Catalytic Conversion of Coconut Pulp into Biodiesel through Transesterification using Calcium Oxide-Based Catalysts

Thivya a/p Keasavan[1], Abdullah bin Dzilalu Khairi[1], Salmiah Jamal Mat Rosid[2], Nurasmat Mohd Shukri[3], Wan Nazwanie Binti Wan Abdullah[1*]

[1]School of Chemical Science, Universiti Sains Malaysia, 11800 USM Penang, Malaysia

[2]Unisza Science and Medicine Foundation Centre, Universiti Sultan Zainal Abidin, Gong Badak Campus 21300 Kuala Nerus, Terengganu, Malaysia

[3]School of Health Sciences, Universiti Sains Malaysia, 16150 Kubang Kerian, Kelantan, Malaysia

*Corresponding author (e-mail: wanazwanie@usm.my)

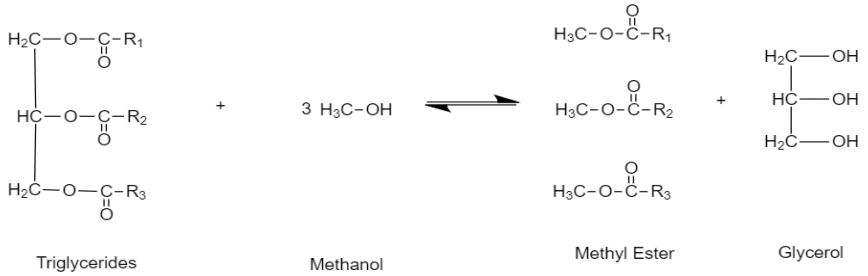
Organic biomasses represent an eco-friendly energy source, while solving problems cause by improper waste disposal. In this research, calcium oxide-based catalysts, namely $CaO/Fe_2O_3/Al_2O_3$ and *Paphia undulatus*, were used to convert coconut pulp waste into biodiesel. 50% of oil was extracted from 10 g of waste coconut pulp at 60℃ in 4 hours using Soxhlet extraction method. Biodiesel was produced from waste coconut pulp through transesterification reaction at a temperature of 55℃ in 2 hr, utilizing calcium oxide-based catalysts. GC-FID results showed the presence of four methyl ester species in the product and this finding revealed that free fatty acids had been successfully converted to methyl esters.

Keywords: Transesterification; biodiesel; Soxhlet Extraction; metal oxide catalyst; coconut pulp

Received: March 2023; Accepted: May 2023

Global environmental issues and inadequate fossil fuels have given rise to wider acceptance of environmentally friendly products. One of the most commonly used fossil fuels in Malaysia is petroleum. However, petroleum-based fossil fuels have disadvantages which may affect human health or the environment. Petrodiesel may consist of some extent of tremendous degrees of pollutants and greenhouse gas (GHG) emissions which contribute to global warming. Some studies have shown that the combustion of petrodiesel may produce nitrogen oxides (NO), carbon monoxide (CO), sulphur dioxide (SO_2), particulate matter, and hydrocarbons [1].

Biodiesel is also known as fatty acid alkyl ester, which is considered to be the greatest alternative to petroleum-based diesel fuel. This is because, biodiesel has high cetane numbers, high efficiency in combustion, and low emission, which contribute to it gaining much attention as a fuel [2]. Apart from that, biodiesel produces less NOx gases and has low emissions compared to normal diesel. Biodiesel helps to reduce pollution and may reduce the effects of global warming. In comparison to petrodiesel, it is less toxic and easier to store. Biodiesel is synthesized from vegetable oils or animal fats with an alcohol (solvent) and in the presence of a catalyst (acid or base), depending on the feedstock used. Vegetable oils and animal fats are insoluble in water [3]. Normally, triglycerides of vegetable oils and animal fats are made up of variety of fatty acids. Triglycerides could be transformed into biodiesel by four main methods, namely transesterification, pyrolysis (thermal cracking), dilution, and micro-emulsification [4]. To reduce oil viscosity and prevent serious damage to biodiesel, vegetable oils and animal fats must undergo transesterification. Transesterification is a process where triglycerides will be converted into fatty acid methyl esters (FAME) in the presence of methanol or ethanol and a catalyst (acid or base), with glycerol as a by-product [5]. The reaction is as shown in Equation 1 [5].



[1]

Table 1. Fatty acid composition (%) using different types of feedstocks.

Fatty acid	Soy bean	Cotton seed	Palm	Lard	Tallow	Coconut	Rubber seed	Waste cooking oil
Lauric	0.1	0.1	0.1	0.1	0.1	46.5	-	-
Myristic	0.1	0.7	1.0	1.4	0.8	19.2	-	-
Palmitic	0.2	20.1	42.8	23.6	23.3	9.8	10.2	38.35
Stearic	3.7	2.6	4.5	14.2	19.4	3.0	8.7	4.33
Oleic	22.8	19.2	40.5	44.2	42.4	6.9	24.6	43.67
Linoleic	53.7	55.2	10.1	10.7	10.7	2.2	39.6	11.39
Linolenic	8.6	0.6	0.2	0.4	0.4	0.0	16.3	0.29

Transesterification is classified into three categories, which are homogeneous, heterogeneous and enzymatic transesterification. Common homogeneous catalysts used are sodium hydroxide (NaOH), sulphuric acid (H_2SO_4), and potassium hydroxide (KOH) [6], while for heterogeneous catalysts are magnesium oxide (MgO) and calcium oxide (CaO). Since homogeneous catalysts cause various problems such as catalysts recovery and saponification, heterogeneous catalysts are used to replace homogeneous catalysts. Enzyme-catalyzed reactions usually utilize lipase, an enzyme which serves as a biocatalyst in transesterification reaction [7]. However, the price and stability of the enzyme are the main challenges yet to be studied. Compositions of fatty acids using different types of feedstocks are summarized in Table 1 [8][9].

Cocos nucifera, or coconut, is well known as the 'tree of life', which grows well in coastal areas of Malaysia. In 2018, Malaysia produced about 538,685 mt of coconut from a planted area of 81,585 ha. [10]. It was reported that million tons of agricultural wastes are produced every year and one of the wastes is from coconut [11]. Sulaiman et al., 2013 [12] reported a high biodiesel yield using coconut waste as a raw material in the presence of KOH catalyst. Recently, Niyas et al. [13] produced biodiesel from waste coconut cooking oil in solar-powered rotating flask oscillatory flow reactor utilizing homogeneous catalyst system. A CaO catalyst derived from natural white bivalve clam shells had been employed to produce biodiesel from waste oil, as reported by Girish et al. [14]. Risso et al. [15] claimed that highly active CaO catalysts were obtained from waste shells for biodiesel production. There is also the lack of study on the conversion of waste coconut pulp into biodiesel using heterogenous catalysts. Therefore, this research focused on the capability of Paphia undulatus as an alternative catalyst to perform the transesterification process utilizing coconut pulp as a feedstock for biodiesel production. The Paphia undulatus catalyst was also compared with different sources of calcium oxide catalyst. Besides, the optimization of extraction and transesterification condition and physicochemical properties of the catalyst were studied.

