

Case Report

Microwave-intensified esterification of high-free fatty acid feedstock into biodiesel using waste chicken eggshells as a heterogeneous catalyst

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ABSTRACT

The efficacy of waste chicken eggshells as a heterogeneous catalyst is investigated for biodiesel production from high-free fatty acid feedstock under microwave irradiation. The calcined waste chicken eggshells were identified using Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray (EDX). The effect of esterification conditions such as catalyst weight, molar ratio of oleic acid to methanol, reaction time and microwave power were determined on biodiesel conversion and yield. The highest conversion and yield of $92.04 \pm 0.8\%$ and $78.75 \pm 1.8\%$, respectively, were achieved under the reaction condition of molar ratio of 1:15, catalyst weight of 6 wt%, reaction time of 20 minutes and microwave power of 60 W. The catalytic stability of calcined waste chicken eggshells revealed that the weight of CaO was decreased after the first cycle. However, the biodiesel conversion was above 80 % after five times usage.

1. Introduction

The major bottleneck in biodiesel production is the oil extraction and purification process which is estimated to consume 75–80 % of biodiesel production cost [1–3]. Moreover, the utilization of edible oil as biodiesel feedstock has raised a fuel vs food problem [4,5]. Hence, low-cost biodiesel feedstocks such as waste cooking oil (WCO) and fat/grease are a potential source [6]. However, the current biodiesel production technology platform which uses a homogeneous alkaline substance as a catalyst could not use this low-cost feedstock as it usually contains high free fatty acids (FFA) [7]. Commonly, two-steps reaction using different types of catalysts was performed to produce biodiesel [8]. Esterification using a homogenous acid substance such as sulphuric acid was first conducted to reduce the FFA content to <2 % to avoid saponification and a homogeneous base is used as a transesterification catalyst in the next step [9]. Photaworn et al. (2017) required 1 hour reaction time to reduce FFA contained in WCO to be <1 % using sulphuric acid as a

catalyst [10]. This long-step process is energy and time-intensive. One-step esterification reaction using a homogeneous acid catalyst and a homogenizer device has been studied in our previous research. The maximum conversion of methyl oleate was achieved after 30 minutes of reaction time at room temperature condition [11]. However, the utilization of a homogeneous acid as a catalyst in an esterification reaction requires a neutralization and purification product process which increases the total biodiesel production cost [12,13].

Recently, heterogeneous catalysts have been developed to overcome this issue [14]. Prinsen et al. (2018) successfully converted 100 % palmitic acid into methyl palmitate in a reaction time of 3 hours using commercial zeolite as a catalyst and concluded that the heterogeneous catalyst was easily recovered and could hold its catalytic activity for up to five cycles of esterification reaction [15]. Transforming the heterogeneous catalyst either to form a nano-particle or impregnated with the sulfonic group could increase the catalytic activity and reduce reaction time [8,16–18]. A biodiesel yield of 90.24 % was achieved in 30 minutes

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reaction time from esterification of waste cooking oil using CuFe_2O_4 nanoparticles as a catalyst [17]. The reaction time could be shortened using the sulfonated carbonaceous catalyst. Rana et al. (2019) achieved a biodiesel yield of 99.8 % after 20 minutes of reaction time using sulfonated biomass derived from rice husk and microalgae biomass [18]. However, the preparation of those catalysts requires additional time and energy hence could increase the total biodiesel production cost.

Microwave has been developed and used to accelerate chemical reactions [19–22]. The effects of microwaves on chemical reactions stem from the heightened molecular motion within a short range which is triggered by the alignment of polar molecules or dipoles in response to the electric fields generated by microwave radiation. The resulting increase in molecular collisions raises the temperature of the medium and accelerates reaction rates [21,23]. Lin et al. (2013) showed that a biodiesel yield of 99.4 % was achieved in a reaction time of 6 minutes using a microwave while the conventional heating method requires 90 minutes to produce similar yield [24]. Further, Yadav et al. (2023) used a heterogeneous catalyst derived from *Oryza sativa* husk in microwave-intensified esterification of oleic acid and obtained a maximum biodiesel yield of 99.6 ± 0.2 % in 60 minutes reaction times and observed that the catalyst could be reused up to 7 cycles [25].

CaO has received special concern among heterogeneous catalysts due to its availability in a wide variety of sources, easy to handle and low cost [26]. Chalapandian et al. (2022) transesterified waste cooking oil to produce biodiesel using CaO nanocatalyst derived from *Acalypha indica* leaves and achieved optimum biodiesel yield of 94.74 % in 70 minutes reaction time [27]. Further, Kodgire et al. (2023) used a combination of microwave and ultrasound to enhance biodiesel production from waste cottonseed oil and obtained a biodiesel yield of 92.11 % in 30 minutes reaction time [28]. However, to date no literatures were found in microwave-intensified esterification high FFA feedstock using CaO as a heterogeneous catalyst.

This study reports the outcomes of microwave-assisted esterification of a high FFA content to biodiesel using CaO derived from calcined waste chicken eggshells as a heterogeneous catalyst. The calcined CaO was characterized using Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray (EDX). The effect of catalyst weight (wt.%), molar ratio of oleic acid to methanol, reaction time (minutes) and microwave power (%power) were systematically investigated to optimize the reaction condition to achieve maximum biodiesel conversion and yield.

2. Methods

2.1. Materials

Waste chicken eggshells were collected from a local restaurant in Medan, Indonesia. The oleic acid and other chemicals were purchased from Sigma-Aldrich and were used as received. The household microwave which has an input and output power of 1200 and 900 W, respectively, was used and modified to connect with a condenser and magnetic stirrer.

2.2. Catalyst preparation and characterization

The waste chicken eggshells were washed, dried overnight, crushed using a homemade coffee crusher and then sieved. The calcination temperature of the waste eggshell powder was determined using TGA (Shimadzu DTG-60). As shown in Fig. 1A, the decomposition of CaCO_3 , the main component in waste chicken eggshell, to CaO occurred at a temperature of 900°C . The calcined CaO were characterized using XRD, XRF and SEM EDX.

2.3. Microwave-intensified esterification of oleic acid to biodiesel using calcined waste chicken eggshells

The biodiesel production from the esterification of oleic acid with methanol using calcined waste chicken eggshells as a heterogeneous catalyst under microwave irradiation was conducted on a laboratory scale. The maximum biodiesel conversion was determined by experimenting with parameters of catalyst weight of 3, 6, 9, 12, 15, 18 and 21 wt% (based on weight of oleic acid), molar ratio of oleic acid to methanol of 1:1, 1:3, 1:6, 1:9, 1:12, 1:15 and 1:8, reaction times of 1, 5, 10, 20, 30, 40, and 60 minutes, and microwave power of 20 %, 40 %, 60 %, 80 % and 100 %. The reaction was performed in a 50 mL round bottom flask which contained 5 mL of oleic and 9.64 mL of methanol (for a molar ratio of 1:1). The calcined CaO of 0.3 g (6 wt% based on oleic acid weight) was added and the irradiation was performed for 20 minutes with microwave power of 60 %. The product mixture was separated from the catalyst using centrifugation and was transferred to a bottle vial for methanol evaporation. The biodiesel conversion was determined based on the acid value before and after the esterification following the ISO 660:2020 procedure. The acid value (AV) was calculated based on equation (1).

$$AV = \frac{V \times N \times 56.1}{W} \quad \text{equation 1}$$

Where V is the volume of KOH (mL), N is the concentration of KOH (mol L^{-1}) and W is the mass of sample (g). The biodiesel conversion (C) was determined following equation (2).

$$C = \frac{AV_0 - AV_1}{AV_0} \quad \text{equation 2}$$

Where AV_0 is the initial acid value and AV_1 is the acid value after the product after the reaction.

