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Sustainable Biodiesel Production via Transesterification of Palm Oil using Waste Oyster Shell-Derived Calcium Oxide Catalysts

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In this study, we investigated the use of waste oyster shells as a sustainable source for calcium oxide catalysts in the transesterification of palm oil for biodiesel production. The modified catalyst was pelletized to facilitate easy separation and handling within the biodiesel reactor. Waste shells were calcined at 900°C for 5 h, converting calcium carbonate to calcium oxide. The innovation lies in the modification of the catalyst by pelletization, enabling efficient separation, handling, and reuse within the biodiesel reactor. The catalyst was characterized using X-ray diffraction (XRD), Thermo-gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and Scanning electron microscopy (SEM). Biodiesel conversion exceeded 98% under optimized conditions (reaction time: 5 h, catalyst loading: 10%, temperature: 80°C, methanol-to-oil ratio: 3:1). Additionally, the reusability of the catalyst pellets was evaluated, showing consistent high yields (over 80%) across ten reaction cycles, showcasing its durability and potential for cost-effective, large-scale biodiesel production.

Keywords: Oyster shell; calcium oxide, biodiesel

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The global surge in energy demand, propelled by population growth, industrial expansion, and advancements in transportation, is met with a concerning decline in conventional energy sources such as coal and crude oil [1]. Amidst this challenge, biodiesel emerges as a compelling alternative; a renewable, biodegradable, and environmentally friendly option synthesized through the transesterification of vegetable oils, waste oils, and fats with alcohol [2, 3].

Transesterification catalysts, operating in both homogeneous and heterogeneous phases, play a pivotal role in this process [4–7]. While homogeneous catalysts have gained prominence in industrial settings due to their rapid reaction rates and mild conditions, they pose significant drawbacks, including excessive wastewater generation and poor reusability [8]. In contrast, heterogeneous catalysts offer an enticing solution, being reusable, environmentally friendly, and easily separable [8,9]. Particularly, waste oyster shell-derived calcium oxide (CaO) has shown potential as a heterogeneous catalyst for biodiesel production. However, there is limited research on optimizing its catalytic performance. Specifically, more work is needed to understand the effects of different calcination temperatures, particle sizes, and surface area modifications to enhance catalytic efficiency and reusability. Thawatchai et al. reported the production of biodiesel through transesterification using CaO catalysts. The CaO catalysts were derived from biomass gasification of bottom ash. The obtained CaO catalysts exhibited high biodiesel production activity, where over 90% yield of methyl ester could be achieved at the optimized reaction conditions [10].

The present study investigated calcined waste oyster shells as catalysts for biodiesel production through transesterification of palm oil and used oil with methanol a resource readily available in the southern regions of Thailand [9]. Moreover, thorough chemical and physical characterization of each catalyst was conducted. Ultimately, the efficiency of biodiesel production hinges on factors such as oil-to-methanol ratio, reaction temperature, reaction time, and catalyst loading.

METHODS

General

In this work, waste oyster shells were obtained from a local fresh market in Pathumthani, Thailand. Palm oil olein (commercially edible grade) was obtained from a local supermarket. Used oil was sourced from Thammasat University and analytical grade methanol used in the synthesis was obtained from Merck.

Catalyst Preparation

The waste oyster shells were first washed with water, then boiled with 2 M concentration of sodium hydroxide solution to remove organic impurities, and subsequently dried in an oven for 24 h. Afterward, the shells were calcined at temperatures ranging from 700ºC to 900ºC for 5 h. After the calcination process, the resulting CaO was crushed using mortar and pestle and then sieved using a 100-mesh size screen, and stored in a desiccator.

