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Exploitation of cost-effective renewable heterogeneous base catalyst from banana (*Musa paradisiaca*) peel for effective methyl ester production from soybean oil

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Abstract

Biodiesel is one of the biofuel alternatives obtained from vegetable oils and animal fats, currently being used globally to lessen environmental pollutions. In this research investigation, waste banana peels impregnated with calcium oxide (CaO) were utilized as a catalyst in the transesterification reaction of soybean oil with methanol. The waste of banana peels was calcined at 700 °C for 4 h and then added with CaO, calcined at 900 °C for 3 h with different concentrations. The results obtained showed that CaO is successfully impregnated based on the SEM–EDX, the surface area of CaO-CBP was smoother than CaO, the BET results revealed that with CaO-CBP the surface area was increased which was exhibited a porous and rough shape on the calcined banana peel (CBP) to give a high yield. Methyl esters (FAME) are produced at the highest conversion of 76.87 wt. % under 7 wt.% of catalyst amounts, 9:1 of molar ratio of methanol to oil and 2 h reaction time, as optimum conditions. The CaO impregnated with CBP (30% CaO-CBP) was used as a potential catalyst for heterogeneous bases that can facilitate transesterification reaction efficiently due to its high catalytic activity.

Keywords *Musa paradisiaca* · Calcium oxide · Heterogeneous catalyst · Fatty acid methyl ester · Banana peel

Introduction

Nowadays due to the depletion of non-renewable energy resources, the production of green energy from waste material has played an important role (Jayakumar et al. 2021; Nguyen et al. 2020). Biodiesel is biodegradable fuel derived from vegetable oils and animal fats, which has similar characteristics to petroleum fuel (Bhuyar et al. 2019; Manmai

et al. 2020). Biodiesel can be produced straight away from vegetable oil, animal oil or fats, tallow, and waste cooking oil. Basumatary (2014) stated, in the current situation, the combustion of petroleum fuel gives adverse effects such as air pollution and release of carbon monoxide toward the environment. Biodiesel is an alternative fuel like conventional petro-diesel or fossil fuels (Saengsawang et al. 2020).

Transesterification is the process to produce biodiesel from oils such as agro-industrial wastes (Abd Malek et al. 2020). The process involves the reaction of vegetable oils or animal waste with alcohols (methanol or ethanol) assisted by catalysts to produce biodiesel (Kumar et al. 2020). The fuel generated is eco-friendly to the environment and has high oxygen content than petroleum (Nakatani et al. 2009). The sources of oils mostly obtained from the extraction of soybean, rapeseed, corn, and sunflower. In recent days, the modern method was used for extraction, oil is straight away extracted from the agricultural industry. However, this method is not preferable for commercial production since the raw oil produced is high in price and has complicated biodiesel processing. The price is too high to compete with petroleum diesel or fossil fuels

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after the cost of converting them to biodiesel. An alternative way to get biodiesel at a low cost is by using waste vegetable oil or animal fats which can often be obtained for free or can be treated for the least price (Manaf et al. 2019).

In the modern era, the scientist stated that biodiesel is an alternative way to substitute the Petro-diesel. The raw materials used for biodiesel production come from vegetable oil or animal fats with the help of catalyst since it enhances the reaction rate. Soybean oil, sunflower oil, coconut oil (copra), groundnut oil, cottonseed oil, palm oil, palm kernel oil, rapeseed oil, and canola oil are the famous vegetable oil used as raw material. Besides, beef and sheep tallow are from animal sources and waste cooking oil, which are also sources of feedstocks used in biodiesel productions (Boakye 2013; Boey et al. 2011). Biodiesel production is mostly done by the chemical process such as base-catalyzed transesterification rather than acid-catalyzed transesterification. The catalyst is the best elements that increase the reaction rate at low temperature and low pressure to enhance the 98% conversion yield produced (Ahmad et al. 2021).

In heterogeneous catalyst transesterification, potassium carbonate (K_2CO_3) is a better alternative alkali catalyst since it provides a practically complete alcoholysis reaction with the least amount of soap production than other base-catalyst such as NaOH, KOH, NaOCH3 and KOCH$_3$. This catalyst is an alternative to biodiesel production. The reaction of KOH with CO_2 will produce potassium carbonate (K_2CO_3) and thus it will consume high cost than KOH. However, most biomass around us contains potassium such as plantain peels, cocoa pods and Jatrophacurcas seedcake. Hence, the production of K_2CO_3 from these biomass sources will help to reduce cost and at the same time can reduce the overall cost of biodiesel production (Boey et al. 2011; Singh et al. 2020).

Soybean oil is the worldwide popular feedstock used in biodiesel production, which is utilized by humans for business and scientists for research. Scientifically, Glycine Max is the popular scientific name soybean from which soybean oil is extracted from the feedstock. As (U.S. Department of Agriculture 2016) stated, in the United Kingdom, soybean oil has been used to produce methyl ester to support about 800 million gallons of biodiesel produce per year in the second half of the project. Besides soybean oil, corn oil, animal fats, and recycled vegetable oil also used to produce biomass-based diesel (Maniam et al. 2015). This study aims to prepare and characterize banana peel adopted with eggshell as a solid heterogeneous catalyst in the transesterification process. The influence of optimizing parameters such as catalyst loading, the ratio of methanol and oil, and the reaction hours on the amount of biodiesel produced from soybean oil using banana peel impregnated with eggshell as a solid catalyst are investigated.

