JOURNAL of the TURKISH CHEMICAL SOCIETY
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CHEMISTRY

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Biodiesel Production from Waste Frying Oil using Catalysts Derived from Waste Materials

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Abstract: Domestic resources such as vegetable oil, animal fats, tallows, and waste frying oil are common raw materials for making biodiesel. In contrast to ordinary diesel, biodiesel helps to reduce CO_2 emissions. This study aimed to produce biodiesel using waste frying oil in the presence of suitable solid waste-derived heterogeneous catalysts. Firstly, CaO/K_2O catalyst was synthesised using eggshells and banana peels. Then, the pre-prepared catalyst (CaO/K_2O) modified with ZnO was utilized for biodiesel production. The prepared catalyst and biodiesel were characterized using X-ray diffraction (XRD) and FTIR spectroscopy. The AOAC and ASTM standard methods were employed to analyze the physicochemical properties of oils and biodiesel. The catalytic efficiency of CaO/K_2O and CaO/K_2O-ZnO tested for the transesterification of purified oil to biodiesel at the catalyst weight (1-7 % wt), temperature (60-80 °C), and methanol to oil ratios ranging from 3:1 to 12:1. The highest biodiesel yield (92%) obtained when 5 % wt CaO/K_2O catalyst used. However, a 95% yield resulted when using a 3 % wt CaO/K_2O-ZnO catalyst load in 2 h with a methanol to oil (v/v) ratio of 9:1 at 65°C. The study revealed that waste frying oil is a good source of biodiesel which could replace nonrenewable energy in the future. The catalysts made from solid waste could also replace an expensive chemical catalyst.

Key words: Biodiesel; frying oils; CaO/K_2O-ZnO catalyst; Transesterification

Submitted: September 19, 2021. **Accepted:** May 31, 2022.

Cite this: Meka Kedir W, Girma Asere T. Biodiesel Production from Waste Frying Oil using Catalysts Derived from Waste Materials. JOTCSA. 2022;9(3):939–52.

DOI: https://doi.org/10.18596/jotcsa.997456.

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INTRODUCTION

Renewable energy generation has been prioritized globally due to the energy and global warming crises (1). Currently, fossil fuel represents 88% of total world energy consumption and is the largest energy source (2). Non-renewable fossil fuels contribute approximately 52% of CO_2 emissions to the atmosphere and are the sources of other greenhouse gases (3). Various renewable resources are considered alternative fossil fuels, including wind, solar, geothermal, wave energy, and biofuel (4, 5). Biodiesel is sold as a diesel engine supplement fuel among various alternative fuels (6). Its advantages are renewability, degradability, non-toxic nature, and compatibility with other energy sources (5, 7). However, the current biodiesel production uses edible oils, which are more expensive than petroleum-based fuels (8). In addition to the high feedstock cost of biodiesel production, the absence of economically and technically viable technology affects its efficient production (9, 10). Thus, using non-edible oil as a biodiesel source may alleviate the existing problems (11, 12).

Transesterification of oil with alcohol with suitable homogeneous or heterogeneous catalysts yielded fatty acid methyl ester or biodiesel (13). The Common used homogeneous catalysts for the transesterification processes are NaOH, KOH, and CH_3ONa, which have high catalytic activity (14). However, separating, purifying, and reusing them is challenging (7). Various heterogeneous catalysts for biodiesel generation have been developed, including zeolite, alkali earth metal oxides, KF/YAl_2O_3, and sodium aluminate (12). However, due to the high cost of catalyst manufacturing, only selective heterogeneous catalysts are used in industry (15). The wise use of waste material as a heterogeneous catalyst can minimize overall biodiesel production costs. CaO and K_2O are common catalysts for biodiesel production because they are abundant in nature, low cost, and show high activity (1). Therefore, this study aimed to produce biodiesel using waste frying oil in the presence of suitable solid waste-derived heterogeneous catalysts.

MATERIAL AND METHODS

Study Area and Study Period

Heterogeneous catalyst preparation, waste frying oil refining, and biodiesel production were carried out at Mattu University, College of Natural and Computational Sciences, Department of Chemistry. The physicochemical properties of the catalysts, oil, and biodiesel were studied by using various analytical techniques. The XRD of catalysts and FTIR analysis of oil and biodiesel were carried out at Jimma University, Institute of Technology, Department of Material Sciences.

Chemicals

Chemicals used for this study include chloroform (99%) and methanol (99.99%) from Blulax, India. Glacial acetic acid, potassium iodide, sodium bisulfate, hydrochloric acid, ammonium chloride, ammonium hydroxide, starch, and phenolphthalein indicator, distilled water, hanus solution, ethanol, ferric chloride, sodium thiosulfate, potassium hydroxide, and sodium hydroxide were used for the physicochemical analysis of oil and biodiesel.

Apparatus and Instrument

Apparatus such as titration flask, burets (300 and 5 00 mm), pestle, and mortar, filter paper, weighing balances, oven, beakers, funnels, Erlenmeyer flasks, magnetic stirrer, crucible dish, water bath, aluminum foil, refrigerator, and rotary evaporator, muffle furnace, and thermometer were used. Instruments such as refractometer, conductometry, pH meter, XRD, and FTIR were used.

Sample Collection

Eggshell, banana peel, and waste frying oil samples were collected from Mattu town, Ilubabara Zone, South-West Ethiopia. A purposive sampling technique was adopted during sample collection.

Purification of Waste Frying Oil

The collected waste frying oil was allowed to pass through the micron-sized holes sieve to remove any solid particles. The filtrate was poured into a separatory funnel. It was followed by adding 40 mL of hot water to remove salt and other soluble particles. The separated oil was put into the oven at 105 °C to remove water. The purified oil was cooled to room temperature and then in a water bath for further analysis and biodiesel production (16).

Catalyst Preparation

The eggshell and banana peel samples were sliced and then washed using hot distilled water (40 °C) to remove waxy material and dirt particles.

Preparation of CaO

The raw waste eggshell is the source of $CaCO_3$ because it converts to CaO when calcined. A 50 g eggshell was dried overnight at 100 °C using an oven. Then, it was powdered and calcined for three hours in a furnace at 900 °C (17). The received CaO catalyst was kept in an airtight container for further use.

Preparation of K_2O

A 50 g banana peel was washed, sliced, and dried at 90 °C in an oven for 48 hours. The dried sample was powdered and calcined at 750 °C for 3 hours (17). The obtained K_2O catalyst was collected and stored in an airtight container for future use.

