Spring International Engineering Research Journal: ISSN: 2384-5058

Volume-13 (Issue): 1, January, Pp 71-78, 2025
Accepted 2nd, **January**, 2024.

Efficient Biodiesel Production from Waste Cooking Oil Using Palm Kernel Shell-Derived Quicklime Catalyst: A Sustainable Approach with Optimal Reaction Conditions

***[1]Olaye Messiah, [2]Egunbambi Mudathir Wale, [3]James Gundat J.**

[1]Department of Industrial Production Engineering, Delta State University of Science and Technology, Ozoro, Nigeria.
[2]Department of Mechanical Engineering, Petroleum Training Institute, Effurun Delta State
[3]Department of Petroleum and Natural Gas Processing, Petroleum Training Institute,
Effurun Delta state-Nigeria.

Email: *olayem@dsust.edu.ng, egunbambi_mw@pti.edu.ng, jonah_jg@pti.edu.ng

Abstract

Biodiesel is a renewable alternative to fossil fuels with less environmental impact. However, conventional production using homogeneous catalysts such as strong acids or bases is costly and environmentally unsustainable due to complex separation and hazardous waste. This paper presents a sustainable route using activated palm kernel shells and quicklime as a heterogeneous catalyst to trans esterify waste cooking oil into biodiesel. X-ray Diffraction (XRD) analysis confirmed the catalyst's structural and catalytic properties. Reactions were carried out in a 250 mL three-necked flask fitted with a digital heating mantle, water-cooled condenser, and magnetic stirrer. Under optimized conditions (molar ratio of oil to methanol-1:12, 3 wt. % catalyst loading, 60°C and 2 hours reaction time) gave 90% biodiesel. This approach uses waste biomass (e.g., palm kernel shells) to further produce applied, biocompatible, low-cost catalysts to sustain the environmental circular economy and waste valorization goals. Its high yield and ease of recovery confirm its potential for industrial application to produce biodiesel on a larger scale. Ultimately, this method provides a viable and sustainable solution to biodiesel production while reducing conventional production methods' environmental and economic drawbacks.

Keywords: Biodiesel, Waste Cooking Oil, Transesterification, Palm Kernel Shells, Catalyst

1. INTRODUCTION

The increasing global population, the rapid demographic changes, and recent technical innovations have significantly improved energy requirements. On the one hand, oil extraction from the earth poses serious threats to the health of humans and the environment by releasing harmful gases into the atmosphere. On the other hand, the extraction has borders. Additionally, the industrial sector predominantly consumes gas, coal, and electricity as energy sources [1], apart from diesel and fuel oil. Due to this fact, the depletion of fossil fuels is moving at a mathematical rate, which shows the importance of exploring alternative fuels to meet the economic needs of growing energy sources [2]. By 2050, energy consumption is expected to increase further with its substitution for the use of costly hydrocarbon fuels, signifying a need to decrease the use of fossil fuels [3]. A rising atmospheric temperature and climate instability result from excess fossil fuel use, leading to more greenhouse gases in the atmosphere [4,5]. Consequently, these actions have led to various environmental issues that harm the environment that humans rely on, such as the energy crisis and the greenhouse effect [6]. Alternative fossil fuels are replaced to prevent the greenhouse effect [7]. Biodiesel is a biofuel that can replace diesel engines [8]. Biodiesel is made from the raw materials of cooking oil, animal fats, and vegetable oils [3]. It has low viscosity and a high cetane number, is non-toxic and ecologically benign, and its manufacturing can easily be adapted to meet specific requirements [9, 10]. Biodiesel, a holocaust gas oil of fat acid alkyl esters, is produced from animal fats by trans esterifying alcohol as the primary raw material into esters [11]. Biodiesel can also be made from renewable oils such as soybean, palm, sunflower, Jatropha curcas, and Moringa oleifera. The process is called transesterification.