Materials and methodology

Sample collection

Soybean oil used in this study was obtained in the nearby supermarket in Pahang state in Malaysia. It was used as a feedstock to produce fatty acids methyl easters (FAME). Besides, the banana peels and eggshell were obtained from supermarket and restaurants and processed them to produce potassium carbonate (K_2CO_3) and calcium oxides (CaO), heterogenous based catalysts. Furthermore, Hammett indicators such as phenolphthalein (H_ = 9.8), 2, 4-dinitroaniline (H_ = 15.0) and 4-nitroaniline (H_ = 18.4) purchased from Sigma (Deisenhofen, Germany). All the chemicals mentioned above are analytical reagent grade.

Oil characterization

Determination of acid value and free fatty acid (FFA)

The acid value is used to measure the breakdown of triacylglycerol into FFA (free fatty acid) through the titration method. The 10.0 g of soybean oil was dissolved in 50 mL of neutralized solvent, isopropanol, and few drops of phenolphthalein indicator were added. Standard potassium hydroxide solution was used to titrate the mixture under 40℃ until the first permanent pink color appeared for 30 s. The amount of potassium hydroxide solution titrated was recorded, and the acid value was calculated by using Eq. (1), whereas free fatty acid (FFA) content was calculated by using Eq. (2):

$$\text{Acid value (mg KOH/g sample)} = \frac{5.61 \times V \times 1}{M} \quad (1)$$

Where, V = Volume of standard potassium hydroxide, mL. M = Molar concentration of standard potassium hydroxide solution used.

$$FFA\ (\%) = \frac{25.6 \times N \times V}{W} \quad (2)$$

Where, N = Normality of alkali, N V = Volume of KOH solution, mL. W = Weight of soybean oil, g.

Determination of moisture content

The water content in soybean oil was utilized by the Karl Fisher method (Blank and Eksperiandova 2007). The titration was carried out by using Karl Fischer Titrator (Methrom, Switzerland). For titration dried methanol was used as a solvent, while Hydranal Composite-2 was used as the titrant. About 0.5 g of oil sample was injected into the

vessel in the titrator, and a heating balance (MX-50) was used to determine the moisture content of the oil.

Determination of iodine value

Iodine value is measured to determine the degree of unsaturation of fats and oils. 0.3 g of oil sample dissolved with 20 mL of cyclohexane in a 500 mL conical flask. Insert the stopper immediately and leave the mixture for 1 h in a dark place. 20 mL of 15% potassium iodide solution and 100 mL of distilled water were added. The sodium thiosulphate solution was used to titrate the solution until the yellow color disappeared. Then, 1–2 mL of starch solution (indicator) was added and continued titration until the blue color disappeared after vigorous shaking. The iodine value was calculated by using Eq. (3)

$$\text{Iodine value (mg I}_2/\text{g sample)} = \frac{(V2 - V1) \times N \times 12.96}{W} \tag{3}$$

Where, $V1$ = Titrated volume of sodium thiosulphate solution, mL. $V2$ = Sodium thiosulphate solution for blank, mL. N = Normality of sodium thiosulphate, N. W = Weight of oil sample, g.

Determination of density

Relative density or specific gravity (SG) is known for measuring the ratio density of a fuel to water at the same temperature with its other properties. The density of soybean oil was measured by an in-house method based on the KEM Density meter (Wagner et al. 2021).

Determination of saponification value

The saponification value is measured to determine the total acid content, both free and combined, of oil. It is determined by measuring the alkali required to saponify the combined acids and neutralize the free acids. 2 g of soybean oil was added into 25 mL of 0.5 N of KOH diluted with ethanol. The sample was refluxed for 1 h on the water bath and shaken occasionally. Then, few drops of phenolphthalein indicator were added to the sample. 0.5 N of hydrochloric acid was used as a titrant to the sample until the pink color disappeared. The procedures were repeated with a blank without an oil sample. The saponification value was calculated by using Eq. (4):

$$\text{Iodine value (mg I}_2/\text{g sample)} = \frac{5.61 \times (V2 - V1) \times N}{W} \tag{4}$$

Where, $V1$ = Volume of titrated hydrochloric acid, mL. $V2$ = Volume of hydrochloric acid for blank, mL. N = Normality of hydrochloric acid, N. W = Weight of soybean, g.

Catalyst preparation and transesterification

Preparation of catalyst

The waste of banana peels and eggshell were washed with tap water to remove any dirt and organic matter that adhered to the surface of peels and eggshells. Banana peels were dried at temperature 1000 °C for 72–80 h, and eggshell was dried at 1050 °C temperature for 24 h in an oven. After cooling at room temperature, the banana peels and eggshells were crushed into powder separately using a grinder. The product is uncalcined banana peel (UCBP) and uncalcined eggshell (UCES). Then, UCBP was calcined at 700 °C in a furnace for 4 h to become calcined banana peels (CBP), while UCES was calcined at 900 °C for 3 h to become calcined eggshell (CES). After the calcination process, different CES concentrations (10 wt. %, 20 wt. %, 30 wt. %, 40 wt. % and 50 wt. %) were adopted to the CBP powder to the intended catalyst, which CaO-K_2CO_3.

Characterization of the catalyst

To determine the suitability of the catalyst for further reaction, characterization was carried out (Singh et al. 2018). The catalyst was characterized using various types of instruments, namely Fourier Transform Infrared Spectroscopy (FTIR), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD) and Hammett indicators test.

Fourier transform infrared spectroscopy (FTIR) analysis FTIR provides information based on the chemical composition and physical state of the whole sample (Bhuyar et al. 2020). The Fourier transform infrared spectroscopy (Perkin Elmer Spectrum 100) was used to investigate the functional groups in CaO-K_2CO_3 catalysts. Each sample was mixed with standard potassium bromide (KBr) to form a disc. The samples were then scanned from 400 to 4000 cm^{-1} of transmittance mode with a resolution of 4 cm^{-1}. All spectra were referenced against the background spectrum.

