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Research Article

Utilization of dairy waste scum oil for microwave-assisted biodiesel production over KOH-waste eggshell based calcium oxide catalyst

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Abstract. The sustainability can be maintained by utilizing the available waste as feedstock and catalyst such as dairy and eggshell waste respectively for biodiesel production. In this study, the calcium oxide (CaO) synthesized from calcined eggshell was doped with potassium hydroxide (KOH-ECaO) via wet impregnation method and analyzed the catalyst performance on biodiesel production from dairy waste scum oil (DWSO) via microwave assisted transesterification. The catalyst was characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy equipped with Energy Dispersive X-ray (SEM-EDX), Brunauer-Emmett-Teller (BET) and Thermogravimetric analysis (TGA). The fatty acid methyl ester (FAME) contents were deduced by Gas Chromatography-Mass Spectrometry (GC-MS). The KOH-ECaO catalyst showed a good potential based on the characterizations analysis such as high pore size (25.5 nm) which supported by SEM pattern analysis. The highest biodiesel production (75%) was obtained at optimum reaction parameters conditions. The optimized conditions were discovered to be 3 wt.% of catalyst, 16:1 of methanol to oil molar ratio, reaction temperature of 65°C and 15 minutes of reaction time as microwave provided faster reaction for the transesterification. These innovative results showed that KOH-ECaO could enhance the biodiesel production from DWSO which encouraged the usage of waste for wealth product.

Keywords: calcium oxide, dairy waste scum oil, eggshell, microwave assisted transesterification, potassium hydroxide.

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1. Introduction

The awareness on various type of pollutions in environment which sources from greenhouse gas emission has increasing publicly due to energy originated from fossil fuels. Up to 75% are coming from greenhouse gas emission and nearly 90% emit from carbon dioxide (Osman *et al.*, 2022) which lead to climate change. The climate change mostly give negative impact towards the mother nature but there is a good behind it such as elevate source of bioenergy (Gernaat *et al.*, 2021). Nevertheless, there were studies that showed the subsided of energy crops due to drastic change of temperature that affected the metabolic pathway of the plants (de Freitas *et al.*, 2021; Nunez *et al.*, 2019; Zhao et *al.*, 2017). The energy demand happens concurrently to fulfil the expectation for vehicles fuel, cooking gas and many mores which give rise to searching for renewable energy, environmentally friendly and less toxic energy (Ahmad *et al.*, 2019). One of the renewable energies is biodiesel which has been publicly known as the replacement for the conventional diesel fuel. The biodiesel is a clean, non-toxic towards the environment, 100% from renewable resources (Ayoub & Abdullah, 2012) and has lesser gas emission which can reduce the air pollution (Granados *et al.*, 2007). Biodiesel can be generated from various type of feedstocks such as vegetable oils (edible and non-edible oil), waste cooking oil, animal fat wastes, microalgae and industrial waste that contain triglycerides (Hadiyanto *et al*, 2016). Industrial waste can be obtained from palm oil industry and food industry included dairy production.

Around 4 to 11 million tons of dairy waste are dumped into the environment each year, posing a major threat to biodiversity and which can probably be reduce by turning it into valuable green energy. The waste production from milk industry only is around 200 – 300 kg of dairy waste scum from dairy plant that runs 500000 litres of milk daily (Binnal *et al.*, 2020; Kavitha *et al.*, 2019; Shareef & Mohanty, 2020). The high waste scum generation caused many problems including environmental pollution since the dairy was scum generally encompasses of lipid, oil and greases, phosphorus, nitrogen and many other organic matters (Ahmad *et al.*, 2019). Kavitha *et al.* (Kavitha *et al.*, 2019) analyzed biodiesel production from dairy waste scum by utilized calcium oxide (CaO) made from eggshell waste. They acquired maximum 96% of biodiesel from optimized condition with temperature at 65°C for 3 hours and methanol: oil ratio of 6:1 as well as presence of 2.4 wt.% of catalyst. They also experimented the biodiesel in compressible diesel engine in term of brake thermal efficiency and specific fuel consumption which showed comparable result with conventional diesel. A distinct recent study by (Krishnamurthy *et al.*, 2020), have

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recorded 98% of biodiesel generation from *Hydnocarpus wightiana* oil and dairy waste scum with presence of nano catalyst snail shell. The optimized condition that they utilized were temperature at 61.6°C for 2.4 hours and methanol: oil ratio was 12.4: 1 with presence of 0.89 wt.% of catalyst. Whilst another study by (Munir *et al.*, 2020) expressed lower yield of biodiesel (83%) from non-edible *Raphnus raphanistrum L.* seed oil. Another previous literature, the study described biodiesel yield from dairy wastewater sludge in laboratory and pilot scale (Balasubramanian *et al.*, 2018). They achieved extraction of 18.81 wt.% and 16.2 wt.% of lipid from laboratory and pilot scale, respectively. The biodiesel generated from both scales were 98.2% and 97.4% respectively.