Catalyst Characterization

The catalysts were characterized using various techniques. The crystal structure and phase purity of the catalysts were characterized by X-ray diffraction (XRD) analysis (Bruker AXS D8 Advance instrument) with Cu Kα1 radiation (λ=1.5406 Å), scanning from 5° to 80° (2θ) with a step size of 0.02°. Surface morphology and surface functional groups of the prepared samples were characterized by Scanning electron microscopy (SEM) (JEOL JSM-6390 instrument) and Fourier-transform infrared (FTIR) (Perkin-Elmer Spectrum GX infrared spectrometer) with KBr pellet technique, providing a resolution of 4 cm^{-1} over a range of 400-4000 cm^{-1}. Thermo-gravimetric analysis (TGA) was carried out using the NERZSCH STA 449 F3 instrument, ramping from room temperature to 1273 K at a rate of 10 K min^{-1} under a nitrogen flow. Energy dispersive X-ray spectroscopy (EDS) (Oxford X-MAX20) was used to analyze the elements and elemental composition of the prepared CaO.

Transesterification Reaction

The transesterification reaction of used palm oil and methanol to synthesize biodiesel was carried out in a round-bottomed flask equipped with a water-cooled condenser, a mechanical stirrer, and a hot plate. The synthesis of biodiesel was examined under various conditions: methanol-to-oil molar ratio (1:1, 3:1, 5:1, and 9:1), catalyst concentration (5, 10, 15, and 20 wt%), and reaction time (3, 4, 5, and 7 h). The mixture was heated to 80°C and stirred until the reaction was complete. After the reaction, the catalyst was removed from the biodiesel by filtration, and the excess methanol was removed using a rotary evaporator. The biodiesel conversion was calculated by the ratio of the integration of the ^1H-NMR signals between the methoxy proton (CH_3O-) of the methyl ester (ACH_3) at a chemical shift of 3.68 ppm and the ethylene proton (CH_2-) of all triglycerides (ACH_2) at a chemical shift of 2.30 ppm, according to Equation 1 [11].

$$\%\ \text{FAME} = \frac{2 \times A_{CH_3}}{3 \times A_{CH_2}} \text{ x } 100\%$$

Equation 1. Equation to calculate biodiesel conversion

RESULTS & DISCUSSION

Catalyst Characterization

Figure 1 illustrates the TGA outcomes for both non-calcined and calcined shells. The non-calcined shell demonstrated a predominant decomposition peak of 14.43% within the 600-700ºC range, primarily attributed to the release of CO_2 during the conversion of $CaCO_3$ to CaO. However, this decomposition process remained incomplete due to the instrument's temperature limitations, capped at 700ºC. In contrast, the TGA analysis of the calcined shell revealed two notable decomposition peaks. The initial decomposition, accounting for approximately 0.62% within the 300-400ºC range, is ascribed to the elimination of organic matter. Additionally, a subsequent decomposition, possibly linked to H_2O removal from the catalyst surface, occurred around 100ºC. It's worth noting that prior research indicates an optimal calcination temperature of 900ºC for waste mussel shells.

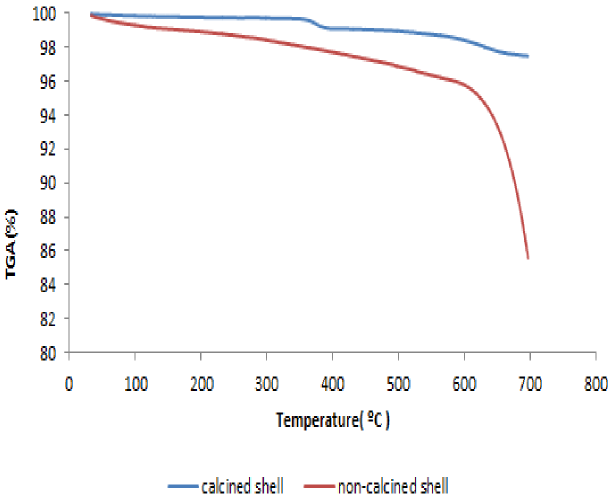

Figure 1. TGA profiles of calcined and non-calcined shells.