Brunauer–Emmett–Teller (BET) analysis Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. BET was used to determine the texture properties and surface area of the catalyst. The surface area analysis of the catalysts was determined by Micromeritics ASAP 2000. The sample was degassed at 105 °C before analysis to remove any gasses attached to the catalyst's surface.

Scanning electron microscopy (SEM) The samples are mounted on a stub of metal with adhesive, coated with

40–60 nm of platinum and then observed in the microscope. Scanning Electron Microscopy coupled with electron dispersive X-ray (SEM–EDX) (FEI QUANTA 450) was used to determine the surface morphology, structure, and chemical composition in the catalyst. The microscope was operated with a vacuum at different magnifications to observe the clear magnified images. The best images are photographed.

X-Ray diffraction (XRD) analysis X-ray diffraction (XRD) was conducted to identify the crystalline structure and surface elemental composition of the CaO and K_2CO_3. XRD instrument was performed on Rigaku with Cu Kα X-ray as a source, 2θ range from 15 ° to 80 ° at a scanning speed of 1 °C/min.

Strength analysis using Hammett indicators Hammett indicators were used to determine the basic strengths of the catalyst. The phenolphthalein (H_ = 9.8), 2, 4-dinitroaniline (H_ = 15.0) and 4-nitroaniline (H_ = 18.4) were used as Hammett indicators. About 0.03 g of catalyst was taken and suspended with 1 mL of Hammett indicators diluted with 10 mL of methanol with methanol for each and left for 2 h equilibrated. After 2 h, the color change of the solution was noted.

Transesterification reaction

Transesterification is the reaction of converting vegetable oil or animal fats into methyl ester. The catalyst output was tested in a 50 mL one-neck round bottom flask with a magnetic stirrer, condenser, and thermometer by transesterification of soybean oil and methanol, immersed in a water bath. The temperature at 65 ± 2 °C was used throughout the experiment by control using a thermometer manually and stirred vigorously. To understand the optimum reaction conditions required, reaction parameters such as wt % of catalyst, reaction hours and the molar ratio of methanol to oil were studied. Using 1–9 wt % of catalyst, methanol to oil ratio was 6:1–18:1 and reaction hours were 1–3 h, the tests were conducted. After transesterification was done, the solution mixture was cooled to room temperature and then sent to centrifugation. Centrifugation was used to separate the three layers of mixture: methyl esters, glycerol, and catalyst further for 4 min at 6000 rpm. After centrifugation, three layers of the product were formed. The catalyst was identified at the bottom layer; the top layer was methyl ester, whereas the middle layer was glycerol. The top layer (methyl ester) was collected and transferred to a glass petri dish carefully to make sure the residual methanol in the layer

was evaporated. The process had done in the fume hood. The methyl esters were then measured and moved with a cap into a small centrifuge and cooled for the next application. For reusability analysis, the catalyst may be reused.

Methyl ester analysis

Qualitative and quantitative analysis of methyl ester

The qualitative and quantitative biodiesel produced was carried out with series of analysis. Thin-layer chromatography (TLC) was conducted for the qualitative study of methyl ester. A small piece of aluminum sheet coated with silica gel 60 (DC- Fertigplatten Kieselgel 60 F254) was used to conduct TLC analysis. A straight line was drawn about 1.0 cm at the bottom and the top of the TLC plate. The mixture of methyl heptadecanoate with heptane was used as solvent at a 10 mg/mL concentration and played as the methyl ester standard. Two methyl ester produced, and methyl ester standard was applied on the bottom of the TLC plate by using a capillary tube. The production solvent used for TLC was a 2:3 ratio mixture of petroleum ether and chloroform, while iodine vapor was used for spot visualization. The reaction was accomplished with the absence of triglyceride spots when the methyl ester spots were formed. The example of methyl ester formation by comparing the spots of mixture internal standard methyl heptadecanoate (C17) and oil.

GC-FID was used to determine the type of FAME presence and determine the conversion of methyl ester produced. The capillary column HP-INNOWAX with (length 30 m × internal diameter 0.25 mm × film thickness 0.25 μm) was used in gas chromatography. The mobile phase and internal standards required were heptane and methyl heptadecanoate. The solution was measured by weighing approximately 12.0 to 16.0 mg of the methyl ester produced in the GC vial and dissolved in a heptane 10 mg/mL concentration of 400 μL of the internal normal dilute. The methyl ester content of the substance is measured in compliance with the European regulation protocol EN 14103 and as an internal requirement using methyl heptadecanoate.

Methyl easter content (%)

$$= \frac{A_{\text{total}} - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{W_{\text{sample}}} \times 100\%$$

where, A_{ISTD} is the area of methyl heptadecanoate. V_{ISTD} is the volume of methyl heptadecanoate in ml. C_{ISTD} is the

concentration of methyl heptadecanoate in mg/ml. W_{sample} is the weight of sample in mg.

Results and discussion

Characteristics of soybean oil

To obtain more detailed information about the soybean oil used, some of the oil properties were studied. The acid, moisture, iodine, free fatty acid, density, and saponification value of the oil have been measured and tabulated in Table 1.

The Table 1 illustrates the difference between the acid value of soybean oil obtained by this study and the published literatures. The acid value for the soybean oil found in this study is 1.01 mg KOH/g; meanwhile, the other kinds of literature found were 0.36 and 0.88 mg KOH/g. The acid value of oils determined the amount of free fatty acid present and the purity of oils. The higher the acidity values, the lower the possibility of the oils being used for cooking purposes (Hasan et al. 2016). Since the results showed much difference, which means the contaminants were present throughout this experiment.

Iodine values use to measures the degree of unsaturation in a fat or vegetable oil. This unsaturation was the form of double bonds that react with iodine compounds. In this work, the iodine value obtained is 64.7 mg I_2/g, and it indicated less than other literature found were 105.47 mg I_2/g and 124.56 mg I_2/g respectively due to parallax error or any contaminants occurred. The higher the iodine value, the greater the number of C=C double bonds present in soybean oil that indicate oleic acid.