Biodiesel production needs presence of methanol and catalyst to ensure the reaction proceeds forward and faster. The catalyst can be divided into three types which are homogenous, heterogenous and enzyme catalyst (Widayat *et al* 2017). Most preferrable catalyst is base heterogenous catalyst due to its easiness to separate from the product and higher yield of biodiesel production (Narasimhan *et al.*, 2021; Nur *et al.*, 2021). This catalyst can be synthesized from organic waste such as fish bone, chicken bone, oyster shells and eggshells due to calcium carbonate composition that can be converted to calcium oxide via calcination at high temperature which is efficient for transesterification process (Hamza *et al.*, 2021). There were many studies utilized eggshells as the catalyst for biodiesel production included (Hua *et al.*, 2015) where they obtained 94% biodiesel yield with presence of 1.5 wt.% off eggshells. Another study by (Kavitha *et al.*, 2019) have utilized 2.4 wt.% of eggshells and obtained 96% of biodiesel yield. To enhance the biodiesel yield, there were researchers (Khatibi *et al.*, 2021) that added metal such as sodium (Na) and potassium (K) to the eggshells and achieved 98% biodiesel yield which higher than eggshells alone. A similar result (98% biodiesel yield) was obtained from (Pavlović *et al.*, 2020) in presence of eggshell with zeolite based catalyst. These studies showed that modified eggshells catalyst could enhance biodiesel yield. To the best of knowledge, there is still no study modified the eggshells with potassium hydroxide (KOH).

Microwave (MW) heating process have been implemented in this past few years to rise the performance in term of rate of reaction such as organic and inorganic chemical synthesis compared to other (Hsiao *et al.*, 2020; Prashanth *et al.*, 2021; Qadeer *et al.*, 2021; Tesfaye & Katiyar, 2016) Microwave heating also has been applied in many experiments associate to biodiesel to promote its yield by lower the reaction time and increase the rates of reaction (Alishahi *et al.*, 2021; Aparamarta *et al.*, 2022; Bundhoo, 2018). The microwave potential to lower the reaction time is due to supply of momentum of the microwave energy to overcome the activation energy barrier and therefore quicken the reaction process. In previous studies, it was found that using microwave heating in the transesterification process for producing biodiesel from macroalgae resulted in lower reaction times compared to the traditional method (Cancela *et al.*, 2012). Despite similar biodiesel yields, the microwave-assisted method only took 3 minutes whereas the basic method required 5 hours. Another study (Hsiao *et al.*, 2020) showed that microwave heating resulted in higher biodiesel production (98.2%) compared to the traditional water bath method (53.6%) for the same reaction time. Whilst in another study (Gupta & Rathod, 2018), the biodiesel yield from waste cooking oil using a calcium diglyceroxide catalyst showed a maximum yield of 94.86% under optimized conditions in a 15 minute reaction time using microwave heating, while the conventional method only produced 42.59% under the same reaction time. These results indicate that microwave heating improved heat transfer efficiency (Hsiao *et al.*, 2020) and reduced reaction times.

This study aims to enhance production of biodiesel from diary waste via catalytical transesterification and the catalyst is also prepared from waste eggshell to economize the cost of the overall process. The synthesized low-cost and environmentally friendly catalyst which is obtained from a completely solid waste such as eggshells with presence of potassium hydroxide (KOH) to produced high quality biodiesel from dairy waste is still limited. Moreover, this study would like to discover the microwave heating transesterification of dairy waste scum oil as it is still not reported yet in presence of base heterogenous catalyst and showed better biodiesel yield compared to conventional heating transesterification. The utilization of two waste is also beneficial for managing and controlling waste via conversion into valuable products especially related to green fuel.

2. Materials and methods

2.1. Materials

Dairy waste for biodiesel production was collected from shop in Kampar, Perak. For raw chicken eggshells, the waste was obtained from kitchen waste from university cafe. The alkali reagent KOH was used as metal precursor purchased from Merck. Methanol (for analysis, Merck) was used as a reagent for acid-esterification and transesterification. Sulphuric acid (95-97%, Merck) was used as the acid catalyst for acid-esterification.