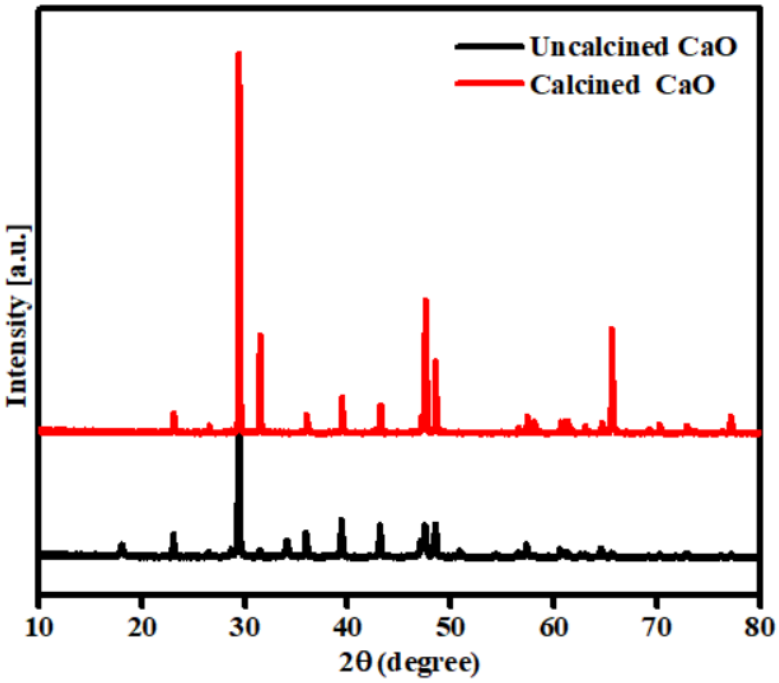

Figure 2. XRD patterns of non-calcined (top) and calcined (bottom) shells.

The XRD patterns of the calcined and uncalcined shells are shown in Figure 2. The XRD pattern of the uncalcined shell displayed relatively lower-intensity peaks and broader diffraction patterns. Additionally, the major peak in the uncalcined shell corresponds to $CaCO_3$ [12], indicating the presence of both aragonite and calcite phases. The characteristic peaks of calcite were observed at 2θ = 23.16°, 29.56°, and 36.07°, while the peaks for aragonite appeared at 2θ = 21.16°, 26.22°, and 27.21°. The weaker diffraction peaks suggest that the calcium carbonate derived from the shell has a less ordered structure. After the calcination process, $CaCO_3$ was converted into calcium oxide (CaO), with significant peaks of CaO observed at 2θ = 32.25°, 36.11°, and 56.56° [13,14]. The XRD pattern of the calcined CaO showed sharp and intense peaks, particularly the dominant peak around 2θ ≈ 32°, which is characteristic of highly crystalline CaO. The cubic phase of CaO was confirmed by ICDD card No. 00-017-0912; thus, having space group Fm-3m. The increased sharpness and intensity of these peaks indicate a well-crystallized structure, confirming the successful conversion of the precursor material into CaO during calcination. This transformation is primarily attributed to the decomposition of $CaCO_3$ into CaO at elevated temperatures, leading to the observed structural changes.