Furthermore, moisture content and FFA% are essential parameters in the determination of quality for soybean oil. The saponification process would occur when the amount of moisture and FFA content is high which leads to the reaction partially change to produced soap (Agustian 2012). The moisture content in the soybean oil was 0.12 wt. %, while the FFA content of soybean oil obtained in this work was 5.89 wt. % which differs from FFA content

as found in the literature (El kady et al. 1993). FFA was the result of the breakdown of the fatty acid chain of the oil.

The density of soybean oil does not differ very much from the literature's values, although the moisture content differs by 0.19 from reviewed literature. The higher the importance of the oil's moisture level, the greater the potential used in the manufacture of soaps, detergents, cosmetics, and oil paints for food texture, baking and frying and industrial (Hasan et al. 2016). The saponification value was determined by the amount of potassium hydroxide required to saponify the 1 g of oil. It also included breaking down the fat or oil into glycerol and fatty acids and leading to 'soap' formation by treating with alkali. As a result, the saponification value of soybean oil was 202.52 mg KOH/g which slightly differs from 184.8 mg KOH/g (Hasan et al. 2016) and 190.5 KOH/g (El kady et al. 1993).

Characterization of catalyst

Fourier transform infrared spectroscopy (FTIR) analysis

FTIR analysis was used to identify the functional groups present in the catalyst. UCBP, CBP, and CaO-CBP were analyzed to study the differences. In the spectrum of UCBP, the broad peak located at the wavenumber 3447.11 cm^{-1} indicated the O–H bonds stretching vibration. The peak for the C-O stretch showed at 1049.83 cm^{-1} and 1653.00 cm^{-1}. The peak at 1506.50 cm^{-1} referred to N–O stretching, while 1384.58 cm^{-1} assigned to carbonate C–O stretching and bending vibrations. 667.71 cm^{-1} indicated C=C bending for alkene.

From the spectrum of CBP, the bands at 3436.03 cm^{-1} were appeared due to O–H stretching and bending vibrations of H_2O while the other bands at 1630.94 and 1384.26 cm^{-1} assigned to carbonate C–O stretching and bending vibrations, which were indicative of the presence of carbonate (CO_3). Aransiola and his coauthors (2010) stated that the characteristic band at 1384.26 cm^{-1} was referred to as K_2CO_3 and this band was prominent only in the calcined sample

Table 1 Characterization of soybean oil

Parameters	This work	(Hasan et al. 2016)	(El kady et al. 1993)
Acid value, mg KOH/g	1.01	0.36	0.88
Moisture content, %	0.12	0.31	–
Iodine value, mg I_2/g	64.7	105.47	124.56
FFA value, %	5.89	–	0.44
Density, g/cm^3	0.9163	0.909	–
Saponification value, mg KOH/g	202.52	184.8	190.5

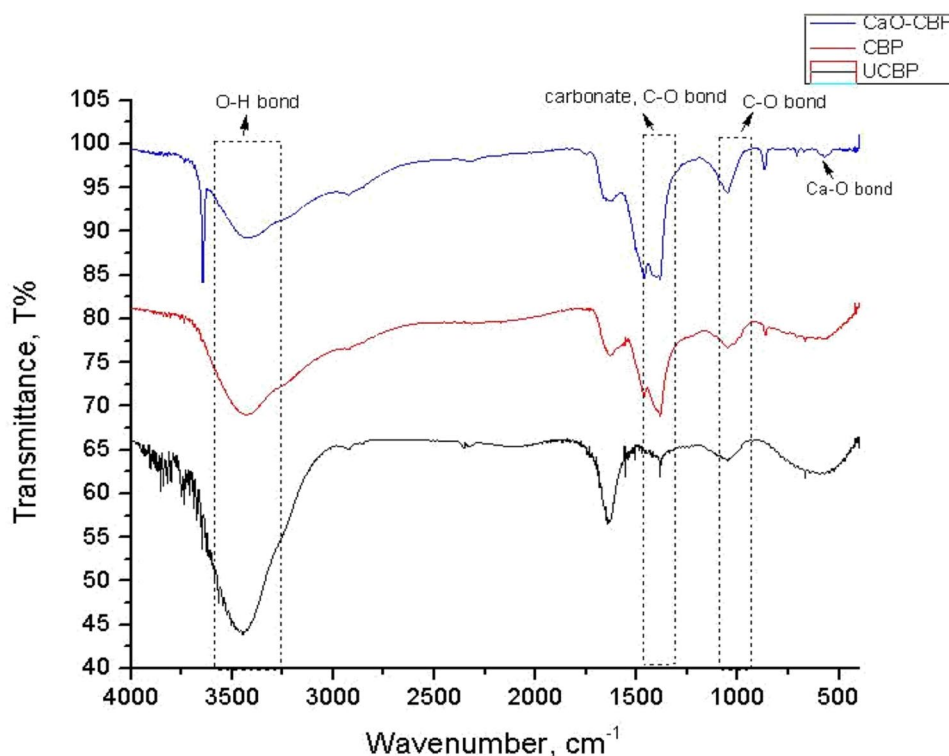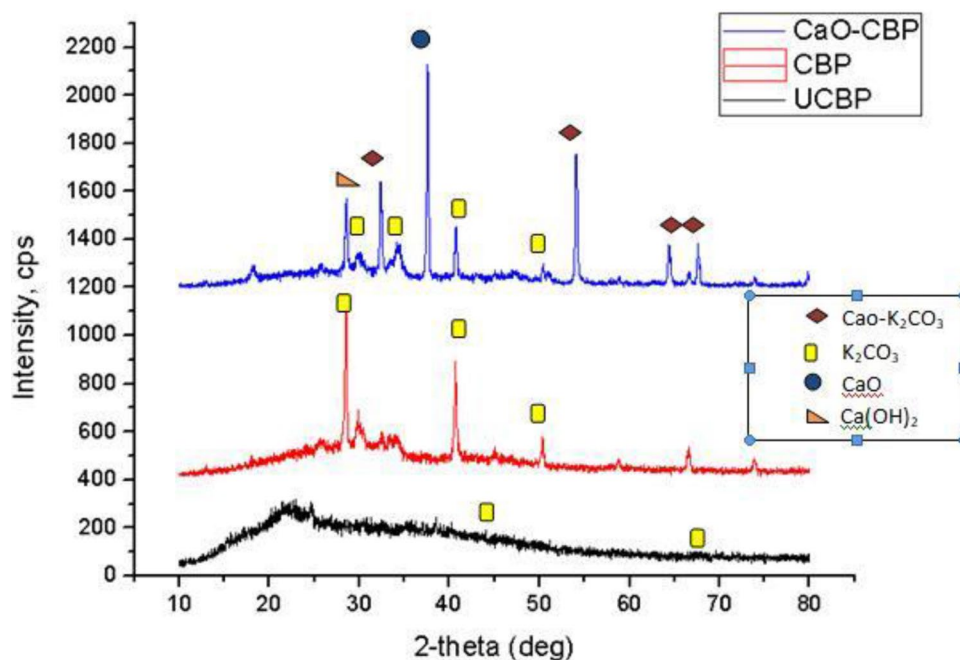**Fig. 1** FTIR spectra of UCBP, CBP and CaO-CBP