2.4. The reusability and leaching test of the catalyst

The reusability of the calcined waste chicken eggshells was investigated at reaction condition of catalyst weight of 6 %, molar ratio of 1:15, reaction time of 20 minutes and microwave power of 60 %. After the reaction was completed the leftover catalyst was directly used to catalyze the next esterification reaction under the same reaction condition. The biodiesel product was separated and purified for conversion analysis. For the leaching test, 1.8 g of calcined waste eggshells were dispersed in 14.56 mL of methanol and irradiated using microwave power of 60 %. After 20 minutes of reaction time, the leftover catalyst was separated, dried in an oven to evaporate methanol, weighed and used for the next leaching study.

2.5. Statistical analysis

The experiments were performed three times and the Statistica v14 software was used to determine the statistical difference between the parameters. The analysis of variance (ANOVA) and Tukey's post hoc were used to confirm the significance.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1A shows the degradation pattern of waste chicken eggshells powder during the heat treatment of the sample in an atmospheric environment. Evaporation and thermal desorption of physically adsorbed materials such as water vapour and hydrocarbons causes very small mass losses observed at temperatures of 100 – 200°C . The next stage was the release of volatile materials due to the decomposition of organic compounds with a weight loss of 28.38 % at temperatures 300 – 600°C .

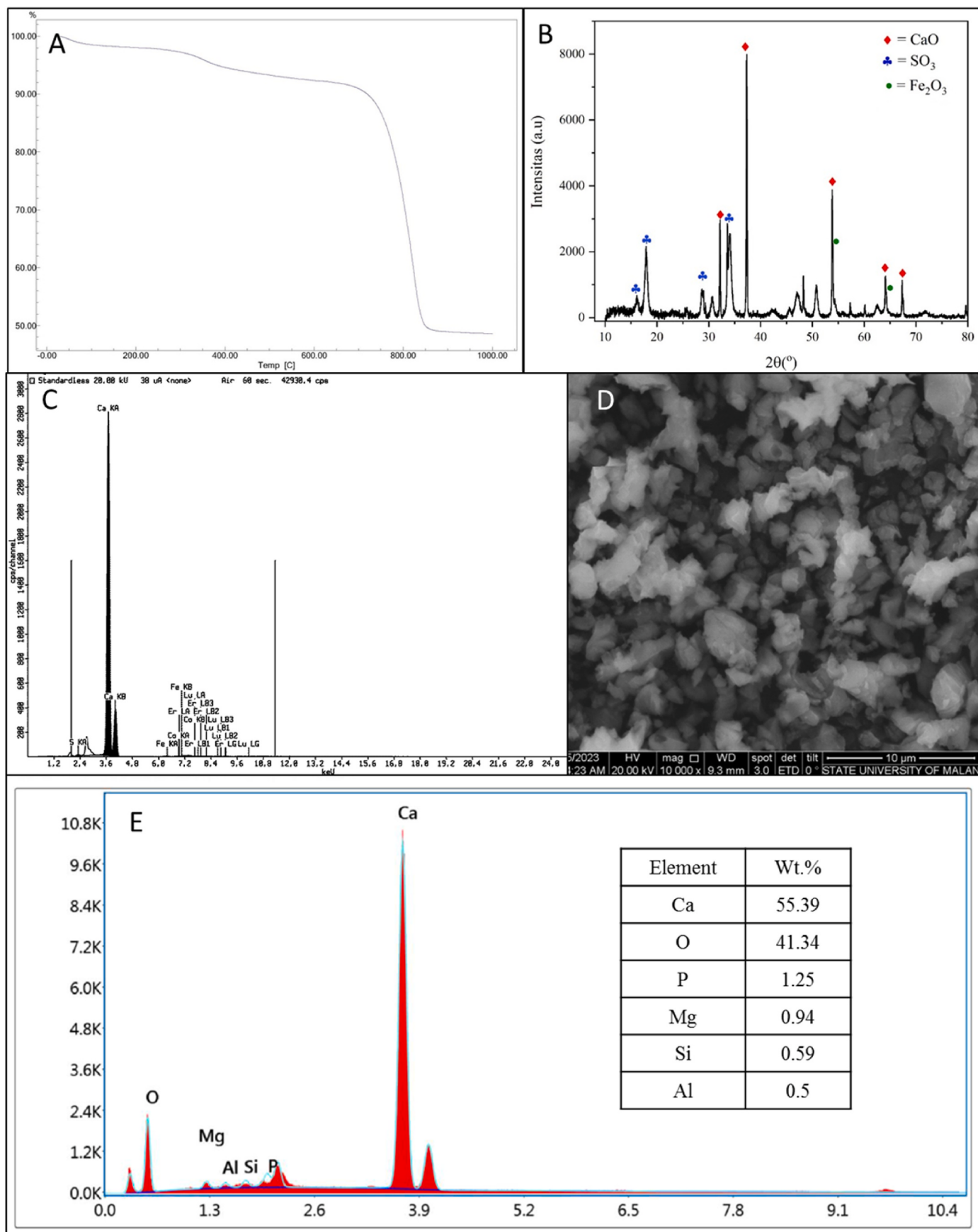


Fig. 1. Calcined waste chicken eggshell characterization: (A) TGA thermogram; (B) XRD pattern; (C) XRF spectra (D) SEM image; and (E) EDX spectra.

The decomposition of calcium carbonate into metal oxide was observed at temperature of 600–850 °C. Furthermore, heating at a temperature above 900 °C did not show any change in the weight of the waste chicken eggshell ash. Hence, a temperature of 900 °C was chosen as the temperature for calcining waste chicken eggshells into a heterogeneous catalyst. These results agreed with the report of Attari et al. (2022), Fayyazi et al. (2018), and Putra et al. (2017) [30,31].

The XRD pattern of the calcined CaO is shown in Fig. 1B. The diffraction pattern of the catalyst shows a strong peak at 37.33° 32.18°; 37.33°; 53.83°; 64.12°; and 67.34° which are CaO crystals with a cubic structure (JCPDS CaO #PDF 01-082-1691). Another diffraction peak of SO₃ and Fe₂O₃ diffraction peaks were not observed which can be assumed to be due to their very small amounts in the sample. This is in agreement with the XRF analysis result (Fig. 1C), where CaO is the dominant compound with a concentration of 99.19 % followed by SO₃ and Fe₂O₃ of 0.42 % and 0.074 %, respectively. As shown in Fig. 1D, the surface morphology of the calcined CaO catalyst is not homogeneous and comprises irregular shapes of the particles. The lumpy structures with several pores are caused by agglomeration during the calcination process. Similar SEM results were reported by Tan et al. (2015) who calcined chicken egg shells at 900 °C for 3 hours [32]. Elemental analysis of the calcined waste chicken eggshells using EDX analysis showed the presence of a mixture of metals as shown in Fig. 1E. The metals are postulated to be in the form of metal oxides due to the presence of oxygen. The significant amount of the mixture of metal oxide in the catalyst verifies the high basicity which exhibits a remarkable potential as a heterogeneous catalyst for biodiesel production [33].