EXPERIMENTAL

Catalyst Preparation

$CaO/FeO/Al_2O_3$ (Catalyst B) was synthesized via wet impregnation method. 5 g of calcium nitrate tetrahydrate and 0.7 g of iron(III) nitrate nanohydrate ($Fe(NO_3)_3.9H_2O$) were respectively dissolved in 10 ml of distilled water. About 2 g of alumina pellet was also weighed. Both solutions were mixed and added with alumina pellet. The mixture was stirred for 6 hours until a slurry solution was produced. The beads were filtered and washed with acetone, then dried in the oven overnight at 120℃. Next, the catalyst was calcined at 500℃ for 5 hours with a ramp rate of 10℃/min. Waste clamshells of *Paphia undulatus* (Asian Clam) were collected, washed, and dried overnight. Then, the clamshells were crushed using a mortar. About 10 to 12 g of clamshell was weighed and calcined at two different temperatures, 500℃ (Lala500) and 900℃ (Lala900), for 5 hours with ramp rates of 10℃/min and 15℃/min, respectively. The calcined clamshells were weighed and stored.

Sample Extraction

Coconut pulp was squeezed various times and dried in the oven at about 90℃ overnight. The dried coconut pulp was ground to increase surface area. The dried coconut pulp was then packed in filter papers. Two extractor setups were used, Soxhlet extractor and in-situ extractor. Both extraction methods used n-hexane as the extraction solvent. For in-situ extraction, the coconut oil was extracted using a simple reflux setup and underwent filtration process to separate dissolved coconut oil from the solid sample. About 10 g of coconut pulp was used to extract coconut oil and refluxed directly for 6 hours in 150 ml of n-hexane at 65℃. The liquid sample and solid waste were separated using a simple buchi-filter setup. For

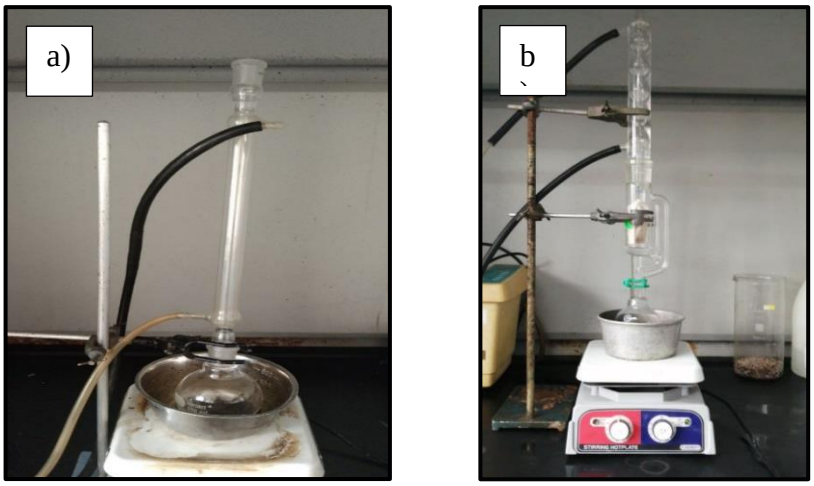


Figure 1. Experimental setups for: (a) In Situ Extraction; and (b) Soxlet Extraction

separation of coconut oil from n-hexane, a rotavapor setup was used at 40℃ and 80 rpm. The extracted coconut oil was later weighed. For Soxhlet extraction, the steps were repeated without filtration with a buchi-filter setup. After the extraction of oil, the mass of the oil extracted was weighed using a measuring balance to calculate the weight percent of oil obtained by using Equation 2. Figure 1 shows the experimental setups for in situ extraction and Soxhlet extraction.

$$\text{Weight percent of oil} = \frac{\text{Weight of oil obtained}}{\text{Weight of coconut pulps used}} \times 100\% \qquad [2]$$

Transesterification Process and Identification of Biodiesel Products

1.2 g of catalyst and 1:12 molar ratio of oil to methanol were added to 5 g of oil. The catalyst was activated by dispersing methanol at 50℃ for 20 minutes at constant stirring. The reflux process was conducted at 55℃ with continuous stirring for 2 hours. When transesterification process finished, the product was cooled down for 10 minutes and filtered through a filter paper to separate the catalyst. The filtered liquid was placed in a separatory funnel and left overnight. By the following day, the liquid separated. The lower layer was removed, and the upper layer was taken for the extraction of biodiesel from excess methanol and byproducts. The extraction of biodiesel was conducted using Heidolph Hei-VAP rotavapor at 40℃ and 80 rpm. The biodiesel liquid obtained was weighed, and by using Equation 3 the weight percent of FAME was calculated.

$$\text{Weight percent of FAME} = \frac{\text{Weight of transesterified liquid}}{\text{Weight of spent bleaching oil used}} \times 100\% \qquad [3]$$

Next, the transesterified liquid was further analyzed using GC-FID (Agilent 78790A GC with Zebron ZB-FAME column) to confirm and identify the FAME produced in biodiesel with 37 FAME Standards. The injection volume was 1.5 µl at 250℃, the detection temperature was 260℃, and the column flowrate was 1 ml/min. The initial temperature program was 80℃ for 1.5 minutes and the first ramping rate was 40℃/min until 160℃. The second ramping rate was 5℃/min until 185℃ and the final ramping rate was 30 ℃/min until 260 ℃.

Characterization

Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer System 2000) was used to predict the functional groups of the catalysts by mounting samples on potassium bromide (KBr) standard pellet. FTIR spectra were obtained at a resolution of 8 cm^{-1} and 400- 4000 cm^{-1} scan range. The surface morphology and elemental composition of the catalysts were determined using field- emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FESEM-EDX) (Hitachi Regulus 8220). X-ray diffraction (XRD) patterns of the catalysts were taken on a Bruker Advance D8 diffracto- meter equipped with a copper anode X-ray tube. Characterization was set at 2θ range between 10° and 80° with a step size of 0.005° and a scan speed of 2.0°/ min.