2.2. Catalyst preparation

Around one kg of eggshells was collected and thoroughly cleaned with water to remove any impurities and organic matter. Then, they were dried in the oven for 24 h at 110 °C. The eggshell was then ground into a powder and sieved with a -200 + 325 mesh. The eggshell powder was then calcined for 3 h at 900 °C. The calcined eggshells were stored in a desiccator to maintain the dry condition of the catalyst. The calcium carbonate ($CaCO_3$) in the eggshell was transformed into calcium oxide (CaO) as follows:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

The calcined eggshell showed white color particles after calcination at 900°C, indicating the highest amount of calcium oxide was produced (Khatibi et al., 2021).

2.3. Impregnation of potassium hydroxide onto calcium oxide

A known amount of calcium oxide from the first calcination was mixed in 200 mL of potassium hydroxide solution with a percentage of 7%. Then, the mixture solution was impregnated by heating at 85°C under constant stirring until the paste was formed. The impregnated catalyst was then dried in an oven at 105°C for 24 hours and then calcined at 600°C for 6 h. A high temperature for calcination is preferred to ensure more vital interaction between the support and active element to build more active sites (Khatibi *et al.*, 2021). The prepared catalyst was named KOH-ECaO.

2.4. Characterization of catalyst

2.4.1 X-ray diffraction (XRD) analysis

XRD analyzed the crystallography and structure of the catalyst. The required amount of ground catalyst was placed in

Table 1
Calcium oxide (CaO) composition in different types of waste

Catalyst	CaO (%)
Calcined eggshell	99.06 (Nath *et al.*, 2021)
Calcined cow bone	64.89 (Ayodeji *et al.*, 2018)
Calcined fish bone	57 – 62 (Widiarti *et al.*, 2017)

the module. The analysis was carried out using Xpert3 powder (Panalytical brand) equipped with Cu K radiation and performed at 45 kV and 40 mA at 2θ from 2° to 90°.

2.4.2 Fourier-transform infrared spectroscopy (FTIR) analysis

Potassium bromide (KBr) was ground in a mortar for 3 to 5 minutes until thoroughly blended. Then, the mixed powder was placed into a salt tablet module and pressed using an oil pressure tamping machine, pressurized to 7 tons for 1 minute. After releasing the pressure slowly, the module was removed, and the sample was applied to the salt tablet. The salt tablet was placed in the holder and transferred to the FTIR.

2.4.3 Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)

The morphology and structure of the catalyst were discovered using Scanning Electron Spectroscopy (SEM) with the EVOLS15 (Zeiss) model, which included taking an image of the sample surface and raster scanning it with a high-energy electron beam. Cutting and encircling the samples was done to prepare them for the impregnation section, and a 20 kV electron beam was used. Additionally, it is equipped with energy dispersive X-ray (EDX) analysis, which was useful in determining the catalysts' elemental makeup. The CaO composition in different types of waste is shown in Table 1.

2.4.4 Brunauer-Emmett-Teller (BET) analysis

The sample was analyzed using the Micromeritic ASAP 2020 instrument model. Before the analysis, the sample was degassed at 120℃ for 2 h. The adsorption and desorption were carried out in a liquid nitrogen bath by utilizing nitrogen gas. The pore volume and size were also examined by N_2 adsorption and desorption isotherm based on the v-t plot method.

2.4.5 Thermogravimetric analysis (TGA)

The sample was ground into powder and sieved through a 200-mesh screen. The fine powder was then put in palladium with a start temperature of 25℃ with a 10℃/min rising gradient to 800℃. The TGA model used was STA6000 with a brand from Perkin Elmer.

2.5. Biodiesel production through conventional and microwave heating assisted transesterification

There are four main processes to produce biodiesel, i.e., blending, transesterification, micro emulsification, and cracking. Among all these, the most suitable is transesterification to produce a better quality of biodiesel. Microwave-assisted transesterification of the dairy scum oil (DWSO) was done to achieve maximum biodiesel productivity with minimum transesterification time.

The free fatty acid (FFA) was determined first by using 10 g of warm DWSO and was dissolved in 50 mL of isopropyl alcohol by adding a few drops of phenolphthalein as an indicator. Then, the sample was titrated against 0.1N potassium hydroxide (KOH) solution until the mixture turned slightly pink. Next, the acid and FFA values were calculated using the titration value based on the Equation (2) and (3) (Krishnamurthy et al., 2020):

$$Acid\ value\ [KOHg^{-1}] = \frac{V \times N \times 56}{W} \quad (2)$$

$$FFA = \frac{Acid\ value}{2} \quad (3)$$

Where V is the volume of titration solution (mL), N is the normality of the KOH solution, W is the weight of the oil sample (g), and 56 is equivalent to the molecular mass of KOH.