3.2. Effect of catalyst weight

Catalyst concentration/weight is one of the important parameters that directly affects the biodiesel conversion/yield [34]. Hence, finding the suitable concentration/weight of the catalyst is necessary to achieve

maximum biodiesel conversion [34–36]. In this study the catalyst weight ranges from 3, 6, 9, 12, 15, 18 and 21 wt% (based on the weight of oleic acid) was explored to determine the maximum biodiesel conversion under reaction conditions of a molar ratio of 1:12, reaction time of 20 minutes and microwave power of 60 %. As expected, the catalyst weight affected the biodiesel conversion as shown in Fig. 2A. The conversion was increased from 75.20 ± 1.5 % using a catalyst weight of 3 wt % to reach the maximum conversion of 90.85 ± 0.9 % using a catalyst dosage of 18 %. However, increasing catalyst weight to 21 wt% decreased the biodiesel conversion to 90.17 ± 1.1 %. A high concentration of CaO in the reactant could increase the viscosity and induce emulsion which decreases the conversion [29,37]. Attari et al. (2022) reported similar results in ultrasonic-assisted transesterification of waste cooking oil using calcined waste chicken eggshells [29]. Similarly, Tan et al. (2015) observed decreasing biodiesel yield in the increasing of CaO weight derived from waste ostrich eggshells [32]. The biodiesel yield has shown a similar graph pattern to the biodiesel conversion. However, the maximum biodiesel yield of 73.87 ± 1.4 % was achieved using a catalyst weight of 12 % (Fig. 3A). Further, the one-way ANOVA showed that catalyst weight has a significant effect both on biodiesel conversion and yield. Tukey's test post hoc identified the significance that was driven by high biodiesel conversion using catalyst weight of 15 and 18 wt% and low biodiesel yield using catalyst dosage of 21 wt%

3.3. Effect of molar ratio of oleic acid: methanol

Even though a molar ratio of 1:1 is stoichiometrically sufficient for the esterification of oleic acid with methanol, an additional mole of methanol is required to drive the reaction towards biodiesel production [22,38]. Hence, in this study the molar ratio of oleic acid to methanol was investigated using seven different ratios of 1:1, 1:3, 1:6, 1:9, 1:12, 1:15 and 1:18 at reaction condition of catalyst weight of 6 wt%, reaction time of 20 minutes and microwave power of 60 %. Fig. 2B and 3B

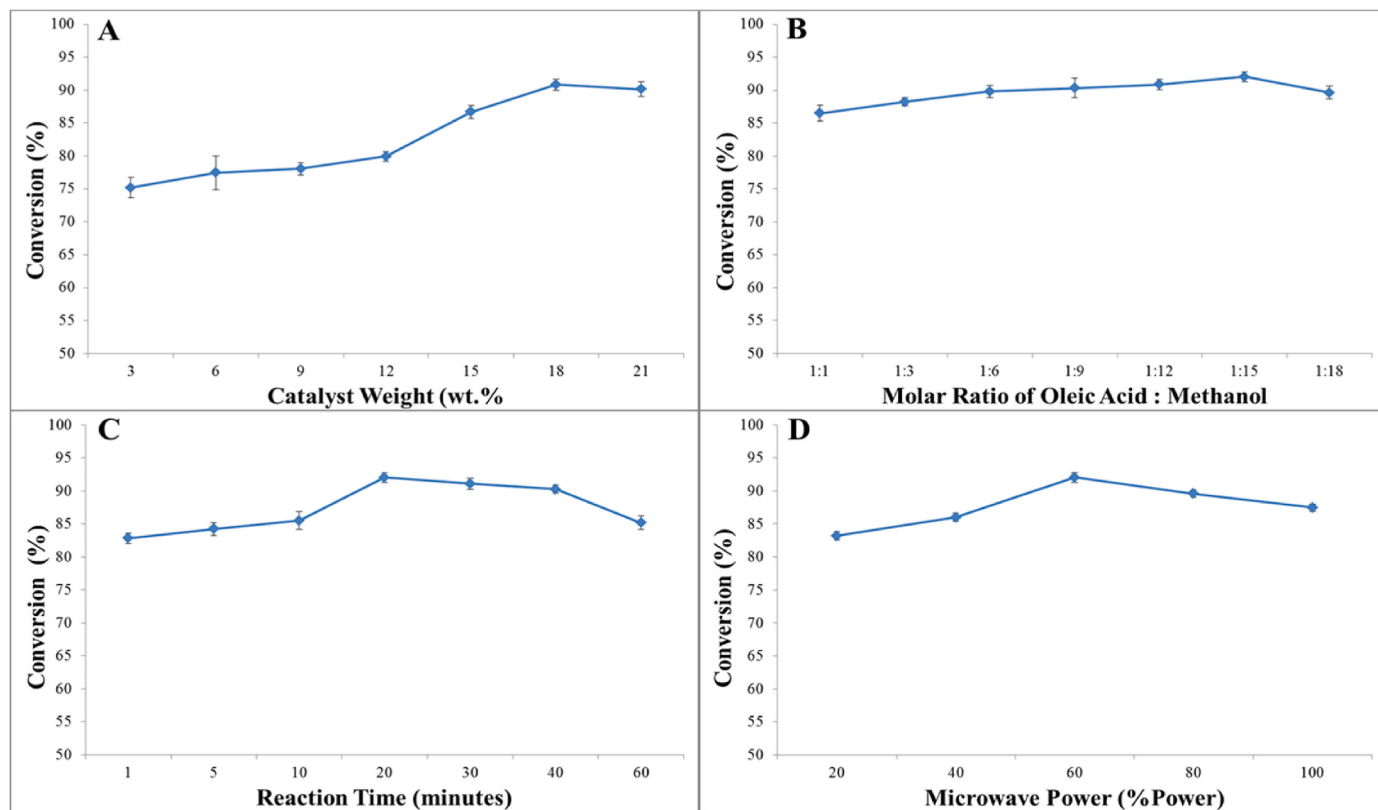


Fig. 2. The effect of (A) catalyst weight (wt.%); (B) molar ratio of oleic acid to methanol; (C) reaction time (minutes); and (D) microwave power (%power) in biodiesel conversion.