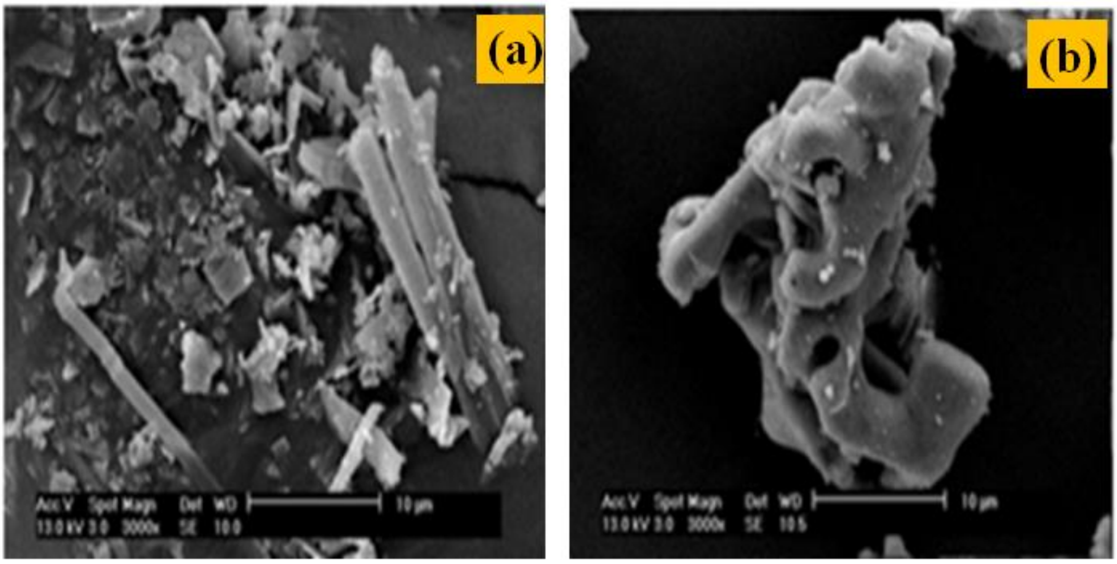

Figure 3. SEM images of (a) natural shell and (b) calcined shell.

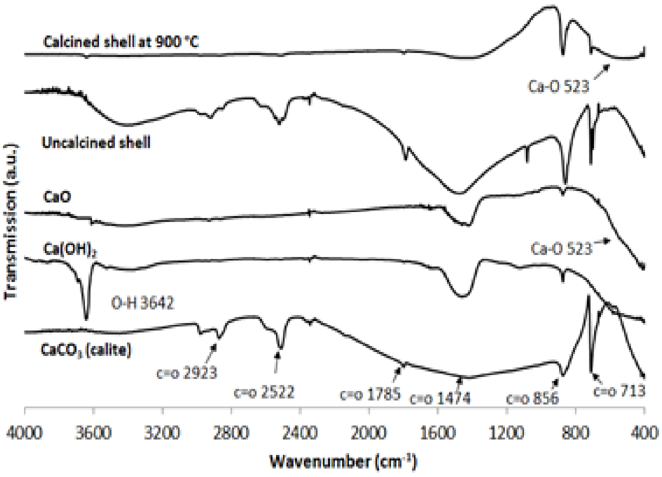

Figure 4. FTIR spectra of $CaCO_3$, CaO, $Ca(OH)_2$, and uncalcined and calcined shells.

The SEM images of both calcined and non-calcined shells are presented in Figure 3. Both images in Figures 3a-b were captured at a magnification of 3000x, with an applied voltage of 13.0 kV during the analysis. This study revealed a smooth and finely porous morphology in the non-calcined shell, whereas the calcined shell exhibited a rougher texture with larger pores. The presence of larger pores in the calcined shell is attributed to the release of CO_2 during calcination [11, 15].

The FT-IR spectra of both the calcined and uncalcined oyster shells were compared with those of $Ca(OH)_2$, $CaCO_3$, and CaO (Figure 4). In the spectrum of the uncalcined shell, absorptions corresponding to $CaCO_3$ were observed. Specifically, peaks associated with the C=O in the CO_3^{2-} group were observed at 1785 cm^{-1} (asymmetric stretching) and 1474 cm^{-1} (asymmetric stretching). Conversely, the calcined shell exhibited a prominent peak at 523 cm^{-1}, indicative of Ca-O bonds similar to CaO [5, 16, 17].