Preparation of CaO/K_2O

After separate preparation of CaO from the eggshell and K_2O from the banana peel, their mixture (1:1 ratio) is immersed in 10 mL of distilled water to form a solution. The solution was continuously stirred at 25 °C for 3 hours, and the obtained product was dried for 24 hours at 80 °C. Then, it was calcined for 5 hours at 500 °C (11). The received product was denoted as CaO/K_2O.

CaO/K_2O/ZnO Catalyst

A wet impregnation method was used to prepared CaO/K_2O/ZnO catalyst by mixing CaO/K_2O catalysts from (eggshells and banana peels) with ZnO in a ratio of 1:1:1 (CaO:K_2O:ZnO). The mixtures were immersed in distilled water (10 mL). Then, the solution was stirred for 3 hours continuously at room temperature, and the recevied product was dried for 24 hours at 80 °C (11). Next, the obtained material was calcined for 5 hours at 500 °C and the resulting catalyst was denoted as CaO/K_2O/ZnO.

Transesterification of Purified Oil Using CaO/K_2O and CaO/K_2O/ZnO Catalyst

The transesterification process was conducted according to the method reported in Khan H.M, et al. 2020 (18) with minor modifications. In a 250 mL two-necked flat bottom flask equipped with a reflux condenser, 20 mL of the purified oil was added, then stirred at 600 rpm for all test runs. The oil was heated at 105 °C for 5 minutes in a heating mantle to evaporate water and other volatile contaminants. A mixture of the oil and a calcined catalyst (1, 3, 5, and 7 % wt.) was stirred at 600 rpm. An oil to methanol ratio was 1:3 to 1:12. Each experiment was allowed to continue at a temperature of 65–80 °C. When the reaction completed, the solution was cooled, and centrifuged or filtered to separate the catalyst. The spent catalyst was regenerated by treating it with methanol. The filtrate mixture was then placed in a separatory funnel for 10 minutes to separate the layers. Methyl esters and unconverted triglycerides make up the top layer. Glycerol, excess methanol, soap generated during the process, and some entrained methyl esters were found in the lower layer. The excess methanol was removed by distillation before the fatty acid methyl esters (FAME) percent analysis. The percentage yield of biodiesel was calculated using Equation 1 (19).

$$\text{Biodiesel yield }\% = \frac{\text{weight of Biodiesel}}{\text{weight of oil used}} \times 100 \quad \text{(Eq. 1)}$$

Biodiesel Purification

The obtained biodiesel was rinsed with distilled water after removing the glycerol layer. The mixture was stirred using mechanical stirring for 10 minutes. The stirring was turned off after 10 minutes, and the water was left to settle for two days. At this point, the process was complete, and the clear crystal product was biodiesel (11, 17).

Physicochemical Analysis of Waste Frying Oil, Purified Oil, and Biodiesel

The physicochemical properties of waste frying oil (WFO), purified oil (PO), and biodiesel were analyzed following the AOAC official method (969.17). The common physicochemical properties include acid value (AV), refractive index (RI), iodine value (IV), saponification value (SV), density, free fatty acid (FFA), moisture content, ash content, pH, and cetane number (20, 21). The biodiesel was also subjected to ASTM standard fuel characterization. Density, flash point, pour point, and cloud point measurements of the ethyl esters produced were made following ASTM D6751 standards.

pH

A 3 g sample of oil or biodiesel was placed in a clean, dry 25 mL beaker, and 15 mL of hot distilled water was slowly poured and stirred. It was cooled in a cold water bath. The pH meter electrode was calibrated with buffer solution and immersed in the sample, and the pH value was recorded (21).

Moisture content

The AOAC official method (969.17) was employed to determine the moisture content. The oil/biodiesel was weighed and dried for 24 hours at 105 °C in an oven. The final weight was taken and recorded (20). The moisture content was calculated by using Equation 2.

$$\text{Moisture }(\%) = \frac{\text{Initial weight of oil - Final weight of oil}}{\text{Initial weight of oil}} \times 100 \quad \text{(Eq. 2)}$$

Ash content

2 g of oil or biodiesel sample was added to a crucible dish. The crucible contained the sample was heated carefully in the muffle furnace at 775 °C for 25 minutes until all carbonaceous materials were disappeared. Then the crucible was cooled at room temperature in a desiccator (20). The ash content was calculated using Equation 3.

$$\text{Ash}(\%) = \frac{W_3 - W_1}{W_2} \times 100 \quad \text{(Eq. 3)}$$

Where, W_1= weight of crucible dish, W_2=weight of oil sample, W_3=Weight the sample plus the crucible dish after calcination.

Acid value (AV)

A 2 g of oil/ biodiesel sample was mixed with neutral ethyl alcohol (30 mL); after boiling for 2 minutes in a water bath, the mixture was titrated with KOH solution (0.1 N) using phenolphthalein as an indicator (20). The AV was calculated by using equation 4.

$$\text{Acid value} = \frac{V \times N \times 56.1}{W} \quad \text{(Eq. 4)}$$

Where, V is the volume in mL of standard KOH used, N is the normality of the KOH solution, and W is the weight in g of the sample.

Determination of free fatty acid (%)

The acid values of the oil samples were used to calculate the percentage of free fatty acid of the samples (20) by using Equation 5.

$$\text{FFA }(\%) = \frac{\text{Acid value}}{2} \quad \text{(Eq. 5)}$$

Peroxide value (PV)

1 g of oil or biodiesel was placed in a conical flask. Then, 30 mL of glacial acetic acid/chloroform (3:2 v/v) was added. The mixture was shaken until the sample was dissolved. Then, 1 mL of saturated potassium iodide solution was added, followed by 0.5 mL of starch indicator solution. 0.1 M $Na_2S_2O_3$ (sodium thiosulfate) was used to titrate the solution until the dark blue color vanished. The PV was determined by using Equation 6 (20).

$$PV = \frac{Titer \times N \times 1000}{\text{weight of the sample}} \quad \text{(Eq. 6)}$$

Where, titer is the mL of $Na_2S_2O_3$ used (blank corrected), and N is the normality of sodium thiosulfate solution.