Transesterification is a slow process; therefore, a catalyst is required to enhance the reaction rate. Both heterogeneous and homogeneous catalysts can be utilized in the transesterification reaction process. NaOH and KOH are homogenous base catalysts commonly used in the transesterification reaction process on biodiesel [12]. Due to the complexity of the biodiesel purification process, homogeneous catalysts utilized in the transesterification process have the drawback of being more expensive [13]. The fact that homogeneous catalysts dissolve in glycerol and biodiesel means that water is required to remove the dissolved catalyst concentration, which is another drawback [14]. Their primary drawback is the inability to reuse homogenous catalysts [16, 17]. One benefit of heterogeneous catalysts is catalyst reuse. Heterogeneous catalysts are the source of one reusable catalyst. Because they may be recycled, heterogeneous catalysts have an advantage over homogeneous catalysts regarding environmental friendliness. Because heterogeneous catalysts may be recycled, are less saponified in the reaction medium during the biodiesel purification, and are easily separated from the product medium, their use in biodiesel transesterification can save production costs [18]. Cathode oxide (CaO) is one of the components of the heterogeneous catalyst type. The most economical and environmentally friendly heterogeneous catalyst is CaO [19]. Catalysts based on calcium oxide (CaO) are abundant, affordable, and diverse. Palm kernel shells (PKS) are one example of a biological waste source that can yield CaO-based catalysts [20]. Calcium carbonate ($CaCO_3$) makes up 99–99% of scallop shells [21]. PKS waste contains calcium that can be used as a catalyst for transesterification reactions, but it must be calcined at high temperatures [22]. PKS's high calcium content offers the potential to serve as the foundation for quicklime, a biodiesel catalyst.

2. MATERIALS AND METHODS

The cooking oil used was gathered from various cafés and restaurants in Effurun and the surrounding areas. The chemicals used were tetraoxosulphate (VI) acid (H2SO4), phenolphthalein, n-hexane, and methanol. They are bought at a chemical laboratory supply store in Effurun, Nigeria. Thermally treated palm kernel shell (PKS) residues were utilized as starting material to make a quicklime (CaO) catalyst. The equipment used in this investigation includes a centrifuge LC-04R, Whatman filter paper, a muffle furnace KSL-1750X-KA3, three (3) neck flasks, a glass funnel, a pyrometer, a WANT brand Analytical Balance Model 2204H with Readability 0.1 mg, Allihn Condenser Glass, a digital stick probe thermometer, a separating funnel, a hotplate magnetic stirrer, a vacuum desiccator NOVUS DN 150 Clear with Porcelain Plate, and a Thread Lid GL32 MOBILEX with PBT.

2.1 Preparation of Waste Cooking Oil (WCO) and Quicklime (CaO)

[23] recommended that waste cooking oil (WCO) gathered from restaurants and other eating establishments in Effurun was cleansed by mixing it with bleaching earth at a 10:1 ratio. Following the recommendation of [24], the bleaching earth and WCO were mixed at 80 °C and left for 24 hours. The resultant sediment was separated and filtered to get rid of the residue. According to [25], a 'planetary ball mill' was used in the wet ball milling process to create the thermally treated PKS. An aqueous medium with a 3:1 mass fraction from the PKS powder sample was used for this procedure [26]. Compared to the mass of the entire ball employed in the procedure, the sample mass ratio was 1:20 [27, 28]. The milling machine rotated clockwise and counterclockwise every fifteen minutes during the forty-hour procedure [26]. After the ball milling, the suspension was filtered through filter paper, and the resulting sediment was baked at 110°C to dry it [29, 30]. After that, the dry sediment was crushed [30] and calcined at a temperature of 900 °C for 2 hours [31]. After calcination, the catalyst was stored in a vacuum desiccator.

2.2 Catalyst Characterization

The phase and crystallite size of the PKS powder was determined using the XRD test on the quicklime (CaO) catalyst made from PKS [32]. Eqn (1) illustrates how the Scherrer [33] formula was used to determine the crystallite size.

$$d = \frac{k \times \lambda}{\beta \times cos\theta} \text{ ....(1)}$$

Where k is a constant (0.9), β is the full-width half maximum, and λ = XRD wavelength (1.5406 Å).