Effect of Reaction Time

Reaction time plays a crucial role in the transesterification process, as it determines how long the reactants have to interact. In the study, reaction times of 3, 5, and 7 h were evaluated, demonstrating that longer reaction time led to higher conversion rates for both palm oil and used oil. At 7 h, the highest conversion rates were observed: 99.33% for palm oil and 98.67% for used oil. These near-complete conversions suggest that 7 h is an optimal time for this process under the given conditions. The slight difference between palm oil and used oil conversions may be attributed to the varying compositions and properties of the oils. Palm oil is typically more homogeneous and has fewer impurities, leading to a slightly higher yield. This trend is common because prolonged exposure allows for more thorough mixing of reactants, greater interaction between the catalyst and oil, and ultimately, more complete reactions.

Effect of Catalyst Loading

The effect of catalyst loading of used oil and palm oil on % conversion is shown in Figure 6. The highest yields were 99.33% for palm oil and 89.33% for used oil when the amount of the catalyst was 10 wt%. However, when the catalyst loading was 15 wt%, the yield of biodiesel was reduced compared to 10 wt% because of the large amount of CaO results in a greater amount of glycerol that slows the mass transfer of methanol on the catalyst surface.

Effect of Oil-to-methanol Ratio

The effect of oil-to-methanol ratio of used oil and palm oil on % conversion is shown in Figure 7. Oil-to-methanol ratio is a key factor in optimizing biodiesel production. Reactions were carried out with 1:1, 1:3 and 1:7 oil-to-methanol ratios. The maximum yield of biodiesel was achieved in oil-to-methanol ratios of 1:3 for palm oil and 1:7 for used oil. The highest yields were 98.67% for used oil and 99.33% for palm oil. For palm oil, 1:3 ratio is optimal, achieving a high yield of 99.33%. Used oil, with its impurities, required a higher methanol ratio (1:7) to achieve a similar yield (98.67%). However, using excess methanol can lead to challenges such as separation difficulties and increased processing costs. Therefore, oil-to-methanol ratio must be carefully optimized for each type of feedstock to ensure maximum yields while maintaining process efficiency.

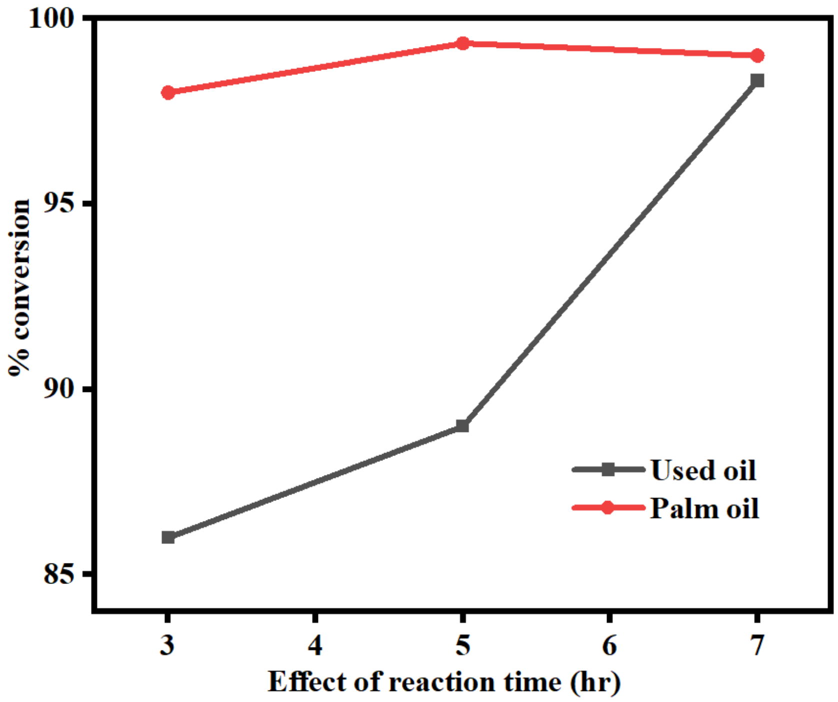

Figure 5. Effect of reaction time.