Fig. 2 XRD diffractogram of UCBP, CBP and CaO-CBP

as in Fig. 1. Then the peak observed at 1048.43 cm^{-1} was assigned to Si–O–Si stretching bands while 1461.82 cm^{-1} indicated C-H bending. The band at 669.04 cm^{-1} shows the presence of C=C bending.

In the spectrum of CaO-CBP, an absorption band at 3420.60 cm^{-1} could be ascribed to the OH stretching

bands. The bands at 1460.01 cm^{-1} and 869.48 cm^{-1} in this spectrum correspond to the C–O bond. The vast and strong bands at around 569.58 cm^{-1} corresponded to Ca–O bonds. The FTIR peak position at 3643.97 cm^{-1} indicated the presence of an isolated hydroxyl group (OH). This isolated OH group becomes responsible for active catalytic

activity (Sahu et al. 2017). The peak of 1048.90 cm^{-1} indicated vital C–O stretching while 1627.25 cm^{-1} referred to as medium C=C stretching of alkene and C–H bending for aldehyde, was shown at 1384.51 cm^{-1}. Concluding the FTIR results shows that the impregnation of CaO on CBP was done successfully.

X-ray diffraction (XRD) analysis

XRD analysis was performed for UCBP, CBP, and CaO-CBP to determine that CBP is a good support material for CaO to produce a catalyst for the transesterification process. Figure 2 illustrated the XRD results for UCBP, CBP, and CaO-CBP. The diffractogram of UCBP showed intense peaks at 43.0°, which correspond to (130) planes. However, the peak at $2\theta = 67.7°$ with (124) plane was not seen. The XRD pattern of CBP has analyzed the presence of compound K_2CO_3 where the intense peak was popped up at 29.867, 40.679 and 50.326 of 2θ, which correspond to (121), (1,3,-2) and (240) planes, respectively. From Fig. 2, the diffractogram in CBP had form crystalline compounds than UCBP.

As CBP was filled with CaO, the CaO-CBP diffractogram revealed a new step of CaO-K2CO3 at 32.379°, 54,035°, 64,403° and 67,611°. The peaks in the catalyst at 29.80°, 34.172°, 40.694° and 50.298° are the features of phase K_2CO_3. Because of $Ca(OH)_2$ (portlandite), the signature peak was observed at 2θ 28.57°. This is created because of the partial hydration of fresh CaO (Sahu et al. 2017). The CaO-CBP diffractogram also indicated the formation at 37,553° of the CaO process formed due to the ion exchange of eggshell calcium ions with K_2CO_3 potassium ions in high-temperature banana peel (Nisar et al. 2017).

Brunauer–Emmett–Teller (BET) analysis

The surface area and pore volume of UCBP, CBP, and CaO-CBP were analyzed by using BET analyzer obtained results are represented in Table 2.

Table 2 indicates the surface area increased from UCBP to CaO-CBP. However, from UCBP to CBP, the pore volume and pore size increase, but there was a decrease from CBP to CaO-CBP. The BET surface area for UCBP, CBP and CaO-CBP were 4.8529 m^2/g, 15.9567 m^2/g, and 23.0722

m^2/g, respectively. The pore volume of UCBP was 0.003133 cm^2/g. The pore volume increased to 0.020469 cm^2/g after calcined and decreased to 0.019104 cm^2/g after undergoing the impregnation method with the CaO compound. The pore size also increased from 25.8222 Å to 51.3117 Å and then decreased to 33.1211 Å. These characteristics occur after calcination of UCBP and impregnation of CaO into CBP. After calcination, the increased surface area with loading amount of CaO may be due to the much higher pore volume or opening of closed pores on the catalyst's surface during calcination (Sahu et al. 2017). The pore size and pore volume of catalyst decreased due to impregnation of CaO into CBP. Furthermore, controlled CaO addition has a positive impact on acid–base properties, limiting pore blocking by coke (Torres et al. 2020).

