Eggshell waste as a catalyst for biodiesel production: A preliminary study

N A Ali¹, N Khairuddin¹,² and B M Siddique³

¹ Department of Science and Technology, Faculty of Humanities, Management and Science, Universiti Putra Malaysia Bintulu Sarawak Campus, 97008 Bintulu, Sarawak, Malaysia
² Institut Ekosains Borneo, Universiti Putra Malaysia Bintulu Sarawak Campus, 97008 Bintulu, Sarawak, Malaysia
³ Faculty of Engineering, Computing and Science, Swinburne University of Technology Sarawak, 93350 Kuching, Sarawak, Malaysia

Email: nozieana@upm.edu.my

Graphical abstract

Abstract. This research aims to observe the usability of waste eggshells as a heterogeneous CaO-based catalyst to produce biodiesel via the transesterification process. The waste eggshell contains CaO and serves as a heterogeneous catalyst that can be extracted using a simple heat treatment technique. The catalyst loading used in this study were 1, 2, 3, 4, and 5 wt.%. The biodiesel yield affects the variables of the reaction, including the amount of catalyst used. According to the findings in this work, the low-weight catalyst produced more biodiesel (64% of yield) than other catalysts in the studies. Using the same CaO catalyst with a 1 wt.% catalyst, previous studies showed a biodiesel yield of 56.64%. Outcomes revealed that waste eggshells could be used as an effective catalyst to transform waste cooking oil into biodiesel, thereby significantly lowering biodiesel costs and improving product yield and fuel properties.
1. Introduction

Along with the rise in human growth, industrial globalisation, and transportation needs, energy demand is constantly rising [1]. Consequent to the growing global population, as well as the development of the economy and industry, petroleum consumption rises every year [2], where there is a great concern on the toxic exhaust emissions from cars that significantly impact the human health and the environment, in addition to the ever-rising prices of petroleum-based fuels [3]. Due to the current strong reliance on petroleum as a main source of fuel for transportation and electricity production, petroleum prices have recently reached new highs [4]. Figure 1 illustrates that the consumption of non-renewable energy keeps increasing. Biodiesel fuel is widely used in most nations since it is eco-friendly, harmless, and environmentally benign, emitting fewer greenhouse gases (GHGs) [5].

![Figure 1. Transitions in energy: Global and national viewpoints & BP world energy's statistical analysis [6].](image)

Efforts to reduce diesel engine emissions without engine modification have accelerated rapid growth and the increased output of biodiesel, which has also been driven by the urgent need to reduce diesel engine emissions to minimise global warming drastically. Biodiesel has become an enticing and sustainable green fuel, recognised as Fatty Acid Methyl Ester (FAME) with a global recognition as an alternate energy source [2]. Biodiesel is typically generated through the transesterification of vegetable oils or tallow with methanol using a suitable catalyst, where it is a healthier option to diesel, whereby the former consists primarily of mono-alkyl esters of unsaturated fatty acids and has similar physical properties to that of diesel, with the added favour of being green and non-toxic biodegradable [7]. In the early 1990s, biodiesel, also known as mono-alkyl ester, became widely available, and production has steadily increased since then [8]. Waste lipids must be used to achieve higher biodiesel yields without compromising the atmosphere or food sources [9]. Transesterification generates FAME while resulting in saponification or soap formation [5]. Biodiesel has been called the most favourable alternative to conventional petroleum diesel because it is renewable and eco-friendly. The downside of biodiesel marketing is the combined high cost of raw materials and processing attributes to the high cost of catalysts and biodiesel feedstocks. Therefore, waste cooking oil (WCO) may be used successfully in biodiesel processing to reduce the expense of raw materials. It also helps to reduce the disposal of WCO, which may cause environmental pollution. Figure 2 shows that the production of cooking oil in Malaysia has a steady increase, where it would increase the amount of WCO required in the present and in the future, therefore, polluting the environment.
Catalyst has a crucial role in biodiesel development. Various homogeneous and heterogeneous catalysts have been used in the manufacture of biodiesel. Furthermore, the use of waste material catalysts would significantly incur an additional rate of biodiesel output. Homogeneous catalysts, such as potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium methoxide (CH\textsubscript{3}OK), and sodium methoxide (CH\textsubscript{3}ONa), are commonly used during the transesterification process [5]. After transesterification on heterogeneous catalysts, a greater grade of FAME can be produced [5]. Calcium oxide (CaO) is among the most extensively used heterogeneous catalysts contained in waste eggshells, which can easily be converted into CaO by high-temperature calcination with a large amount of calcium compounds (CaCO\textsubscript{3}) [2]. The CaO catalyst from chicken eggshell can be used for successful transesterification [11]. An average egg is estimated to weigh between 60.0–60.2 g, whereas an empty shell weighs between 6.6–7.3 g [12]. Calcium carbonate in the form of calcite accounts for 94–97 % [13–14] of the chemical composition of eggshells, with organic matter accounting for 3–4.5 % [12]. This shows that chicken eggshells are reliable sources of CaO. The CaO catalysts are easy to obtain, as the production of chicken eggs showed higher increment every year. Figure 3 demonstrates that the production of chicken eggs in Peninsular Malaysia have increased year by year, where the eggshell waste containing valuable sources of CaO can be easily obtained from restaurants, among other places [15].
A substantial increase of 91% in biodiesel yield for the catalyst compared with a 78% yield for the unsupported CaO catalyst was obtained [17].