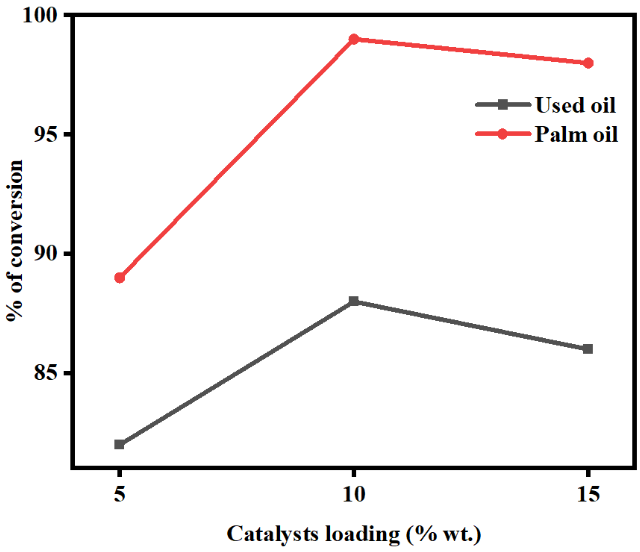

Figure 6. Effect of catalyst loading.

Reusability

Figure 8 illustrates the catalyst's reusability. Employing optimal conditions of 10% by weight catalyst loading, reaction time of 5 h, and oil-to-methanol ratio of 1:7, the catalyst was reused. Remarkably, the catalyst demonstrated the capacity for three cycles of reuse, consistently yielding biodiesel with a conversion rate exceeding 60%.

Fuel Properties

Table 1 presents the fuel properties of the biodiesels or methyl esters obtained through the transesterification process of palm oil and waste cooking oil, utilizing a catalyst derived from waste oyster shells.

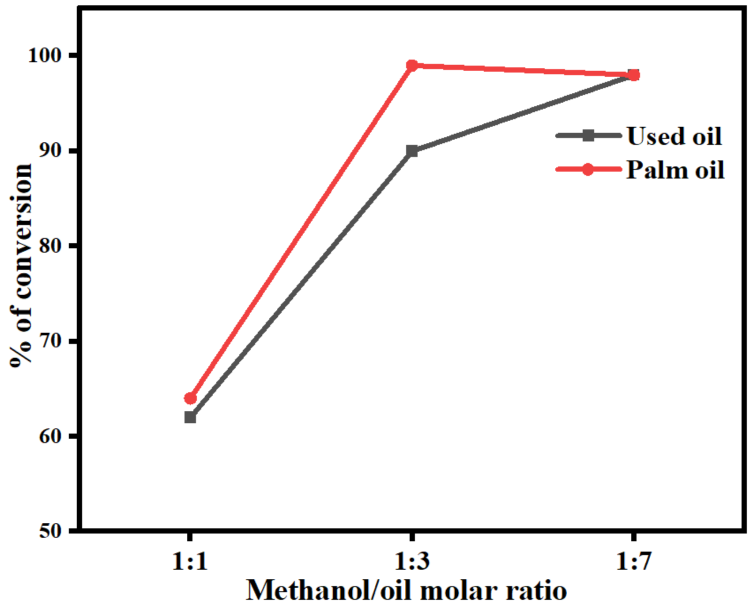

Figure 7. Effect of oil-to-methanol ratio.

