

# Biodiesel from fresh and waste sunflower oil using calcium oxide catalyst synthesized from local limestone

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## Abstract

*A study of converting fresh and waste sunflower oil to biodiesel through transesterification reaction using heterogeneous catalysts is established. Calcium Oxide (CaO) was selected as a basic heterogeneous catalyst because it is the cheapest and the most available comparing with other options. The characteristics of the catalyst were evaluated using several evaluation tests. The results confirm that the best preparation condition is at 850°C and 2 hours. This catalyst has demonstrated positive results, high productivity and good recycling potential. The best conditions for reaction were obtained by varying the reaction conditions to obtain the highest bio-fuel production. The reaction has been studied in various operating conditions of methanol to oil molar ratio, catalyst loading, agitation speed and reaction time at temperature 65°C. The maximum yield of biodiesel was 97.4% for fresh vegetable oil.*

*Moreover, the catalyst shows perfect results for transesterification of waste vegetable oil. It was tested for market waste sunflower oil and home waste sunflower oil, where the yield was 88.2% and 91.6% respectively. The reuse of the catalyst showed good activity with no less than 5 cycles. So, the production of biodiesel using calcium oxide as a catalyst is a perfect promising approach.*

**Keywords:** Biodiesel, Calcium oxide, Sunflower oil, Transesterification, Heterogeneous Catalyst.

## Introduction

Presently, the world is facing great challenges because of global warming and environmental pollution due to greenhouse gas emissions by fossil fuels. Therefore, it is necessary to find another energy sources that are renewable, economically practicable and friendly to the environment. In addition, the depletion of petroleum worldwide has also stimulated the search for alternative sources<sup>1</sup>.

Biodiesel is considered a suitable choice that is friendly for the environment because of its low emission of carbon monoxide, biodegradability, non-toxic nature and free sulfur<sup>2</sup>. It may be defined as an alternative fuel that is manufactured by reacting triglycerides obtained from vegetable oils or fats with short chain alcohols such as methanol to produce fatty acid methyl ester (FAME) and

glycerin through a transesterification reaction which is a reversible catalytic reaction<sup>3</sup>.

Catalysts are usually utilized in the production of biodiesel to increase yield and the rate of reaction<sup>8</sup>. Three various kinds of catalysts can be used in the transesterification process for biodiesel synthesis: base catalysts, acid catalysts and biocatalyst<sup>1</sup>.

However, although several basic catalysts have shown promising activities like basic zeolites<sup>10</sup>, alkali and alkali earth oxides<sup>11,12</sup>, alkali and alkali earth carbonates<sup>10</sup>, supported guanidines<sup>13,14</sup> and basic hydrotalcites<sup>15,16</sup>. Among the alkali and alkali earth oxides, CaO is one of the solids that has displayed higher transesterification activity<sup>17-19</sup>. The process of transesterification using CaO as a solid base catalyst has many features such as mild reaction conditions, higher activity, low cost and catalyst reusability<sup>20</sup>. CaO has excellent catalytic features such as acceptance of high free fatty acid and high basic strength, less environmental risk effect due to its low solubility in alcohol<sup>21,22</sup>.

CaO as a heterogeneous catalyst can be achieved from several sources such as chicken eggshell, limestone, seashells<sup>23</sup>. Calcium oxide does not exist naturally; it is produced from the calcination process of calcium carbonate at high temperatures. Several studies have focused on the application of CaO as a catalyst and they reported successful production in the last decade. Tan et al<sup>24</sup> studied the use of ostrich eggshells to prepare CaO catalyst and its application in the transesterification of soybean oil using a 12:1 methanol to oil ratio, a reaction time of 3 hours, 8% of CaO per oil mass and they obtained 96% yield with the calcined shells.

