Eng. Sci., 2024, **28**, 1053

Engineered Science
DOI: https://dx.doi.org/10.30919/es1053

Two-step Biodiesel Production from Black Acid Oil Waste Using Calcium Oxide from Charcoal Ash as a Catalyst

Jindaporn Jamradloedluk[1,#] and Somsuk Trisupakitti[2,#,*]

Abstract

Black acid oil is a liquid waste from the production of coconut oil. Here we used this waste to synthesize biodiesel by two-step reaction: esterification and transesterification. Charcoal ash was calcined to obtain a CaO-based catalyst. The black acid oil was heated to evaporate and esterified to reduce the amount of Free Fatty Acid (FFA) to less than 2% before transesterification. The results showed that calcium oxide (CaO) from charcoal ash incineration increased with increasing temperature and calcination time at 1000 °C and 240 min, the maximum calcium oxide content was 85%. FFA in black acid oil decreased from 82% to 1.8% from esterification using a 18:1 v/v methanol:oil ratio, catalyst concentration as 5% w/w, 60 °C and 180 min. Transesterification at a 12:1 v/v methanol:oil ratio, catalyst concentration as 3% w/w, 60 °C and 60 min gave the highest yield of biodiesel equal to 81%. Properties of the biodiesel obtained from black acid oil in the transesterification lay within the specified standards, except for the viscosity value, which is higher than the standard value.

Keywords: Biodiesel; Esterification; Transesterification; Black acid oil.
Received: 22 September 2023; Revised: 01 December 2023; Accepted: 04 December 2023.
Article type: Research article.

1. Introduction

At present, energy consumption is continuously increasing in line with economic growth rate thus the energy demand increases. Especially fuel energy, in the form of refined oil, is in high demand, and is an important proportion in the transportation and industrial sectors of every country. Much of the oil comes from depleted fossil fuels with declining reserves and is likely to run out in the near future.[1,2] Therefore government agencies are pushing the search for new energy sources to replace existing ones. Biodiesel therefore plays an important role, because it has similar properties to petroleum and can be used in diesel engines without modification.[3-8] Biodegradable low emissions to the environment in the form of carbon dioxide or sulfur provide complete combustion. The exhaust gas has better quality than that from combustion of diesel fuel, and is therefore environmentally friendly.

The raw materials for biodiesel production are vegetable oils, animal fats and short chain alcohols. The oils most used for biodiesel production are derived from rapeseed,[9] soybean,[10] palm,[11] jatropha,[12] and sunflower,[13] although other oils are also used, including waste cooking oil,[14,15] and also animal fats.[16-19] Transesterification uses an alcohol (e.g. methanol, ethanol) to chemically break the molecule of the renewable feedstock into methyl or ethyl esters (biodiesel) with glycerol as the only by-product.[20] The transesterification reaction is represented by the general overall reaction shown in Fig. 1.

Biodiesel is an alternative energy source synthesized by transesterification of vegetable oils or animal fats, containing triglyceride organic compounds, using acids or bases as catalysts to convert oil molecules into alkyl esters.[21] Catalysts, reviewed by researchers,[22-24] include homogeneous catalysts such as sodium hydroxide,[25] potassium hydroxide,[26] sulfuric acid,[27] and hydrochloric acid *etc*.[28] Heterogeneous catalysts, for example various single metal oxides (MgO, CaO, SnO_2, ZnO, CeO_2, ZrO_2 (mixed metal oxides, zeolites, Al–Mg hydrotalcites, have also been used.[29]

The homogeneous catalyst, NaOH, is commonly used due to its rapid solubility in methanol, so the reaction is faster than with acids.[30] For this reason, water is required to flush the product, which wastes energy to separate the catalyst from the product. Further large quantities of contaminated washing

---

[1] *Solar Energy and Energy Resources Research Unit, Faculty of Engineering, Mahasarakham University, Kantharawichai District, Maha Sarakham 44150, Thailand.*

[2] *Chemistry Department, Faculty of Science and Technology, Rajabhat Maha Sarakham University, Mueang District, Maha Sarakham 44000, Thailand.*

[#] *These authors contributed to this work equally.*

**Email:* somsukrmu@gmail.com (S. Trisupakitti)

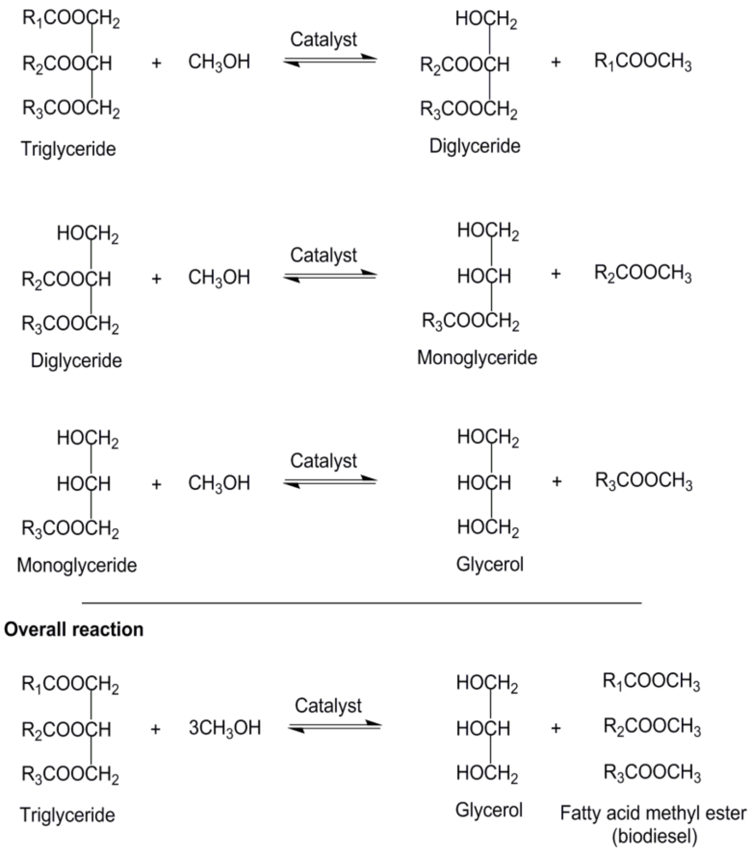


Fig. 1 The overall transesterification reaction of triglyceride. Reproduced with the permission from [20], Copyright 2016 Elsevier Ltd.

water affect the environment and waste energy in the needed wastewater treatment.[31,32] Easy to restore and reuse, CaO is a natural solid base catalyst, easily extracted from waste, such as eggshells, containing $CaCO_3$, which is readily converted to CaO through high-temperature calcination. Thus, CaO is an inexpensive, environmentally safe, non-corrosive, eco-friendly, substance, which is very active, under mild conditions and can be regenerated.[33-36] $CaCO_3$ in eggshells, when calcined at sufficiently high temperatures (700 – 1,000 °C) converts to CaO.[37] Natural CaO can be used as a substitute for commercial catalysts for biodiesel production and in addition to being useful as a catalyst, its production from waste increases the value of the waste as well. However, CaO has some limitations, particularly easy gelation in methanol and a low specific surface or active site area, resulting in a decrease in catalytic efficiency.[38,39]

2. Experimental section

Black Acid Oil (BAO) was obtained Saengsook Industry Company and was filtered to remove impurities. All chemicals used in the experiments such as methanol of 99% purity and sulfuric acid (95%) were of analytical reagent grade.

