, provide a readily available, low-cost, and renewable resource, particularly when used to minimize pollutants in biodiesel production. NaOH is a strong base used in various chemical reactions; eggshells offer a more environmentally friendly option for specific applications like biodiesel synthesis.

Conclusion

Waste cooking oil can be used to produce biodiesel, but free fatty acids should be kept below 2% to avoid soap formation. NaOH catalysts showed higher biodiesel production yields, but eggshell catalysts yielded different results. Reducing the catalyst ratio and reaction time increased yields. Recycled calcined eggshell produced good biodiesel yields. The cost of producing a ton of biodiesel from eggshell and NaOH catalysts is $1,560 and $1,566, respectively.

It is recommended to prepare nanoscale eggshell catalysts and study their efficiency in biodiesel production. Tests should be conducted on the produced biodiesel samples, such as cetane number and kinematic viscosity. The effect of changing reaction temperature on biodiesel production should be studied. Zeta potential tests should be conducted on used oil and eggshell samples to determine the oxygen group.

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