Piker et al<sup>25</sup> conducted the same reaction with fresh soybean oil and yielded 97 % of FAMES at a molar ratio of 1:6 and 5.8% of CaO catalyst. Sirisomboonchai et al<sup>26</sup> studied transesterification of WCO by using calcined scallop shells as a catalyst with a loading amount of 5 wt% at 65 °C and they yielded 86%. Pandit and Fulekar<sup>27</sup> utilized waste chicken eggshells for the synthesis of CaO Nanocatalyst to transesterify dry biomass into biodiesel and reported a yield of 86.41%. Teo et al<sup>28</sup> prepared a nanocatalyst derived from the waste eggshell of Gallus to produce biodiesel and applied neural network model to obtain a predicted yield of 97% at 60 °C and 5 hours reaction time. Viriya-empikul et al<sup>29</sup> derived CaO catalyst from waste shells of eggs, a golden apple snail and meretrix Venus and applied them in a

transesterification of palm olein oil and obtained 90% yield at 60 °C and 2 hrs.

The main target of this research is to develop and characterize calcium oxide catalyst produced from local limestone in transesterification reaction for sunflower oil to produce biodiesel. Moreover, it is desired to study the reusability of this catalyst.

### Material and Methods

**Materials:** The limestone collected from natural sources is washed with tap water several times to remove any undesired materials like salts, soil and planktons, then washed with distilled water to ensure purity; after that, these rocks are crushed by mortar and then sieved by laboratory vibrating sieve (YS-02, Germany), to achieve particles less than 90µm. The waste vegetable sunflower oil was collected from two sources: a home waste and cafeteria waste; each one has different free fatty acid content dependent on the time and temperature of using.

**Catalyst preparation:** In order to convert limestone (CaCO<sub>3</sub>) to quicklime (CaO), the fine particles were calcified with electrical muffle furnace (MF-14, Hanyang, South Korea), under different temperatures (750, 850 and 950 °C) and different time from 1–3 hours. Different samples of the calcified catalyst were put in desiccators in presence of potassium hydroxide and silica gel to prevent calcium oxide reconverted to calcium carbonate and calcium hydroxide by carbonation with CO<sub>2</sub> and hydration with (H<sub>2</sub>O) moisture. Figure (1) shows a sample of calcified CaO catalyst.

**Catalyst characterization:** X-ray fluorescence (XRF) spectroscopy is used to identify the element available in the rocks (limestone) utilized as a source for catalyst preparation. XRF is a qualitative and quantitative analysis. The analysis was carried out using X-Ray fluorescence meter (FT150-XRF/Germany), also XRD analysis was done on the local limestone to identify its characterization; the analysis was carried out using X-Ray diffractometer (XRD-6000, Shimadzu, Japan) to show images and the morphology of catalyst of a sample. Scanning electron microscope analysis was done. The analysis was carried out using TESCAN, Vega III / Czech Republic. All samples of calcium oxide (CaO) catalyst prepared under different conditions were analyzed by Fourier transform infrared spectrophotometer (IR Affinity-1 Shimadzu / Japan), The surface area and pore volume properties were calculated based on the nitrogen adsorption-desorption isotherm using the apparatus of Brunauer-Emmett-Teller (HORIBA, SA-900 series, USA).

**Waste vegetable oil FFA test:** Vegetable oil was collected from two sources, first from home utilizing and second from restaurant; utilizing each one filtered by vacuum filtration system to get rid of all impurities and food remains. Then WVO was heated to 120°C to discharge any associated

humidity (H<sub>2</sub>O) if existing.

Then the titration method was adopted to evaluate the free fatty acid content and acid number. The general procedure was summarized as taking a weighted sample of WVO and adding three drops of phenolphthalein as an indicator, then adding drops of determined solution of methanol and potassium hydroxide (KOH) until the mixture color changed to purple.