2.1 Preparation of calcium oxide from charcoal ash by calcination

The biomass was burned in the atmosphere to form ash at the bottom of the stove; the ash sieved through a 40 mesh sieve into a crucible and closed tightly; then calcined in a muffle furnace model Carbolite RHF1600, Germany at 700, 900 and 1,000 °C for 120 min and at 1000 °C for 240 min. The ash was stored in a zip-lock bag to prevent moisture adsorption and stored in a desiccator with silica gel.

2.2 Black acid oil preparation

The raw black acid oil was first filtered through a white cloth folded in five layers to remove impuritie. It was then boiled to expel water (boil, 60 min). After that, the oil was cooled and vacuum filtered through 110 mm filter paper and the oil properties were checked.

2.3 Acid-catalyzed esterification process

The objective of the first step is to reduce free fatty acid of the black acid oil to about 2%. The black acid oil (300 g) was poured into the reactor. The reaction mixtures consist of black acid oil, 99% methanol and 95% sulfuric acid. Sulfuric acid catalyst was added in 0.5%, 0.75% and 1.5% concentrations (w/w) of the mass of oil in methanol and then added to the reactor. The methanol and oil mixtures in 6:1, 18:1 and 21:1 v/v ratios were added to reactor. The reaction temperature was 30 ^{o}C and time was 120 min. After completion of the reaction, the mixture was allowed to settle for 24 h. Then, gumming, methanol and water fraction at the bottom layer was removed. FFA of the product was determined by titration. The condition produced the least free fatty acid was selected and used for the base catalyzed trans-esterification reaction.

2.4 Base-catalyzed trans-esterification process

In the second step, optimal CaO concentrations were investigated. Firstly, the oil from the first step was poured into the reactor. CaO powder, at 1.0% to 7.0% (w/w) as a catalyst, was added to a 200 g mass of methanol and oil mixture (12:1 v/v) and poured in the reactor, which was heated to 60 °C, slightly less than the methanol boiling point – 68 °C, 60 min reaction time. After completion of the reaction, the mixture was allowed to settle for 24 h. The mixing of CaO and methanol settles at the bottom of the funnel, where is small amount of catalyst, methanol and glycerol are in the upper biodiesel layer. The upper layer was collected for further purification by washing with hot water. After final washing and drying, the yield of biodiesel and its properties were determined.

2.5 Investigation of properties of acid black oil

Free Fatty Acid (FFA) – 25 mL 0.1 N NaOH solution was placed in a burette and 50 mL isopropyl alcohol placed in a 250 mL conical flask to which a few drops of 0.1 N NaOH solution was added. 10 g oil was added to the conical flask, shaken well and heated to 60 °C. Then, the mixture was allowed to cool at room temperature and titrated against 0.1 N NaOH from the burette using phenolphthalein indicator. The volume of NaOH used in the titration to obtain a pink solution as Fig. 2a, was recorded and used to calculate the free fatty fraction as in Equation (1):

$$\%\mathrm{FFA} = \frac{\mathrm{V_{NaOH}\ x\ 0.1\ x\ 28.2}}{\mathrm{W_{oil}}} \tag{1}$$

where, V is the volume of NaOH used (mL) and W is the mass of oil used (g).

Density – The mass of oil needed to fill a volumetric flask was determined by difference and the density calculated as in Equation (2):

$$\mathrm{Density} = \frac{\mathrm{W_{oil}}}{\mathrm{V_{flask}}} \tag{2}$$

where, W is the mass of oil (g) and V is the volume of Pycnometer (mL).

Viscosity – Viscosity was measured by timing the flow of a fixed volume of oil in a Cannon-Fenske Viscometer TUBE No. 100/32 (Direct type) and converting to viscosity using the calibration constant. The viscometer tube was held in a water-bath at 40°C for at least 20 min. From Fig. 2b, record the time and calculate the kinematic viscosity as in Equation (3):

$$V = \mathrm{Ct} \tag{3}$$

where, V is kinetic viscosity (centistoke, cSt), C is calibration factor of the bulb of the viscometer tube used for testing (cSt/s) and t is the time (s).

Flash point – The flash point of a volatile liquid is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Pensky-Marten's closed cup tester measures the lowest temperature at which the application of the test flame causes the vapor above the biodiesel sample to ignite. It is used to assess the overall flammability hazard of the biodiesel. Specifically, the flash point is used in safety regulations to define the "flammable" and combustible materials. Higher values indicate materials that are less likely to ignite accidentally. Flash point experiment is shown in Fig. 2c.

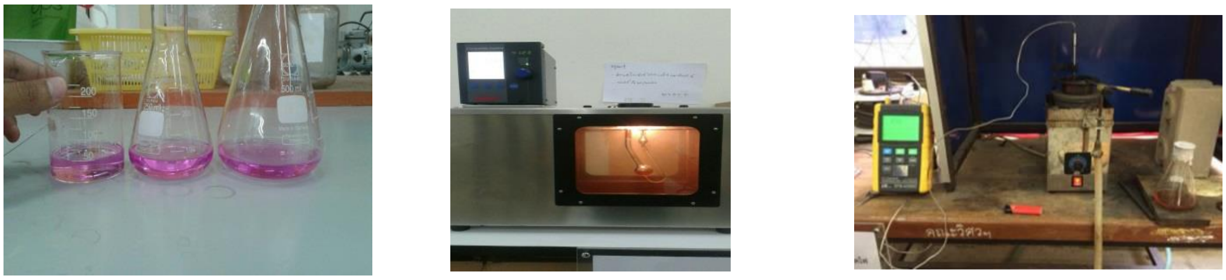
Heating value – was determined using Bomb calorimeter brand GALLENKAMP model ADIAMBATIC using firing cotton model CBA-535-B, length 10 cm, crucible type nickel-chromium type model CBA-450-C and water jacket thermometer model THL-630-070N.

3. Results and discussion

We produced biodiesel from black acid oil by a two-step chemical process. The first step esterifies the oil using sulfuric acid as a catalyst to reduce the free fatty acid content. After that, the oil obtained from the optimal esterification (in the conditions giving the least amount of free fatty acid) was then passed through transesterification using CaO as a catalyst to determine the biodiesel oil yield and its properties.

3.1 Preparation of CaO from charcoal ash by calcination

When the ash obtained from burning charcoal was examined by an X-Ray diffractrometer. Peaks for $CaCO_3$ were found at 2θ angles = 24.1, 29.5, 36.2, 39.4, 43.3, 47.8 and 48.6 with sub-peaks at angles 2θ = 31.5, 56.7, 57.7, 61.7, 63.2, 64.9, 66.0, 70.5, 73.2, 76.5, 77.5, 82.0, 84.0 and 85.2. CaO has main peaks at 2θ = 32.2, 37.5, 54.0, 64.5 and 67.5, see Fig. 3, which are the X-ray diffraction positions corresponding to CaO,[40,41] and when burning charcoal ash at 700 °C for 120 min, the X-ray diffraction pattern of calcium oxide was not different from unburned charcoal ash with CaO 8% but when calcined at 900-



(a) %FFA (b) Viscosity (c) Flash point

Fig. 2 Apparatus used to determine the properties of sampled oils.