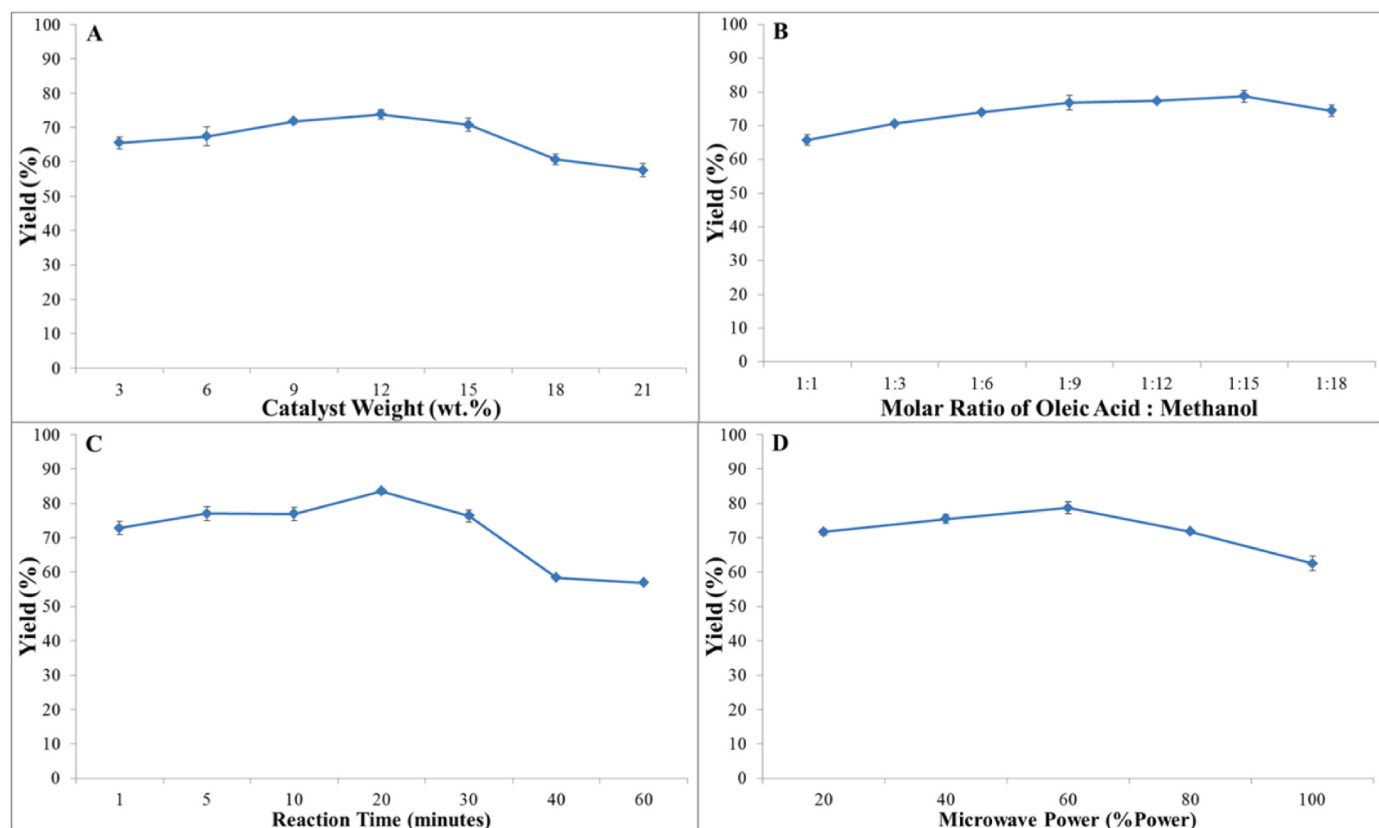


Fig. 3. The effect of (A) catalyst weight (wt.%); (B) molar ratio of oleic acid to methanol; (C) reaction time (minutes); and (D) microwave power (%power) in biodiesel yield.

showed the biodiesel conversion and yield when different molar ratios of oleic acid to methanol were used. As shown in those figures, either biodiesel conversion or yield was increased with the increase of molar ratio to achieve a maximum conversion of 92.04 ± 0.76 % and a maximum yield of 78.75 ± 1.8 % both using a molar ratio of 1:15. Interestingly, increasing the molar ratio from 1:15 to of 1:18 did not promote the esterification reaction. The decreasing either biodiesel conversion or yield after reaching the maximum point in the addition of methanol volume is presumably due to the deactivation of CaO in the excess of methanol [39]. A similar phenomenon was also observed by Ezzah-Mahmudah et al. (2016) in the transesterification reaction of waste cooking oils using $\text{Fe}_2\text{O}_3/\text{CaO}$ derived from cockle shells [40]. Our previous study in room temperature biodiesel production using calcined bio-waste durian peels concluded that an excess volume of methanol could dilute the catalyst concentration leading to decreasing conversion and yield [35]. A one-way analysis of variance displayed that either biodiesel conversion or yield was significantly affected by the molar ratio which was driven by low conversion and yield at a molar ratio of 1:1.

3.4. Effect of reaction time

The esterification reaction is a reversible reaction and reaction time is one important factor that affects the biodiesel production cost [41–43]. Hence, to study the effect of reaction time against biodiesel conversion and yield, experiments were performed by varying reaction time from 1 to 60 minutes under reaction condition of molar ratio of 1:12, catalyst weight of 18 wt% and microwave power of 60 %, as shown in Fig. 2C and 3C. With the increase in reaction time, the collision between reactants becomes intense, leading to an increase in both biodiesel conversion and yield. The maximum biodiesel conversion and yield of 92.04 ± 0.8 % and 83.61 ± 0.8 %, respectively, were achieved

both at a reaction time of 20 minutes. A similar finding was observed by Maafa et al. (2024) for biodiesel production using CaO derived from chitosan [44]. Further increasing reaction times do not affect both the biodiesel yield and conversion. This is presumably due to reversible reaction and deactivation of the catalyst by water as the esterification by-product [25]. This result is in agreement with the previous researcher which used commercial CaO as a catalyst and assisted by conjoint ultrasound and microwave to produce biodiesel from a blend of waste cooking oil and *Ricinus communis* oil [28]. The significant effect of changing the reaction time both on biodiesel conversion and yield was detected using ANOVA. Further, the Tukey test revealed the significance of the biodiesel conversion was driven by low conversion at a reaction time of 1 minute while low biodiesel yield at a reaction time of 60 minutes drives the significance.

3.5. Effect of microwave power

As reported in the previous works [20–22,36,45–47], the microwave input power has a positive effect on the electromagnetic radiation. The reaction rate is raised due to intense localized heating leading to high biodiesel conversion or yield in short reaction time [20]. The effect of microwave power on biodiesel conversion and yield is shown in Fig. 2D and 3D. All experiments were conducted at a constant molar ratio of oleic acid to methanol of 1:15, catalyst weight of 6 wt% and reaction time of 20 minutes. As expected, there was an increase in the biodiesel conversion and yield as the microwave power increased. The biodiesel conversion gradually increased until it reached 60 % where the conversion raised to 92.04 ± 0.8 % before it decreased to 89.6 ± 0.6 % at 80 %. Similarly, the biodiesel yield also increases to reach the maximum yield of 78.75 ± 1.8 % using microwave power of 60 % and decreases with the increasing microwave power. This clearly shows that in the high microwave power, the reaction temperature is excessively high

generating more methanol vapour in the system. Hence, less methanol was reacted with oleic acid resulting in low both biodiesel conversion and yield [48]. Similar observations were reported in emollient ester production using enzyme lipase as a catalyst under the influence of microwave irradiation [21]. The authors reported that the increasing microwave power could accelerate the reorientation of reactant molecules resulting in high emollient products. However, the ester yield was decreased due to the denaturation of enzyme lipase in the high reaction temperature [21]. Further, the ANOVA revealed that microwave power has a significant effect on biodiesel conversion and yield. Tukey's test showed that the significance in the biodiesel conversion was driven by all values tested while the low biodiesel yield at a microwave power of 100 % drove the significance.

3.6. The reusability and leaching study

The prospect of reusing the heterogeneous catalyst several times without losing its catalytic activity is one of the most important advantages in biodiesel production. The reusability and leaching of the CaO catalyst are of high priority in deciding if the waste catalyst is viable or not. Hence, the reaction condition of a molar ratio of 1:15, catalyst weight of 6 wt%, reaction time of 20 minutes and microwave power of 60 % was used to determine the reusability of the calcined waste eggshells. The biodiesel conversion decreased by 6.84 % in cycle 2 as shown in Table 1. The decline continues to occur in the subsequent cycle. Lin et al. (2012) in the transesterification of rapeseed oil using CaO as a catalyst showed that the biodiesel conversion gradually decreased in each cycle [49]. The decreasing biodiesel conversion was presumably due to catalyst loss during filtration and the reaction between CaO with methanol to form Ca(OH)_2 which was inactive [50]. Therefore, a leaching study was conducted to prove the assumption. A 1.8 g of calcined waste eggshells was mixed with 14.56 mL and irradiated using microwave power of 60 % for 20 minutes. As shown in Table 1, the weight of the calcined waste eggshells was decreased by 22 % after the first cycle. The amount of CaO remains constant in the following cycle with an insignificant decrease. In contrast, Huang et al. (2013) in the study of deep eutectic solvent-activated commercial CaO to catalyze transesterification of rapeseed oil, did not observed decreasing in biodiesel yield after reuse several times [51]. Further, some researchers suggested incorporating the CaO in the supporting material such as Al_2O_3 , silica, carbon, and more to maintain its catalytic activity [52–54].