2.3 Preparation of Biodiesel using Waste Cooking Oil and Quicklime Catalyst Recycling

The transesterification procedure made use of the prepared waste frying oil. Using the manufactured quicklime as a catalyst, the WCO transesterification reaction produced biodiesel. A 250 mL three-necked flask, a digital heater, a water-cooling condenser, and a magnetic stirrer were used in the experiment. Twenty grams of waste cooking oil were mixed with varying concentrations of prepared catalyst (0.4–2.6% by oil weight) for varying reaction times (1, 2, and 3 hours) and reaction temperatures (30–75 °C) using various oil/methanol ratios (1:5, 1:10, and 1:15). Centrifugation was used to extract the catalyst from the reaction medium following each experiment. The leftover liquid was held in the separating funnel for a full day to allow the mixture to separate into two layers (biodiesel on top and glycerol on bottom). After removing alcohol, glycerine, and catalyst residues from the top layer with hot distilled water, it is filtered to remove glycerol residue and dried at 110 °C for two hours to remove water residue. Using the following equation [34], the conversion reaction's efficiency (biodiesel yield%) was calculated.

$$Biodiesel\ yield\ (\%) = \frac{Volume\ of\ biodiesel}{Volume\ of\ waste\ cooking\ oil} \times 100 \text{ ....(2)}$$

3. RESULTS AND DISCUSSION

The obtained calculated XRD results are summarized in Table 1.

Table 1. Intensity, full-width half maximum (FWHM), d-spacing and crystallite size of the Quicklime catalyst

Sample	XRD Peak			
	Intensity (counts)	FWHM (rad)	d-spacing (Å)	Crystallite size (nm)
Quicklime Catalyst	889	0.001373562	2.39161	68.75

The quicklime catalyst made from PKS material has a crystal size of 68.75 nm, as Table 1 illustrates. Quicklime peaks at 32.15° (112), 37.25° (205), 54.65° (225), 65.06° (315), 68.13° (226), 80.01° (025) and 89.11° (405) are shown in Figure 1, which shows the catalyst that was synthesized and sintered from PKS material at 950°C for two hours. These results are consistent with the data found in the International Centre for Diffraction Data (ICDD) database No. 00-004-0777 [35,36]. Stated differently, at 18.28° (001), 34.11° (101), 47.17° (102) and 51.82° (110) [60–62], slaked lime was also detected on the catalyst as described in Fig. 1. The peaks of the slaked lime are similar to those found in ICDD database No. 00-004-0733. The interaction of quicklime with atmospheric water produces slaked lime [37]. Since quicklime is known to be hygroscopic and can absorb moisture from the air, the water molecules absorbed on its surface are the source of the slaked lime phases [38]. Information regarding the quicklime's crystal structure from the PKS powder was also obtained through analysis with the MATCH program. The crystal structure of the quicklime catalyst is cubic [39].