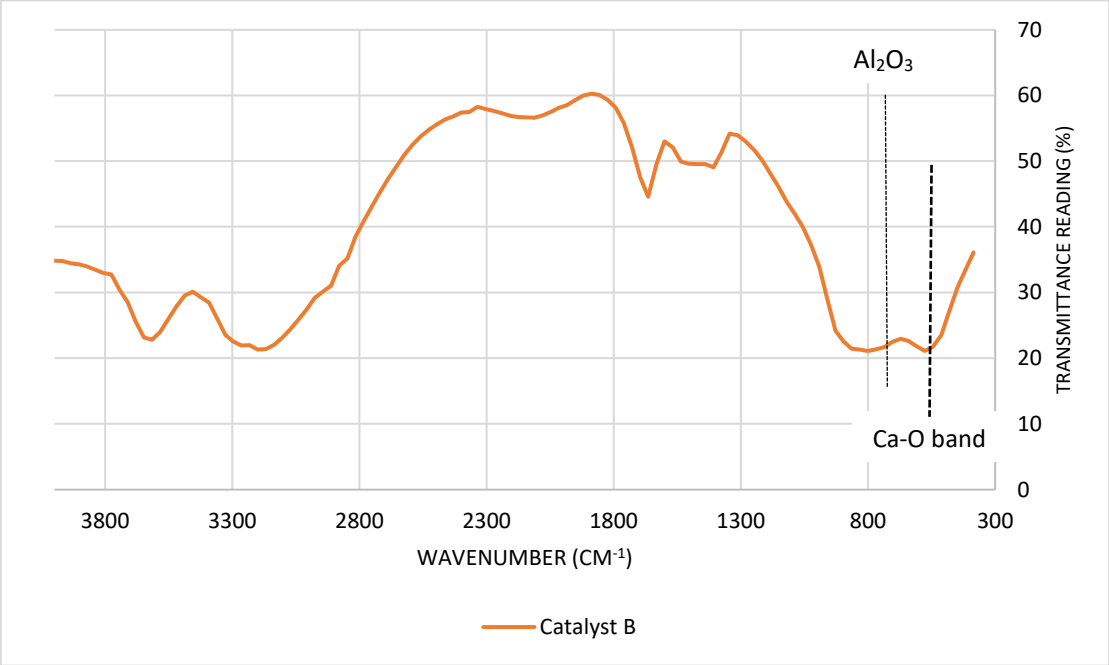


Figure 2. FTIR-KBr spectrum of $CaO/FeO/Al_2O_3$ (Catalyst B).

RESULTS AND DISCUSSION

Characterization of Catalysts

The surface functional groups present on the catalysts were determined by FTIR analysis. Figure 2 shows the FTIR spectrum for $CaO/FeO/Al_2O_3$ (Catalyst B). The presence of a peak at 700 cm^{-1} was due to amorphous structured or disordered defects of Al_2O_3 on the catalyst $CaO/FeO/Al_2O_3$ (Catalyst B). Furthermore, the peak at 512 cm^{-1} corresponded to Ca-O vibration [16].

Figure 3 shows the FTIR spectra for Lala500 and Lala900. There were peaks between 864 cm^{-1} and 1440 cm^{-1} for Lala500 and Lala900, which were attributed to C-O bond since the catalyst might react with CO_2 in the air [17]. Besides, the peak at 1415 cm^{-1} represented $CaCO_3$, which is the basic component of the Asian clamshell. Furthermore, the peak at 512 cm^{-1} corresponded to the strong vibration of Ca-O band [16].

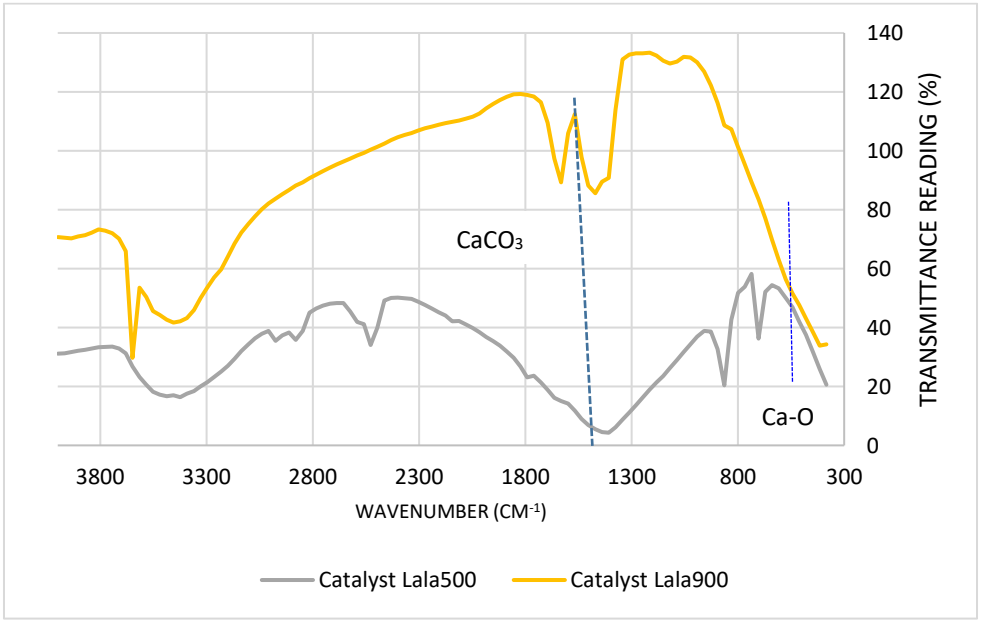


Figure 3. FTIR-KBr spectra of clamshell calcined at 500°C (Lala500) and at 900°C (Lala900).

FESEM-EDX analysis was performed to verify the presence of CaO in the catalysts. Based on Figure 4, the morphology of the particles on the surfaces was irregular in shape and size. As depicted in Figure 4(c), upon calcination of the clamshell of *Paphia undulatus*, a cluster of well agglomerated crystal with obvious edges formed [18].

The EDX analysis was performed to ensure that the active element was present in the catalysts. From Table 2, we can conclude that about 2.27% of calcium, 6.19% of iron, 29.52% of aluminium, 16.37% of carbon, and 45.64% of oxygen were present in $CaO/FeO/Al_2O_3$ catalyst. In Lala500 and Lala900, the percentage of aluminium present was due to the detection from the sample holder during the EDX analysis [19]. Small amounts of carbon were detected in the EDX analysis. This may be ascribed to reagents that were used in the preparation of the catalysts, e.g., carbonate ($[CO_3]^{2-}$), which could remain as impurities in the sample. There was about 27.62% and 62.38% of calcium in Lala500 and Lala900, respectively. The percentage of Ca was shown to increase as temperature increased. This might be due to the growth of the Ca particles which led to agglomeration and sintering when exposed to the higher temperature. The higher composition of calcium in Lala900 might affect the performance of transesterification in biodiesel production.