Determination of iodine value (IV)
1 g of sample was placed in a 250-mL conical flask, followed by adding 30 mL of Hanus iodine solution and mixing. Then, the mixture was kept in the drawer for 30 minutes. The mixture was titrated against 0.14 M $Na_2S_2O_3$ until the solution became light yellow. After the addition of a starch indicator (1%, 2 mL), the titration continued until the blue colors disappeared (20). A similar procedure was employed to determine the blank solution. The IV was calculated by using Equation 7.

$$IV=\frac{(B-S)\times N\times 12.69}{\text{Weight of sample}} \quad \text{(Eq. 7)}$$

Where, B is the volume in mL of standard $Na_2S_2O_3$ solution required for the blank, S is the volume in mL of standard $Na_2S_2O_3$ solution required for the sample, and N is the normality of the standard $Na_2S_2O_3$ solution.

Saponification value (SV)
The AOAC official method (920.160) was used to determine the saponification value (SV). A 2.5 g of oil or biodiesel sample was heated with alcoholic potassium hydroxide (25 mL, 0.5%) for 30 minutes. The resulting solution was cooled and titrated with an HCl solution (0.5 N) using phenolphthalein as an indicator. The same volume of alcoholic KOH solution without oil was treated as a blank (20). The SV was calculated by using Equation 8.

$$SV=\frac{(B-S)\times N\times 56.1}{\text{Weight of sample}} \quad \text{(Eq. 8)}$$

Where, B is the volume in mL of standard hydrochloric acid required for the blank; S is the volume in mL of standard hydrochloric acid required for the sample; and N is the normality of the standard hydrochloric acid.

Cetane number (CN)
The calculated SV and IV were employed to calculate the cetane number (CN), which is the capacity of fatty acid methyl esters as a fuel to burn quickly after injection. The greater the value, the better the quality of the ignition. Cetane number is among the crucial factors must be considered when choosing fatty acid methyl esters for biodiesel production (21). The CN was determined by using Equation 9.

$$\text{Cetane Number (\%)}=46.3+\frac{5458}{SV-0.225\times IV} \quad \text{(Eq. 9)}$$

Where, SV is the saponification value, and IV is the iodine value.

Refractive index (RI)
An Abbé Refractometer (NYRL-3-Leica Mark, Leica Inc., Buffalo, New York) was used to determine the refractive index of the oil or biodiesel sample (20).

Density
The mass of an empty container weighed using a digital weighing balance to estimate the density of the biodiesel. A 5 mL of the produced biodiesel was added to the pre-weighed container and weighed again. The mass of mass of the biodiesel was calculated by subtructing the mass of the empty container from the mass of the container plus the biodiesel (20). The density was then determined by dividing the sample mass by its volume.

Determination of the Cloud Point
A few drops of biodiesel was poured right into a test tube. Then a thermometer was inserted into the test tube. The setup was put on a beaker containing ice. After a few minutes, the biodiesel was discovered to form a cloud of gel. The temperature at which the biodiesel form a cloud of gel record (22).

Determination of the pour point
The same setup as in the cloud point test was immersed in the ice and left to solidify. The test tube was withdrawn and inverted after the biodiesel form a solid, and the solid was closely examined until it began to flow. The temperature at which the solid biodiesel begin to flow was considered its pour point (22).

Determination of the flash point
A few drops of biodiesel were poured into a flask with a branch opening fitted with a cork. A thermometer was inseted into the flask through the cork with caution the thermometer tip not to contact the bottom of the flask. The biodiesel contained flask produced fume upon heating. The temperature at which the fume ignites considered as the flashpoint temperature (22).

Characterization of Synthesized Catalyst, Purified Oil, and Biodiesel

XRD measuremnts of the prepared catalysts (K_2O/CaO and K_2O/CaO/ZnO) performed to determine their composition and phase. FTIR spectroscopy was used to determine the functional groups present in the biodiesel.

RESULTS AND DISCUSSION

Physicochemical Analysis of Frying Oils

The oxidative breakdown of lipids is accelerated by repeated heating of the oil, creating dangerous reactive oxygen species and decreasing the frying oil's natural antioxidant content (23). The quality of biodiesel depends on the quality of oil used to produce it. The quality of the oil depends on its physicochemical properties. Thus, it is crucial to determine the physicochemical properties of the oil to prepare good quality biodiesel.

Physical Properties of Frying Oil

The physicochemical properties of waste frying oil and purified oil were determined to evaluate their suitability for biodiesel production. Table 1 summarizes the obtained results.

Table 1: Physical properties of oils.

Physical properties	Local oil (Hayat)	WFO	PO	AOAC Standard (20)
Moisture (%)	0.2	0.3	0.1	≤0.3
Ash (%)	NS	0.2	0.012	0.015
pH at 25 °C	6.5	5	6.32	5-7
Density g/ml) 25 °C	NS	0.644	0.510	0.840
Odor	Agreeable	Unpleasant	Agreeable	Agreeable
State at 25 °C	Smooth-S	Viscous-L	liquid	liquid
Conductivity (µS/cm)	-	0.04	0.5	NS
RI (at 25 °C (nD)	1.4665	1.443	1.3453	1.4694
Color	White-yellowish	Reddish-brown	yellowish	yellowish

WFO= waste frying oil, PO= purified oil, NS=not specified, S=solid

The percentage moisture content of purified oil (0.1%) was lower than waste frying oil (0.3%), but the moisture content of WFO was higher than the raw un-frying oil (0.2%). The higher moisture content can cause difficulties such as water accumulation and growth of microbes in fuel handling and storage, as well as inappropriate post-processing treatment (24). The low moisture content of purified oil samples may improve their storability and suitability (25). The ash value refers to the amount of solid material left behind when the oil burns. The results showed that the WFO samples have a significant amount of ash compared to PO; it indicates a high amount of solid materials left over after frying (25). In addition, the ash value of WFO (0.2%) is much higher than the AOAC standard (0.015) (20). The RI value of oils varies depending on molecular weight, fatty acid chain length, unsaturation, and conjugation. The RI value of the purified oil (1.3453) was lower than that of unpurified oil (1.443). This lower RI of PO can be explained as the oxidation of double bonds of the oil during frying and then up on treatment with hot water reduces the oil unsaturation. The pH of WFO is lower than that of PO (Table 1). The higher pH of PO may be due to the removal of some free fatty acids during the purification. The lower density of PO (0.510 g/mL) indicates that the WFO (0.644 g/mL) had lost some soluble particles upon treatment.