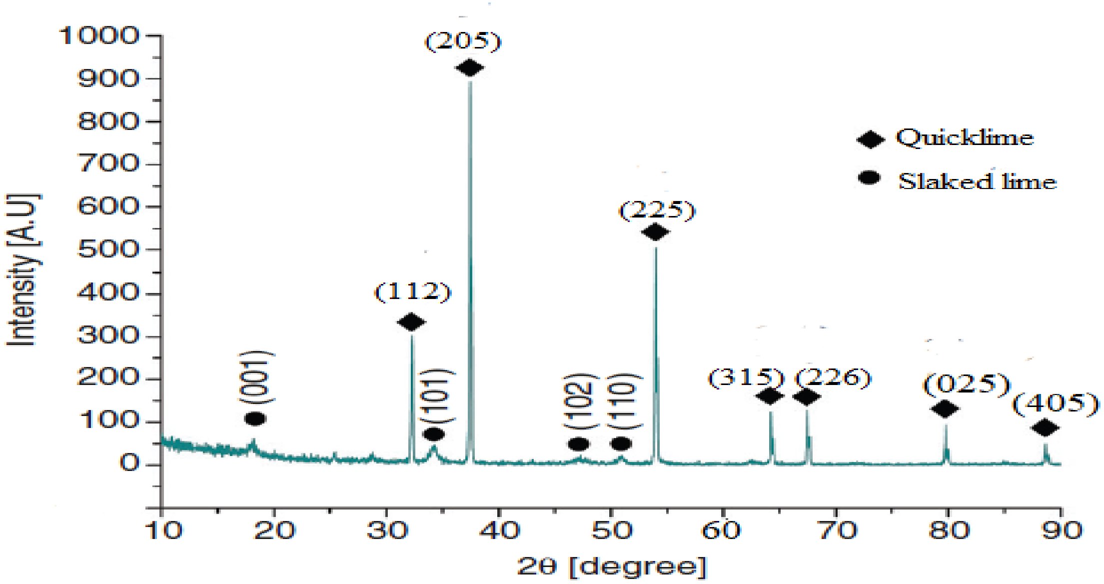

Fig. 1. XRD results for quicklime catalyst from PKS

At a reaction temperature of 60 ◦C, the effects of utilizing different molar ratios (1:8, 1:12, and 1:14) were investigated. Three hours was the reaction time, and the catalyst was used equal to 3% of the oil's weight. Figure 2 illustrates that the transesterification reaction was not completed when utilizing a molar ratio of less than 1:12. It is evident, therefore, that the maximum biodiesel output (90%) was reached when the molar ratio was raised from 1:8 to 1:12. This may be explained by the fact that the amount of methanol added was adequate to convert the oil and wasn't too much to surpass the glycerin's dissolution as a result of the oil's transesterification process, which was the problem found using the molar ratio (1:12). It appears that the production of biodiesel drops when the methanol content is increased over the recommended ratio (1:12) as shown in Fig. 2. It is clear that the rise in glycerin solubility, which makes glycerine separation from the reaction solution challenging, is one of the reaction limits. Moreover, glycerin in the reaction solution causes the reaction to be shifted in the direction of the reactants, which lowers the yield of biodiesel [40].

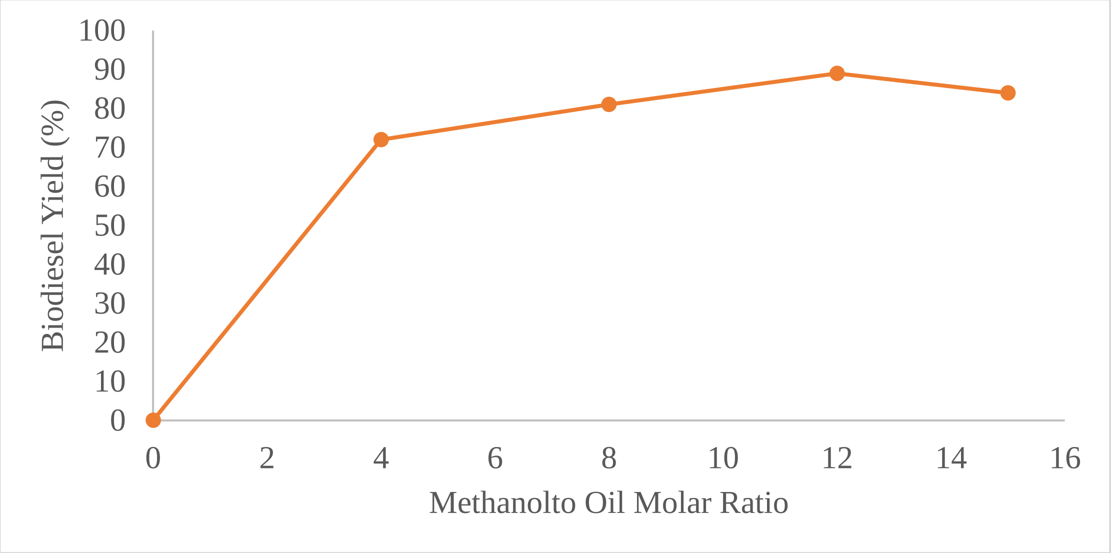

Fig. 2. Evaluation of the effect of methanol/oil molar ratio

Catalyst ratios to oil weight were varied (1, 2, 3, 4). Every experiment was run with a molar ratio of 1:12, a reaction time of three hours, and a temperature of 60 ◦C. Figure 3 illustrates how the reaction yield rises as catalyst concentration increases, peaking at 3%. The reaction yield decreases as the catalyst is increased more. This is because too much catalyst makes the mixture more viscous, which prevents the system from reaching the right homogeneous mixture, where the diffusion coefficient is crucial to the yield [41, 42]. Conversely, a reduction in yield is noted when ratios smaller than 3% are used, as there aren't enough active centres on the catalyst to finish the reaction as Fig. 3. Consequently, the catalyst level of 3 per cent was ideal for the highest biodiesel production of 90%.