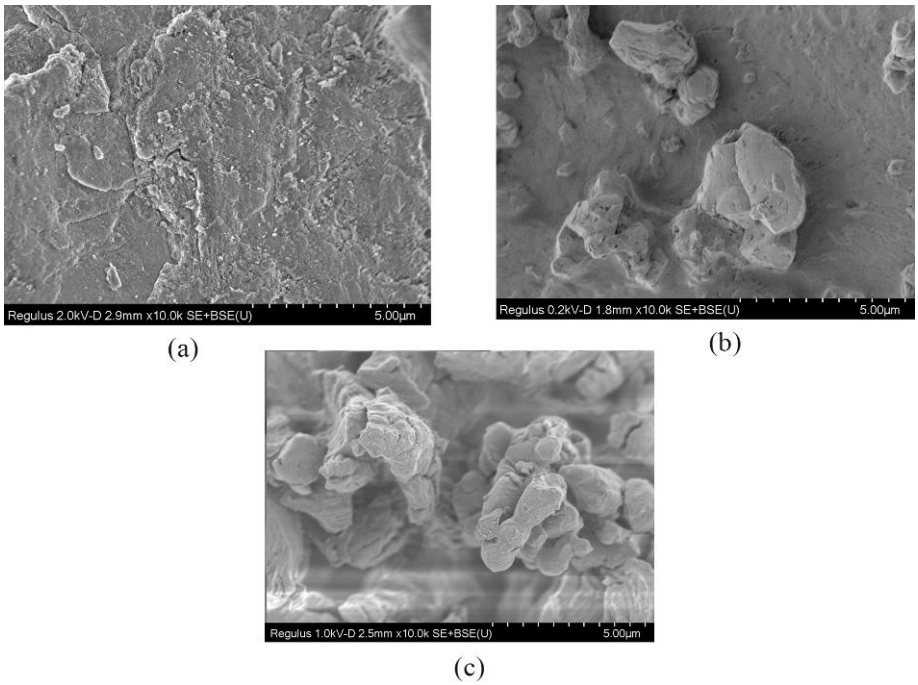


Figure 4. FESEM micrographs of catalysts: (a) $CaO/FeO/Al_2O_3$ (Catalyst B); (b) clamshell calcined at 500℃ (Lala500); and (c) clamshell calcined at 900℃ (Lala900); at 10 000× magnification

Table 2. Elemental composition by EDX analysis of $CaO/FeO/Al_2O_3$ (Catalyst B), clamshell calcined at 500℃ (Lala500) and clamshell calcined at 900℃ (Lala900)

Catalyst	Loading (wt%)				
	Ca	Fe	Al	O	C
$CaO/FeO/Al_2O_3$ (Catalyst B)	2.27	6.19	29.52	45.64	16.37
Lala500	27.62	-	0.41	46.89	11.40
Lala900	62.38	-	0.5	31.03	6.09

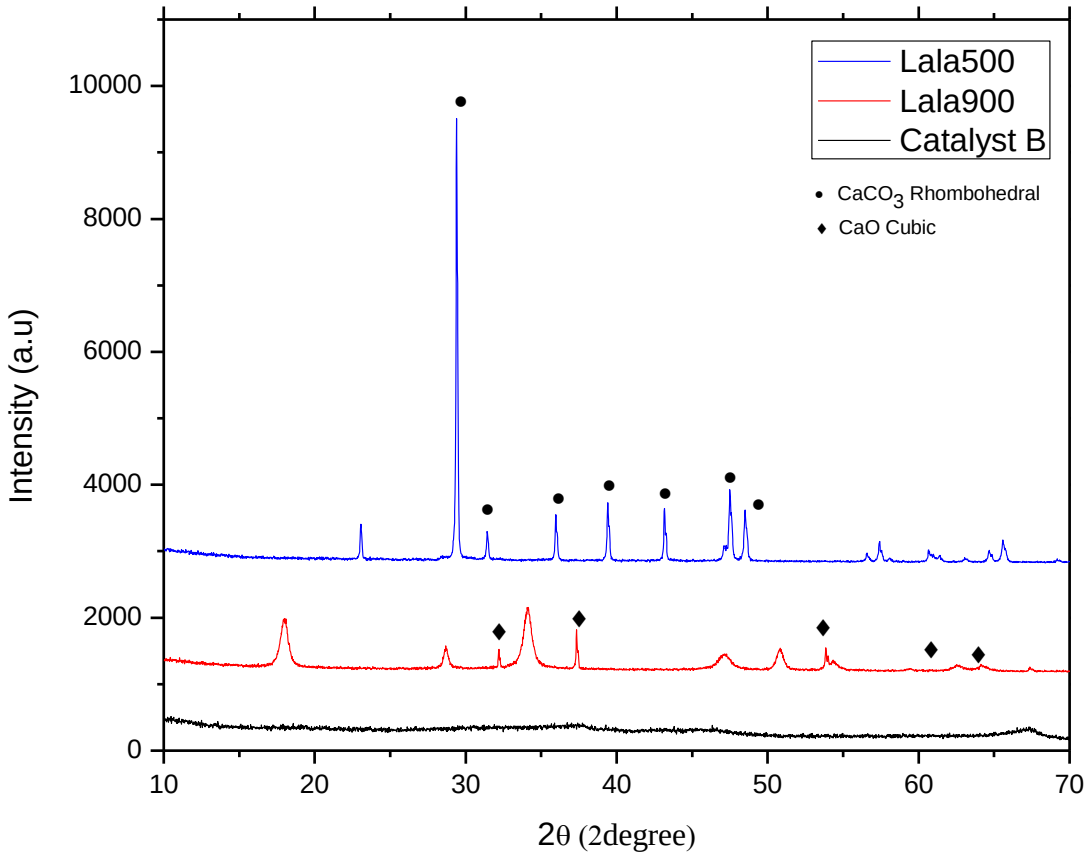


Figure 5. XRD diffractogram of catalyst CaO/FeO/Al_2O_3 (Catalyst B), clamshell calcined at 500℃ (Lala50) and clamshell calcined at 900℃ (Lala900).

Figure 5 shows the XRD patterns of CaO/FeO/Al_2O (Catalyst B), Lala500, and Lala900. The analysis was used to identify the crystal structures and phases in the samples. Based on the analysis of Lala500, rhombohedral $CaCO_3$ was observed at 2Θ(*hkl*) of 29.40 °(104), 31.42 °(104), 35.98 °(300), 39.41 °(113), 43.17 °(202), 47.50 °(018), and 48.49 °(116). As expected, calcination at 900℃ resulted in the conversion of $CaCO_3$ to CaO, as evidenced by the appearance of peaks at 32.62 °(111), 37.43 °(200), 53.84 °(220), and 64.06 °(311). At higher calcination temperatures, no presence of $CaCO_3$ was recorded, which indicates that $CaCO_3$ had reacted and converted to CaO. These results, supported by previous reports, suggest that the calcination temperature of $CaCO_3$ to CaO is in the range of 850–1000°C, due to the highest crystallinity and the formation of a single phase of CaO [20]. Other peaks might also appear due to the formation of $Ca(OH)_2$. Singh et al. [21] mentioned that CaO is easily converted to Ca(OH) by absorbing moisture or water from the surrounding atmosphere. Figure 5 displays the peak of CaO as the dominant mineral composition in the catalyst [22]. This view is also supported by the FTIR and EDX analyses that CaO is the major metal oxide present in the prepared catalyst, which have been proven to possess good activity for transesterification of coconut oil to produce biodiesel.