**Transesterification process:** The reaction occurred at a batch reactor consisting of the three-necked round-bottomed flask, one neck connected with a condenser, the second neck connected with thermocouple, the last for mechanical overhead stirrer (PHOENIX, RSO 20D/Germany) with a digital screen to achieve perfect mixing reaction. The reactor was heated by an electrical fabric digital heater (Type 98-1-C, the numeral controls temperature Electric Heated sleeves) and the condenser cooled by water from the electrical chiller, so all alcohol used in this experiment refluxed to the reactor. Experiments occurred at this fitted system shown in fig. 2 consisting of methanol, vegetable oil and catalyst. Different weights of sunflower oil were heated to 60 °C using a magnetic heater and mixed with different weights of methanol and catalyst. When the reaction mixture reaches the desired temperature, the reaction initial time has been recorded.



Fig. 1: Prepared calcium oxide



Fig. 2: Experiment fitted system

Several sets of experiments were done to cover different working parameters such as methanol to oil molar ratio, catalyst load, agitation speed and reaction time. At the end of each experiment, the mixing was stopped and the mixture allowed to be cooled at room temperature. Then the mixtures were filtered to remove all the catalyst by a vacuum filter system consisting of Buchner funnel, filter flask, filter paper and vacuum pump.

After that, the excess methanol was removed from the produced mixture by using a rotary evaporator system and the discharged methanol could be reused in other experiments. Later on, the mixture was put in the separating funnel where two layers have been observed. The upper layer is FAME which has a light golden color and the lower layer is glycerin which has a brown color as shown in fig. 3. The bottom layer has been withdrawn from the separating funnel and the upper layer was weighed and stored in a cloudy glass small bottle. The produced biodiesel was analyzed by gas chromatography-mass spectrometer GC-MS to evaluate the conversion and yield.



Fig. 3: Biodiesel and glycerin

**Transesterification of (WVO):** After WVO preparation (filtration, drying and analyzing), WVO was heated to 60°C and then added to a mixture of methanol and catalyst and then agitated. After the reaction time end, the mixture was cooled to stop the reaction and filtered by a vacuum filtration system. The excess methanol was evaporated by rotary evaporator and the mixture was put in separating funnel to separate FAME and glycerin.

## Results and Discussion

### Catalyst characterization

**Assessment of raw material:** The previously prepared sample of limestone rocks collected from local sources was subjected to XRD analysis test. Fig. 4 illustrates the analysis pattern of XRD test. The results show that the major compound is calcium carbonate when the intensity is between 28-30 2 $\theta$  waveform spectrum. This indicates the ratio of about 97.4% of calcium carbonate; XRD analysis

was done using X-Ray diffractometer (XRD-6000).

**Limestone evaluation by FTIR:** A test sample of limestone which was previously prepared is subjected to FTIR spectra investigation. Fig. 5 properly illustrates the adsorption band peaks at 2939 cm<sup>-1</sup>, 1452 cm<sup>-1</sup>, 879 cm<sup>-1</sup> and 767 cm<sup>-1</sup>. The percent of these peaks at such intensity was attributed to CO<sub>3</sub> groups in the sample, after the calcination process, the prepared catalysts were analyzed by FT-IR. The catalyst prepared at 850 °C for two hours shows best-converted bonds from CO<sub>3</sub> groups to CO as shown in fig. 6. Fig. 6 indicates that most CO<sub>3</sub> groups were discharged and a strong adsorption band at a wavelength less than 600 cm<sup>-1</sup> appeared which was attributed to Ca – O group as a good result of calcination process.

**BET analysis:** Surface area is a fundamental characteristic of most heterogeneous catalysts and liable to change during preparation. The catalyst showed higher yield prepared at 850 C /2 hr, was analyzed by BET and it has a surface area of 8.18 m<sup>2</sup>/g.

**Selection of the best catalytic conditions:** Several samples of CaO catalyst were prepared successfully by calcination of limestone CaCO<sub>3</sub> at different temperatures and times since the different conditions affect the catalyst structure and activity. Nine catalytic samples were prepared under different range of temperatures 750, 850 and 950 °C and variable times from 1 to 3 hours. Each of the nine samples of catalysts was employed in transesterification reaction under specific conditions to find out the yield of biodiesel produced. The same reaction conditions of temperature 65°C, 24/1 methanol to oil ratio, 400 rpm agitation speed and 3% catalyst load were employed. It was found that the highest yield of biodiesel was achieved when using the catalyst prepared under 850°C and 2 hours of calcination.