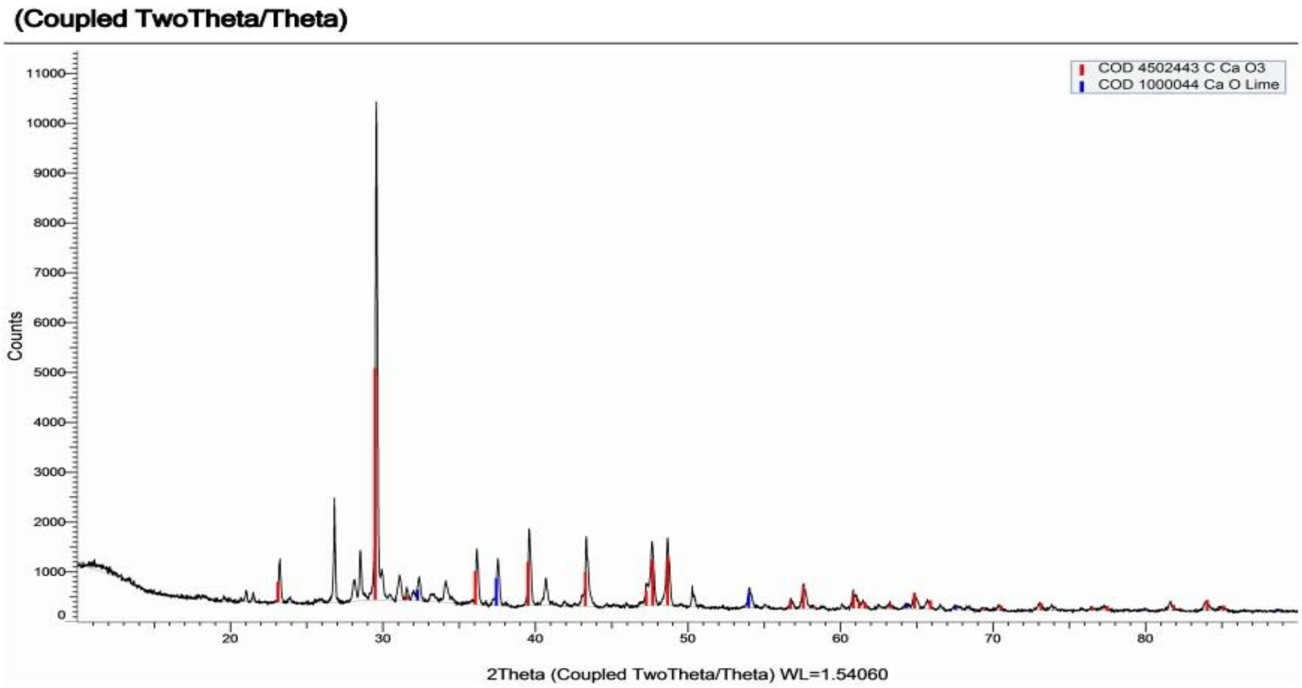


Fig. 3 XRD pattern of uncalcinated charcoal ash.

1,000 °C for 120 min, CaO peaks increased by 61% to 66%, when the calcination time was increased to 240 min at 1,000 °C as Fig. 4. The CaO amount increased by 85%, accompanied by a corresponding decrease in all CaCO$_3$ peaks. The calcium oxide peak at -2Theta angle = 38.5 is the highest concentration as Fig. 4. CaO catalyst prepared from charcoal ash is shown in Fig. 5.

3.2 Properties of acid black oil

The initial properties of the black oil were measured before processing – see Table 1. Viscosity, FFA and densities were very high, whereas the calorific value and the flash point were in the low range and cannot bring oil into the transesterification. The amount of free fatty acids is an important factor in biodiesel synthesis, because values greater than 2 – 2.5% will cause lower yields, because saponification will form soap in the product.[12] Therefore, the esterification step is necessary to reduce free fatty acid content first.

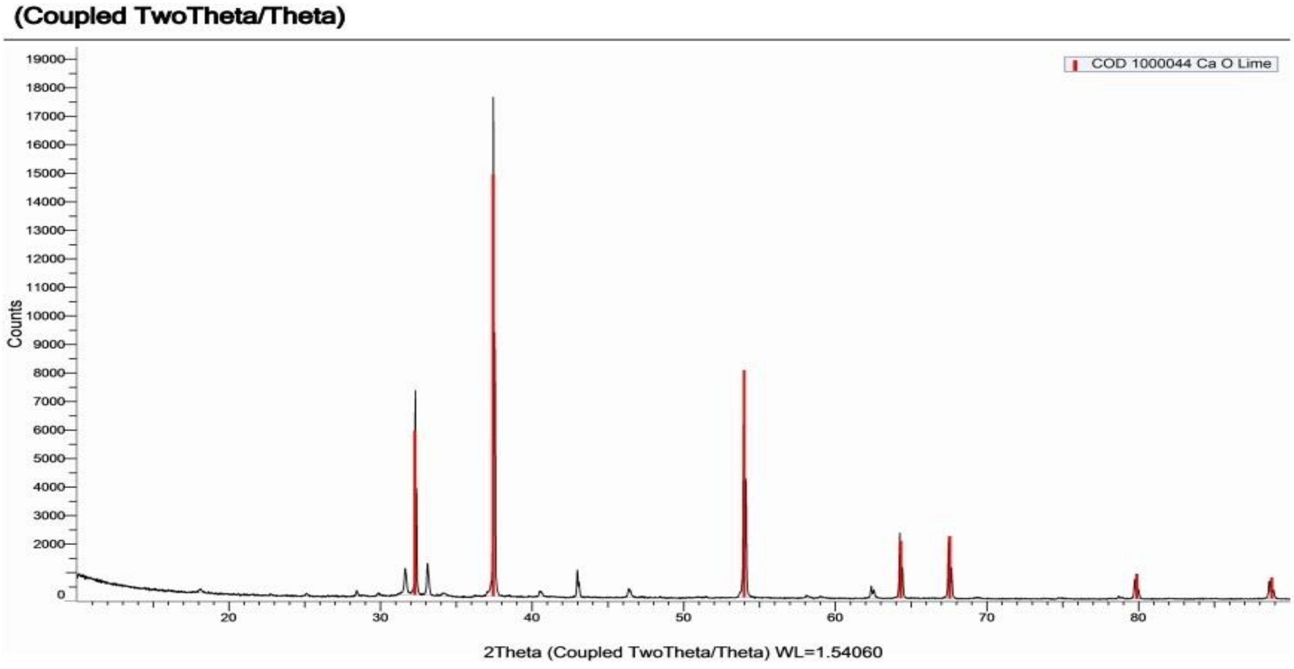


Fig. 4 XRD pattern of charcoal ash calcined at 1000 °C, 240 min (CaO 85%).

Fig. 5 CaO catalyst prepared from charcoal ash.

Table 1. Physicochemical properties of black acid oil.