Hammett indicators

The H_ value of the CaO-CBP can determine by using Hammett indicators. It is used to determine the basicity of the catalysts. In this case, phenolphthalein (H_ = 9.8), 2,4-dinitroaniline (H_ = 15.0) and 4-nitroaniline (H_ = 18.4) were used as Hammett indicators when the base strength of the catalyst exceeded the H_ range of the Hammett indicators, the color-changing as illustrated in Table 3.

As stated by (Wu et al. 2015), if the color of indicators has changed, it shows that the primary strength of the catalyst was higher than the indicator pH range; meanwhile, if the indicator has failed to change color, the pH range of the catalyst was lower than the indicator pH range. Based on Table 3, the pH range of the CaO-CBP catalyst was higher than 9.8 in the phenolphthalein indicator due to changing color from colorless to pink. However, the other two indicators which were 2,4-dinitroaniline and 4-nitroaniline not showing unchanged color. This revealed that catalyst had basicity in the range of 9.8 < H_ < 15.0, indicating a lower base strength.

Scanning electron microscopy (SEM) analysis

The surface morphologies with EDX for elemental composition of the UCBP, CBP, and CaO-CBP catalysts were studied by scanning electron microscopy (SEM) and the

Table 2 Surface area and pore volume profile of UCBP, CBP and CaO-CBP

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
UCBP	4.8529	0.003133	25.8222
CBP	15.9567	0.020469	51.3117
CaO-CBP	23.0722	0.019104	33.1211

Table 3 Basicity determination of CaO-CBP catalyst

Catalyst	Color change		
	Phenolphthalein (H_ = 9.8)	2,4-dinitroaniline (H_ = 15.0)	4-nitroaniline (H_ = 18.4)
CaO-CFB	Colorless to pink	Yellow remain unchanged	Yellow remain unchanged

Fig. 3 SEM images of (**a**) UCBP, **b** CBP and **c** CaO-CBP under 5 k magnification
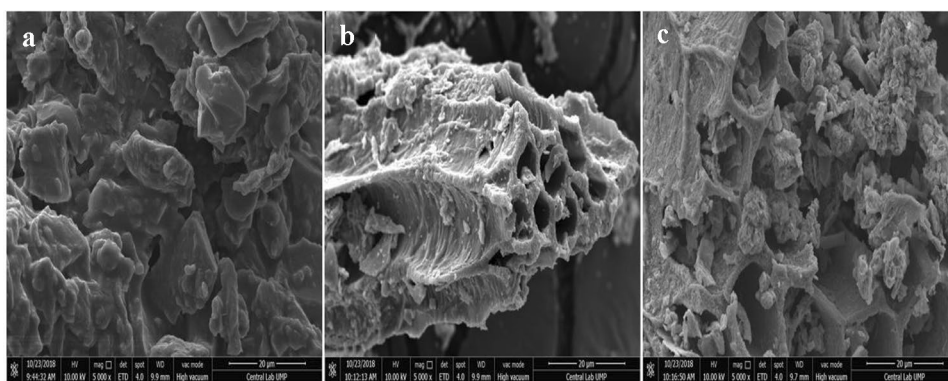
images obtained were very irregular in shape are shown in Fig. 3a–c respectively. The images were taken at a resolution of 5000. Figure 3a shows that the UCBP is in a highly irregular and clustered form. Uncalcined material could not give high conversion efficiency due to less active surface availability (Sahani et al. 2018). The surface of CBP in Fig. 3b showed the presence of the nodule with a relatively rough surface where the agglomerated particles are evenly dispersed after calcination at 900 °C over the irregular-shaped flat surface of the formed catalyst. However, the surfaces of catalysts impregnated with metal are shown in Fig. 3c was commonly correlated with the development of smaller aggregates with variable morphologies throughout the catalysts. The formation of clusters of CaO-K_2CO_3 particles would lead to irregularities in the morphologies of metal impregnated catalysts during their impregnation method (Aransiola et al. 2010). The smaller the size of aggregates could provide the higher specific surface areas.

The elemental components of UCBP, CBP, and CaO-CBP, were determined through energy dispersive X-ray analysis (EDX). Figure 4 representing the spectra of SEM–EDX of the catalyst samples that showed elements

like carbon, oxygen, calcium, and potassium. Quantitative analysis in UCBP, as observed in Fig. 4a indicates the presence of 57.53% C–K, 21.34% O–K, 7.66% K–K, and 3.61% Cl–K in UCBP; meanwhile in CBP, Fig. 4b, there is 49.48% C–K, 10.98% O–K, 20.95% K–K and 8.06% Cl–K. Figure 4c shows the elements found on CaO-CBP are O–K, K–K, and Ca–K with weight content of 37.23%, 1.89% and 48.48%, respectively.

Qualitative and quantitative analysis of methyl ester

TLC method is a test used to confirm the yield of methyl ester present as the transesterification product. This test was conducted before the product was subjected to GC analysis. TLC result of methyl ester under transesterification reaction for the catalyst amount of 7 wt% at 2 h reaction with MeOH: oil ratio, 1:9 and standard. Although the procedure to carry out TLC analysis is rapid and straightforward, the quantitative test cannot be determined accurately because the volume of sample applied is not consistent on the TLC plate. The percentage of conversion of soybean oil into methyl ester can