**SEM analysis:** The analysis was carried out using TESCAN, Vega III / Czech Republic. The scanning electron microscope (SEM) was utilized to illustrate the microstructure of limestone before and after calcination process. Figures 7 and 8 show the images of natural limestone and calcined lime respectively with 20 $\mu$ m zoom scale which shows the difference in particles shape. Fig. 7 shows the SEM image of local limestone before calcination. It indicated ball like particles. Some of them are bonded together as aggregates. After calcination at 850 C/ 2 hr illustrated in fig. 8, it shows a larger size of aggregated particles and it is expressed as micromorphological particles. This explains the rise in surface area after calcination process.

**EDX analysis:** The change in the elements composition between natural limestone and the calcined lime was examined by EDX and the results are illustrated in fig. 8 and 9 respectively. The calcium content of the calcined catalyst increased from 64.7 to 74.3 wt. % compared to the raw rocks. The oxygen contents of the limestone, on the other hand,

decreased from 35.3 to 24.2 wt. % compared to the calcined catalyst.

**Determination of biodiesel composition:** After the transesterification process was completed, the product FAME was weighed and the yield was determined using the equation:

$$\text{FAME yield} = \frac{\text{weight of biodiesel}}{\text{weight of oil}} \times 100\%$$

The samples of FAME were tested by gas chromatography-mass spectrometer GC-MS to determine its composition. The results showed many esters like Methyl palmitate, Methyl linoleate, Methyl lino-elaidate, Methyl Elaidate, Methyl oleate and Methyl stearate. Methyl palmitate concentration was about 7% and it appears at retention time 22.8 min; methyl linoleate and methyl lino-elaidate have concentration of about 46% of retention time at 26.1 min, methyl elaidate and methyl oleate have a concentration of about 37% and retention time of about 26.25 min, methyl stearate has a concentration of about 10% and retention time of about 26.58 min and about 0.5% monoglycerides appears at retention time 36.24 min. Thus, the concentration of FAME in biodiesel produced was about 99.5%.

#### Effect of process parameter

**Effect of catalyst load:** The biodiesel yield achieved over different loading (1, 3, 5, 7, 9) of CaO weight % catalyst at constant reaction conditions (24:1 alcohol: oil molar ratio, reflux temperature (65°C), time 2 hours, 600 agitation speed) was 47.1, 89.5, 93.65 and 95.2% as depicted in fig. 11. The results show that the biodiesel yield increases as the catalyst loading increases due to an increase in the number of active sites. Low yield (47.1%) was obtained with low catalyst loading (1wt. %), which was not enough to catalyze the reaction for completion. However, as the catalyst charging was increased above 7 wt. %, the biodiesel yield begins to decline at the same reaction conditions. This case occurs due to the reaction mixture becoming more viscous.

**Effect of methanol to oil molar ratio:** Several samples of methanol to oil molar ratios (8:1, 16:1, 20:1, 24:1, 30:1) were accomplished during reaction temperature of 65°C, catalyst load 7% by weight, agitation speed of 600 rpm and 2hr reaction time. The FAME yield was 55.0, 87.7, 90.2, 95.2 and 94.9 for molar ratio 8:1, 16:1, 20:1, 24:1 and 30:1 respectively as shown in fig 12. It is clearly shown from this figure that the yield increases dramatically with increasing alcohol/oil ratio, because of the impact of the excessive methanol load on the reaction equilibrium. The highest yield of biodiesel was achieved at 95.2 weight% with a ratio of (24:1) alcohol/oil and little bit decreases when alcohol/oil molar ration increases to (30:1). The behavior could be explained as the dilution effect of excess methanol which reduced the reaction rate.