Firstly, acid-esterification was done prior to base-transesterification to reduce the FFA content of the oil. The esterification of DWSO was done in a 100 ml three-necked round bottom flask equipped with a condenser and magnetic stirrer. The center neck was used to connect with the condenser. One neck was inserted with a thermometer, and another was closed with a stopper. DWSO was preheated at 110°C for 30 minutes to evaporate moisture in the oil. 1 wt.% of sulphuric acid and methanol (15:1) were added to the heated oil. The reaction time and temperature were set for 1 h and 65°C, respectively. Then, the mixture was transferred to a separating funnel to separate into two layers overnight. The top layer containing excess methanol and acid was removed, while the bottom layer was taken for the next step, which was transesterification. The acid value of the bottom layer, consisting of DSO, was measured as per American Society for Testing and Materials (ASTM) D 664, and the % conversion of esterification is calculated based on Equation (5) as follows (Binnal *et al.*, 2020):

$$Conversion\ of\ esterification\ \left(\%\frac{w}{w}\right) = \frac{AV_0 - AV}{AV_0} \times 100 \quad (5)$$

Where AV_0 and AV are the initial and final acid values of DWSO, respectively.

First, the specified amount of catalyst was mixed with a proper amount of methanol and heated at 65℃ for 1 h to produce a methoxide solution. For transesterification, a known amount of treated dairy waste scum oil (<0.5% FFA) was performed in a microwave with a three-neck round bottom flask connected with a water-cooled condenser at the center neck. Another neck was inserted with a thermocouple for temperature detector purposes, and another was closed with a stopper. The methoxide solution and heated DWSO were mixed in the round bottom flask and transferred into the microwave. The reaction time and temperature were set according to the desired parameters. After the reaction, the mixture was transferred to the separating funnel to allow for the separation of the phases (2 phases). The top layer consisted mainly of biodiesel, and the lower layer had glycerol as the byproduct and catalyst. The upper biodiesel layer was washed with warm distilled water and dried overnight at 105℃ to remove the water content.

2.6. Conditions of reaction parameters

The catalyst loading of KOH-ECaO was fixed at 3 wt.%, 16:1 for methanol to oil molar ratio, and the temperature was set at 65℃. The reaction times of the process were tested for 5 – 25 minutes for microwave heating and 1 – 4 h for conventional heating.

2.7. Gas chromatography-mass spectrometry (GC-MS) analysis for biodiesel

The biodiesel composition (fatty acid methyl esters) was analyzed using Agilent Gas chromatography-Mass Spectrometry (GC-MS) model GC 7890A. The column used was DB-5ms with a measurement of 30 m x 250 µm x 0.25 µm. The inlet temperature was set at 250℃, pressure at 23.68 psi, total flow of 79.5 mL/min and septum purge flow was 3 mL/min. The sample components were identified by comparing their mass spectra with the National Institute of Standards and Technology Research Library (NIST-2014).

Biodiesel yield in terms of volume percentage was calculated by using Equation (6) as follows (Kavitha *et al.*, 2019):

$$\text{Biodiesel yield} = \frac{g\ of\ \ biodiesel}{g\ of\ dairy\ scum\ oil\ waste\ added} \text{ x } 100 \qquad (6)$$

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The powder X-ray diffraction analysis was performed using a Panalytical diffractometer model Xpert3 Powder, over a 2θ range of 2 – 90°. The XRD pattern of the calcined eggshell impregnated with KOH (KOH-ECaO) catalyst was shown in Fig. 1.

Clear peaks were observed, which can be identified based on the library from the Joint Committee on Powder Diffraction Standards (JCPDS). Peaks of $Ca(OH)_2$ appeared at 2θ = 18.2°, 28.9°, 34.1°, 47.3°, 50.9°and 63.4° which is most probably due to hygroscopic properties of the catalyst that absorb water from surroundings after calcination (Ferraz *et al.*, 2019; *Nur et al.*, 2021) The peaks were similar to the previous study (Kirubakaran & Selvan, 2021). However, the most intense peaks belonged to CaO at 2θ = 37.6° and 54.1°, indicating that the amount of CaO was the highest compared to other compounds. Peaks of CaO are also shown in other small peaks at 2θ = 32.4°, 64.4° and 67.6°. These peaks showed that the eggshell had been converted to CaO at a calcination temperature of 900°C. The potassium carbonate (K_2CO_3) can be seen at 2θ = 41.9º which showed the present of KOH from the wet impregnation method (Ding *et al.*, 2017). The KOH most probably combined with CO_2 from calcium carbonate and formed K_2CO_3 (Blasi *et al.*, 2009). There was only one peak corresponding to $CaCO_3$ at 2θ of 28.2° which means there were some traces of the unconverted $CaCO_3$ to CaO.