3.7. Comparison microwave-assisted CaO catalyzed esterification/transesterification

The result of the microwave-assisted esterification of oleic acid using calcined waste eggshells as a catalyst obtained in this study was compared with those of various biodiesel production using similar methods. The biodiesel conversion/yield was varied with most of them occurring >90 % except for the study which used CaO derived from oyster shells. As shown in Table 2, the molar ratio used in all of those studies was more than the stoichiometric ratio required. The presence of an excessive amount of methanol could increase the solubility of fatty acids generating high biodiesel yield [32]. The catalyst weight varied from 4 to 8 wt%. Interestingly, the lowest catalyst weight used produced the highest biodiesel yield compared with other studies. The authors

Table 1
Reusability and leaching test of CaO catalyst.

Cycle	Biodiesel Conversion (%)	Weight of CaO (gram)
Cycle 1	92.04 ± 0.8 %	1.8
Cycle 2	85.2 ± 0.4	1.416
Cycle 3	83.6 ± 0.9	1.378
Cycle 4	82.6 ± 0.5	1.368
Cycle 5	81.7 ± 0.9	1.361

Table 2

Comparison of microwave-assisted esterification/transesterification using CaO as a catalyst.

Type of reaction/ Oil/Catalyst	Reaction Condition (molar ratio, catalyst weight, reaction time, microwave power)	Biodiesel Conversion/ Yield (%)	Ref.
Waste cooking oil Commercial CaO	1:8, 4 wt%, 75 minutes, 300 W	98.2	[55]
Waste cooking oil Oyster shells	1:9, 6 wt%, 180 minutes, 800 W	87.3	[58]
Waste lard CaO-Zeolite	1:30, 8 wt%, 75 minutes, 595 W	90.89	[59]
Jatropha curcas oil Eggshells	1:9, 5 wt%, 165 minutes, 800 W	92	[60]
Jatropha curcas oil Oyster and Pyramidella shells	1:15, 4 wt%, 5 minutes, 800 W	93	[56]
Oleic acid Eggshells	1:15, 6 wt%, 20 minutes, 540 W	92.04	This study

concluded that the addition of bromooctane could improve the catalytic activity of commercial CaO [55]. In terms of reaction time, the biodiesel production from Jatropha curcas oil using calcined Oyster and *Pyramidella* shells used a shorter reaction time to achieve comparable biodiesel conversion. However, the reaction was conducted under microwave irradiation with a power of 800 W [56]. Other studies were conducted with varied reaction time from 20 to 180 minutes. The long reaction time is presumably due to the reaction temperature being fixed at 65 °C in which the irradiation will stop when reaches the temperature. Hence, the higher collision among the reactants due to rapidly changing electromagnetic was discontinued [57]. The microwave power used in all studies was varied with the lowest power used by Hsiao et al. (2020) generating the highest biodiesel yield [55].

3.8. Propose reaction mechanism for CaO catalyze esterification

The mechanism esterification reaction of fatty acid to produce biodiesel using a homogeneous acid catalyst is different from using a heterogeneous catalyst. In acid acid-catalyzed esterification reaction, the fatty acid was protonated by the catalyst forming an intermediate that can ease the acceptance of the nucleophilic alcohol molecule attack [61]. The mechanism esterification reaction of fatty acid with methanol using CaO as a catalyst is similar to the transesterification reaction which has been proposed and published elsewhere [39,62,63]. As shown in Fig. 4, the reaction begins with the activation of the alcohol to form methoxide anion. This anion further attacks the carbon atom of the carbonyl species to form a tetrahedral intermediate substance. Due to the unstable condition, the intermediate substance underwent a rearrangement. The lone pair electron in the hydroxyl species attracts the proton from the alcohol. The methyl oleate or biodiesel as the main product was formed as the water molecule and CaO were released. This proposed reaction mechanism is similar to the previous research which uses $\text{Fe}_2\text{O}_3/\text{CaO}$ as the heterogenous catalyst in the esterification of free fatty acid [40].

4. Conclusion

The CaO derived from waste eggshells was successfully prepared and employed for microwave-assisted biodiesel production from high-free fatty acid feedstocks. A maximum biodiesel conversion and yield of $92.04 \pm 0.8 \%$ and $78.75 \pm 1.8 \%$, respectively were achieved under the reaction condition of molar ratio of 1:15, catalyst weight of 6 wt%, reaction time of 20 minutes and microwave power of 60 %. This result indicates that calcined waste eggshells can be employed for sustainable biodiesel production from oleic acid using microwave irradiation. Moreover, the catalytic activity of the heterogeneous catalyst remains

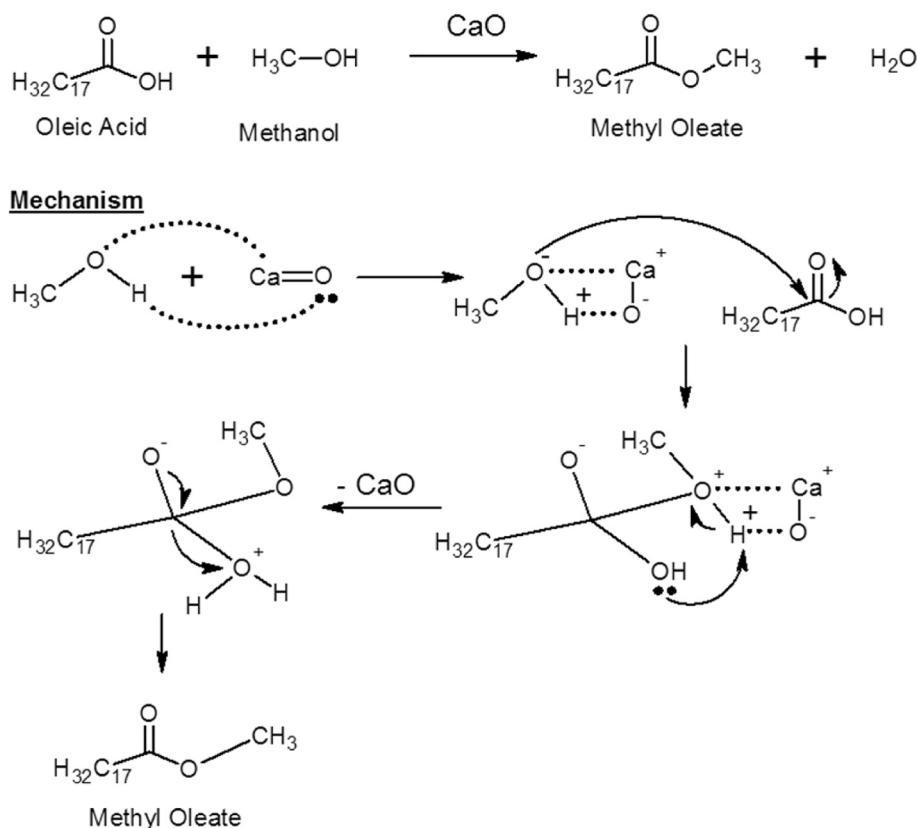


Fig. 4. The mechanism of esterification reaction of oleic acid with methanol using CaO as a catalyst.

higher to produce biodiesel conversion up to 80 % after use five times. However, the leaching study showed that the stability of the catalyst needs to improve.