Extraction Conditions of Coconut Oil

Type of Extraction

In this study, in-situ extraction and Soxhlet extraction were used to determine which method is best to extract oil from coconut pulp. Figure 6 illustrates the percentage of coconut oil extracted from dried coconut pulp using both in-situ extraction and Soxhlet extraction, at 60℃ with the same volume of n-hexane as solvent. From Figure 6, we can conclude that Soxhlet extraction showed the highest percentage (32%) of oil extract from dried coconut pulp compared to in-situ extraction (29%). A step for the separation of the desired solution from the solid waste using vacuum pump was required in in-situ extraction before continuing to the rotary evaporator. Furthermore, in-situ extraction may cause the desired chemical to react with the solid waste (coconut pulp), resulting in a lower yielding product. In in-situ extraction, the coconut pulp was directly heated in n-hexane and this may cause the disruption of cell walls of the coconut pulp and

chemicals such as lignocellulosic substances might react with n-hexane [23]. Moreover, this could also decrease the percentage yield of the product formed. In Soxhlet extraction, since the sample was frequently exposed to the solvent, and the temperature of the extraction was higher than room temperature, thus more analytes could be extracted from the sample. Additionally, no filtration was required, resulting a higher yield than insitu method.

Most researchers recommend the use of Soxhlet extraction compared to in-situ extraction to extract oil from coconut pulp because a small amount of solvent can extract a large quantity of oil. Therefore, we can conclude that Soxhlet extraction shows the best method to extract oil from dried coconut pulp.

Number of Squeezes of Coconut Pulp Waste

Figure 7 shows a higher percentage of oil extraction when the coconut pulp waste was squeezed 3 times. The result showed that by increasing the number of squeezes of the coconut pulp waste more than 3 times, the percentage yield remained constant or no much changes could be seen. According to Senphan & Benjakul et al. (2017), coconut milk is a milky white oil-in-water emulsion and can be extracted from coconut flesh [24]. The oil-in-water emulsion naturally occurs due to the presence of coconut proteins such as globulin and albumin.

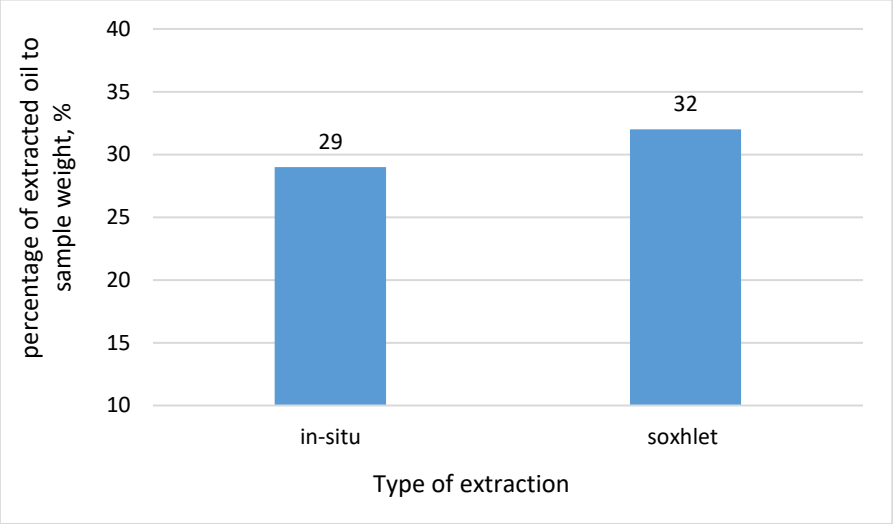


Figure 6. Effect of different types of extraction.

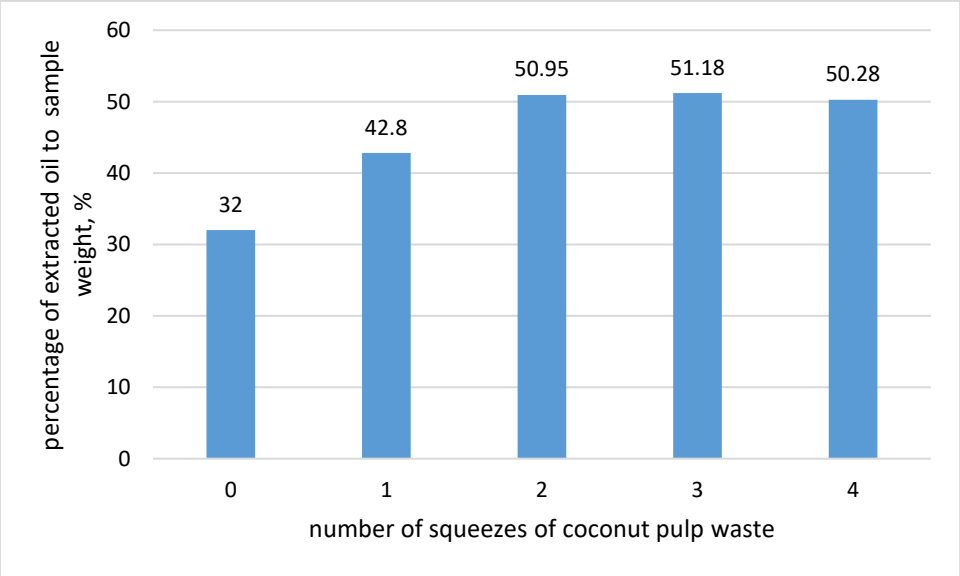


Figure 7. Number of squeezes of coconut pulp waste.

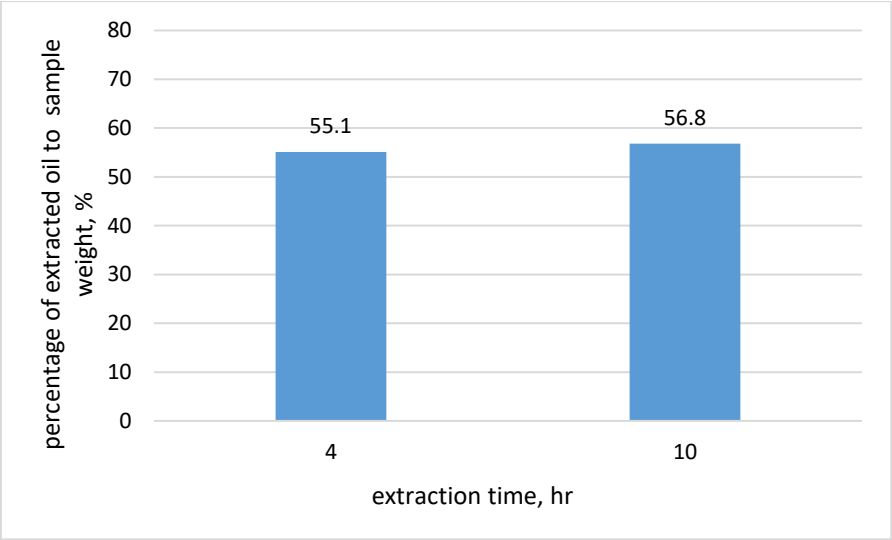


Figure 8. Effect of time of extraction.