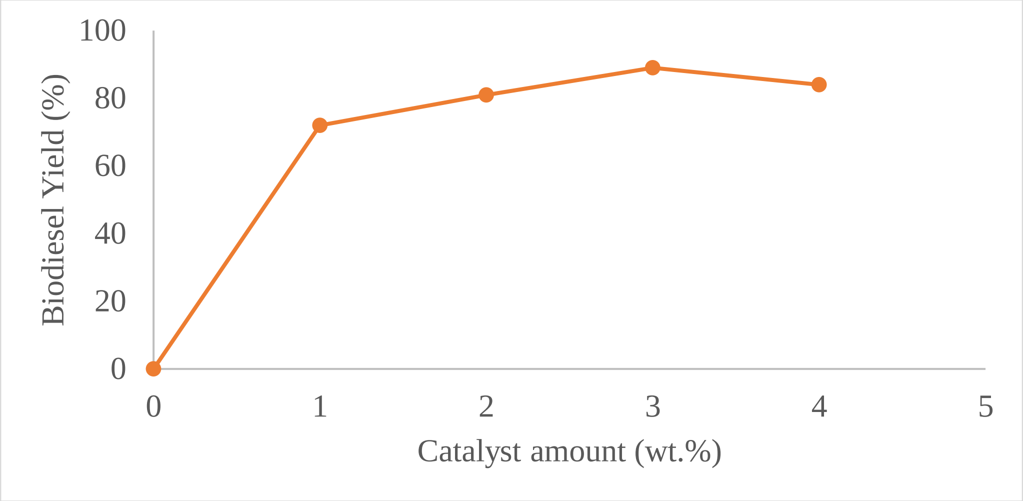

Fig. 3. Evaluation of the effect of catalyst amount

It investigated how temperature affected the output of biodiesel. At a molar ratio of 1:12, a catalyst quantity of 3% of the oil weight, and a reaction duration of 2 hours, the reaction temperature fluctuated between 30 and 45, 60 and 75 ◦C. As the temperature rises to 60 °C, the transesterification reaction rate increases as the oil's viscosity reduces, leading to improved mixing between the processes and the increase in reaction rate [38]. However, over 60 °C, the output of biodiesel drops because the temperature exceeds the boiling point of methanol, which is 64.7 °C, as illustrated in Fig. 4. This causes some of the methanol to evaporate, which lowers the yield. The results are like those of other research [42, 43]. To obtain the maximum production of 90% biodiesel, the transesterification reaction temperature was conducted at 60 ◦C.

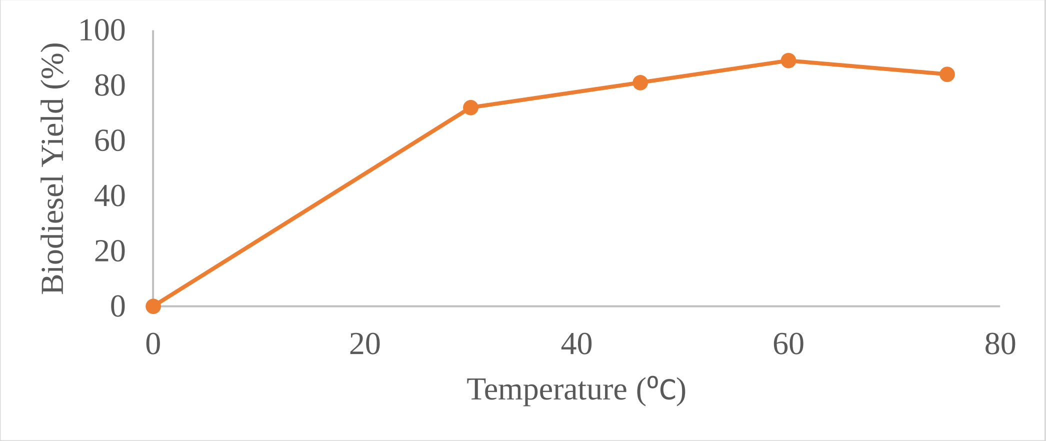

Fig. 4. Evaluation of the effect of temperature

The impact of reaction duration on yield was investigated at one-hour, two-hour, and three-hour intervals; the temperature was maintained at 60 ◦C, the molar ratio was 1:12, and 3% of the oil weight was used as catalyst. At a reaction time of two hours, the reaction rate increased to its maximum. 90% of the biodiesel was produced, as illustrated in Fig. 5. This represents how long it takes to complete a transesterification reaction. It may be concluded that 1 hour was insufficient to get the highest biodiesel output. Furthermore, extending the reaction duration beyond two hours reduced the yield. Doing so could cause biodiesel to decompose and shift the reaction in another direction, affecting the yield [42].