This research aims to study the development of biodiesel using a low-cost, heterogeneous CaO-based catalyst from waste eggshells. The development of biodiesel through the transesterification method using WCO was carried out using the established catalyst. In addition, the influence of eggshell catalyst loading on biodiesel yield was observed.

2. Methodology

2.1. Materials
In Malaysia, the wide availability of WCO in all eateries has led to its use as raw material in this study. The WCO used in this experiment was acquired from the restaurant in Bintulu, Sarawak. Methanol was purchased from HmbG Chemicals (Hamburg, Germany) to produce high-quality biodiesel fuel. The chicken eggshells were collected from bakery and restaurant in Bintulu, Sarawak.

2.2. Catalyst preparation
To minimise impurities present on the surface and inside of the eggshells, the waste chicken eggshells collected were rinsed with distilled water several times. The eggshells were then washed and dried in a 100 °C oven for 24 hours. Then, using a 0.08-mm sieve wire, the waste eggshell was crushed into powder and sieved. Finally, the powdered eggshell experienced a calcination process at 900 °C for 3 hours.

The following equation (1) demonstrates the conversion of chicken eggshells into calcium oxide (CaO) under calcination process:

\[
\text{Chicken eggshells (CaCO}_3\text{)} \xrightarrow{900^\circ C} \text{CaO} + \text{CO}_2 \uparrow
\]  

Figure 3. Weekly output of chicken eggs every year [16].
2.3. Reaction of transesterification

The following reaction of transesterification procedure described by [2] shows a slight modification. The transesterification reaction was performed using a 100-mL three-necked round-bottom glass flask fitted with a reflux condenser, magnetic stirrer, and thermometer. To regulate the temperature, a water bath at a constant temperature was also used. Molar ratio: methanol/oil using in the experiment carried out was 6:1. Time taken to carry out the process of transesterification was 1 hour. At a stirring rate of 600 rpm for the length of the reaction, the catalyst was dispelled in methanol at 100 °C and subsequently add on oil. The reaction mixture was separated using the separating funnel. The latter occurred in the separation between the two phases, where the upper layer consisted of biodiesel, and the lower layer is the glycerol. With a mass yield of 10 %, the glycerol obtained as a by-product of biodiesel processing is referred to as crude glycerol because it contains free fatty acids (FFA) [18]. Figure 4 below shows the transesterification reaction, where biodiesel is made from triglycerides in the presence of alcohol and a catalyst.

![Figure 4](image)

**Figure 4.** The reaction equation of process conversion from triglycerides to biodiesel in the presence of alcohol with a catalyst through the transesterification process [19].