**Effect of agitation speed:** Agitation speed affects biodiesel production yield. Varying mixing speeds were experimented

to optimize giving the highest output 200,400, 600 and 800 rpm with constant reaction conditions of 24:1 alcohol: oil, time 2 hr., reflux temperature, 7% catalyst load. The results were 82.0, 91.5, 95.2 and 88.8% respectively, perfect speed was 600 round per minute with output about 95.2% .as shown in fig. 13. Increasing mixing speed led to enhance the mass transfer of reactants toward active sites of catalyst surface due to reduction in the boundary layer between the fluid bulk and catalyst surface. This leads to decreasing the external diffusion resistance between reactants and products around the catalyst surface. A decrease with the increase of agitation speeds above 600 rpm occurs because higher stirring speed favors the formation of soap.

**Effect of reaction time:** The transesterification reaction was carried out at different times 1.2.3 and 4 hours, the FAME yield was 83.1, 95.2, 97.3 and 95.2 respectively as illustrated in fig. 14.

The lesser yield of biodiesel was 83.1% at reaction time one hour because the reaction has not achieved the equilibrium state yet, the reactants and catalyst need to contact more than one hour, after two hours reaction the yield was 95.2%; after three hours the yield was 97.3%. This is the highest result achieved at catalyst loud 7%, agitation speed 600 rpm, 24:1 methanol to oil ratio and at reflux temperature 65°C. These results display that the productivity of biodiesel has increased with the increased reaction time. A little decrease in the content of FAME at 4 hrs. due to the nature of transesterification causes a reverse reaction.

**Catalyst reusability:** The reusability of CaO catalyst was studied by varying the reaction cycles. After using of catalyst for the first time, the mixture was left to let the catalyst particles settled, the products removed and methanol was added immediately to the remainder catalyst in the round flask, then methanol and catalyst heated to about 60C with mixing and vegetable oil added. This moment was recorded as the beginning time. Figure shows the yield of FAME after the catalyst reusing. The yield decreases gradually after 5 cycles; the yield was 55%.

This is caused by the formation of calcium hydroxide by the hydration reaction of calcium oxide that can lower catalyst activity and also due to CaO sensitivity to CO<sub>2</sub> in any cyclic process and leaching of CaO for reuse.

**Measured properties of the produced biodiesel:** In order to know the quality and physical properties of the biodiesel produced and compare it to the diesel produced from fossil fuels, properties Viscosity, Flashpoint, Acid number, Cetane, Color and Density were measured and compared. The properties are illustrated in table 1.

#### Conclusion

The present study revealed that the limestone rocks from local sources consist of a high concentration of calcium carbonate with a ratio of 97.4 wt. Calcium oxide with high

purity as a heterogeneous catalyst is successfully produced by calcination of limestone at different temperatures and time. The highest yield of biodiesel is obtained with catalyst synthesized under 850°C and 2 hours of calcination. The

optimal reaction conditions were 24:1 methanol to oil ratio, 7wt% catalyst load, 3 hours reaction time, 65°C and 600 rpm mixing speed.