Chemical Properties of Frying Oil

Table 2 gives the chemical properties of WFO and PO oils like AV, FFA, SV, IV, and PV. The acid values (mg/KOH/g) of WFO and PO were 8.42 and 5.61, respectively. The acid values of both WFO and PO oils were higher than the value in the AOAC standard (20). The increase in acid value on WFO may be due to the formation of small monomeric acids and FFA on thermal oxidation. The saponification values (mg/KOH/g) of WFO and PO were 213.2 and 190, respectively (Table 2), where these values are in good agreement with the value given in the AOAC standard (20). The higher the SV of WFO could be due to the presence of lower molecular weight fatty acid in glycerides than that of PO (11). The iodine value (IV) measures the degree of unsaturation in fatty acids. In general, the degree of polymerization increases as the IV of unsaturated fatty acids increases (26).

Table 2: Chemical properties of waste frying and purified oil.

Chemical Properties	Local oil (Hayat)	WFO	PO	AOAC Standard (20)
Acid value(mg/KOH/g)	3	8.42	5.61	≤4.00
% FFA (mg/KOH/g)	1.5	4.208	2.805	≤1.304
Saponification value (mg/g)	190	213.2	190	≥ 180
Iodine value (g/100g)	90	76	69	80-100
Peroxide value (meqO_2/kg)	10	13	8	2-10

WFO=waste frying oil, PO=purified oil

The IV of WFO (76 g/100 g) was higher than that of PO (69 g/100 g), but the IV of WFO and PO were less than the AOAC standard. Similarly, the peroxide value of WFO (13 meq/kg) was higher than that of PO (8 meq O_2/kg). PV is the most widely used test for determining the state of oxidation in fats and oils. It also indicates the fats/oil's rancidity or degree of oxidation, not its stability. The PV value of WFO was higher than the maximum limit of the AOAC standard (2-10 meq O_2/kg), but PO was within the range of the AOAC standard (20). The high PV of WFO may be due to the high moisture content of oil since increased moisture content increases PV.

Physicochemical Properties of Catalysts

Table 3 gives the physicochemical properties of banana peels, eggshells, and the prepared catalysts. The pH values of the raw and the synthesized materials were in the alkaline range (Table 3). The percentage moisture content of banana peels (50%) was higher than that of the eggshell (20%). The ash content of the catalysts was 42% (C.E. S) to 45% (ZnO/B.P /E.S). The highest ash content of the ZnO/B.P/E.S may be due to the impregnation of ZnO.

Table 3: Physicochemical properties of the catalyst.

Physical properties	BP	ES	C.B.P	C.E.S	ZnO/B.P /E.S
pH	9.91	9.33	11.9	8.5	11.81
Moisture content (%)	50	20	-	-	-
Ash content (%)	44	43	42	42	45
Conductivity (μs/cm)	3.5	4.6	2.5	3	2.7
Colour	Black	White	Black	White-black	Bluish
Calcination T(°C)	-	-	700	900	500
Calcination time (h)	-	-	3	3	5

B.P = banana peel, E.S = eggshell, C.B.P= Calcined banana peel, C.E.S= Calcined eggshell

Transesterification of Purified Oils

The transesterification of purified oil was evaluated under the conditions of catalyst weight (1–7 % wt.), temperature 60–80 °C, and methanol to oil ratio of 3:1 to 12:1. For the CaO/K_2O catalyst; the highest biodiesel yield (92%) obtained for a 9:1 methanol to oil ratio, at 5% wt catalyst load in 3 h at 65 °C. However, with CaO/K_2O-ZnO catalyst, the methanol/oil molar ratio of 9:1 resulted in the highest biodiesel yield (95%) with a 3 % wt catalyst load in 2 h at 65 °C. It means that incorporating ZnO into CaO/K_2O catalyst can facilitate the conversion of oil to FAME (biodiesel) and shorten the reaction time. This study resulted in a higher yield of biodiesel (95%) compared to the previously reported by Zuleta et al. (26), which claimed that 2% wt. K_2O/CaO-Zinc oxide catalyst showed the highest activity with a FAME yield of 81% at a 15:1 methanol to oil ratio at a temperature of 60 °C in 4 h. The observed yield difference may be due to the difference in the amount of ZnO presented in the catalyst, the size and purity level of the catalysts.

Effect of Reaction Parameters on the Biodiesel Yield

The parameters that affect biodiesel yield: the methanol to oil ratio, the catalyst load, catalyst reusability, temperature, and reaction time evaluated; the obtained results are given in Figures 1, 2, 3, 4, and 5, respectively.

Effect of Methanol/Purified Oil Ratio

Figure 1 illustrates the influence of the methanol/oil ratio on the formation of methyl ester. The highest

FAME yields were obtained (95%) for 6:1 and 9:1 using CaO/K_2O-ZnO (3% wt.), but a 92% yield was obtained using CaO/K_2O (5% wt), a 9:1 methanol to oil ratio in 3 h. However, the FAME yield was lower for both CaO/K_2O and CaO/K_2O-ZnO catalysts in the 3:1 and 12:1 methanol to oil ratios. These indicate that the optimum methanol to oil ratio was 9:1. The results contradicted the one reported by Madhuvilakku and Piraman (27), the optimum methanol to oil ratio for FAME production is 6:1. This disagreement may be due to the difference in the catalyst, the oil quality, and the reaction condition. On the other hand, the results of this study were in agreement with the results reported by Refaat (28), who prepared biodiesel from waste cooking oil at an optimum 9:1 oil to methanol ratio.

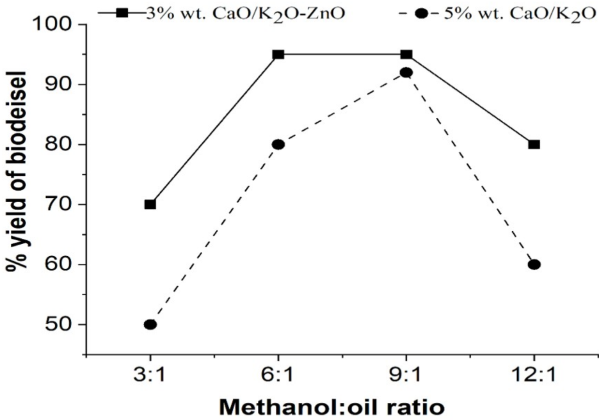

Figure 1: Effect of methanol to oil on biodiesel yield with time 3 h and temperature 65 °C.