Fig. 4 SEM–EDX spectra of **a** UCBP, **b** CBP and **c** CaO-CBP
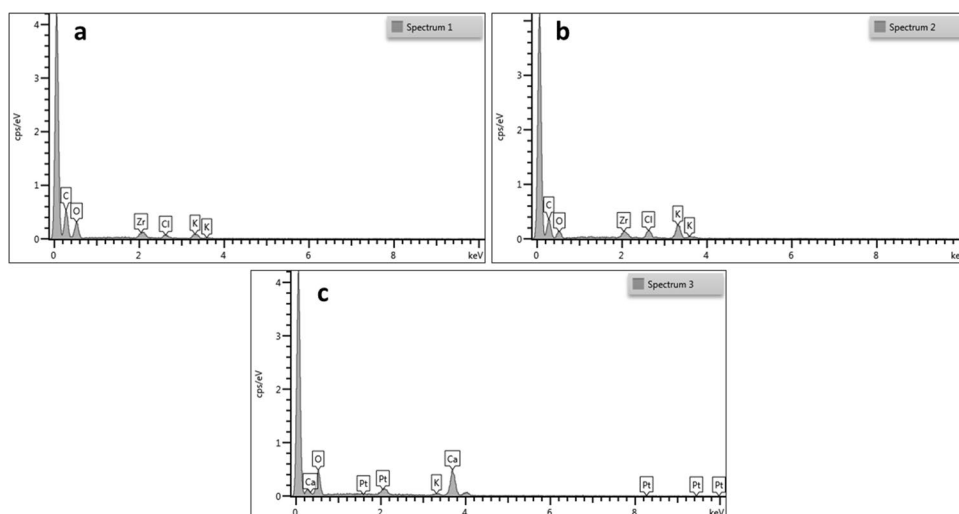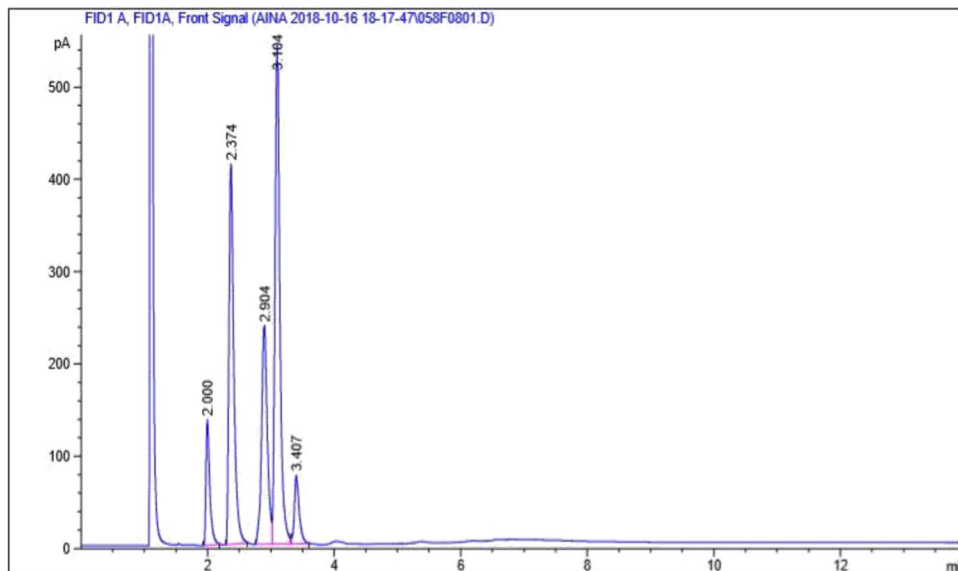
Fig. 5 Gas chromatogram (FID) of methyl ester of soybean oil

be calculated by carrying out GC-FID analysis. Conversion of methyl ester can be obtained by calculating the area of peaks on the GC-FID result. Figure 5 shows the GC-FID result for methyl ester of soybean oil.

Optimization of transesterification reaction parameters

Effect of CaO concentration

The CBP catalysts were synthesized with a varied concentration of CaO from 10 wt. % to 50 wt. % To determine the effect of CaO loading on the catalyst performance. Figure 6a shows the relationship between the CaO concentration and the yield of methyl ester produced. The yield of biodiesel slowly improved from 25.93 wt. %, 76.55 wt. % to 93.31 wt. % when CaO concentration increased from 10 wt. % to 30 wt. %. The active site (basic site) had increased as the total basicity increased in transesterification reaction (Irmawati et al. 2014). Unfortunately, when the concentration of CaO increased to more than 30 wt. %, the yield of methyl ester decreased. The conversion dropped to 27.27% for 40 wt. % of CaO due to the crystallization and agglomeration on the excessive active species at the surface of the catalyst, leading

Fig. 6 **a** Effect of CaO concentration on ME conversion at MeOH/oil ratio of 15:1 and catalyst amount of 5 wt% for 4 h (**b**) Effect of catalyst amount on ME conversion for 30 wt.% CaO-CBP at MeOH to oil molar ratio of 9:1 for 2 h (**c**) Effect of reaction time on ME conversion for CaO-CBP at MeOH to oil molar ratio of 9:1 and catalyst amount of 7 wt% (**d**) Effect of MeOH to oil molar ratio on ME conversion for CaO-KCB at catalyst amount of 7 wt% for 2 h
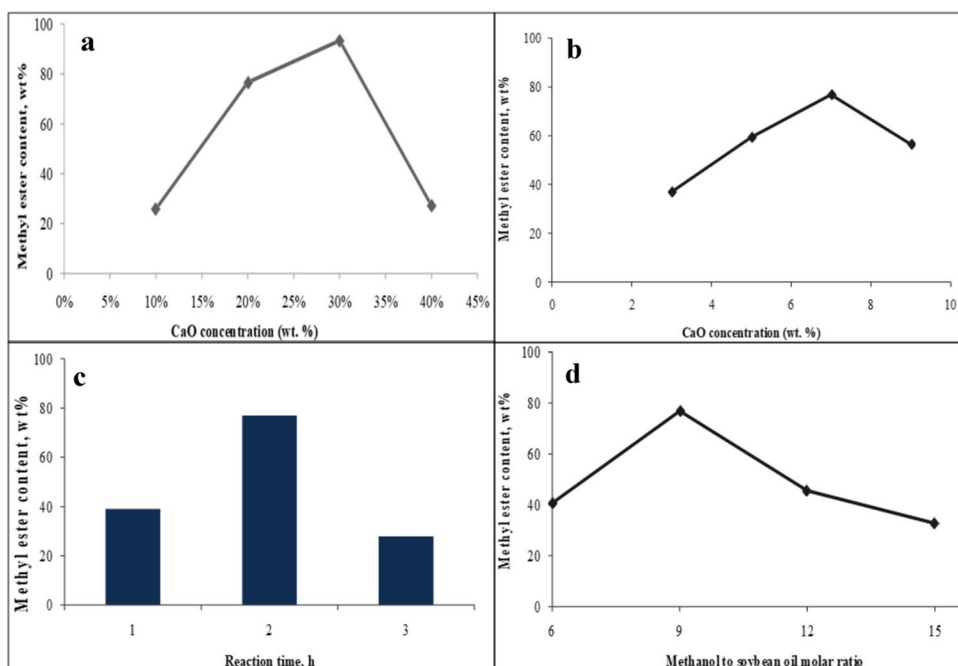
to poor dispersion of CBP species. Hence, the impregnation of 30 wt. % CaO on CBP was chosen to be the best for solid catalyst.