2.4. Post - treatment process

To extract unreacted oil and impurities, biodiesel with excess methanol and unreacted oil was washed with hot distilled water at 90.3 °C. Next, the final mixture was heated for 30 min at 100 °C to eliminate excess moisture content and obtain pure biodiesel.

2.5. Fourier-Transform Infrared Spectroscopy (FTIR) analysis of biodiesel and WCO

The biodiesel content C=O was determined using the Shimadzu IRAffinity-1 equipment of the Fourier-Transform Infrared Spectroscopy (FTIR) for the biodiesel characterisation study of the functional group and composition of the biodiesel, where the infrared absorption spectra were obtained in the range of 600 to 4000 cm⁻¹.

3. Results and discussion

3.1. Effect of calcination temperature

The temperature for calcination was one of the parameters of nanocatalytic synthesis, where it demonstrates improvement in the catalytic surface and improves the action of a catalyst [20–22]. Table 1 shows that the biodiesel production yield is inconsistent when the loading catalyst increases. Logically, it demonstrates that 1 wt.% of catalyst can produce high yields for others. According to previous studies conducted by Goli and Sahu [23], a biodiesel yield of 63.2% is obtained at 2 wt.% of catalyst loading and at a low reaction duration of 1 hour; yet, at the same reaction time, the catalyst loading of 12 wt.% had reduced the biodiesel yield by 55.2%. The 2 wt.% catalyst, on the other hand, shows that it produced the second highest biodiesel yield. Results showed a somewhat similar outcome to that of the previous study, where a high catalyst was used, showing a reduction rate of biodiesel compared with that using a low catalyst. For every catalyst loading weight percentage, the biodiesel yield obtained was distinct. Maximum biodiesel yield of 64% was achieved at 100 °C. The biodiesel
yield, as shown in table 1, showed a decrease when 4 wt.% of catalyst loading was used. As shown in table 1, the yield of biodiesel was quite low (34.0%) at 100 °C. High oil viscosity causes a decreased diffusion rate and irreversible transesterification process conversion on the catalyst surface, which can be attributed to this [24]. The excess catalyst was shown to make the reaction mixture more viscous, resulting in poor diffusion of reactants in the methanol–oil–catalyst systems and a reduction in the yield and conversion of the reactions [25–30]. The yield reduced as the catalyst quantity increased for two possible reasons, which are, firstly, at increasing catalyst concentrations, diffusion in methanol-oil-catalyst systems is inhibited [25]. Whilst, secondly, greater catalyst concentrations might adsorb more products, lowering yield [31–32].

| Catalyst loading, (wt.%) | Biodiesel yield, (% ± S.E.) |
|-------------------------|-----------------------------|
| 1                       | 64.0 ± 0.00                 |
| 2                       | 56.0 ± 1.00                 |
| 3                       | 53.4 ± 0.65                 |
| 4                       | 45.0 ± 2.75                 |
| 5                       | 52.0 ± 1.00                 |

3.2. Characterisation of biodiesel

Figure 5 illustrates the FTIR biodiesel output and WCO spectra with different catalyst loading percentage and mid-infrared between 600 and 4000 cm⁻¹. The FTIR study was conducted to analyse the percentage of biodiesel in the biodiesel transesterification reaction, depending on the catalyst. Chemically, biodiesel is a blend of mono-alkyl esters of long-chain fatty acids (C₁₆–C₁₈) derived from vegetable oils and animal fats [33].

The methyl ester peaks showed strong C=O and O–CH₃ group bands, demonstrating the occurrence of transesterification process. It is vital to identify the O–CH₃ group, as it plays a significant role in ensuring the transesterification had occurred. For biodiesel and WCO, there were no noticeable peaks in the bands 1800–2700 cm⁻¹ and 3000–4000 cm⁻¹. Furthermore, the difference is seen in the area between band 3400–2600 cm⁻¹, where the C–H stretch is indicated at different absorption spectra. Therefore, all of the spectra in figure 5 displayed high peaks at precise bands of 2922.16 and 2852.72 cm⁻¹ prior to C–H vibrations.