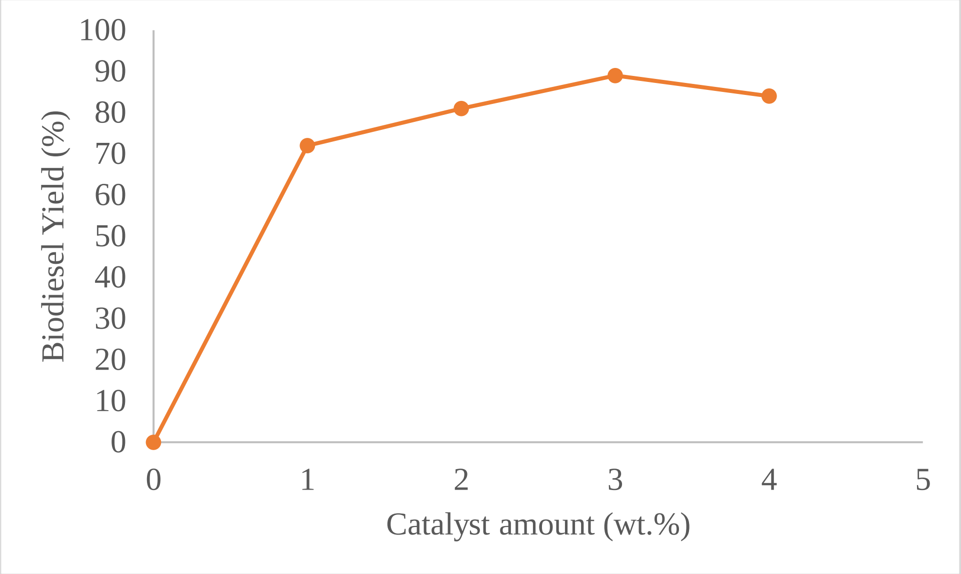

Fig. 5. Evaluation of the effect of catalyst amount

4. CONCLUSION

The present study confirms that utilizing WCO as biodiesel feedstock with a PKS-derived QLC catalyst is a courteous and practical process. At optimum reaction conditions, that was achieved with a methanol-to-oil molar ratio of 1:12 and catalyst loading of 3 wt. % of oil, 60°C reaction temperature, and 2 hours reaction time, 90% biodiesel yield was achieved. The high yield indicates the efficacy of PKS-derived CaO as a low-cost, renewable, and eco-friendly heterogeneous catalyst. This solution could contribute to meeting this energy demand, as it can significantly reduce pollution and waste generation by replacing standard diesel fuel with research biodiesel produced from spoiled cooking oil. The study further highlights the potential reusability of the catalyst, with the quicklime retaining substantial catalytic activity after being recycled and reused for three cycles of transesterification. This reusability enhances the economic and environmental advantages of catalytical methanol and ethanol chemical recycling in this proposed method by minimizing catalyst waste and cost, which is also a prerequisite for its large-scale industrialization. The results highlight the double benefits of valorising agro-waste materials such as palm kernel shells and solving pollutant problems such as used cooking oils. The advantage of this method lies in supporting cleaner production processes while applying the principles of a circular economy, serving as a sustainable and scalable solution for biodiesel production processes. In future work, we will scale up & recycle the catalyst for further cycles and optimize more parameters for industrial applications.

REFERENCES

[1] Susvira D. Synthesis of biodiesel from waste cooking oil using heterogeneous catalyst (CaO) based on duck eggshell with transesterification reaction. *Jurnal Kartika Kimia*, 2022, 5:40–43.

[2] Premkumar S, Radhakrishnan K, Kalidoss R, *et al*. Synthesis, characterization and application of SnO2 @ rGO nanocomposite for selective catalytic reduction of exhaust emission in internal combustion engines. *Catalyst*, 2023, 13:381

[3] Babadi, Arman Amani, et al., Emerging technologies for biodiesel production: processes, challenges, and opportunities. *Biomass Bioenergy,* 163 (2022), 106521.

[4] Martins F, Felgueiras C, Smitkova M, *et al*. Analysis of fossil fuel energy consumption and environmental impacts in European countries. *Energies*, 2019, 12:964.

[5] Lamb WF, Wiedmann T, Pongratz J, *et al*. A review of trends and drivers of greenhouse gas emissions by sector from 1990 to 2018. *Environ Res Lett*, 2021, 16:073005.