Properties	Measured value
Density (kg/m^3)	0.9109 ±0.1
Viscosity (mm^2/s)	37.04±0.02
Flash point (^{O}C)	213.3±0.1
Calorific value (MJ/kg)	29,806.03±0.26
Free Fatty Acid (FFA)	82.2±0.2

3.3 Esterification

We varied the oil: methanol ratio and catalyst loading to determine optimal esterification conditions at 60 °C – just less than the methanol boiling point, with results shown in Table 2.

Table 2. Final Free Fatty Acid levels *vs* Esterification Conditions.

Parameter	Condition						
	1	2	3	4	5	6	7
MeOH: oil ratio, v/v	6:1	18:1	21:1	12:1	15:1	18:1	18:1
H_2SO_4 (%w/w)	0.5	1.5	0.75	5	5	3	5
Reaction time (min)	120	120	120	180	180	180	180
Free Fatty Acid (FFA)	25.3	2.5	2.7	2.66	2.0	2.4	1.8

Table 2 shows that free fatty acids could be reduced to < 1.8% under the conditions in the highlighted column. The triglyceride was hydrolyzed to convert FFAs and alcohols according to Equation (4).[42]

Triglyceride + Water = FFA + low weight molecular alcohols (4)

In Fig. 6, it can be seen after esterification, the mixture separated into two phases: The top layer was lighter and represented the biodiesel, whereas the darker lower phase represented glycerine. From Fig. 7 shows black acid oil before esterification (Fig. 7a) and after esterification (Fig. 7b).

3.4 Transesterification

Figure 8 shows the oil after transesterification using the CaO catalyst. Fig. 8a, separation of the biodiesel (top) and glycerol (bottom) layers as by-products of the reaction, and Fig. 8b shows the biodiesel washed with water: the water layer became turbid with contaminants removed from the biodiesel.

Fig. 6 Separation after esterification.

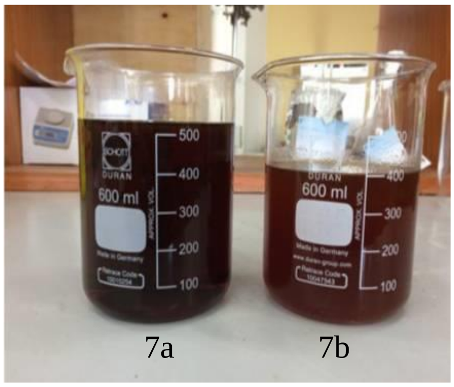


Fig. 7 Black acid oil before esterification (7a) and after esterification (7b).

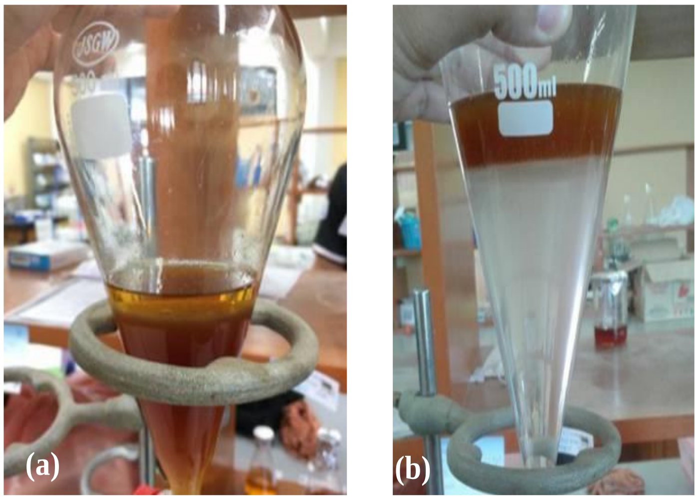


Fig. 8 Biodiesel from transesterification and washing, a) From transesterification, b) After methyl ester washing.

Transesterification conditions were 60 °C, 60 min, 12:1 methanol to oil v/v, 1–7% w/w catalyst, the percentage results are shown in Fig. 9.

Figure 9 shows that using 3% w/w catalyst at 60 °C for 60 min, with methanol to oil at 12:1 v/v gave the highest methyl ester yield of 76%. When the catalyst was increased to 5% and 7%, the yield of actually decreased. It is believed that inadequate diffusion of the active species on the catalyst surface was caused by the crystallization or agglomeration of Ca compounds,[43] resulting in ineffective mixing, due to high viscosity leading to significantly lower yield. Thus, higher catalyst loading made the catalyst less accessible or less active. Makes the precursor more viscous the chance of entering a reaction between the reactants is less resulting in reduced product content.[44,45]

Figure 10 illustrates the process of CaO-catalyzed transesterification, as described in reference.[46] Initially, methanol undergoes proton removal by basic sites, resulting in the formation of a methoxide anion. Subsequently, the methoxide anion interacts with the carbonyl carbon of the triglyceride, leading to the formation of an alkoxy carbonyl intermediate. This intermediate then undergoes a transformation into a more stable structure known as fatty acid methyl ester (FAME) and an anion of diglyceride. The methoxide cation attracts the anion of a diglyceride, resulting in the formation of a diglyceride. This sequence is repeated twice for the carbon chain of fatty acids (R_2 and R_3).

3.5 Physicochemical properties of biodiesel

Properties of methyl esters obtained from transesterification, including density, viscosity, flash point and calorific value, were measured.

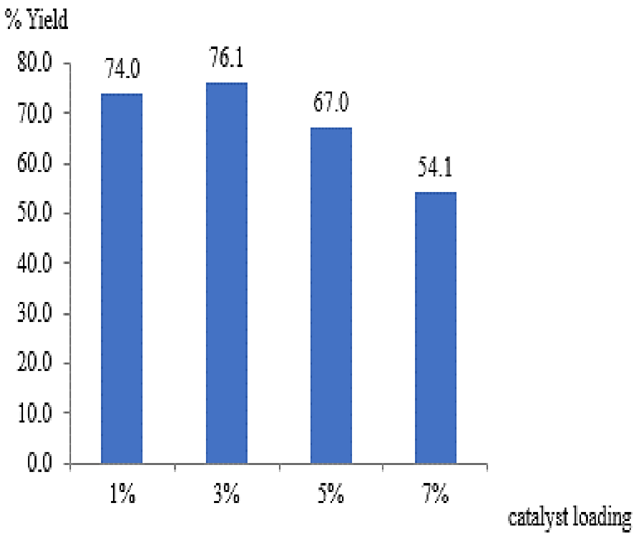


Fig. 9 Effect of catalyst content on methyl ester yield, 60 °C, 60 min, 12:1 v/v methanol:oil ratio, and catalyst mass fraction 1-7% acceleration.