Effect of Temperature on Biodiesel Yield

The effect of temperature on the yield of FAME was evaluated using a 9:1 methanol to oil ratio at a fixed reaction time (3 h). At lower temperatures, the FAME conversion efficiency was very low. The temperature around the boiling point of alcohol resulted in the maximum FAME yield. Therefore, 65 °C was the optimum temperature with 95% and 92% FAME yields for CaO/K_2O-ZnO (3% wt) and CaO/K_2O (5% wt.) catalysts, respectively. The FAME yields decreased as the temperature increased to 80 °C (Figure 2). It may be due to the methanol in the vapor form (beyond its boiling point) less interacting with the oil. The result of this study agrees with the previously reported data by Birla A, et al. 2012 (15), and stated that the reaction temperature must be lower than the boiling point of the alcohol to avoid loss of alcohol through vaporization from the reaction media. Therefore, alcoholysis of vegetable oils is usually carried out at atmospheric pressure at the boiling point of the alcohol.

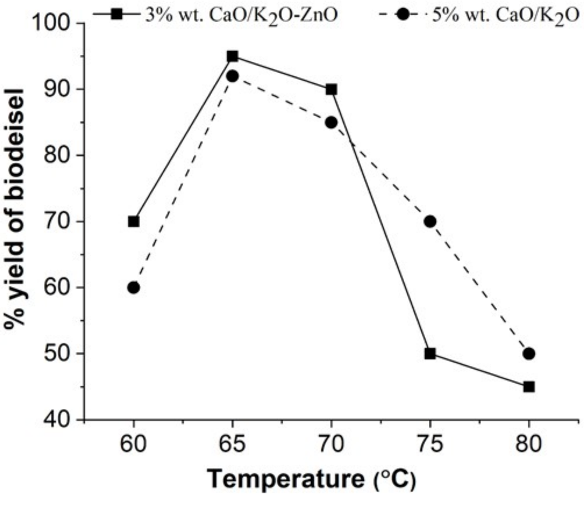

Figure 2: Effect of temperature on biodiesel yield with 9:1 methanol to oil ratio in 3 h.

Effect of Catalyst Load on Biodiesel Yield

The effect of catalyst load on the biodiesel production was evaluated for both CaO/K_2O-ZnO and CaO/K_2O catalysts with a 9:1 methanol to oil ratio in 3 h reaction time by varying the doses from 1 to 7% wt, keeping the temperature at 65 °C. Figure 3 shows the obtained results. The ZnO doped catalyst (1%) converted 60% of the oil into FAME, but as the catalyst load increased to 3% wt, the conversion oil to FAME reached 95%.

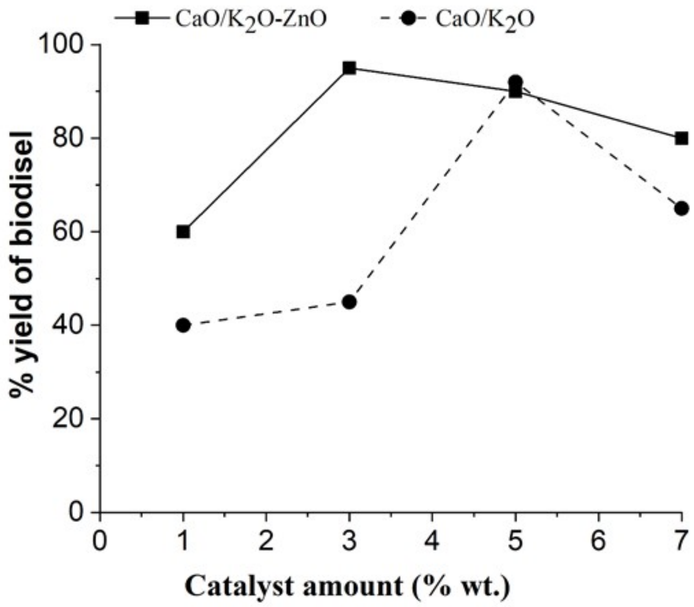

Figure 3: Effect of catalyst load on biodiesel yield with a 9:1 methanol/oil ratio for 3 h at 65 °C.

The result indicates that a 3% CaO/K_2O-ZnO catalyst was sufficient to convert 95% oil to biodiesel with a 9:1 methanol to oil ratio in 3 h. The catalyst without ZnO converts 92% of oil to biodiesel (FAME) with a 9:1 methanol to oil ratio in 3 h. In the previous report, the percentage yield of biodiesel from *Citrullus vulgaris* seeds oil using NaOH as a catalyst was only 70% (19). This variation may be due to the higher amount of NaOH (0.13 g) employed may convert oil to soap rather than biodiesel. Further, increasing the catalyst amount does not increase the yield due to a mixing problem involving reactants, products, and solid catalyst (29).

The Effect of Reaction Time (h) on Biodiesel Yields

The effect of reaction time on the biodiesel formation evaluated using CaO/K_2O-ZnO (3% wt.),and CaO/K_2O (5% wt.) catalysts at constant temperature (65 °C), methanol to oil ratio of 9:1. Figure 4 illustrates the effect of reaction time on the conversion of oil to biodiesel. The conversion of the oil to biodiesel using either catalyst increased up to 3 h. However, the CaO/K_2O-ZnO catalyst reached 95% conversion in 2 h. These indicate that modifying CaO/K_2O catalyst using ZnO can improve the biodiesel yield and shorten the reaction time. As the reaction time goes beyond 3 h, the conversion of oil to biodiesel decrease for CaO/K_2O-ZnO and CaO/K_2O catalysts. Therefore, a reaction time of 3 h is assumed to be an optimum time for the maximum biodiesel yield for CaO/K_2O-ZnO (3% wt.) and CaO/K_2O (5% wt.) catalysts using methanol and an oil ratio of 9:1 molar ratio at 65 °C. The effective conversion of oil to FAME in a short time using the prepared catalysts is favorable for industrial applications (5).