[6] Li W, Ma J, Liu H, *et al*. Investigations on combustion system optimization of a heavy-duty natural gas engine. *Fuel*, 2023, 331:125621.

[7] Papież M, Śmiech S, Frodyma K, *et al*. Decoupling is not enough: evidence from fossil fuel use in over 130 countries. *J Clean Prod*, 2022, 379:134856.

[8] Espootin S, Sameti M, Zaker S. Biodiesel from fish waste oil: synthesis via supercritical methanol and thermodynamic optimization. *Clean Energy*, 2021, 5:187–195.

[9] Sulaiman NF, Hashim ANN, Toemen S, *et al*. Biodiesel production from refined used cooking oil using co-metal oxide catalyzed transesterification. *Renew Energy*, 2020, 153:1–11.

[10] Thangaraj B, Solomon PR. Biodiesel production by the electrocatalytic process: a review. *Clean Energy*, 2021, 5:19–31.

[11] Ndiaye M, Arhaliass A, Legrand J, *et al*. Reuse of waste animal fat in biodiesel: biorefining heavily-degraded contaminant-rich waste animal fat and formulation as diesel fuel additive. *Renew Energy*, 2020, 145:1073–1079

[12] Ramirez J, Buest L, Lopez-Maldonado EA. Preparation and physicochemical characterization of biodiesel from recycled vegetable oil in Cuenca, Ecuador by transesterification catalyzed by KOH and NaOH. *Eng*, 2023, 4:954–963.

[13] Barros S, Pessoa Junior WAG, Sá ISC, *et al*. Pineapple (Ananás comosus) leaves ash as a solid base catalyst for biodiesel synthesis. *Bioresour Technol*, 2020, 312:123569.

[14] Li S, Cheng S, Cross JS. Homogeneous and heterogeneous catalysis impact on pyrolyzed cellulose to produce bio-oil. *Catalysts*, 2020, 10:178.

[15] Junior WAGP, Takeno ML, Nobre FX, *et al*. Application of water treatment sludge as a low-cost and eco-friendly catalyst in the biodiesel production via fatty acids esterification: process optimization. *Energy*, 2020, 213:118824.

[16] Mendonça IM, Paes OARL, Maia PJS, *et al*. New heterogeneous catalyst for biodiesel production from waste tucumã peels (Astrocaryum aculeatum Meyer): parameters optimization study. *Renew Energy*, 2019, 130:103–110.

[17] Gobikrishnan S, Park J-H, Park S-H, *et al*. Sonication-assisted production of biodiesel using soybean oil and supercritical methanol. *Bioprocess Biosyst Eng*, 2013, 36:705–712.

[18] Zhang Y, Niu S, Han K, *et al*. Synthesis of the SrO–CaO–Al2O3 trimetallic oxide catalyst for transesterification to produce biodiesel. *Renew Energy*, 2021, 168:981–990.

[19] Mazaheri H, Ong HC, Amini Z, *et al*. An overview of biodiesel production via calcium oxide-based catalysts: current state and perspective. *Energies*, 2021, 14:3950.

[20] Srichanachaichok W, Pissuwan D. Micro/Nano structural investigation and characterization of mussel shell waste in Thailand as a feasible bioresource of CaO. *Materials (Basel)*, 2023, 16:805.

[21] Azzahro UL, Broto W. Utilization of waste shells as CaO catalyst in biodiesel production from used cooking oil. *Acta Chimica Asiana*, 2022, 5:147–152.

[22] Ooi HK, Koh XN, Ong HC, *et al*. Progress on modified calcium oxide derived waste-shell catalysts for biodiesel production. *Catalysts*, 2021, 11:194.[27] Degfie TA, Mamo TT, Mekonnen YS. Optimized biodiesel production from waste cooking oil (WCO) using calcium oxide (CaO) nano-catalyst. *Sci Rep*, 2019, 9:18982

[23] Akbar T, Hendro A. Pemurnian Minyak Goreng Bekas dengan Menggunakan Adsorbent Zeolit dan Bleaching Earth. *Indonesian J Halal*, 2022, 4:16–24.

[24] Trisnaliani L, Ridwan KA, Fitriyanti D. Pretreatment Minyak Jelantah Dengan Menggunakan Adsorben Sebagai Bahan Baku Biodiesel. KINETIKA, 2019, 10:19–24.