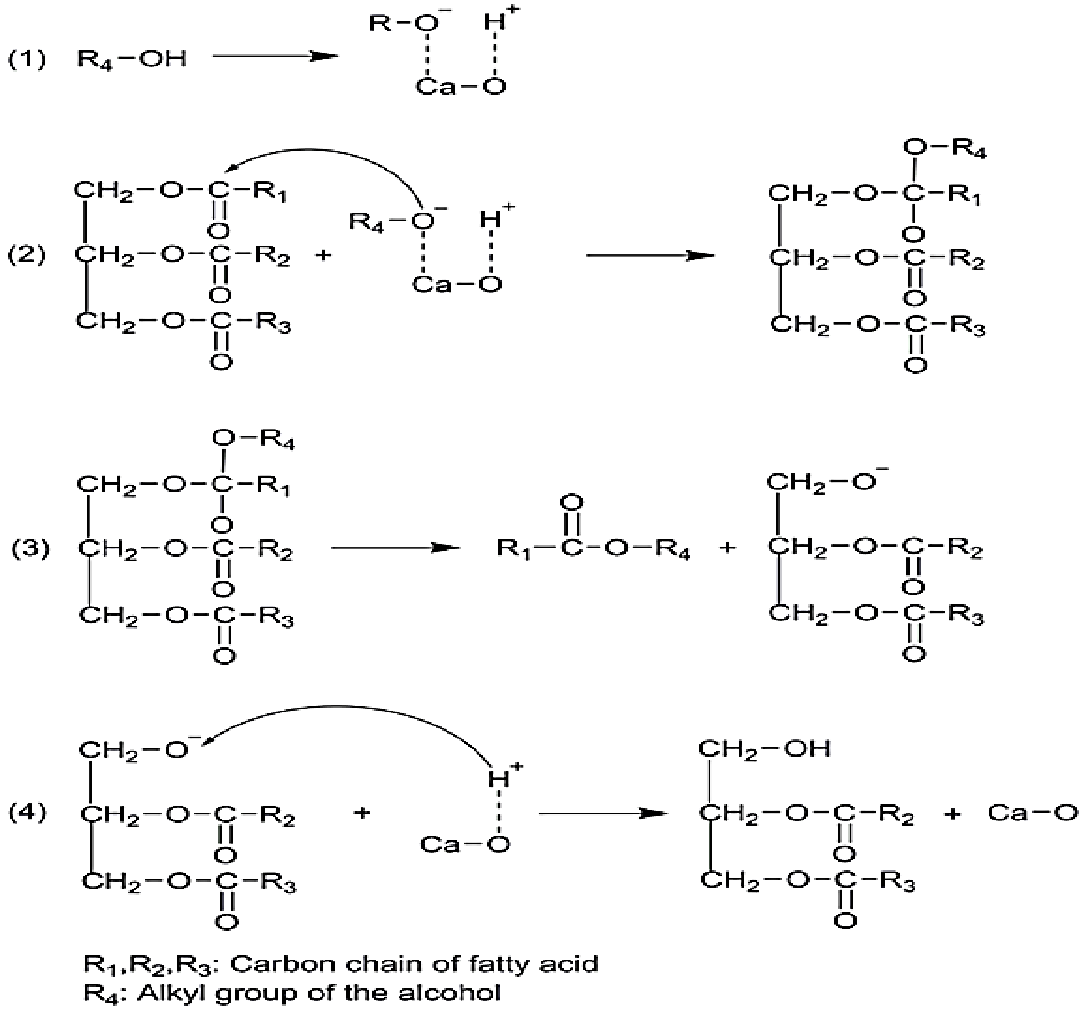


Fig. 10 Mechanism of CaO-catalyzed transesterification. Reproduced with the permission from [46], Copyright 2010 Elsevier Inc. R_1, R_2, R_3 are fatty acid carbon chains and R_4 is an alkyl group of the alcohol.

If the oil is dense, an engine will emit black smoke and if it is too low, engine power will be affected. ASTM D1298 standard determines that biodiesel should have a density between 860–900 kg/m^3. From Fig. 11, increasing amount of catalyst still led to densities within the ASTM D1298 limits, but the best catalyst loading was 1% because it reduced the amount of catalyst needed and the density differed by less than 2%. The optimum conditions were 60 °C, time 60 min, and methanol to oil ratio 12:1 v/v.

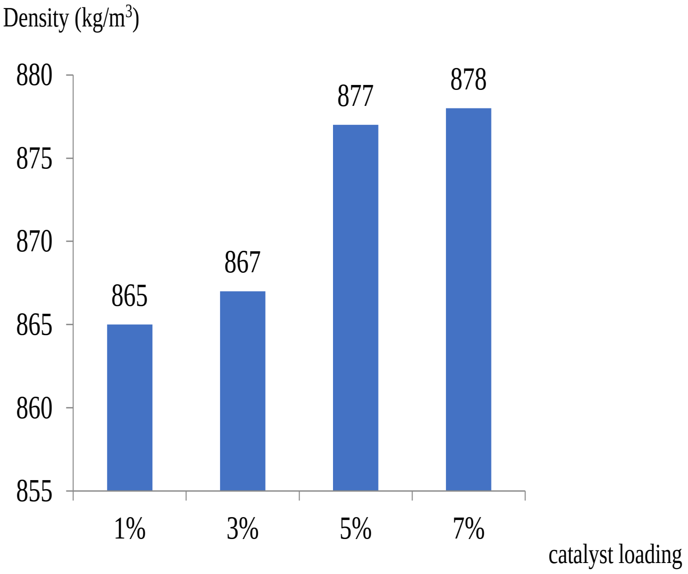


Fig. 11 Methyl ester density *vs* catalyst loading in the transesterification step.

The standard requires the measurement of biodiesel density at 15 °C.[47] This measurement is crucial in determining the quantity of biodiesel injected into the fuel combustion system.[48] The density of biodiesel is affected by the level of unsaturation in the fatty acid methyl esters. Generally, biodiesel is denser than conventional diesel, but when blends with petroleum diesel, the density of the fuel blend decreases.[49] Table 3 provides a comparison of the density at 15 °C for various biodiesel sources, ranging from 889 kg/m^3 for mustard biodiesel to 867 kg/m^3, for sesame and coconut biodiesel.

Table 3. Properties of biodiesels from 8 different vegetative oil sources.[49-53]

Biodiesel sources	Density (kg/m^3)	Viscosity (cSt)	Flash point (ºC)	Calorific value (MJ/kg)
Soybean	882	4.15	160	39.8
Coconut	867	3.14	118	38.2
Mustard	888.9	5.53	169	41.9
Sunflower	869	4.10	183	40.6
Palm	880	4.52	175	34.4
Sesame	867	4.58	180	40.1
Camelia	885	4.53	150	52.2
Jatropha	880	4.80	176	40.8

Viscosity affects the engine combustion, because if it is too low or too high the fuel injector will not atomize optimally and combustion will produce black smoke in the exhaust: ASTM D445 specifies a viscosity in the range of 1.8–4.1 cSt, whereas biodiesel requires a viscosity in the range of 3.5–5 cSt. Fig. 12 shows that our biodiesel had a somewhat higher viscosity than the ASTM target for every catalyst loading, but the 1% loading led to an insignificantly higher viscosity than the lowest value.