The O–CH₃ group is present in biodiesel but absent in WCO, which indicates the WCO successfully converted to biodiesel where can be found between band 1188–1200 cm⁻¹. According to a prior study by Goli and Sahu [23], peak of O–CH₃ can be found at 1170.16 cm⁻¹ with 19.5% for eggshell based FAME product.

The peaks that show in figure 5, the presence of C–O group can be found precisely at bands 1159.22 cm⁻¹, and some of the bands at 1234.44, 1159.22, 1114.86, and 1097.50 cm⁻¹ perchance attributed towards the category of (C–O) ester group stretching vibrations. The cis C=C bond produced a small band with a wavelength between 1750–1500 cm⁻¹.

The bands of CH₂ and CH₃ aliphatic groups resulted at band 1460.11 cm⁻¹. Other biodiesel diagnostic peaks were found at positions 1743.65 cm⁻¹ for the C=O group of glycerides. The greater the amount of free fatty acid, the less likely it is to convert into fatty acid methyl ester. Because of the variety of bending and stretching within the molecule, the area between 600–1500 cm⁻¹ is usually a very complicated absorption sequence. Previous research by Goli and Sahu [23] confirmed the eggshell-based FAME obtain was 21.5%, where the –CH₃ asymmetric bending vibration at 1458.19 cm⁻¹. This study refers to a band spectra that summarise the functional groups assigned to the main
and minor absorption bands from previous studies [34]. Both the biodiesel and WCO did not show a significant difference. In the FTIR, the only difference is that glycerine had been removed from the hydrocarbon chain and replaced with methanol, where the difference can be found between 600–1500 cm⁻¹. Some are recognisable in a specific band, such as 1425–1447 cm⁻¹ and 1188–1200 cm⁻¹, where the biodiesel spectrum differs slightly [35–37]. In the biodiesel spectrum, these peaks are not present in the oil spectrum [35].

Figure 5 illustrates the probable mechanistic feature of the transesterification reaction in the presence of the calcined eggshells. The calcinated eggshell containing mainly calcium oxide (CaO) acts as a catalyst in the transesterification reaction by drawing protons from the reacting media to the solid catalyst surface, forming an extremely fundamental and active methoxide anion(I) [15]. As a strong nucleophile, methoxide anion targets the oil's carbonyl carbon atom to form a tetrahedral intermediate. CaO proton attacks the intermediate species with simultaneous tetrahedral rearrangement to generate biodiesel or methyl ester (FAME) and glycerol fatty acids [38–39].

According to Zaman et al. [40], CaO calcined at 800 °C had a higher degree of crystallinity than others, implying that this is the optimal temperature for the synthesis of CaO. Besides, a prior study conducted by Habte et al. [41] also indicated that the absence of a greater absorption at 1415.52 cm⁻¹ in the FTIR analysis implies that the CaCO₃ as an essential element of the eggshell was no longer present because it has been transformed to CaO. According to the XRD analysis performed by Kirubakaran and Selvan [42], calcium hydroxide Ca(OH)₂ was generated during the decarbonation of CaCO₃ into CaO due to reactive moisture adsorption displays at 2θ = 47.1° and 2θ = 18° and 47.2°, respectively, in contrast, calcium carbonate was noticed at 2θ = 28.7° due to incomplete conversion.

![Figure 5. FT-IR spectrum of biodiesel and WCO.](image)

### 3.3. Acid value of biodiesel

The acid value of the biodiesel is different for each catalyst loading. It was found that 3 wt.% of catalyst loading was found to be 2.02 mg of titration oil CaO/g corresponding to the 1.01% FFA value. Extensive research was done on the yield of biodiesel in terms of FFA content, where it was learnt that transesterification will not occur if the FFA content in the oil is more than 2 wt.%; hence, the FFA value must be reduced to below 1% [43–44]. A pre-treatment step was necessary for oils with acid value greater than 2 mg KOH/g, [45]. A high acid value may cause rubber seals and hoses in the
engine to lose their solvency, resulting in early failure causing deposits that can clog the fuel filter and lower fuel pressure. [46–47].