CRediT authorship contribution statement

Juliati Br Tarigan: Writing – original draft, Supervision, Resources, Methodology, Conceptualization. **Anzelina F. Barus:** Project administration, Investigation. **Nabilah T. Simamora:** Investigation, Formal analysis. **Ribka S. Tarigan:** Investigation, Formal analysis. **Sabarmin Perangin-angin:** Methodology, Formal analysis. **Junedi Ginting:** Resources, Project administration, Investigation. **Eko K. Sitepu:** Writing – review & editing, Supervision, Formal analysis. **Y.H. Taufiq-Yap:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cscee.2025.101107>.

Data availability

Data will be made available on request.

References

- [1] E.K. Sitepu, K. Heimann, C.L. Raston, W. Zhang, Critical evaluation of process parameters for direct biodiesel production from diverse feedstock, *Renew. Sustain. Energy Rev.* 123 (1) (2020) 109762, <https://doi.org/10.1016/j.rser.2020.109762>.
- [2] F. Harahap, S. Silveira, D. Khatiwada, Cost competitiveness of palm oil biodiesel production in Indonesia, *Energy* 170 (2019) 62–72, <https://doi.org/10.1016/j.energy.2018.12.115>.
- [3] M.J. Haas, A.J. McAloon, W.C. Yee, T. A. Foglia, A process model to estimate biodiesel production costs, *Bioresour. Technol.* 97 (4) (2006) 671–678, <https://doi.org/10.1016/j.biortech.2005.03.039>.
- [4] H.M. Khan, T. Iqbal, S. Yasin, M. Irfan, M. Kazmi, H. Fayaz, M.A. Mujtaba, C.H. Ali, M.A. Kalam, M.E.M. Soudagar, N. Ullah, Production and utilization aspects of waste cooking oil based biodiesel in Pakistan, *Alex. Eng. J.* 60 (6) (2021) 5831–5849, <https://doi.org/10.1016/j.aej.2021.04.043>.
- [5] E.K. Sitepu, S. Perangin-angin, G.J. Ginting, S. Machmudah, R.N. Sari, J. B. Tarigan, Controlled crushing device-intensified direct biodiesel production of Black Soldier Fly larvae, *Heliyon* 9 (6) (2023) e16402, <https://doi.org/10.1016/j.heliyon.2023.e16402>.
- [6] V. Mandari, S. K. Devarai, Biodiesel production using homogeneous, heterogeneous, and enzyme catalysts via transesterification and esterification reactions: a critical review, *BioEnergy Res.* 15 (2021) 935–961, <https://doi.org/10.1007/s12155-021-10333-w>.
- [7] J.B. Tarigan, S. Perangin-angin, S.R. Simanungkalit, N.P. Zega, E. K. Sitepu, Utilization of waste banana peels as heterogeneous catalysts in room-temperature biodiesel production using a homogenizer, *RSC Adv.* 13 (9) (2023) 6217–6224, <https://doi.org/10.1039/D3RA00016H>.
- [8] V. Mandari, S. K. Devarai, Biodiesel production using homogeneous, heterogeneous, and enzyme catalysts via transesterification and esterification reactions: a critical review, *BioEnergy Res.* 15 (2) (2022) 935–961, <https://doi.org/10.1007/s12155-021-10333-w>.
- [9] S. Joshi, P.R. Gogate, P.F. Moreira, R. Giudici, Intensification of biodiesel production from soybean oil and waste cooking oil in the presence of heterogeneous catalyst using high speed homogenizer, *Ultrason. Sonochem.* 39 (2017) 645–653, <https://doi.org/10.1016/j.ultsonch.2017.05.029>.
- [10] S. Photaworn, C. Tongurai, S. Kungsanunt, Process development of two-step esterification plus catalyst solution recycling on waste vegetable oil possessing high