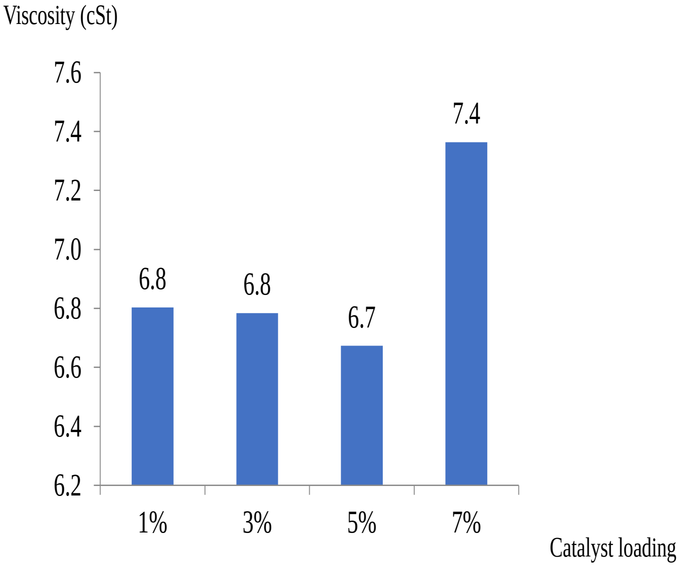


Fig. 12 Methyl ester viscosity *vs* catalyst content.

Biodiesel exhibits a higher kinematic viscosity value compared to petroleum diesel due to its larger molecular mass.[50] The presence of high kinematic viscosity can lead to inadequate fuel atomization, resulting in inefficient combustion and the accumulation of dirt and debris. Conversely, low kinematic viscosity promotes the formation of small fuel droplets, facilitating fuel transfer for combustion and enhancing thermal efficiency.[49] The standard measurement for kinematic viscosity is conducted at 40 °C.

The flash point is the temperature at which the fuel will spontaneously ignite. High flash point fuels are safe from accidental combustion during use. For storage and transportation, ASTM D93 requires diesel fuel to have a flash point of at least 52°C and may be slightly lower in colder countries. For biodiesel fuel, the flash point was required to be higher than 120 °C. Fig. 13 that all biodiesels produced in this study considerably exceeded the ASTM D93 requirement. In standard atmospheric conditions, the ignition point of biodiesel fuel is the lowest temperature point.[51] The flash point value of biodiesel is always higher than that of fossil fuel diesel. The flash point value of conventional diesel ranges between 55 – 65°C. The reason for the higher flash point values of biodiesel is its low volatility. This characteristic makes biodiesel safer during transportation and storage.[52] Table 3 shows that the flash point values of various biodiesel sources range from 118.5°C to 183°C for coconut and rubber biodiesel, respectively.

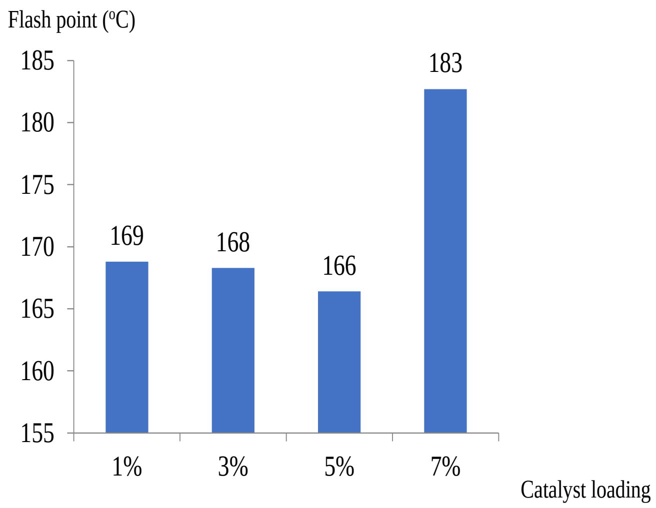


Fig. 13 Methyl ester flash point *vs* catalyst loading.

Calorific value generally describes the energy produced per unit mass of fuel or per unit volume, i.e. the heat that will be obtained from the fuel combustion and has a direct effect on engine efficiency. If the heat value is high, it will make the engine stronger round speed. The heating value of biodiesel (39 MJ/kg) is usually lower than that of diesel (48.6 MJ/kg), due to the oxygen content. Fig. 14 shows that the calorific value of our methyl ester was lower than the target for diesel engines, but may be adequate for applications, e.g. burners, where the calorific value is less critical.

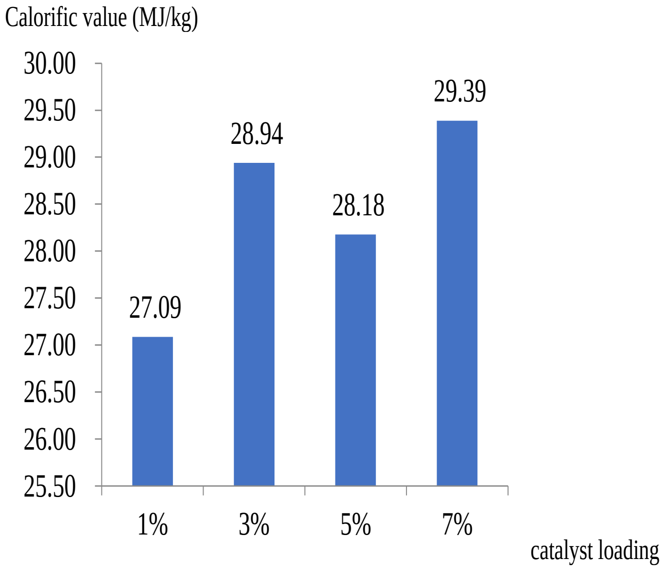


Fig. 14 Methyl ester calorific value *vs* catalyst content in transesterification.

4. Conclusions

Optimal conditions for methyl ester production from acid black oil in a two-step chemical process, used esterification of the oil and methanol with sulfuric acid as a catalyst, followed by transesterification catalyzed by CaO. In the esterification reaction, increasing the molar ratio of methanol to oil and increased sulfuric acid content resulted in free fatty acids reduced to the level less than 1.8%. For the transesterification, optimal conditions were 60 °C, reaction time 180 min, catalyst volume 5% w/w, methanol: oil ratio 18:1 v/v.

The flash point and viscosity of the methyl ester decreased with the CaO catalyst loading. Also the calorific value of our esters (27–29 MJ/kg) was lower than the target for diesel engines (39–42 MJ/kg), but increasing catalyst loading tended to result in a higher calorific value. The density was found to be in the standard range of 840–900 kg/m^3 but tended to increase with increasing amount of catalyst compared to diesel The flash point, viscosity and density of the methyl esters were higher than those of diesel. However, the calorific value was lower than that of diesel fuel and lower than the standards, it was found that the resulting oil was still below the ASTM standard.

Acknowledgements

This Research was financially supported by Faculty of Engineering, Mahasarakham University. The authors would like to express their sincere gratitude to Saengsook Industry Co., Ltd for providing black acid oil.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Applicable.

References

[1] D. F. Correa, H. L. Beyer, H. P. Possingham, S. R. Thomas-Hall, P. M. Schenk, Biodiversity impacts of bioenergy production: Microalgae *vs.* first generation biofuels, *Renewable and Sustainable Energy Reviews*, 2017, **74**, 1131-1146, doi: 10.1016/j.rser.2017.02.068.

[2] B. Azeem, K. KuShaari, M. Naqvi, L. Kok Keong, M. K. Almesfer, Z. Al-Qodah, S. R. Naqvi, N. Elboughdiri, Production and characterization of controlled release urea using biopolymer and geopolymer as coating materials, *Polymers*, 2020, **12**, 400, doi: 10.3390/polym12020400.