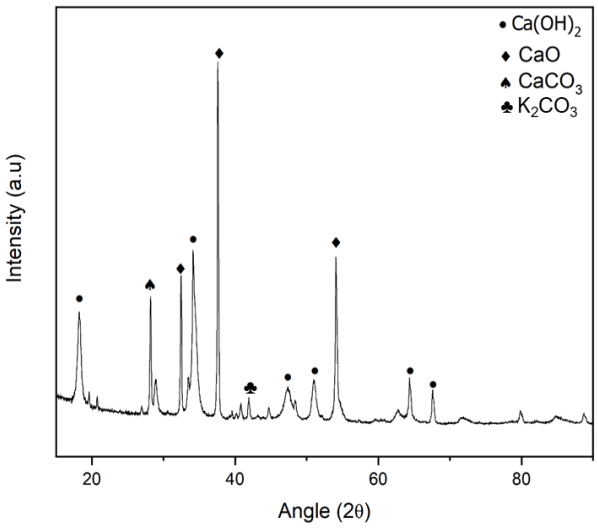


Fig. 1. XRD pattern for KOH-ECaO catalyst

3.2 Brunauer-Emmett-Teller (BET) analysis

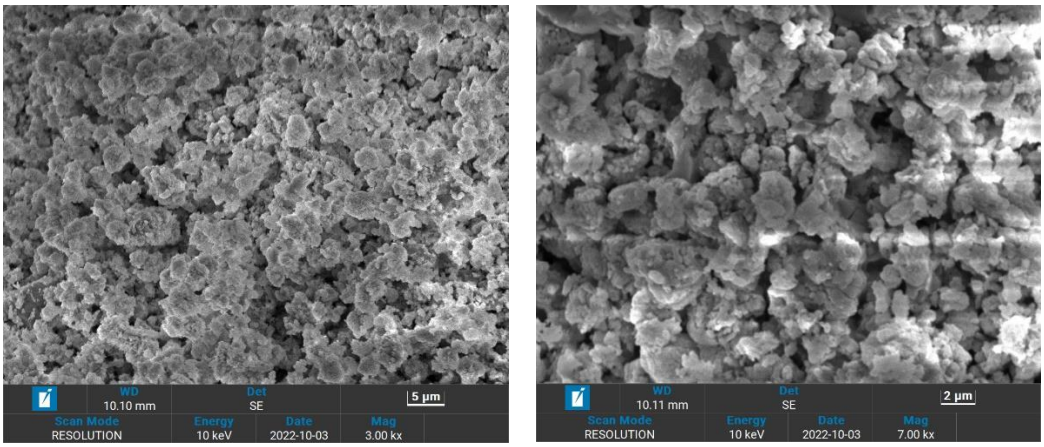
The structural characteristics of the KOH-ECaO catalyst are displayed in Table 2. The surface area, pore volume and pore size of KOH-ECaO showed higher values compared with CaO alone. These results indicated that impregnation of KOH could increase the structural properties of the catalyst. Based on recent study by (Ali *et al.*, 2023), the pore size of their catalyst was only 3.5 nm which indicated a very small pore compared to this study (25.54 nm). Small pore size would cause less selectivity of the catalyst and thus lead to low performance of the desired application (Gallagher, 2019). The BET surface area of KOH-ECaO was higher than CaO (Awogbemi *et al.*, 2020) which was not the same as the previous studies. This is most probably due to the addition of KOH, it might trigger the formation of new crystal ($Ca(OH)_2$) which formed from chemical reaction between KOH and CaO (Khatibi *et al.*, 2021). This $Ca(OH)_2$ crystal most probably caused a new formation of pore size which led to increase of surface and pore size to 9.85 m^2/g and 25.54 nm respectively (Aziz *et al.*, 2016). These results can be supported by (Khatibi *et al.*, 2021) where their K/CaO catalyst had bigger surface area than CaO alone. The larger surface area of the catalyst the better the activity of catalyst in transesterification process (Rahman *et al.*, 2019). This result can be supported from SEM pattern at Fig. 2 as it can be seen many pores existed at 7k magnification.

3.3 Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)

To learn more depth in surface morphology of the KOH-ECaO, SEM analysis with magnification of 3.0 and 7.0 Kx was done as shown in Fig. 2. In Fig. 2c, the SEM image was taken from a previous study that utilized CaO from eggshell for their biodiesel production chicken fat. The SEM micrograph displays amorphous structure with small and dispersed particles which similar with the earlier studies where they used CaO derived

Table 2
BET surface area, pore volume and pore size of the KOH-ECaO catalyst.