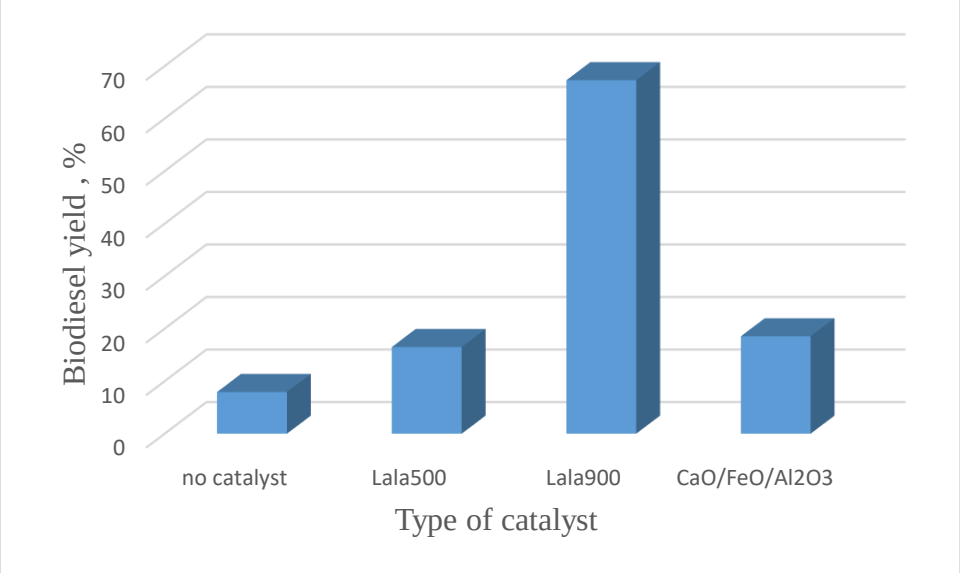


Figure 9. Effect of type of catalyst for biodiesel production.

Effect of Extraction Time

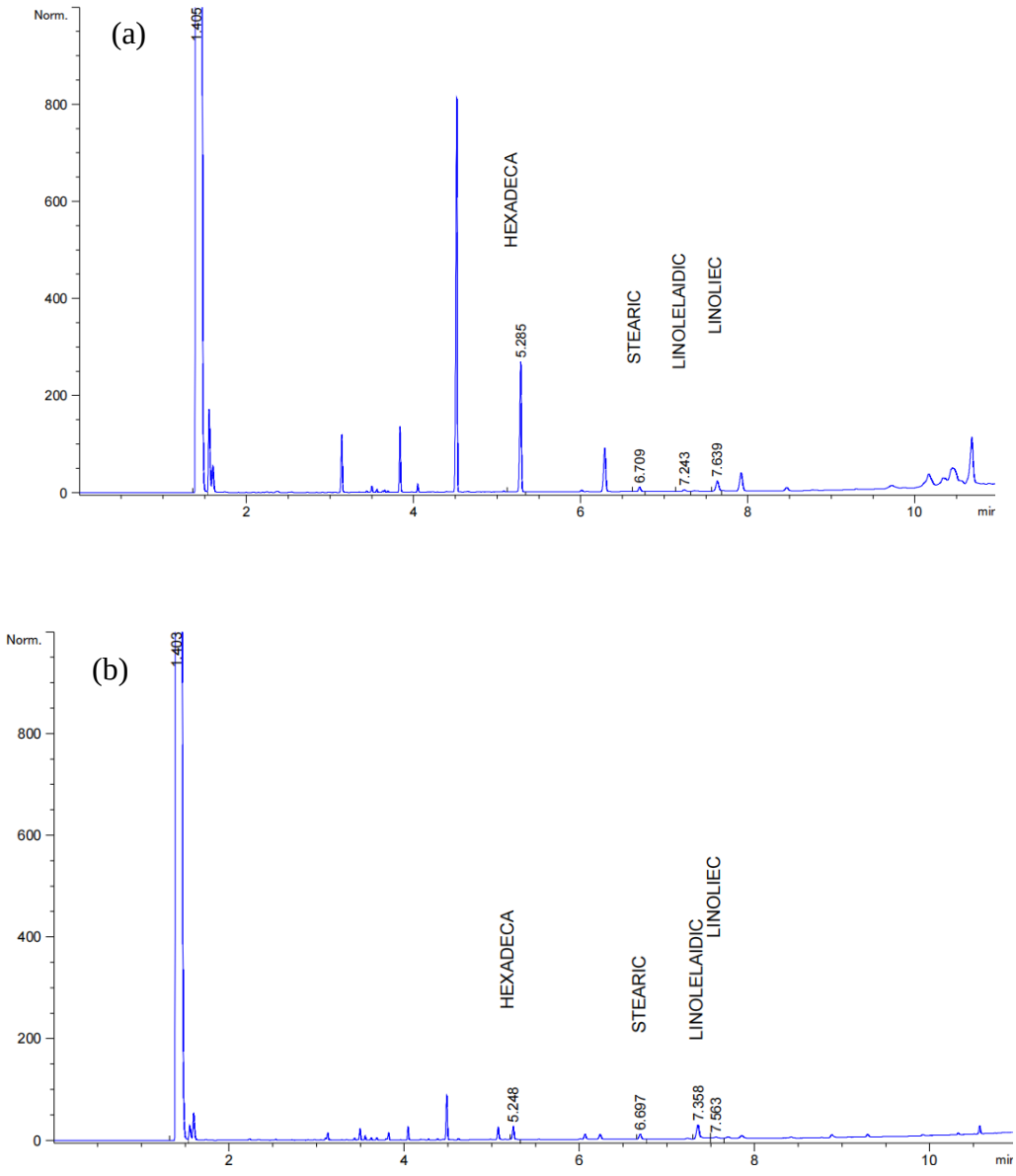
Based on Figure 8, the percentage of extracted oil to solid mass using Soxhlet extraction for 4 hr and 10 hr were 55.1% and 56.8%, respectively. It can be concluded that, increasing the extraction time had no effects on the percentage yield. According to Suwari et al. (2017), the suggested time of extraction using Soxhlet extractor is between 3 to 5 hours [25]. Therefore, 4 hours was chosen as the optimum due to the difference in percentage oil yield at longer times was not highly significant.