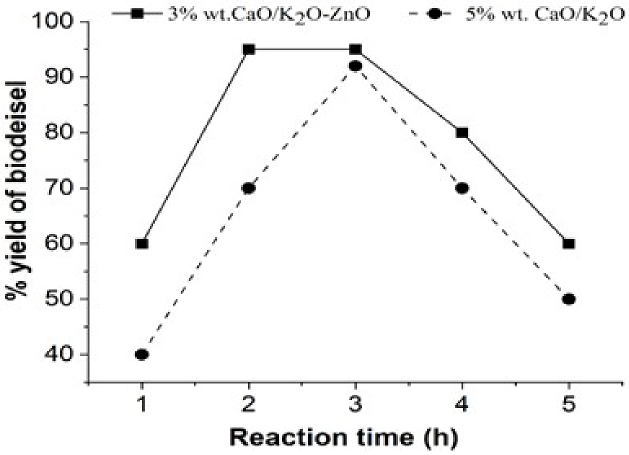

Figure 4: Effect of reaction time (h) on biodiesel yield with 9:1 methanol to oil ratio.

The Effect of Catalysts Reusability on Biodiesel Yields

The reuse of CaO/K_2O and CaO/K_2O-ZnO catalysts in the transesterification PO was evaluated at optimum conditions. Figure 5 shows the obtained results. The spent catalyst was separated using filter paper and washed with methanol. Then, the dried adsorbent was re-activated with a muffle furnace at 500 °C for reuse. The CaO/K_2O-ZnO catalyst resulted in a high yield (95%) of biodiesel in the first cycle, and the catalyst without ZnO converted 92% of the oil to biodiesel. The result was consistent with the previously reported by Navas, M. B. et al. (30); the recycling test of catalyst 0.5 Zn/Mg in the transesterification of castor oil showed a higher yield than in the first cycle.

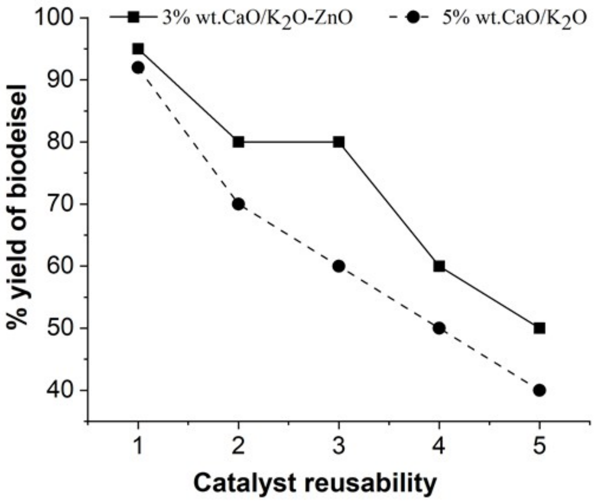

Figure 5: Effect of catalyst reusability on biodiesel yield with methanol: oil of 9:1 for 3 h at 65 °C.

After the first cycle, the percentage yield of biodiesel decreased until the fourth cycle. That is, the efficiency of both catalysts decreased when they were used repetitively. The 3% wt CaO/K_2O-ZnO catalyst could convert 80% of oil to biodiesel in up to 3 cycles. However, the biodiesel conversion efficiency of the CaO/K_2O catalyst declined to 60% in the 3rd cycle. These indicate that modifying CaO/K_2O catalyst with ZnO can improve both the biodiesel yield and durability of the catalyst. The decrease in efficiency of a catalyst for successive cycles in the conversion of oil to biodiesel is because of the active site metal ion leaching into the reaction medium. Bond cleavage and the formation of Ca^{2+} and CH_3O^- ions and leaching into the alcoholic phase are responsible for the loss of active sites (5).

Physicochemical Analysis of Biodiesel

Biodiesel was produced from waste frying oil using 3% wt CaO/K_2O-ZnO and 5% wt CaO/K_2O catalysts. Tables 4 and 5 present the physical and chemical properties of the biodiesel.

Physical Properties of Biodiesel

The physical properties of biodiesel: moisture (%), ash (%), pH, and density (g/cm^3) at 25 ºC, cloud point, flash point, and RI are depicted in Table 4. The moisture content of biodiesel prepared using 3% wt CaO/K_2O-ZnO (0.2%) was a lower moisture content than that of using 5% wt CaO/K_2O (0.5%). The lower moisture content of biodiesel improves its storability and adaptability for long-term preservation (31). The percentage ash content of BPO using CaO/K_2O catalyst (0.02%) was higher than the biodiesel obtained from CaO/K_2O-ZnO (3% wt.) (0.01%). However, the ash content of produced biodiesels was higher than the ASTM-D6751 standard. The density and refractive index of the prepared biodiesel matched the standard. However, the flash point of the synthesized biodiesel was higher than the standard.

Table 4: Physical properties of biodiesel from 9:1 methanol to oil a period of 3 h.

Physicochemical	**BPO using CaO/K_2O (5% wt.)**	**BPO using CaO/K_2O-ZnO (3% wt.)**	**Standard [ASTM D6751], (21,29)**
Moisture (%)	0.5	0.2	0.050
Ash (%)	0.02	0.01	0.01
pH	5.20	6.35	6.99
Density g/cm^{3}25°C	0.88	0.88	0.82-0.90
Color	Yellowish	Yellowish	Yellowish
Cloud point	1.1	1.2	-3-12
Pour point	1.5	2	-5-10
Flash point	198	150	130
RI(at 25 ˚C(nD)	1.459	1.457	1.45

BPO= Biodiesel from purified oil, RI = Refractive index.

Chemical properties of Biodiesel

The chemical properties such as AV (mg/KOH/g), %FFA (mg/KOH/g), IV (g/100g), SV (mg/g), PV, and CN were depicted in Table 5. The AV reflects how much lubrication has degraded. A higher AV in the fuel supply system and the internal combustion engine might cause severe corrosion (4, 32). Both the American and European Standards permit a maximum of 0.8 mg KOH/g acid and a minimum of 0.5 mg KOH/g acid. In this study, the AV of the biodiesel was 0.6 and 0.4 mg KOH/g, and the free fatty value was 0.3 and 0.2 mg KOH/g, CaO/K_2O (5 % wt.) and CaO/K_2O-ZnO (3% wt.) catalysts respectively, which is closer to the ASTM-D6751 standard. The %FFA of BPO using CaO/K_2O-ZnO (3% wt.) was lower than BPO using CaO/K_2O (5% wt.), but both BPO using CaO/K_2O (5% wt.) and BPO using CaO/K_2O-ZnO (3% wt.) were less than the ASTM D6751 standard. The iodine value of BPO using CaO/K_2O (5% wt.) and BPO using CaO/K_2O-ZnO (3% wt.) were 77 and 80, respectively. The iodine value of BPO was less than the iodine value of oil from the previously reported study, which is 104 g/100 g. The observed variation may be due to the oil type and the amount of catalyst used (33).