Table 2. Free fatty acid biodiesel oil and acid value.

| Catalyst loading, (wt%) | Acid value, (mg) | Free fatty acid, (%) |
|-------------------------|-----------------|---------------------|
| 1                       | 1.36            | 0.68                |
| 2                       | 1.67            | 0.84                |
| 3                       | 2.02            | 1.01                |
| 4                       | 1.60            | 0.80                |
| 5                       | 1.39            | 0.70                |

4. Conclusion
This study demonstrates that the different weight percentages of CaO catalyst used had produced different yield of biodiesel production, demonstrating the highest biodiesel production at 64%. The biodiesel yield varied depending on the amount of catalyst used. It appears that a low-cost, heterogeneous CaO-based catalyst made from waste eggshells was used to produce biodiesel by using powdered eggshell that was calcined at 900 °C, which majorly helped to ensure the success of the transesterification conducted. The presence of CaO with high basicity in eggshell after calcination is directly linked to these findings. Eggshell waste served as a catalyst give an outstanding contribution as a heterogeneous catalyst to synthesis biodiesel production. The development of biodiesel through the transesterification method using WCO was carried out using the established catalyst. Therefore, the compatibility of the CaO catalyst and WCO as a potential candidate for biodiesel production in future fuel regimes are found to be promising. Further investigation needs to be done on more parameters such as reaction time and temperature and catalyst loading to observe the suitability of waste eggshell as a catalyst for biodiesel production. Meanwhile, the experimental approach used in this study can be expanded. Thus, additional catalyst reusability experiments might be conducted to determine the biodiesel yield production at which the catalyst could be further tuned. Thus, it may assist biodiesel manufacturing by enhancing product quality and significantly reducing purification procedures and ancillary wastes.

Acknowledgment
The authors are grateful to the Universiti Putra Malaysia Bintulu Sarawak Campus, Malaysia, and Ministry of Higher Education (MOHE). This study was supported by (GP-IPB vot no: 9671301) and Fundamental Research Grant Scheme (Ref.: FRGS/1/2018/TK05/UPM/02/8) that enabled the success of this work.

References
[1] Putra M D, Ristianingsih Y, Jelita R, Irawan C and Nata I F 2017 RSC Adv. 7 55547–54
[2] Borah M J, Das A, Das V, Bhuyan N and Deka D 2019 Fuel 242 345–54
[3] Mansir N, Teo S H, Rabiu I and Taufiq-Yap Y H 2018 Chem. Eng. J. 347 137–44
[4] Sahar, Sadaf S, Iqbal J, Ullah I, Bhatti H N, Nouren S, ur Rehman H, Nisar J and Iqbal M 2018 Sustain. Cities Soc. 41 220–6
[5] Hamzah N H C, Khairuddin N, Siddique B M and Hassan M A 2020 Processes 8 1–11
[6] Ritchie H and Roser M 2017 Published online at OurWorldInData.org
[7] Savaliya M L, Bhakhar M S and Dholakiya B Z 2016 Catal. Letters 146 2313–23
[8] Mishra V K and Goswami R 2018 Biofuels 9 273–89
[9] Jamal Y, Shah I H and Park H S 2019 Biofuels 0 1–7
[10] Hirschmann R 2019 Production of blended/deodorized cooking oil in Malaysia from 2013 to 2020 Statista

[11] Chung Z L, Tan Y H, Chan Y S, Kansedo J, Mubarak N M, Ghasemi M and Abdullah M O 2019 Biocatal. Agric. Biotechnol. 21 101317

[12] John-Jaja S A, Udoh U H and Nwokolo S C 2016 Beni-Suef Univ. J. Basic Appl. Sci. 5 389–94

[13] Mittal A, Teotia M, Soni R K and Mittal J 2016 J. Mol. Liq. 223 376–87

[14] Mohan T P and Kanny K 2018 J. Compos. Mater. 52 3989–4000

[15] Kavitha V, Geetha V and Jacqueline P J 2019 Process Saf. Environ. Prot. 125 279–87

[16] Federation of Livestock Farmers’ Associations of Malaysia 2020 Weekly output of broiler, chicken eggs and meat duck in Peninsular Malaysia 2006—forecast in 2020 industry statistics Federation of Livestock Farmers’ Associations of Malaysia.