[25] Puspitasari P, Fauzi AF, Susanto H et al. Synthesis and characterization of $CaCO_3$/CaO from Achatina fulica in various sintering time. In: International Conference on Mechanical Engineering Research and Application (iCOMERA
2020), Vol. 2, Malang, Indonesia, 7–9 October, 2020, 012093.

[26] Gbadeyan OJ, Adali S, Bright G, et al. Optimization of milling procedures for synthesizing Nano-$CaCO_3$ from

Achatina fulica shell through mechanochemical techniques. *J Nanomater,* 2020, 2020:4370172.

[27] Sargheini J, Ataie A, Salili SM, et al. One-step facile synthesis of $CaCO_3$ nanoparticles via mechano-chemical route. *Powder Technol,* 2012, 219:72–77.

[28] Dulian P, Bąk W, Wieczorek-Ciurowa K, et al. Controlled mechanochemical synthesis and properties of a selected perovskite-type electroceramics. *Mater Sci Poland,* 2013, 31:462–470.

[29] Camargo ILD, Lovo JFP, Erbereli R, *et al*. Influence of media geometry on wet grinding of a planetary ball mill. *Mater Res*, 2019, 22: e20190432.

[30] Ozkan A, Yekeler M, Calkaya M. Kinetics of fine wet grinding of zeolite in a steel ball mill in comparison to dry grinding. *Int J Miner Process*, 2009, 90:67–73.

[31] Boey P-L, Maniam GP, Hamid SA, *et al*. Utilization of waste cockle shell (Anadara granosa) in biodiesel production from palm olein: optimization using response surface methodology. *Fuel*, 2011, 90:2353–2358.

[32] Bunaciu AA, Udriştioiu E, Aboul-Enein HY. X-ray diffraction: instrumentation and applications. *Crit Rev Anal Chem*, 2015, 45:289–299.

[33] Puspitasari P, Putra CS, Permanasari AA *et al*. Physical and magnetic properties of nickel cobalt oxide ($NiCo_2O_4$) as synthesized by self-combustion method. In: Karim SAA, Puspitasari P (eds). *Advanced Materials towards Energy Sustainability.* 1st edn. Boca Raton: CRC Press, 2023, 5–35.

[34] Nasim Hasan, M. Venkata Ratnam, Biodiesel production from waste animal fat by transesterification using H2SO4 and KOH catalysts: a study of physiochemical properties, *Int. J. Chem. Eng.* (2022) 2022.

[35] Rujitanapanich S, Kumpapan P, Wanjanoi P. Synthesis of hydroxyapatite from oyster shell via precipitation. *Energy Procedia*, 2014, 56:112–117.

[36] Alobaidi YM, Ali MM, Mohammed AM. Synthesis of calcium oxide nanoparticles from waste eggshell by thermal decomposition and their applications. *Jordan J Biol Sci*, 2022, 15:269–274.

[37] Linggawati A. Preparation and characterization of calcium oxide heterogeneous catalyst derived from Anadara Granosa shell for biodiesel synthesis. *KnE Eng*, 2016, 1:1–8. https://doi. org/10.18502/keg.v1i1.494.

[38] Puspitasari P, Iftiharsa MA, Zhorifah HFN, *et al*. Analysis of physical properties and compressibility of avian eggshell nanopowders in solid state reaction. *EUREKA: Phys Eng*, 2021, 5:110–120.
[39] Supriyanto NSW, Sukarni S, Puspitasari P *et al*. Synthesis and characterization of CaO/CaCO3 from quail eggshell waste by solid state reaction process. In: *International Conference on Biology and Applied Science (ICOBAS)*, Vol. 1, Malang, Indonesia, 13–14 March 2019, 040032

[40] ERCHAMO, Yeshimebet Simeon, et al., Improved biodiesel production from waste cooking oil with mixed methanol–ethanol using enhanced eggshell-derived CaO nano-catalyst, *Sci. Rep.*, 11 (1) (2021) 1–12.

[41] Wuttichai Roschat, et al., Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst, Energy Convers. Manag. 108 (2016) 459–467. [42] ¨Ozlem Bedir, Do˘gan, Tuba Hatice, Use of sugar industry waste catalyst for biodiesel production, Fuel 286 (2021), 119476.

[43] Xing-Xia Yang, et al., Catalytic transesterification to biodiesel at room temperature over several solid bases, Energy Convers. Manag. 164 (2018) 112–121.