Table 5: Chemical properties of biodiesel from 9:1 methanol to oil a period of 3 h.

Physicochemical	**BPO using CaO/K_2O (5% wt.)**	**BPO using CaO/K_2O-ZnO (3% wt.)**	**Standard [ASTM D6751], (21,29)**
Acid value (mg/KOH/g)	0.6	0.4	$\leq$0.8
%FFA(mg/KOH/g)	0.3	0.2	2.5
Iodine value (g/100g)	77	80	80-106
Saponification value (mg/g)	127.6	182.3	150.1
PV (meq O_2/kg)	4	3	8
Cetane number	79	96.1	$\geq$50

BPO=biodiesel from waste purified oil, PV =peroxide value

Saponification value (SV) indicates the average molecular weight of triglycerides. The lower the SV, the larger the molecular weight of fatty acids in the glycerides (33). The SV of BPO using CaO/K_2O (5% wt) and CaO/K_2O-ZnO (3% wt) were 127.6 and 182.3, respectively. These values are not consistent with the previously reported by Ogunkunle and Ahmed (34), 167 mg of KOH g/L. The amount of PV in fats indicates primary oxidation and rancidity in oil. The peroxide value increased with increasing moisture content. The PV of BPO using CaO/K_2O (5% wt.) and CaO/K_2O-ZnO (3% wt.) was 4 and 3, respectively. The peroxide value for BPO using CaO/K_2O (5% wt) was higher than that of BPO using

CaO/K_2O-ZnO (3% wt). However, the peroxide values of both BPO using CaO/K_2O (5% wt) and BPO using CaO/K_2O-ZnO (3% wt.) were less than the ASTM-D6751 Standard. The low peroxide and acid values indicate good quality of the biodiesel.

Characterization of Oils, Biodiesels, and Catalyst

The FTIR analysis of PO was only determined because WFO showed a lower potential to make biodiesel. X-ray diffraction spectroscopy (XRD) was employed to characterize the synthesized catalysts CaO/K_2O and CaO/K_2O-ZnO that converted oils to biodiesel.

FTIR Characterization of Purified Oil

The FTIR spectra of purified oil showed a peak aaround 3500 cm^{-1} and an intense peak at 2900 cm^{-1} due to OH (emulsified water) and CH_3 (sp^3) stretching, respectively, as depicted in Figure 6. The high-intensity peak at 1700 cm^{-1} is assigned to the carbonyl stretching (C=O stretching) of the oil.

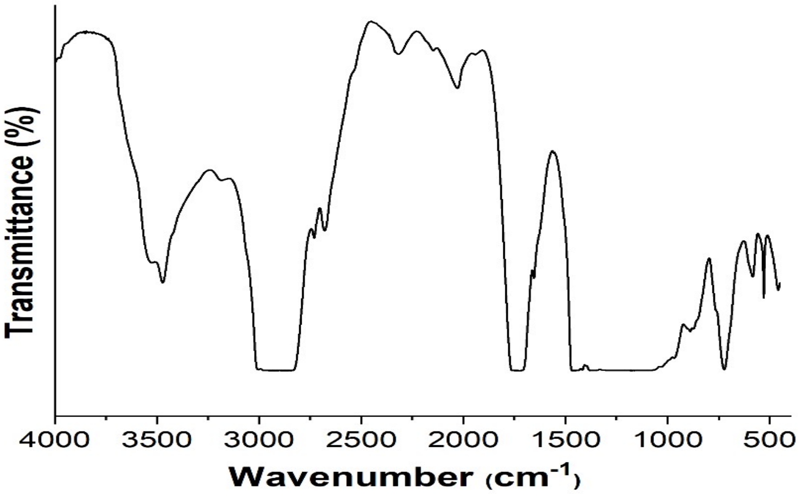

Figure 6: FTIR spectra of purified oil.

FTIR Characterization of Biodiesel

Figure 7 depicts the FTIR spectra of biodiesel from the purified oil. The strong band around 3400 cm^{-1} indicates the OH stretching of the residue alcohol in the biodiesel. Medium intense peaks around 2900 cm^{-1} and 2800 cm^{-1} indicate the presence of CH_2 and CH_3 groups. The medium peak at 1650 cm^{-1} indicates carbonyl (C=O) stretching of the ester. The peaks at 1416-1470 cm^{-1} were assigned for CH bending of sp^3 carbon. The intense peak around 1100 cm^{-1} indicates the presence of C-O stretching of the ester functional group (35, 36).

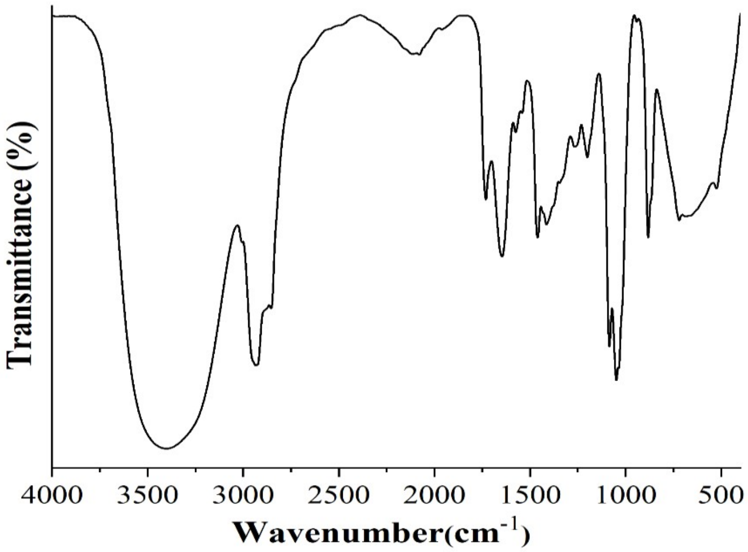

Figure 7: FTIR characterization of biodiesel.

Powder XRD Analysis of Catalysts

The crystalline structures of the prepared CaO/K_2O and CaO/K_2O-ZnO heterogeneous catalysts were characterized by using XRD. Figures 8 and 9 shows the obtained results. At a 2 theta angle, the diffraction patterns were recorded in the range of 10º to

90º with a scanning speed of 4º min^{-1} at ambient temperature.