- free fatty acid, *Chem. Eng. Process: Process Intensif.* 118 (2017) 1–8, <https://doi.org/10.1016/j.cep.2017.04.013>.
- [11] M. Supeno, J.P. Sihotang, Y.V. Panjaitan, D.S.Y. Damanik, J.B. TariganE, K. Sitepu, Room temperature esterification of high-free fatty acid feedstock into biodiesel, *RSC Adv.* 13 (47) (2023) 33107–33113, <https://doi.org/10.1039/D3RA06912E>.
 - [12] E.K. Nazloo, N.R. MoheimaniH, Ennaceri, Graphene-based catalysts for biodiesel production: characteristics and performance, *Sci. Total Environ.* 859 (2023) 160000, <https://doi.org/10.1016/j.scitotenv.2022.160000>.
 - [13] A.S. Abou-Elyazed, A.K.F. Shaban, A.I. Osman, L.A. Heikal, H.F.M. Mohamed, W. M.I. Hassan, A.M. El-Nahas, B.E. KeshtaA, S. Hamouda, Comparative catalytic efficacy of cost-effective MIL-101(Cr) based PET waste for biodiesel production, *Curr. Res. Green Sustain. Chem.* 8 (2024) 100401, <https://doi.org/10.1016/j.crgsc.2024.100401>.
 - [14] S. Chozhavendhan, M. Vijay Pradhap Singh, B. Fransila, R. Praveen KumarG, Karthiga Devi, A review on influencing parameters of biodiesel production and purification processes, *Curr. Res. Green Sustain. Chem.* 1–2 (2020) 1–6, <https://doi.org/10.1016/j.crgsc.2020.04.002>.
 - [15] P. Prinsen, R. LuqueC, González-Arellano, Zeolite catalyzed palmitic acid esterification, *Microporous Mesoporous Mater.* 262 (2018) 133–139, <https://doi.org/10.1016/j.micromeso.2017.11.029>.
 - [16] T. Kushwaha, S. Ao, K. Ngaosuwana, S. Assabumrungrat, B. GurunathanS, L. Rokhum, Esterification of oleic acid to biodiesel using biowaste-based solid acid catalyst under microwave irradiation, *Environ. Progress Sustain. Energy n/a (n/a)* (2023) e14170, <https://doi.org/10.1002/ep.14170>.
 - [17] R.M. Ali, M.R. ElkatoryH, A. Hamad, Highly active and stable magnetically recyclable CuFe₂O₄ as a heterogenous catalyst for efficient conversion of waste frying oil to biodiesel, *Fuel* 268 (2020) 117297, <https://doi.org/10.1016/j.fuel.2020.117297>.
 - [18] A. Rana, M.S.M. Alghazal, M.M. Alsaedi, R.S. Bakdash, C. BasheerA, A. Al-Saadi, Preparation and characterization of biomass carbon-based solid acid catalysts for the esterification of marine algae for biodiesel production, *BioEnergy Res.* 12 (2) (2019) 433–442, <https://doi.org/10.1007/s12155-019-9965-0>.
 - [19] Y.D. Bizualema, G. Nurie, A review on recent biodiesel intensification process through cavitation and microwave reactors: yield, energy, and economic analysis, *Heliyon* 10 (2) (2024) e24643, <https://doi.org/10.1016/j.heliyon.2024.e24643>.
 - [20] R. D. N. Ghosh, S. Lalthazuala RokhumG. Halder, Current progress and future outlooks of microwave-irradiated biodiesel production: a holistic review, *Chem. Eng. J.* 482 (2024) 149033, <https://doi.org/10.1016/j.cej.2024.149033>.
 - [21] E.K. Sitepu, S. Hudiyo, Z.A.P. Sinaga, R. Pramudhita, D. Desmita, Y.F. Ginting, F. SebayangJ, B. Tarigan, Microwave-assisted enzymatic esterification production of emollient esters, *ACS Omega* 8 (42) (2023) 39168–39173, <https://doi.org/10.1021/acsomega.3c04336>.
 - [22] J.B. Tarigan, D.A. Barus, G. Brahmana, D.A. Hulu, W.S. Sembiring, S. Perangin-AnginE, K. Sitepu, Microwave facilitated the synthesis of isopropyl myristate and palmitate using heterogeneous catalyst, *Rasayan J. Chem.* 16 (1) (2023) 176–181, <https://doi.org/10.31788/RJC.2023.1618078>.
 - [23] N. Yadav, G. YadavM. Ahmaruzzaman, Microwave-assisted biodiesel production using –SO₃H functionalized heterogeneous catalyst derived from a lignin-rich biomass, *Sci. Rep.* 13 (1) (2023) 9074, <https://doi.org/10.1038/s41598-023-36380-1>.
 - [24] Y.-C. Lin, P.-M. Yang, S.-C. Chen, Y.-T. Tu, J.-F. Lin, Biodiesel production assisted by 4-allyl-4-methylmorpholin-4-ium bromine ionic liquid and a microwave heating system, *Appl. Therm. Eng.* 61 (2) (2013) 570–576, <https://doi.org/10.1016/j.applthermaleng.2013.08.038>.
 - [25] G. Yadav, N. YadavM. Ahmaruzzaman, Microwave-assisted sustainable synthesis of biodiesel on Oryza sativa catalyst derived from agricultural waste by esterification reaction, *Chem. Eng. Process-Process Intensification* 187 (2023) 109327, <https://doi.org/10.1016/j.cep.2023.109327>.
 - [26] M.G. Weldele, N.E. Benti, M.A. DestaY, S. Mekonnen, Maximizing biodiesel production from waste cooking oil with lime-based zinc-doped CaO using response surface methodology, *Sci. Rep.* 13 (1) (2023) 4430, <https://doi.org/10.1038/s41598-023-30961-w>.
 - [27] K. Cholanpandian, B. Gurunathan, N. Rajendran, Investigation of CaO nanocatalyst synthesized from Acalypha indica leaves and its application in biodiesel production using waste cooking oil, *Fuel* 312 (2022) 122958, <https://doi.org/10.1016/j.fuel.2021.122958>.
 - [28] P. Kodgire, A. SharmaS, S. Kachhwaha, Optimization and kinetics of biodiesel production of Ricinus communis oil and used cottonseed cooking oil employing synchronised 'ultrasound + microwave' and heterogeneous CaO catalyst, *Renew. Energy* 212 (1) (2023) 320–332, <https://doi.org/10.1016/j.renene.2023.05.016>.
 - [29] A. Attari, A. Abbaszadeh-Mayvāna, Taghizadeh-Alisaraei, Process optimization of ultrasonic-assisted biodiesel production from waste cooking oil using waste chicken eggshell-derived CaO as a green heterogeneous catalyst, *Biomass Bioenergy* 158 (2022) 106357, <https://doi.org/10.1016/j.biombioe.2022.106357>.
 - [30] E. Fayyazi, B. Ghobadian, H.H. van de Bovenkamp, G. Najafi, B. Hosseinzadehsamani, H.J. HeeresJ. Yue, Optimization of biodiesel production over chicken eggshell-derived CaO catalyst in a continuous centrifugal contactor separator, *Ind. Eng. Chem. Res.* 57 (38) (2018) 12742–12755, <https://doi.org/10.1021/acs.iecr.8b02678>.
 - [31] M.D. Putra, Y. Ristianingsih, R. Jelita, C. IrawanI, F. Nata, Potential waste from palm empty fruit bunches and eggshells as a heterogeneous catalyst for biodiesel production, *RSC Adv.* 7 (87) (2017) 55547–55554, <https://doi.org/10.1039/C7RA11031F>.
 - [32] Y.H. Tan, M.O. Abdullah, C. Nolasco-HipolitoY, H. Taufiq-Yap, Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: catalyst characterization and biodiesel yield performance, *Appl. Energy* 160 (2015) 58–70, <https://doi.org/10.1016/j.apenergy.2015.09.023>.
 - [33] E. Bekhradinasab, M. Haghighi, M. Shabani, A review on acidic metal oxide-based materials towards heterogeneous catalytic biodiesel production via esterification process, *Fuel* 379 (2025) 132986, <https://doi.org/10.1016/j.fuel.2024.132986>.
 - [34] J.L. Aleman-Ramirez, P.U. Okoye, U. PalP, J. Sebastian, Agro-industrial residue of Pouteria sapota peels as a green heterogeneous catalyst to produce biodiesel from soybean and sunflower oils, *Renew. Energy* 224 (2024) 120163, <https://doi.org/10.1016/j.renene.2024.120163>.
 - [35] E.K. Sitepu, R.P.A. Sinaga, B.E.N. Sitepu, A. Santoso, B. Susilo, B. Ginting, S. Perangin-anginJ, B. Tarigan, Calcined biowaste durian peel as a heterogeneous catalyst for room-temperature biodiesel production using a homogenizer device, *ACS Omega* 9 (13) (2024) 15232–15238, <https://doi.org/10.1021/acsomega.3c09642>.
 - [36] B. Ginting, M.P. Sitepu, A. Santoso, B. Susilo, J.B. TariganE, K. Sitepu, Optimization of biomass durian peel as a heterogeneous catalyst in biodiesel production using microwave irradiation, *Green Process. Synth.* 13 (1) (2024), <https://doi.org/10.1515/gps-2023-0209>.
 - [37] M. Zhang, G. Ramya, K. Brindhadevi, M. Alsehlhi, A. Elfakhany, C. Xia, N.T.L. Chi, A. Pugazhendhi, Microwave assisted biodiesel production from chicken feather meal oil using Bio-Nano Calcium oxide derived from chicken egg shell, *Environ. Res.* 205 (2022) 112509, <https://doi.org/10.1016/j.envres.2021.112509>.
 - [38] N. Yadav, G. Yadav, M. Ahmaruzzaman, Fabrication of surface-modified dual waste-derived biochar for biodiesel production by microwave-assisted esterification of oleic acid: optimization, kinetics, and mechanistic studies, *Renew. Energy* 218 (2023) 119308, <https://doi.org/10.1016/j.renene.2023.119308>.
 - [39] M.R. Abukhadra, A.S. Mohamed, A.M. El-Sherbeen, A.T.A. SolimanA, E.E. Abd Elgawad, Sonication induced transesterification of castor oil into biodiesel in the presence of MgO/CaO nanorods as a novel basic catalyst: characterization and optimization, *Chem. Eng. Process-Process Intensification* 154 (2020) 108024, <https://doi.org/10.1016/j.cep.2020.108024>.
 - [40] S. Ezzah-Mahmud, I.M. Lokman, M.I. SaimanY, H. Taufiq-Yap, Synthesis and characterization of Fe₂O₃/CaO derived from Anadara Granosa for methyl ester production, *Energy Convers. Manag.* 126 (2016) 124–131, <https://doi.org/10.1016/j.enconman.2016.07.072>.
 - [41] P. Moradi, M. SaidiA, T. Najafabadi, Biodiesel production via esterification of oleic acid as a representative of free fatty acid using electrolysis technique as a novel approach: non-catalytic and catalytic conversion, *Process Saf. Environ. Protect.* 147 (2021) 684–692, <https://doi.org/10.1016/j.psep.2020.12.032>.
 - [42] H.K. Ismaeel, T.M. Albayati, F.T. Al-Sudani, I.K. Salih, H.A. Dhahad, N.M.C. Saady, S. Zendeheboudil, M.R. Fattah, The role of catalysts in biodiesel production as green energy applications: a review of developments and prospects, *Chem. Eng. Res. Des.* 204 (2024) 636–653, <https://doi.org/10.1016/j.cherd.2024.02.048>.
 - [43] B.M. KurjiA, S. Abbas, MCM-48 from rice husk ash as a novel heterogeneous catalyst for esterification of glycerol with oleic acid: catalyst preparation, characterization, and activity, *Case Stud. Chem. Environ. Eng.* 8 (2023) 100382, <https://doi.org/10.1016/j.csee.2023.100382>.
 - [44] I.M. Maafa, A.A. Sayed Alahl, M.O. Abd El-Magied, X. CuiA, S. Dhmees, Eco-friendly self-terminated process for preparation of CaO catalyst based on chitosan production wastes for biodiesel production, *J. Mater. Res. Technol.* 30 (2024) 1217–1227, <https://doi.org/10.1016/j.jmrt.2024.03.091>.
 - [45] B.S. Ginting, A. Ginting, E.K. SitepuJ, B. Tarigan, Non-catalytic synthesis of fatty acid alkanolamides from palm fatty acid distillate and monoethanolamine under microwave irradiation, *Rasayan J. Chem.* 16 (1) (2023) 391–397, <https://doi.org/10.31788/RJC.2023.1618188>.
 - [46] C. Bao, A. Serrano-Lotina, M. Niu, R. Portela, Y. Li, K.H. Lim, P. Liu, W.-j. Wang, M. A. BañaresQ. Wang, Microwave-associated chemistry in environmental catalysis for air pollution remediation: a review, *Chem. Eng. J.* 466 (2023) 142902, <https://doi.org/10.1016/j.cej.2023.142902>.
 - [47] S. Allende, G. BrodieM, V. Jacob, Breakdown of biomass for energy applications using microwave pyrolysis: a technological review, *Environ. Res.* 226 (2023) 115619, <https://doi.org/10.1016/j.envres.2023.115619>.
 - [48] K. Fiala, A. ThongjaradR. Leesing, Valorization of durian peel as a carbon feedstock for a sustainable production of heterogeneous base catalyst, single cell oil and yeast-based biodiesel, *Carbon Resour. Convers.* 7 (3) (2024) 100224, <https://doi.org/10.1016/j.crccon.2024.100224>.
 - [49] L. Lin, X. Li, F. Cui, H. Zhou, X. ShenM. Dong, Transesterification of rapeseed oil to biodiesel on CaO/α-Fe hollow fiber catalyst: optimization by response surface methodology, *BioEnergy Res.* 5 (4) (2012) 949–957, <https://doi.org/10.1007/s12155-012-9209-z>.
 - [50] G. Chen, R. Shan, J. ShiB. Yan, Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts, *Bioresour. Technol.* 171 (2014) 428–432, <https://doi.org/10.1016/j.biortech.2014.08.102>.
 - [51] W. Huang, S. Tang, H. ZhaoS. Tian, Activation of commercial CaO for biodiesel production from rapeseed oil using a novel deep eutectic solvent, *Ind. Eng. Chem. Res.* 52 (34) (2013) 11943–11947, <https://doi.org/10.1021/ie401292w>.
 - [52] V. MahdaviA, Monajemi, Optimization of operational conditions for biodiesel production from cottonseed oil on CaO–MgO/Al₂O₃ solid base catalysts, *J. Taiwan Inst. Chem. Eng.* 45 (5) (2014) 2286–2292, <https://doi.org/10.1016/j.jtice.2014.04.020>.
 - [53] W. XieL. Zhao, Heterogeneous CaO–MoO₃–SBA-15 catalysts for biodiesel production from soybean oil, *Energy Convers. Manag.* 79 (2014) 34–42, <https://doi.org/10.1016/j.enconman.2013.11.041>.
 - [54] H. Li, Y. Wang, Z. Han, T. Wang, Y. Wang, C. Liu, M. Guo, G. Li, W. Lu, M. Yu, X. Ma, Nanosheet like CaO/C derived from Ca-BTC for biodiesel production