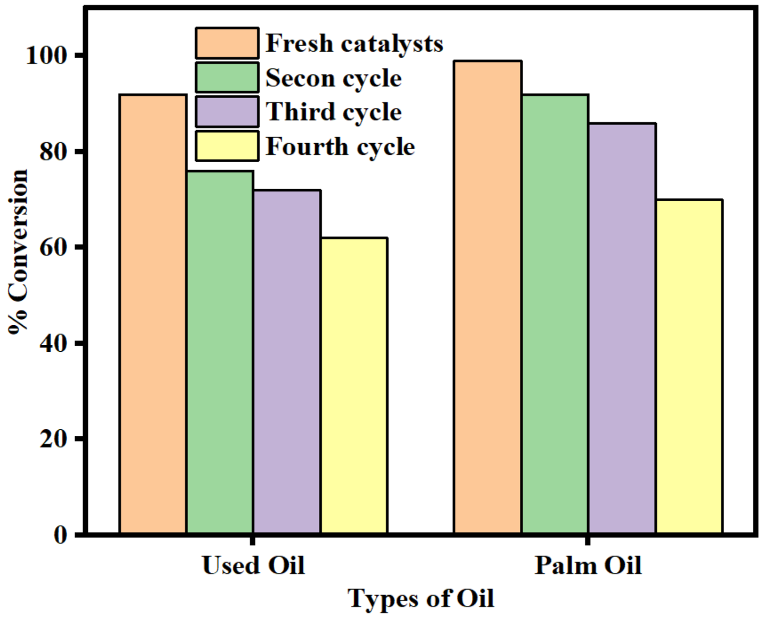

Figure 8. Reusability of calcined shell with waste cooking oil and palm oil.

Table 1. Fuel properties of prepared biodiesels.

Property	Unit	Waste cooking oil biodiesel	Palm oil biodiesel
bomb calorimeter revel energy	J/g	39,679	39,659.5
acidity	mg KOH/g	0.20	0.15

CONCLUSION

This study utilized calcined waste oyster shells in the transesterification process of palm and waste cooking oils. Following calcination at 900°C, the shells completed their conversion from $CaCO_3$ to CaO. Optimal conditions for the process included 10% by weight catalyst loading, 1:3 molar ratio of palm oil to methanol, and 1:7 molar ratio of waste cooking oil to methanol. Reaction times of 5 h for palm oil and 7 h for waste cooking oil, both at a reaction temperature of 80°C, were found to be most effective. Furthermore, the reusability of the calcined shell catalyst was investigated for up to three cycles. Impressively, yields exceeding 70% across all cycles underscore the significant potential of calcined waste oyster shells as a catalyst for heterogeneous biodiesel production, with promising prospects for commercial applications.

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Research Ethics / Declarations

Authors declare no conflict of interest

REFERENCES

1. Tariq, M., Ali, S., Khalid, N. (2012) Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of -biodiesel: A review. *Renewable and Sustainable Energy Reviews*, **16,** 6303–6316. https://doi.org/10.1016/j.rser.2012.07.005.

2. Boey, P. -L., Maniam, G. P., Hamid, S. A. (2009) Biodiesel production via transesterification of palm olein using waste mud crab (*Scylla serrata*) shell as a heterogeneous catalyst. *Bioresource Technology*, **100**, 6362–6368. https://doi.org/10.1016/ j.biortech.2009.07.036.

3. Atadashi, I. M., Aroua, M. K., Abdul Aziz, A. R., Sulaiman, N. M. N. (2013) The effects of catalysts in biodiesel production: A review. *Journal of Industrial and Engineering Chemistry*, **19**, 14–26. https://doi.org/10.1016/j.jiec.2012.07.009.

4. Boro, J., Thakur, A. J., Deka, D. (2011) Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production. *Fuel Processing Technology*, **92**, 2061–2067. https://doi.org/10.1016/j.fuproc.2011.06.008.

5. Shanmugam, P., Parasuraman, B., Boonyuen, S., Thangavelu, P., AlSalhi, M. S., Zheng, A. L. T., Viji, A. (2024) Hydrothermal synthesis and photocatalytic application of ZnS-Ag composites based on biomass-derived carbon aerogel for the visible light degradation of methylene blue. *Environ Geochem Health*, **46**, 92. https://doi.org/10.1007/s10653-024-01871-1.

6. Prabhakar, U. P. S., Shanmugam, P., Boonyuen, S., Chandrasekar, L. P., Pothu, R., Boddula, R., Radwan, A. B., Al-Qahtani, N. (2024) Non-covalent functionalization of surfactant-assisted graphene oxide with silver nanocomposites for highly efficient photocatalysis and anti-biofilm applications. *Materials Science for Energy Technologies*, **7**, 205–215. https://doi.org/10.1016/j.mset.2023.10.005.