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
CaO from eggshell (Kirubakaran & V, 2018)	0.11	0.0012	5.66
CaO from eggshell	5.58	0.027	15.33
KOH-ECaO	9.85	0.073	25.54



(a) (b)

Fig. 2. SEM image of KOH-ECaO catalyst with a) 3 kx and b) 7 kx resolutions

Table 3
Atomic and weight elemental concentration of KOH-ECaO catalyst

Element	Atomic (%)	Weight (%)
Calcium	20.05	38.98
Carbon	28.23	16.45
Oxygen	47.77	37.08
Potassium	3.95	7.49

from eggshell (Kavitha *et al.*, 2019; Krishnamurthy *et al.*, 2020). To compare with CaO alone, the morphology surface shows irregular and rod-like shape with a lot of pores which could be the place where the KOH was impregnated. Moreover, there were some pores and some filled pores that can be seen in 7.0 Kx magnification that indicates high surface area and high basicity with presence of KOH that can enhance the biodiesel production. From Table 3, it has shown that Ca and O were the highest in weight percentage which means that the major compound was CaO with less contaminant.

The potassium also presented with 7.49% which came from KOH and proved that KOH had been successfully impregnated onto the CaO eggshell.

3.4 Fourier-transform infrared spectroscopy (FTIR) analysis

Fig. 3 shows the FTIR band for the KOH-CaO. The range of wavenumber of 4000 to 500 cm^{-1} was conducted to determine the functional group presented in the catalyst. The sharp and intense peak at 3643 cm^{-1} corresponds to the stretching of -OH bond due to the water presence in the catalyst (Tan *et al.*, 2019). Next, a broad peak is shown at 3426 $cm^{-1,}$ which indicates as -OH bond in Ca $(OH)_2$ built due to water adsorption on the CaO surface, which was similar to the 3643 cm^{-1} band (Kirubakaran & V, 2018; Krishnamurthy *et al.*, 2020). The presence of broad peak at 1453 cm^{-1} attributed to C-O bond from CO_3^{2-} which have been migrated at higher energy from 1394 and 1422 cm^{-1} for uncalcined eggshell that can be supported from previous studies (Awogbemi *et al.*, 2020; Kirubakaran & V, 2018). This situation is most likely because of exposure to high temperature (900℃) during calcination (Kirubakaran & V, 2018). The occurrence of 1072 cm^{-1} and 870 cm^{-1} also resulted from a stretching of C-O bond in the residue of CO_3^{2-} compound (Kavitha *et al.*, 2019; Krishnamurthy *et al.*, 2020). The final sharp peak at 560 cm^{-1} was most probably the CaO band, which can be supported by (Habte *et al.*, 2019) where they detected the peak at 512 cm^{-1} and identified it as a CaO compound. In addition, (Tatzber *et al.*, 2007; Varrica *et al.*, 2019) have reported that the range of wavenumber at 400 to 800 cm^{-1} is inorganic area.

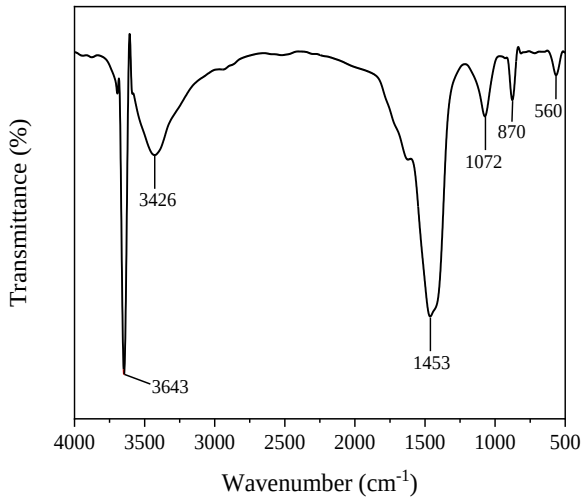


Fig. 3. FTIR pattern for KOH-ECaO catalyst

3.5 Thermogravimetric analysis (TGA)

To investigate the effect of calcination temperature on weight loss, the KOH-ECaO catalyst was analyzed for thermal analysis and differential thermogravimetry (DTG) at a range of 30 – 800℃. The thermogram in Fig. 4 displays a preliminary weight loss of 15.00% in the form of H_2O and CaO from Ca $(OH)_2$ at a range of temperature of 360 – 430℃.