- assisted with microwave, *Appl. Energy* 326 (2022) 120045, <https://doi.org/10.1016/j.apenergy.2022.120045>.
- [55] M.-C. Hsiao, J.-Y. Kuo, S.-A. Hsieh, P.-H. Hsieh, S.-S. Hou, Optimized conversion of waste cooking oil to biodiesel using modified calcium oxide as catalyst via a microwave heating system, *Fuel* 266 (1) (2020) 117114, <https://doi.org/10.1016/j.fuel.2020.117114>.
- [56] A. Buasri, T. Rattanapan, C. Boonrin, C. Wechayan, V. Loryuenyong, Oyster and Pyramidella shells as heterogeneous catalysts for the microwave-assisted biodiesel production from *Jatropha curcas* oil, *J. Chem. (1)* (2015) 578625, <https://doi.org/10.1155/2015/578625>, 2015.
- [57] H.M. Khan, T. Iqbal, M.A. Mujtaba, M.E.M. Soudagar, I. VezaI, M.R. Fattah, Microwave assisted biodiesel production using heterogeneous catalysts, *Energies* 14 (23) (2021) 8135.
- [58] Y.-C. Lin, K.T.T. Amesho, C.-E. Chen, P.-C. ChengF, C. Chou, A cleaner process for green biodiesel synthesis from waste cooking oil using recycled waste oyster shells as a sustainable base heterogeneous catalyst under the microwave heating system, *Sustain. Chem. Pharm.* 17 (2020) 100310, <https://doi.org/10.1016/j.scp.2020.100310>.
- [59] I. Lawan, Z.N. Garba, W. Zhou, M. Zhang, Z. Yuan, Synergies between the microwave reactor and CaO/zeolite catalyst in waste lard biodiesel production, *Renew. Energy* 145 (2020) 2550–2560, <https://doi.org/10.1016/j.renene.2019.08.008>.
- [60] K.T.T. Amesho, Y.-C. Lin, C.-E. Chen, P.-C. ChengV, K. Ponnusamy, Optimization and kinetics studies of biodiesel synthesis from *Jatropha curcas* oil under the application of eco-friendly microwave heating technique: an environmentally benign and sustainable bio-waste management approach, *Sustain. Environ. Res.* 32 (1) (2022) 41, <https://doi.org/10.1186/s42834-022-00151-w>.
- [61] Y. Liu, E. LoteroJ, G. Goodwin Jr., Effect of water on sulfuric acid catalyzed esterification, *J. Mol. Catal. Chem.* 245 (1–2) (2006) 132–140, <https://doi.org/10.1016/j.molcata.2005.09.049>.
- [62] X. Liu, H. He, Y. Wang, S. Zhu, X. Piao, Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst, *Fuel* 87 (2) (2008) 216–221, <https://doi.org/10.1016/j.fuel.2007.04.013>.
- [63] M. Kouzu, J.-s. Hidaka, Transesterification of vegetable oil into biodiesel catalyzed by CaO: a review, *Fuel* 93 (2012) 1–12, <https://doi.org/10.1016/j.fuel.2011.09.015>.