XRD Pattern of CaO/K_2O Catalyst

The powder XRD patterns of CaO show that the intensified and narrowed peaks at 2θ angles of 17.5°, 26.3°, 28.13°, 33.5°, 37.3°, 47.1°, and 53.8°, respectively. The K_2O impregnation into the CaO catalyst surface (1:1, 5 % wt.) revealed a second peak of intensity at 2θ angles of 23.05°, 25.10°, 28.60º, 33.2°, 40.7º, and 48.90° which assigned to the presence of K_2O on the surface of the catalyst, respectively (JCPDS File No. 47-1701; 77-2176) (39). The result matched the (JCPDS File No. 37-1497) and the previous study data (38, 39). However, the observed shift in 2θ degree may be due to the effect of K_2O on the crystal surface of the calcium oxide catalyst (Figure 8). The result indicates that the heterogeneous catalyst, CaO/K_2O, was successfully produced, and the narrow band indicates the smaller crystalline size of the catalyst (Figure 8).

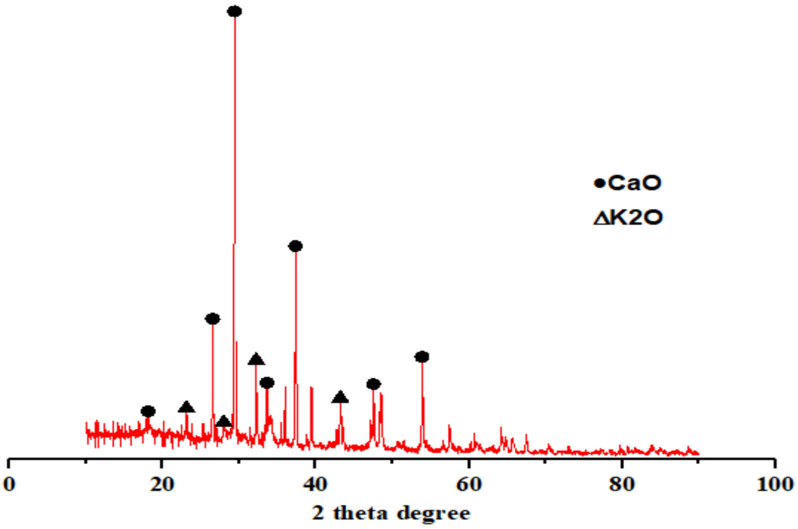

Figure 8: XRD pattern CaO/K_2O catalyst.

XRD Pattern of CaO/K_2O/ZnO Catalyst

Figure 9 shows the XRD patterns of the prepared catalyst by using a mixture of CaO/K_2O and modified with ZnO. After impregnating ZnO into the prepared CaO/K_2O catalyst, some of the peaks of CaO and K_2O vanished, and others shifted to the higher 2θ value, indicating that the ZnO affects the crystal structure of the CaO/K_2O catalyst.

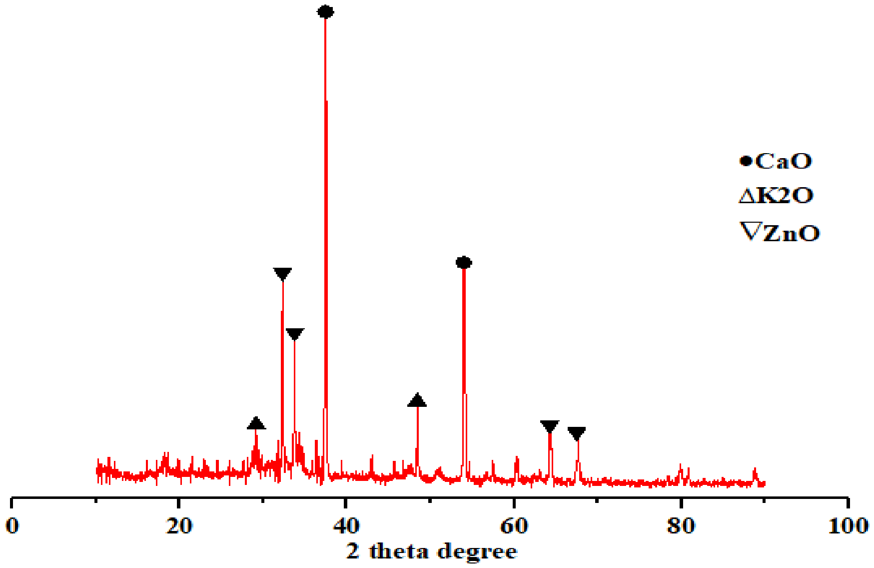

Figure 9: XRD pattern CaO/K_2O-ZnO catalyst.

The peak of CaO 2θ at 28.13° in Figure 8 shifted to 37.3°, which may be due to the addition of ZnO affecting the crystal structure of CaO/K_2O (Figure 9). The peak at 2θ values of 28.607° and 48.8° correspond to K_2O, similar to peaks observed in the previous report (39). The XRD result showed that the 2θ value of ZnO at 31.6°, 34.52°, 47.31°, 66.21°, and 67.6°, indicating that the ZnO was in the wurtzite hexagonal phase. The shift in the 2θ value on the ZnO peak may be due to the impact of CaO and K_2O.

CONCLUSION

In this study, biodiesel is produced from waste frying oil after purification. Catalysts such as eggshells (CaO) and banana peels (K_2O) were prepared and employed for biodiesel production. The methanol to oil ratios of 6:1 and 9:1 resulted in the highest biodiesel yield (95%) than 3:1 and 12:1 using CaO/K_2O-ZnO catalyst (3% wt), but 9:1 gave the highest product (92%) for the CaO/K_2O at 5% wt catalyst load. It is conceivable to deduce that both catalysts were effective at a 9:1 methanol to oil ratio and yielded the highest biodiesel. The catalyst prepared from eggshell and banana peels (CaO/K_2O) was most effective at a 5% wt load and converted around 92% of the oil to biodiesel. After modification of the CaO/K_2O catalyst with ZnO, the percentage yield of biodiesel increased to 95%. The CaO/K_2O and CaO/K_2O-ZnO were effective up to four cycles resulting in 60 and 50% biodiesel yield, respectively. Transesterification of purified oil with CaO/K_2O-ZnO (3% wt.) and CaO/K_2O (5%) wt.) catalysts at 65 °C produced the highest yield.

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