Next, there is a slight loss in weight of 6.97% at a range temperature of 540 – 720℃. This weight loss indicated the decomposition of $CaCO_3$ into CO_2 and CaO. The CaO compound can be confirmed from the result of XRD (Fig. 1) as the CaO peak is the highest, indicating that CaO was successfully synthesized. The temperature of decomposition for calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) were reported at 350℃ and 600℃ by (Hsiao *et al.*, 2020). The

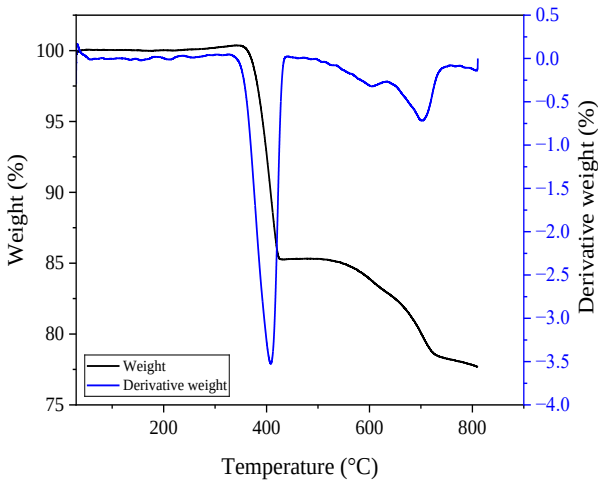


Fig. 4. TGA-DTG graph of KOH-ECaO catalyst

difference in decomposition temperature with the previous study was most probably due to the presence of organic matter on the CaO which in this case is KOH (Hsiao *et al.*, 2020). The derivative thermogravimetric (DTG) shows two prominent peaks at 410℃ and 703℃ which are comparable to the temperature of thermal decomposition of $Ca(OH)_2$ to generate H_2O and temperature of thermal decomposition of $CaCO_3$ to CO_2 respectively (Hsiao *et al.*, 2020). The high temperature of thermal decomposition discovered in this study verifies that KOH-ECaO has high thermal stability. The KOH-ECaO catalyst preparation has been successfully characterized in terms of chemical composition, morphology structures with elemental composition, surface area, and pore size, as well as the thermal stability of the catalyst. Overall, the characterization analysis shows that KOH-ECaO displays an adequate amount of CaO and $Ca(OH)_2$ based on XRD analysis, better pore size than CaO eggshell alone, which can be convinced with SEM image and exhibits an excellent thermal stability with more temperature of than 700°C.

3.6 Biodiesel yield from dairy waste scum oil (DWSO)

3.6.1 DSWO via conventional heating method

The conventional heating transesterification was done via a three-neck round bottom flask connected with a condenser and placed on a hot plate under constant stirring (320 rpm). The temperature was set at 65°C, with catalyst loading of 3 wt.% of KOH-ECaO, 16:1 for methanol to oil molar ratio, while varying the reaction time (1 – 4 hrs). Based on Fig. 5, the biodiesel production increased as the time increased and achieved the highest output of 73.74% at 3 h due to the longer time of contact between the reactants. This result indicated that the KOH-ECaO catalyst has higher basicity properties due to the addition of alkali metal (K), which increased the biodiesel yield compared with CaO alone, which produced only 58.44% at the same reaction time. The EDX analysis can prove that 7.49% of K could enhance the basicity of the catalyst, which can be supported by earlier studies (Khatibi *et al.*, 2021; Watkins *et al.*, 2004).

This result aligned with the previous study by *(Kavitha et al.*, 2019), where the biodiesel yield from dairy waste scum improved from 60 min to 180 min and then decreased at 240 min with less than 20% yield. Another study by (Khatibi *et al.*, 2021) varied the reaction time from 2 h to 5 h and obtained a similar pattern where increased time increased the biodiesel yield from canola oil until 3 hrs and decreased after that. The reversible nature of transesterification mainly causes this result due to a longer reaction time that passed the equilibrium state at 3 hrs (Çakırca *et al.*, 2019).

3.6.2 DSWO via microwave heating transesterification

In this section, only one parameter affecting biodiesel production was discussed, which is reaction time. At the same time, the other parameters were fixed, such as 3 wt.% of KOH-ECaO, 16:1 for methanol to oil molar ratio, and 65℃. The biodiesel production from DWSO in the presence of KOH-ECaO catalyst showed better production due to the catalyst's higher basicity caused by the presence of potassium (K), which could be supported by a previous study (Khatibi *et al.*, 2021). Moreover, the surface area of the KOH-ECaO was higher than CaO alone, contributing to better biodiesel yield as the transesterification of DWSO can acquire the active site without restraint (Chukwuka *et al.*, 2023).

Based on Fig. 6, the highest biodiesel yield (75.40 wt.%) was achieved at 15 min of reaction time and decreased when increased up to 25 min. The reason was probably because the time taken for the transesterification was beyond the favorable time for the equilibrium to be in a forward direction (Tesfaye & Katiyar, 2016; Yadav *et al.*, 2023). It means that a higher reaction time could favor the reverse direction of the process. This situation was similar to earlier studies where the biodiesel yield decreased when the time was above 60 min (Yadav *et al.*, 2023).