[3] S. Jain, M. P. Sharma, Prospects of biodiesel from Jatropha in India: a review, *Renewable and Sustainable Energy Reviews*, 2010, **14**, 763-771, doi: 10.1016/j.rser.2009.10.005.

[4] N. C. Om Tapanes, D. A. Gomes Aranda, J. W. de Mesquita Carneiro, O. A. Ceva Antunes, Transesterification of Jatropha curcas oil glycerides: theoretical and experimental studies of biodiesel reaction, *Fuel*, 2008, **87**, 2286-2295, doi: 10.1016/j.fuel.2007.12.006.

[5] Z. Helwani, M. R. Othman, N. Aziz, W. J. N. Fernando, J. Kim, Technologies for production of biodiesel focusing on green catalytic techniques: a review, *Fuel Processing Technology*, 2009, **90**, 1502-1514, doi: 10.1016/j.fuproc.2009.07.016.

[6] I. B. Banković-Ilić, O. S. Stamenković, V. B. Veljković, Biodiesel production from non-edible plant oils, *Renewable and Sustainable Energy Reviews*, 2012, **16**, 3621-3647, doi: 10.1016/j.rser.2012.03.002.

[7] A. Abbaszaadeh, B. Ghobadian, M. R. Omidkhah, G. Najafi, Current biodiesel production technologies: a comparative review, *Energy Conversion and Management*, 2012, **63**, 138-148, doi: 10.1016/j.enconman.2012.02.027.

[8] E. F. Aransiola, T. V. Ojumu, O. O. Oyekola, T. F. Madzimbamuto, D. I. O. Ikhu-Omoregbe, A review of current technology for biodiesel production: state of the art, *Biomass and Bioenergy*, 2014, **61**, 276-297, doi: 10.1016/j.biombioe.2013.11.014.

[9] Y. Tang, Y. Yang, H. Liu, T. Yan, Z. Zhang, Preparation of nano-CaO and catalyzing tri-component coupling transesterification to produce biodiesel, *Inorganic and Nano-Metal Chemistry*, 2020, **50**, 501-507, doi: 10.1080/24701556.2020.1720726.

[10] A. U. Badnore, N. L. Jadhav, D. V. Pinjari, A. B. Pandit, Efficacy of newly developed nano-crystalline calcium oxide catalyst for biodiesel production, Chemical Engineering and Processing - Process Intensification, 2018, **133**, 312–319, https://doi.org/10.1016/j.cep.2018.09.007.

[11] J. Poosumas, K. Ngaosuwan, A. T. Quitain, S. Assabumrungrat, Role of ultrasonic irradiation on transesterification of palm oil using calcium oxide as a solid base catalyst, *Energy Conversion and Management*, 2016, **120**, 62-70, doi: 10.1016/j.enconman.2016.04.063.

[12] A. Bouaid, N. El Boulifi, M. Martinez, J. Aracil, Optimization of a two-step process for biodiesel production from Jatropha curcas crude oil, *International Journal of Low-Carbon Technologies*, 2012, **7**, 331-337, doi: 10.1093/ijlct/ctr047.

[13] Ž. Kesić, I. Lukić, M. Zdujić, Č. Jovalekić, V. Veljković, D. Skala, Assessment of $CaTiO_3$, CaMnO3, $CaZrO_3$ and $Ca_2Fe_2O_5$ perovskites as heterogeneous base catalysts for biodiesel synthesis, *Fuel Processing Technology*, 2016, **143**, 162-168, doi: 10.1016/j.fuproc.2015.11.018.

[14] R. Yahyaee, B. Ghobadian, G. Najafi, Waste fish oil biodiesel as a source of renewable fuel in Iran, *Renewable and Sustainable Energy Reviews*, 2013, **17**, 312-319, doi: 10.1016/j.rser.2012.09.025.

[15] P. Imani-Mofrad, Z. H. Saeed, M. Shanbedi, Experimental investigation of filled bed effect on the thermal performance of a wet cooling tower by using ZnO/water nanofluid, *Energy Conversion and Management*, 2016, **127**, 199-207, doi: 10.1016/j.enconman.2016.09.009.

[16] F. Toldrá-Reig, L. Mora, F. Toldrá, Trends in biodiesel production from animal fat waste, *Applied Sciences*, 2020, **10**, 3644, doi: 10.3390/app10103644.

[17] J. Abraham, R.S. Kumar, F. Xavier, D. Mathew, Biodiesel production from broiler chicken waste, *International Agricultural Engineering Journal*, 2015, **9**, 1190-1193, doi: 10.5281/ZENODO.1110157.

[18] D. Papargyriou, E. Broumidis, M. de Vere-Tucker, S. Gavrielides, P. Hilditch, J. T. S. Irvine, A. D. Bonaccorso, Investigation of solid base catalysts for biodiesel production from fish oil, *Renewable Energy*, 2019, **139**, 661-669, doi: 10.1016/j.renene.2019.02.124.

[19] 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, *Renewable Energy*, 2020, **145**, 2550-2560, doi: 10.1016/j.renene.2019.08.008.

[20] N. A. Tajuddin, A. F. Lee, K. Wilson, Production of biodiesel via catalytic upgrading and refining of sustainable oleagineous feedstocks, *In Handbook of Biofuels Production*, Woodhead Publishing: Sawston, UK, 2016, 121-164, doi: 10.1016/B978-0-08-100455-5.00006-0.

[21] A. Macario, G. Giordano, B. Onida, D. Cocina, A. Tagarelli, A. M. Giuffrè, Biodiesel production process by homogeneous/heterogeneous catalytic system using an acid–base catalyst, *Applied Catalysis A: General*, 2010, **378**, 160-168, doi: 10.1016/j.apcata.2010.02.016.

[22] R. Ahmed, K. Huddersman, Review of biodiesel production by the esterification of wastewater containing fats oils and grease (FOGs), *Journal of Industrial and Engineering Chemistry*, 2022, **110**, 1-14, doi: 10.1016/j.jiec.2022.02.045.

[23] M. Catarino, S. Martins, A. P. Soares Dias, M. F. Costa Pereira, J. Gomes, Calcium diglyceroxide as a catalyst for biodiesel production, *Journal of Environmental Chemical Engineering*, 2019, **7**, 103099, doi: 10.1016/j.jece.2019.103099.

[24] A. P. S. Dias, J. Puna, J. Gomes, M. J. S. Correia, J. João Bordado, Biodiesel Production over Lime Catalyst: Bulk and Surface Catalyst Dynamics, *Renewable Energy*, 2016, **99**, 622-630, doi: 10.1016/j.renene.2016.07.033.

[25] J. K. Efavi, D. Kanbogtah, V. Apalangya, E. Nyankson, E. K. Tiburu, D. Dodoo-Arhin, B. Onwona-Agyeman, A. Yaya, The effect of NaOH catalyst concentration and extraction time on the yield and properties of Citrullus vulgaris seed oil as a potential biodiesel feed stock, *South African Journal of Chemical Engineering*, 2018, **25**, 98-102, doi: 10.1016/j.sajce.2018.03.002.

[26] Z. Abelniece, L. Laipniece, V. Kampars, Biodiesel production by interesterification of rapeseed oil with methyl formate in presence of potassium alkoxides, *Biomass Conversion and Biorefinery*, 2022, **12**, 2881-2889, doi: 10.1007/s13399-020-00874-z.