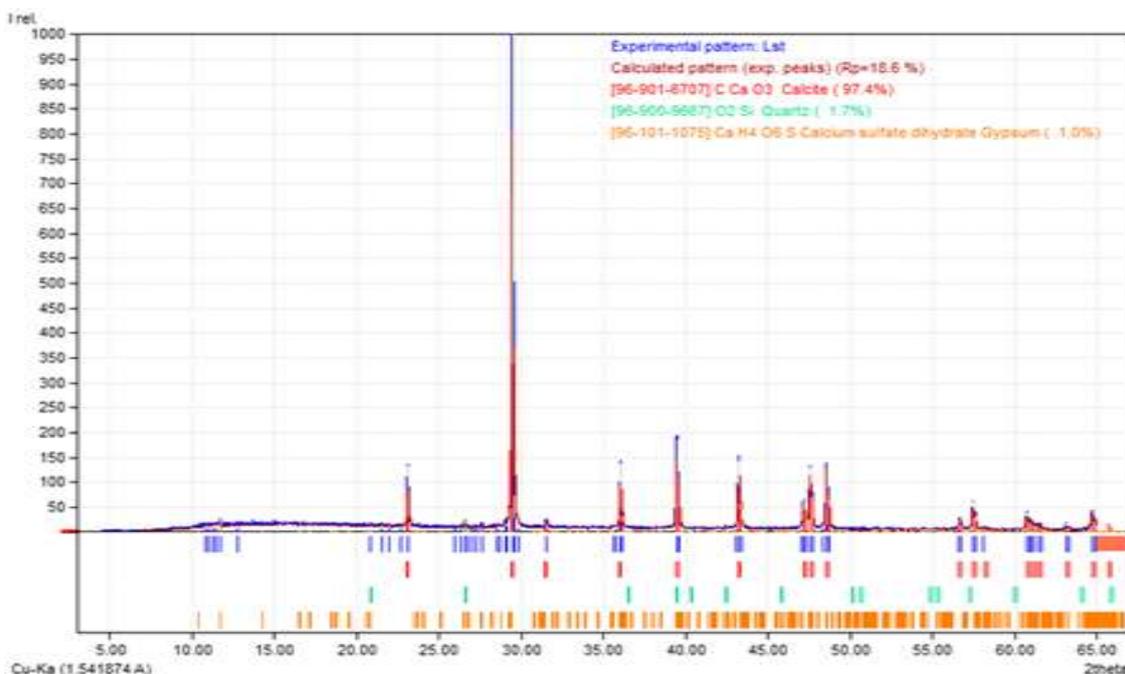


Fig. 4: XRD analysis

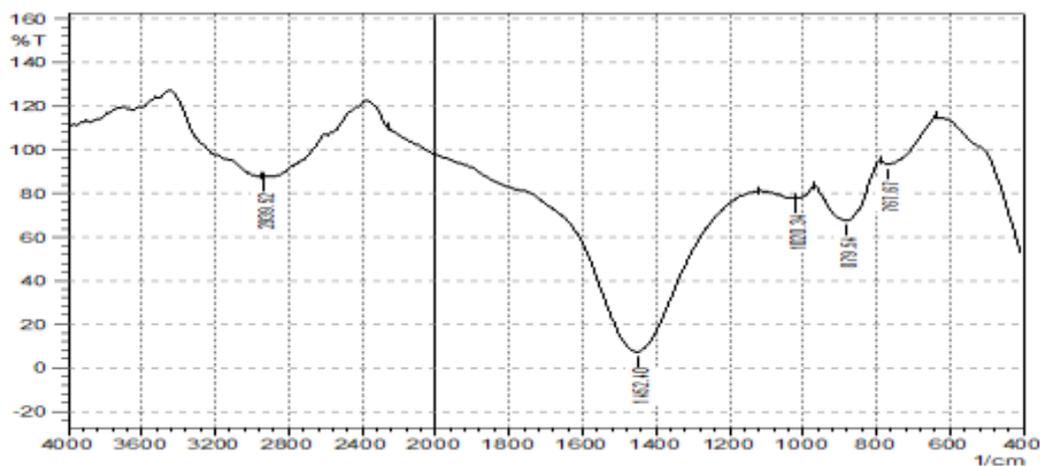


Fig. 5: FTIR analysis of CaCO<sub>3</sub>

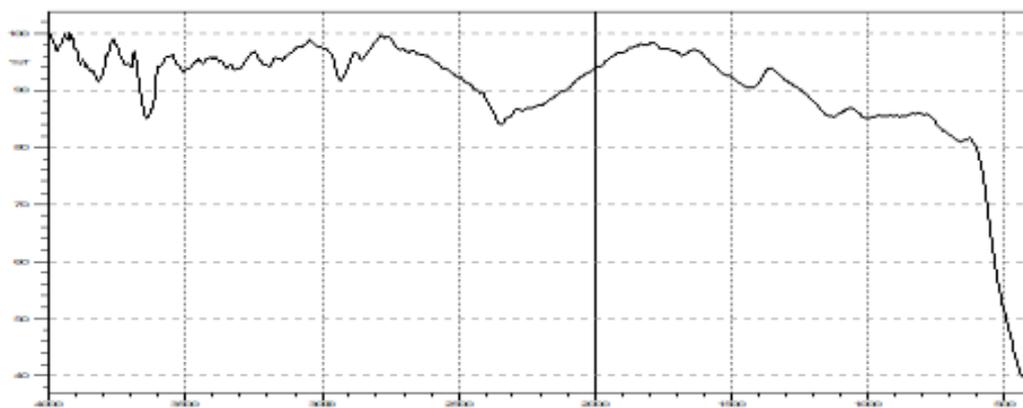