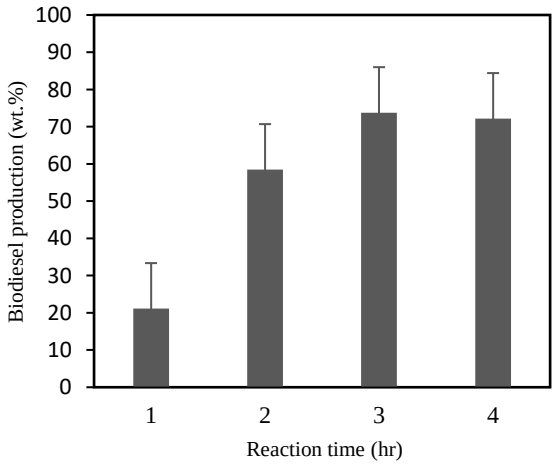


Fig. 5. Influence of reaction time on biodiesel production from DWSO by using conventional heating

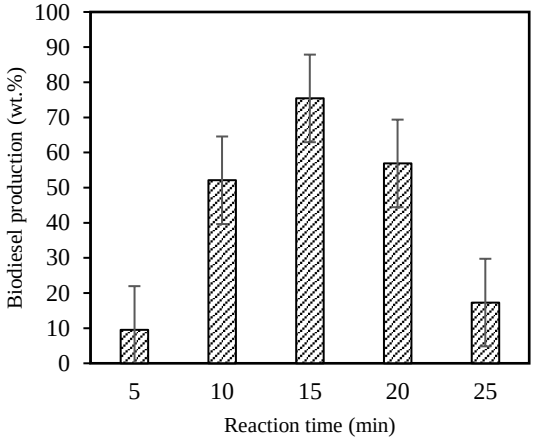


Fig. 6. Influence of reaction time on biodiesel production from DWSO by using microwave heating

Table 4
FAME composition in biodiesel from DWSO

Structural Name	Chemical Formula	Systematic Name
Methyl Palmitate	$C_{17}H_{34}O_2$	Hexadecanoic acid
Methyl Palmitoleate	$C_{17}H_{32}O_2$	Cis-9- hexadecanoic acid
Methyl Stearate	$C_{19}H_{36}O_2$	Octadecanoic acid
Methyl Oleate	$C_{19}H_{36}O_2$	Cis-9- octadecanoic acid
Methyl Linoleate	$C_{19}H_{34}O_2$	Cis-9,12-octadecenoic acid

Another study achieved a 99% biodiesel yield at 5 min and then reduced it after exceeding that time (Tesfaye & Katiyar, 2016). Another reason is that the longer reaction time affected the function of the catalyst amount due to adverse reactions (Rashtizadeh *et al.*, 2014).

For conventional heating transesterification (3 h), the biodiesel yield was 73.74 wt.%, less than microwave heating. This result indicated that microwave heating is faster and better in biodiesel production than conventional heating because the heat from the microwave penetrates the flask and directly heats the sample, thus promoting better thermal efficiency (Hsiao *et al.*, 2020). The fatty acid methyl ester (FAME) composition was analyzed by GC-MS and is shown in Table 4, which indicated the oil produced from the DWSO was biodiesel.

In essence, the microwave assisted transesterification of DWSO shows an interesting biodiesel production with a good composition of FAME, which is in line with the previous studies (Binnal *et al.*, 2020; Kavitha *et al.*, 2019; Sarno & Iuliano, 2020). The application of microwave energy in this study created faster reaction time and simultaneously saved electricity usage. With the addition of a high basic catalyst (KOH-ECaO), the reaction was fast and better yielded biodiesel production. The utilization of wastes for both the feedstock and catalyst give a lot of benefits, including cost-effectiveness, reducing pollution from the environment, and improving biodiesel production from DWSO.

4. Conclusion

The present work shows the synthesis of KOH impregnated with CaO derived from eggshell and recognizes the favorable properties and characterization of the catalyst. The presence of K and CaO can be proved through the FTIR analysis, which means the KOH is confirmed to be impregnated with CaO from the eggshell, which is also supported by EDX analysis. Plus, the catalyst showed a high pore size that was good for catalytic activity. The KOH-ECaO has been successfully utilized in the microwave heating transesterification of DWSO. The optimized reaction time for conventional heating was 3 h with 73.7% biodiesel production while 75% biodiesel production was generated only within 15 min via microwave heating. These results showed that shortened reaction time was required when microwave heating was applied and thus more cost-effective and time-saving. Further study on synthesizing CaO with other potential metals, such as lithium or sodium, for biodiesel production can upgrade the catalytic performance and thus improve the biodiesel yield.

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