Transesterification of Coconut Oil into Biodiesel

Type of Catalyst Used

After oil was obtained through Soxhlet extraction, it was then proceeded with transesterification process for biodiesel production. As shown in Figure 9, percentage yields of biodiesel using $CaO/FeO/Al_2O_3$ (Catalyst B), clamshell calcined at 500℃ (Lala500), and clamshell calcined at 900℃ (Lala900) were 18.54%, 16.49% and 67.30%, respectively. According to Jayakumar et al. (2021), calcination at higher

temperatures for 4 hours can activate Ca^{2+} ions present in CaO and convert waste shells into a heterogeneous base catalyst [26]. These results are in agreement with the XRD analysis, which showed the formation of CaO at a higher calcination temperature. Awogbemi et al. (2021) reported that calcination of wastes at appropriate temperatures and time lead to improved conversion efficiency during transesterification [27]. The higher activity of Lala900 than the other catalysts maybe due to strong basic properties, which resulted in the increase in biodiesel production. Besides, from a previous study, coconut oil conversion into biodiesel using a homogeneous catalyst, KOH reported conversion up to 60% of biodiesel yield [28]. Budhwani et al., (2019) [29] obtained 70% of biodiesel yield from crude coconut oil using enzymatic transesterification. The biodiesel obtained from this study was 67%, which is quite high, thus showing Lala900 has a potential as a catalyst in transesterification.



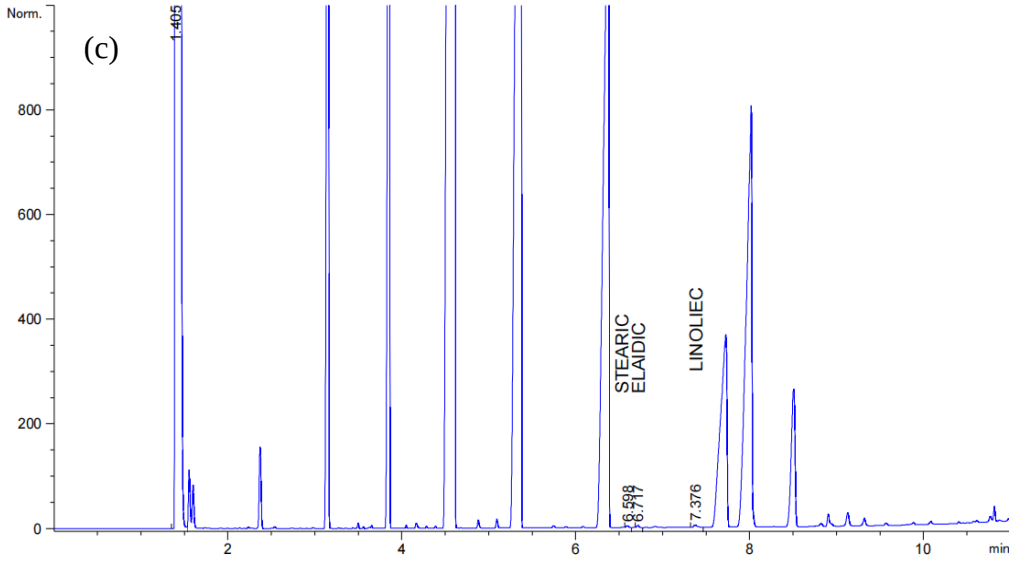


Figure 10. Characterization of biodiesel using gas chromatography-flame ion detector (GC-FID) for (a) $CaO/FeO/Al_2O_3$ (Catalyst B), (b) clamshell calcined at 500°C (Lala500) and (c) clamshell calcined at 900°C (Lala900).

Table 3. Fatty acid methyl ester (FAME) composition of biodiesel.

Catalyst	Reference Retention time (min)	Retention time (min)	ID (Peak)	Fame compound
B ($CaO/FeO/Al_2O_3$)	5.40	5.285	C16:0 (12)	Hexadecanoic Acid Methyl Ester
	6.80	6.709	C18:0 (16)	Stearic Acid Methyl Ester
	7.20	7.243	C18:2 (19)	Linolelaidic Acid Methyl Ester
	7.40	7.639	C18:2 (20)	Linoliec Acid Methyl Ester
Lala500	5.40	5.243	C16:0 (12)	Hexadecanoic Acid Methyl Ester
	6.80	6.697	C18:0 (16)	Stearic Acid Methyl Ester
	7.20	7.358	C18:2 (19)	Linolelaidic Acid Methyl Ester
	7.40	7.563	C18:2 (20)	Linoliec Acid Methyl Ester
Lala900	6.60	6.598	C18:0 (16)	Stearic Acid Methyl Ester
	6.80	6.717	C18:1 (17)	Elaidic Acid Methyl Ester
	7.40	7.376	C18:2 (20)	Linoliec Acid Methyl Ester

Characterization of Oil

In this study, coconut oil was obtained after extraction from coconut pulp. Major fatty acids found in coconut oil include lauric acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, and stearic acid. Lauric acid is 12 carbons in length, while other fatty acids are 16 and 18 carbons in length [30]. The analysis results of the biodiesel were compared, and the composition of fatty acids is tabulated in Table 3.

The identified FAME were hexadecanoic acid, stearic acid, linoliec acid, and linolelaidic acid. Based on the chromatogram, Lala900 showed higher FAME intensities compared to the other catalysts, supporting the catalytic activity result that showed a higher FAME yield using Lala900.

CONCLUSION

$CaO/FeO/Al_2O_3$ and *Paphia undulatus* were found to be potential catalysts in transesterification reaction for conversion of pulp waste into biodiesel. FAME yield of 67% was obtained at a temperature of 55°C in 2 hours using a calcium oxide-based catalyst. This study revealed the potential of coconut pulp waste to be converted into energy, and the valorization of biomass waste represents an eco-friendly approach to maximize the generation of energy while solving the waste management issue.

ACKNOWLEDGEMENT

This work was supported by Universiti Sains Malaysia, Special (Matching) Short Term Grant with Project No: 304/PKIMIA/6315704.

REFERENCES

1. Syafiuddin, A., Chong, J. H., Yuniarto, A. & Hadibarata, T. (2020) The current scenario and challenges of biodiesel production in Asian countries: A review. *Bioresource Technology Reports*, **12**, 100608.

2. Hamza, M., Ayoub, M., Shamsuddin, R. B., Mukhtar, A., Saqib, S., Zahid, I., Ameen, M., Ullah, S., Al-Sehemi, A. G. & Ibrahim, M. (2021) A review on the waste biomass derived catalysts for biodiesel production. *Environmental Technology & Innovation*, **21**, 101200.