Fig. 6: FTIR analysis of CaO

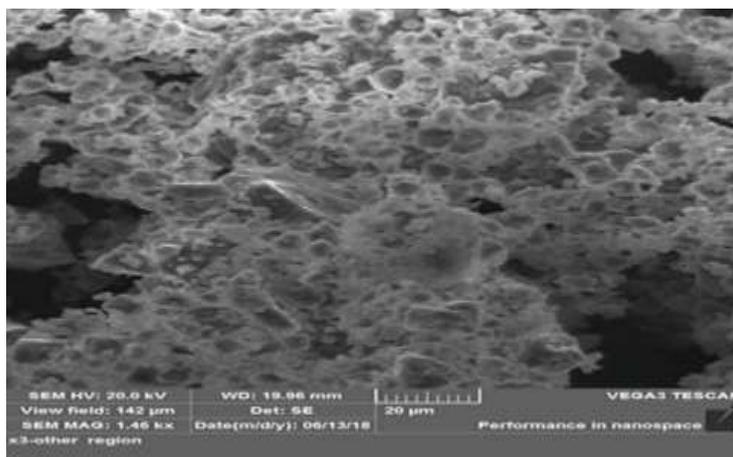


Fig. 7: SEM image CaCO<sub>3</sub>

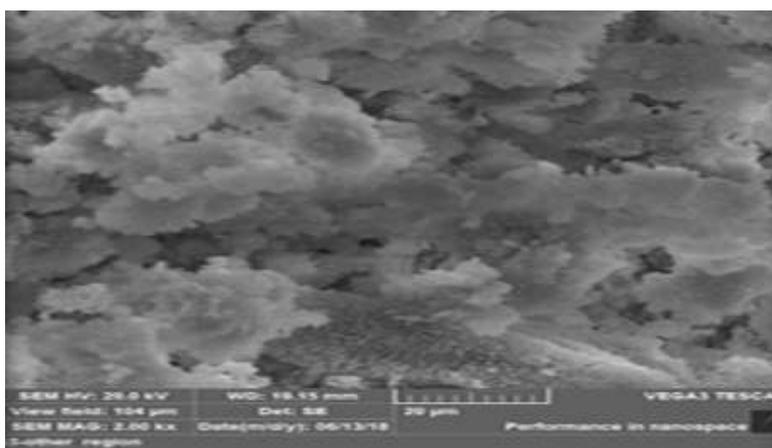


Fig. 8: SEM image of CaO

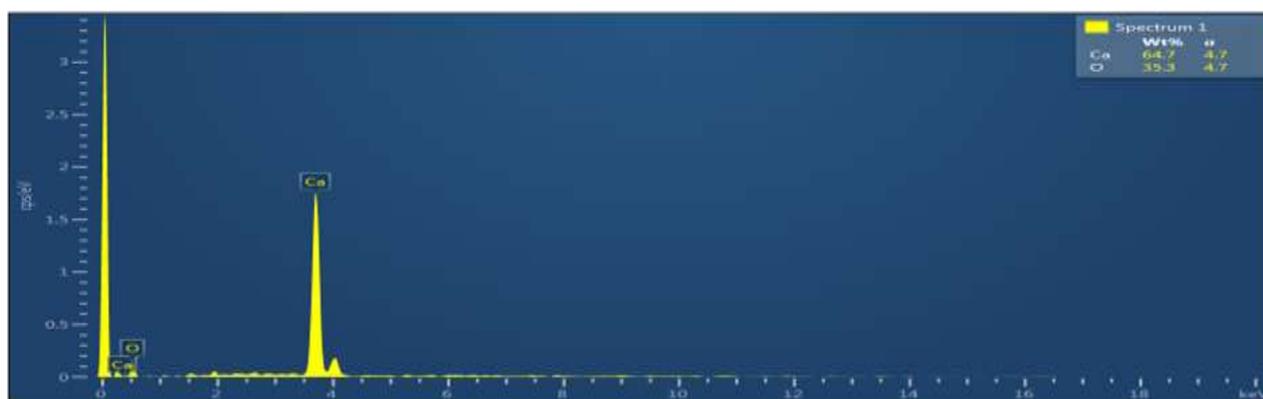