7. Ngullie, R. C., Bhuvaneswari, K., Shanmugam, P., Boonyuen, S., Smith, S. M., Sathishkumar, M. (2022) Magnetically Recoverable Biomass-Derived Carbon-Aerogel Supported ZnO (ZnO/MNC) Composites for the Photodegradation of Methylene Blue. *Catalysts*, **12**, 1073. https://doi.org/10.3390/catal12091073.

8. Boey, P. -L., Maniam, G. P., Hamid, S. A., Ali, D. M. H. (2011) Utilization of waste cockle shell (*Anadara granosa*) in biodiesel production from palm olein: Optimization using response surface methodology. *Fuel*, **90**, 2353–2358. https://doi.org/10.1016/j.fuel.2011.03.002.

9. Chakraborty, R., Chatterjee, S., Mukhopadhyay, P., Barman, S. (2016) Progresses in Waste Biomass Derived Catalyst for Production of Biodiesel and Bioethanol: A Review. P*rocedia Environmental Sciences*, **35**, 546–554. https://doi.org/10.1016/j.proenv.2016.07.039.

10. Maneerung, T., Kawi, S., Wang, C. -H. (2015) Biomass gasification bottom ash as a source of CaO catalyst for biodiesel production via transesterification of palm oil. *Energy Conversion and Management*, **92**, 234–243. https://doi.org/10.1016/j.enconman.2014.12.057.

11. Mazaheri, H., Ong, H. C., Masjuki, H. H., Amini, Z., Harrison, M. D., Wang, C. -T., Kusumo, F., Alwi, A. (2018) Rice bran oil based biodiesel production using calcium oxide catalyst derived from *Chicoreus brunneus* shell. *Energy*, **144**, 10–19. https://doi.org/10.1016/j.energy.2017.11.073.

12. Reis, M. C., Sousa, M. F. B., Alobaid, F., Bertran, C. A., Wang, Y. (2018) A two-fluid model for calcium carbonate precipitation in highly super-saturated solutions. *Advanced Powder Technology*, **29**, 1571–1581. https://doi.org/10.1016/j.apt.2018.03.022.

13. Roschat, W., Kacha, M., Yoosuk, B., Sudyoadsuk, T., Promarak, V. (2012) Biodiesel production based on heterogeneous process catalyzed by solid waste coral fragment. *Fuel*, **98**, 194–202. https://doi.org/10.1016/j.fuel.2012.04.009.

14. García, J., López, T., Álvarez, M., Aguilar, D. H., Quintana, P. (2008) Spectroscopic, structural and textural properties of CaO and CaO–SiO2 materials synthesized by sol–gel with different acid catalysts. *Journal of Non-Crystalline Solids*, **354**, 729–732. https://doi.org/10.1016/j.jnoncrysol.2007.07.074.

15. Chen, G. -Y., Shan, R., Shi, J. -F., Yan, B. -B. (2015) Transesterification of palm oil to biodiesel using rice husk ash-based catalysts. *Fuel Processing Technology*, **133**, 8–13. https://doi.org/10.1016/j.fuproc.2015.01.005.

16. Nisar, J., Razaq, R., Farooq, M., Iqbal, M., Khan, R. A., Sayed, M., Shah, A., ur Rahman, I. (2017) Enhanced biodiesel production from *Jatropha* oil using calcined waste animal bones as catalyst. *Renewable Energy*, **101**, 111–119. https://doi.org/10.1016/j.renene.2016.08.048.

17. Parasuraman, B., Shanmugam, P., Govindasamy, P., Nangan, S., Gnanasekaran, L., Thangavelu, P. (2023) Photocatalytic degradation of tetracycline contaminated wastewater over Bi2S3/BiWO6/rGO ternary nanocomposite under visible light irradiation. *Journal of the Taiwan Institute of Chemical Engineers*, **105249**. https://doi.org/10.1016/j.jtice.2023.105249.