3. Galadima, A. & Muraza, O. (2020) Waste materials for production of biodiesel catalysts: Technological status and prospects. *Journal of Cleaner Production*, **263**, 121358.

4. Yaakob, Z., Mohammad, M., Alherbawi, M., Alam, Z. & Sopian, K. (2013) Overview of the production of biodiesel from Waste cooking oil. *Renewable and Sustainable Energy Reviews*, **18**, 184–193.

5. Vasudevan, P. T. & Briggs, M. (2008) Biodiesel production—current state of the art and challenges. *Journal of Industrial Microbiology & Biotechnology*, **35(5)**.

6. Tran, D. T., Chang, J. S. & Lee, D. J. (2017) Recent insights into continuous-flow biodiesel production via catalytic and non-catalytic transesterification processes. *Applied Energy*, **185**, 376–409.

7. Moazeni, F, Chen, Y. -C, Zhang, G. (2019) Enzymatic transesterification for biodiesel production from used cooking oil, a review. *Journal of Cleaner Production*, **216**, 117–128.

8. Mlay, H., Katima, J. & Minja, R. J. A. (2014) Modifying Plant Oils for Use as Fuel in Rural Contexts Tanzania: Techno-Economic Analysis. *Open Journal of Modelling and Simulation*.

9. Konwar, L. J., Boro, J. & Deka, D. (2014) Review on latest developments in biodiesel production using carbon-based catalysts. *Renewable and Sustainable Energy Reviews*, **29**, 546–564.

10. Nor, N. A. A. M, Ariff, E. E. E, Omar, N. R. N., Abidin, A. Z. Z, Muhammad, R. M. M., Rahim, H., Nazmi, M. S. and Sulaiman, N. H. (2022) Total productivity and technical efficiency of coconuts in Malaysia. *Economic and Technology Management Review*, **15**, 11–22.

11. Suman, S. & Gautam, S. (2017) Pyrolysis of coconut husk biomass: Analysis of its biochar properties. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, **39(8)**, 761–767.

12. Sulaiman, S., Abdul Aziz, A. R, Aroua, M. K. (2013) Reactive extraction of solid coconut waste to produce biodiesel. *Journal of the Taiwan Institute of Chemical Engineers*, **44**, 233-–238.

13. Niyas, M. M., Shaija, A. (2023) Biodiesel production from coconut waste cooking oil using novel solar powered rotating flask oscillatory flow reactor and its utilization in diesel engine. *Thermal Science and Engineering Progress*, **40**, 101794.

14. Girish, N., Niju, S. P., Begum, K. M. M. S, Anantharaman, N. (2013) Utilization of a cost-effective solid catalyst derived from natural white bivalve clam shell for transesterification of waste frying oil. **111**, 653–658.

15. Risso, R., Ferraz, P., Meireles, S., Fonseca, I., Vita, J. (2018) Highly active Cao catalysts from waste shells of egg, oyster and clam for biodiesel production. **567**, 56–64.

16. Roy, A. & Bhattacharya, J. (2011) Microwave-assisted synthesis and characterization of CaO nanoparticles. *International Journal of Nanoscience*, **10(03)**.

17. Liu, T., Zhu, Y., Zhang, X., Zhang, T., Zhang, T. & Li, X. (2010) Synthesis and characterization of calcium hydroxide nanoparticles by hydrogen plasma-metal reaction method. *Materials Letters*, **64(23)**, 2575–2577.

18. Mazaheri, H., Ong, H. C., Masjuki, 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.

19. Djebaili, K., Mekhalif, Z., Boumaza, A. & Djelloul, A. (2015) XPS, FTIR, EDX, and XRD Analysis of Al_2O_3 Scales Grown on PM2000 Alloy. *Journal of Spectroscopy*, **2015**, 1–16.

20. Kamalanathan, P., Ramesh, S., Bang, L. T., Niakan, A., Tan, C. Y., Purbolaksono, J., Chandran, H., Teng, W. D. (2014) Synthesis and sinter-ing of hydroxyapatite derived from egg-

shells as a calcium precursor. *Ceram Int*., **40(10)**, 16349–16359.

21. Singh, A. (2012) Hydroxyapatite, a biomaterial: its chemical synthesis, characterization and study of biocompatibility prepared from shell of garden snail, Helix aspersa. *Bull Mater Sci*., **35(6)**, 1031–1038.

22. Nath, B., Das, B., Kalita, P. & Basumatary, S. (2019) Waste to value addition: Utilization of waste Brassica nigra plant derived novel green heterogeneous base catalyst for effective synthesis of biodiesel. *Journal of Cleaner Production*, **239**, 118112.

23. Archana, A., Singh, M. K., Chozhavendhan, S., Gnanavel, G., Jeevitha, S. & Pandian, A. M. K. (2020) Coconut Shell as a Promising Resource for Future Biofuel Production. *Energy, Environment, and Sustainability*, 31–43.

24. Senphan, T. & Benjakul, S. (2016) Comparative Study on Virgin Coconut Oil Extraction Using Protease from Hepatopancreas of Pacific White Shrimp and Alcalase. *Journal of Food Processing and Preservation*, **41(1)**, 12771.

25. Suwari, Kotta, H. Z. & Buang, Y. (2017) Optimization of soxhlet extraction and physico-chemical analysis of crop oil from seed kernel of Feun Kase (Thevetia peruviana). *AIP Conference Proceedings*, **1911**.

26. Jayakumar, M., Karmegam, N., Gundupalli, M. P., Bizuneh Gebeyehu, K., Tessema Asfaw, B., Chang, S. W., Ravindran, B. & Kumar Awasthi, M. (2021) Heterogeneous base catalysts: Synthesis and application for biodiesel production – A review. *Bioresource Technology*, **331**, 125054.

27. Awogbemi, O., Kallon, D. V. V. & Aigbodion, V. S. (2021) Trends in the development and utilization of agricultural wastes as heterogeneous catalyst for biodiesel production. *Journal of the Energy Institute*, **98**, 244–258.

28. Sulaiman, S., Raman, A. A. A., Aroua, M. K. (2010) 2nd International Conference on Chemical, Biological and Environmental Engineering, **254**.

29. Budhwani, A. A. A., Maqbool, A., Hussain, T., et al. (2019) Production of biodiesel by enzymatic transesterification of non-edible *Salvadora persica* (Pilu) oil and crude coconut oil in a solvent-free system. *Bioresour. Bioprocess.*, **6**, 41. https://doi.org/10.1186/s40643-019-0275-3.

30. Zhang, J. (2019) Fatty Acid Methyl Esters (FAMEs) Analysis on an Agilent 8890 GC and Its Application to Real Samples. *Application Note Food Testing Fatty*, **5994–0549**, 1–8.