[17] Yaşar F 2019 Fuel 255 115828

[18] Rodrigues A, Bordado J C and Dos Santos R G 2017 Energies 10

[19] Degfie T A, Mamo T T and Mekonnen Y S 2019 Sci. Rep. 9 1–8

[20] Naveenkumar R and Baskar G 2019 Biocatal. Agric. Biotechnol. 21 101317

[21] Baskar G, Aberna Ebenezer Selvakumari I and Aiswarya R 2018 Biocatal. Technol. 250 793–8

[22] Meng Y L, Wang B Y, Li S F, Tian S J and Zhang M H 2013 Biocatal. Technol. 128 305–9

[23] Goli J and Sahu O 2018 Renew. Energy 120 142–54

[24] Afsharizadeh M and Mohsennia M 2019 React. Kinet. Mech. Catal. 128 443–59

[25] Maneerung T, Kawi S, Dai Y and Wang C H 2016 Energy Convers. Manag. 123 487–97

[26] Birla A, Singh B, Upadhyay S N and Sharma Y C 2012 Biocatal. Technol. 106 95–100

[27] Yan S, Kim M, Salley S O and Ng K Y S 2009 Appl. Catal. A Gen. 360 163–70

[28] Kotwal M S, Niphadkar P S, Deshpande S S, Bokade V V and Joshi P N 2009 Fuel 88 1773–8

[29] Jitputti J, Kitiyanan B, Rangsunvigit P, Bunyakiat K, Attanatho L, and Jenvanitpanjakul P 2006 Chem. Eng. J. 116 61–6

[30] Kim H J, Kang B S, Kim M J, Park Y M, Kim D K, Lee J S and Lee K Y 2004 Catal. Today 93–95 315–20

[31] Khatibi M, Khorasheh F and Larimi A 2021 Renew. Energy 163 1626–36

[32] Mansir N, Teo S H, Rashid U and Taufiq-Yap Y H 2018 Fuel 211 67–75

[33] Da Silva H R G, Quintella C M and Meira M 2017 J. Braz. Chem. Soc. 28 2348–56

[34] Wembabazi E, Mugisha P J, Ratibu A, Wendiro D, Kyambadde J and Vuzi P C 2015 J. Spectrosc. 2015

[35] Rosset M and Perez-Lopez O W 2019 Vib. Spectrosc. 105 102990

[36] Mahamuni N N and Adewuyi Y G 2009 Energy and Fuels 23 3773–82

[37] Siatis N G, Kimbaris A C, Pappas C S, Tarantilis P A and Polissiou M G 2006 JAOCS, J. Am. Oil Chem. Soc. 83 53–7

[38] Dhmees A S, Rashad A M and Abdulla E S 2020 Egypt. J. Chem. 63 1033–44

[39] Boro J, Thakur A J and Deka D 2011 Fuel Process Technol. 92 2061–7

[40] Zaman T, Mostari M S, Mahmood M A Al and Rahman M S 2018 Cerâmica 64 236–41

[41] Habte L, Shiferaw N, Khan M D, Thriveni T and Ahn J W 2020 Sustain. 12 1174

[42] Kirubakaran M and Arul Mozhi Selvan V 2021 Biocatal. Technol. Reports. 14 100658

[43] Idowu I, Wylie S, Teng K H, Kot P, Phipps D and Shaw A 2019 Renew. Energy 142 535–42

[44] Canakci M 2007 Biocatal. Technol. 98 183–90

[45] Bouaida A, Vázquez R, Martinez M and Aracil J 2016 Fuel 174 54–62

[46] Yesilyurt M K 2020 Fuel 275 117893

[47] Hossain A B M S and Mazen M A 2010 Aust. J. Crop Sci. 4 550–5