[27] H. Cao, Z. Zhang, X. Wu, X. Miao, Direct biodiesel production from wet microalgae biomass of Chlorella pyrenoidosa through *in situ* transesterification, *BioMed Research International*, 2013, **2013**, 930686, doi: 10.1155/2013/930686.

[28] A. Sagiroglu, I. Selen, M. Ozcan, H. Paluzar, N. Toprakkiran, Comparison of biodiesel productivities of different vegetable oils by acidic catalysis, *Chemical Industry and Chemical Engineering Quarterly*, 2011, **17**, 53-58, doi: 10.2298/ciceq100114054s.

[29] M. Tariq, S. Ali, N. Khalid, Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of biodiesel: a review, *Renewable and Sustainable Energy Reviews*, 2012, **16**, 6303-6316, doi: 10.1016/j.rser.2012.07.005.

[30] H. Fukuda, A. Kondo, H. Noda, Biodiesel fuel production by transesterification of oils, *Journal of Bioscience and Bioengineering*, 2001, **92**, 405-416, doi: 10.1263/jbb.92.405.

[31] S. H. Y. S. Abdullah, N. H. M. Hanapi, A. Azid, R. Umar, H. Juahir, H. Khatoon, A. Endut, A review of biomass-derived

heterogeneous catalyst for a sustainable biodiesel production, *Renewable and Sustainable Energy Reviews*, 2017, **70**, 1040-1051, doi: 10.1016/j.rser.2016.12.008.

[32] Natasha, I. Bibi, M. Shahid, N. K. Niazi, F. Younas, S. R. Naqvi, S. M. Shaheen, M. Imran, H. Wang, K. M. Hussaini, H. Zhang, J. Rinklebe, Hydrogeochemical and health risk evaluation of arsenic in shallow and deep aquifers along the different floodplains of Punjab, Pakistan, *Journal of Hazardous Materials*, 2021, **402**, 124074, doi: 10.1016/j.jhazmat.2020.124074.

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

[34] N. Nakatani, H. Takamori, K. Takeda, H. Sakugawa, Transesterification of soybean oil using combusted oyster shell waste as a catalyst, *Bioresource Technology*, 2009, **100**, 1510-1513, doi: 10.1016/j.biortech.2008.09.007.

[35] M. Kouzu, A. Kajita, A. Fujimori, Catalytic activity of calcined scallop shell for rapeseed oil transesterification to produce biodiesel, *Fuel*, 2016, **182**, 220-226, doi: 10.1016/j.fuel.2016.05.111.

[36] Z. Wei, C. Xu, B. Li, Application of waste eggshell as low-cost solid catalyst for biodiesel production, *Bioresource Technology*, 2009, **100**, 2883-2885, doi: 10.1016/j.biortech.2008.12.039.

[37] R. Ahmad, R. Rohim, N. Ibrahim, Properties of waste eggshell as calcium oxide catalyst, *Applied Mechanics and Materials*, 2015, **754**, 171-175, doi: 10.4028/www.scientific.net/amm.754-755.171.

[38] H. Liu, L. Su, Y. Shao, L. Zou, Biodiesel production catalyzed by cinder supported CaO/KF particle catalyst, *Fuel*, 2012, **97**, 651-657, doi: 10.1016/j.fuel.2012.02.002.

[39] Y. Tang, M. Meng, J. Zhang, Y. Lu, RETRACTED: efficient preparation of biodiesel from rapeseed oil over modified CaO, *Applied Energy*, 2011, **88**, 2735-2739, doi: 10.1016/j.apenergy.2011.02.033.

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

[41] N. Subramonia Pillai, P. S. Kannan, S. C. Vettivel, S. Suresh, Optimization of transesterification of biodiesel using green catalyst derived from Albizia Lebbeck Pods by mixture design, *Renewable Energy*, 2017, **104**, 185-196, doi: 10.1016/j.renene.2016.12.035.

[42] X. Deng, Z. Fang, Y.-H. Liu, Ultrasonic transesterification of Jatropha curcas L. oil to biodiesel by a two-step process, *Energy Conversion and Management*, 2010, **51**, 2802-2807, doi: 10.1016/j.enconman.2010.06.017.

[43] A. Hameed, S. R. Naqvi, U. Sikandar, W.-H. Chen, One-step biodiesel production from waste cooking oil using CaO promoted activated carbon catalyst from prunus persica seeds, *Catalysts*, 2022, **12**, 592, doi: 10.3390/catal12060592.

[44] V. G. Deshmane, Y. G. Adewuyi, Synthesis and kinetics of biodiesel formation via calcium methoxide base catalyzed transesterification reaction in the absence and presence of ultrasound, *Fuel*, 2013, **107**, 474-482, doi: 10.1016/j.fuel.2012.12.080.

[45] J. Boro, L. J. Konwar, A. J. Thakur, D. Deka, Ba doped CaO derived from waste shells of T striatula (TS-CaO) as heterogeneous catalyst for biodiesel production, *Fuel*, 2014, **129**, 182-187, doi: 10.1016/j.fuel.2014.03.067.

[46] M. K. Lam, K. T. Lee, A. R. Mohamed, Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review, *Biotechnology Advances*, 2010, **28**, 500-518, doi: 10.1016/j.biotechadv.2010.03.002.

[47] E. Alptekin, M. Canakci, Determination of the density and the viscosities of biodiesel–diesel fuel blends, *Renewable Energy*, 2008, **33**, 2623-2630, doi: 10.1016/j.renene.2008.02.020.

[48] R. Sakthivel, K. Ramesh, R. Purnachandran, P. Mohamed Shameer, A review on the properties, performance and emission aspects of the third-generation biodiesels, *Renewable and Sustainable Energy Reviews*, 2018, **82**, 2970-2992, doi: 10.1016/j.rser.2017.10.037.

[49] D. Singh, D. Sharma, S. L. Soni, S. Sharma, D. Kumari, Chemical compositions, properties, and standards for different generation biodiesels: a review, *Fuel*, 2019, **253**, 60-71, doi: 10.1016/j.fuel.2019.04.174.

[50] A. Demirbas, Progress and recent trends in biodiesel fuels, *Energy Conversion and Management*, 2009, **50**, 14-34, doi: 10.1016/j.enconman.2008.09.001.

[51] N. D. D. Carareto, C. Y. C. S. Kimura, E. C. Oliverira, M. C. Costa, A. J. A. Meirelles, Flash points of mixtures containing ethyl esters or ethylic biodiesel and ethanol, *Fuel*, 2012, **96**, 319-326, doi: 10.1016/j.fuel.2012.01.025.

[52] M. M. K. Bhuiya, M. G. Rasul, M. M. K. Khan, N. Ashwath, A. K. Azad, M. A. Hazrat, Prospects of 2nd generation biodiesel as a sustainable fuel–Part 2: properties, performance and emission characteristics, *Renewable and Sustainable Energy Reviews*, 2016, **55**, 1129-1146, doi: 10.1016/j.rser.2015.09.086.

[53] A. A. Refaat, Correlation between the chemical structure of biodiesel and its physical properties, *International Journal of Environmental Science & Technology*, 2009, **6**, 677-694, doi: 10.1007/BF03326109.