Effect of catalyst concentration

The catalyst used in the reaction would play an essential role in influencing the yield of the synthesized Renown by speeding the reaction by decreasing the reaction's activation energy 30 wt. in this research report. Throughout the transesterification reaction, CaO-CBP % was used as the catalyst. The volume of the catalyst was optimized to achieve the best yield of methyl ester. The sum of the catalyst ranged from 3 Wt. % up to nine wt. % dependent on soybean oil's weight. The ME yield has risen from 36.93 wt, as seen in Fig. 6b. %age of 59.40 wt. 76.87% to wt. %age. As the catalyst quantity has increased, Methyl easter yield steadily increases due to the increase in the active reactant site to undergo reaction. Due to the maximum Renown yield produced, a %age of the catalyst was used. The ME content decreased to 56.55 wt. % when the amount of catalyst used increased to 9 wt. %. Hence, the optimization of catalyst amount at 7 wt % was used in the transesterification reaction. Thus, the higher amount of catalyst would lead to the lower conversion of methyl ester (Vicente et al. 2004).

Effect of reaction time

The critical parameter, which is the reaction time, can impact the yield of biofuel production. Based on Fig. 6c had shown the effect of different reaction times on the methyl ester conversion. The ME conversion increased from 38.95 wt. % to 76.87 wt. % when the reaction time increased from 1 to 2 h. but after 3 h, the yield of ME conversion decreased rapidly to 27.84 wt. %. Obtained results indicated that 2 h of transesterification reaction is the best to get the highest yield of FAME. As the interaction of oil and methanol is simple, the total yield of ME conversion can be achieved quickly. But Talha and Sulaiman (2016) suggested that FAME's yield would remain unchanged when the equilibrium state was achieved. If the reaction time were much longer than the optimal reaction time, extreme reactions such as saponification would occur, and the FAME yield would decrease. When the soaps were made, the FAME conversion yield decreased rapidly when the optimal reaction time was surpassed (Zainal et al. 2018).

Effect of methanol on soybean oil molar ratio

Methanol to oil molar ratio was one of the parameters used in the optimization of methyl ester yield. Figure 6d shows the %age conversion of methyl ester by 7 wt % constant the catalyst amount and 2 h reaction time. The methyl ester conversion was investigated at 6:1, 9:1, 12:1 and 15:1 of methanol to oil molar ratio. In Fig. 6d, the methanol to oil molar ratio increased from 6:1 to 15:1 to show the effect on ME % of conversion. The yield conversion of ME-oil increased from 40.72 wt. % to 76.87 wt. % when the amount of methanol to oil ratio increased from 6:1 to 9:1. However, when the methanol to oil molar ratio further increased to 12:1, which beyond the optimum value, the yield of production decreased to 45.60 wt. %. At a methanol to oil ratio of 151, the conversion yield of ME-oil further decreased to 32.74 wt. %. In transesterification reaction, the excess amount of alcohol used would lead to the increased solubility of glycerin and causing difficulties in the separation of biodiesel and glycerol, especially under high temperature. (Basumatary 2014) stated that the lower ME conversion occurred due to glycerolysis reaction under this unfavorable condition for biodiesel.

Conclusion

A heterogeneous catalyst was successfully synthesized from waste calcinated banana peels impregnated with CaO in this research. The catalyst was calcined at 700 °C and, using the dry impregnation process, CaO is added from the calcined (at 900 °C) eggshells. The catalysts prepared were subjected to various characterizations such as BET, SEM–EDX, FTIR, XRD, and the Hammett indicators test for their basicity. The catalysts were then used for the transesterification of soybean oil to produce FAME. Transesterification reactions were done at different parameters to find out the optimum conditions. The XRD diffractogram clearly showed the different crystalline structures between CBP and CaO-CBP catalyst. The FTIR results clearly shown at the catalyst CaO-CBP peak was presented at 569.58 cm^{-1} indicating the Ca-O bonds. The BET results revealed that with CaO-CBP the surface area was increased, but the pore volume and pore size were decreased. Based on the SEM–EDX image, the surface area of CaO-CBP was smoother than CaO, which was exhibited a porous and rough shape. The pH range of CaO-CBP was identified at the range of H_ = 9.8 by Hammett indicators testing. Due to the high methyl ester conversion, CaO-CBP catalyst tends to be a promising solid base catalyst for biodiesel manufacture. In this analysis, the maximum methyl ester conversion was found at 76.87 wt.%. under 7 wt.% catalyst, methanol to oil molar ratio of 9:1 and reaction time of 2 h.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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