Fig. 9: EDX analysis of CaCO<sub>3</sub>

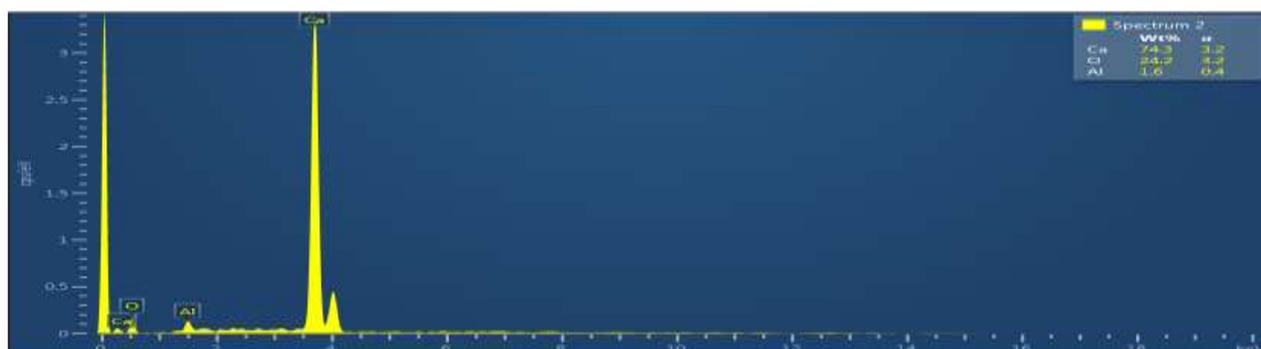


Fig. 10: EDX analysis of CaO

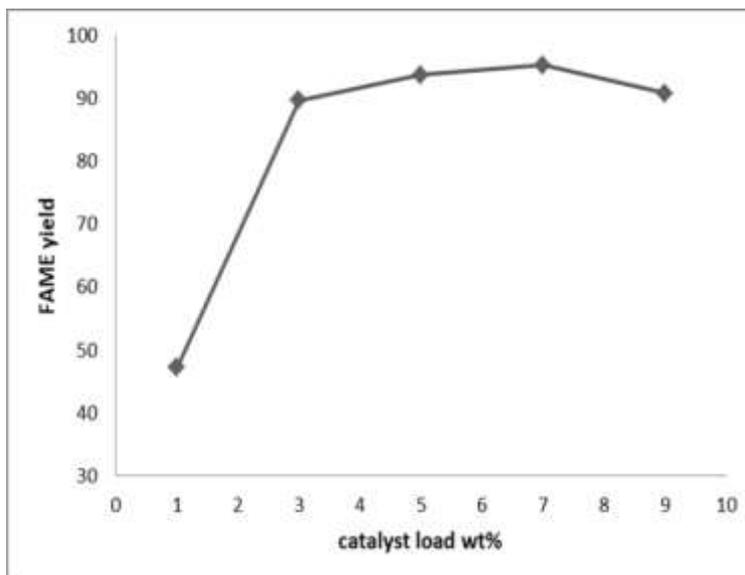


Fig. 11: Effect of catalyst load on FAME yield

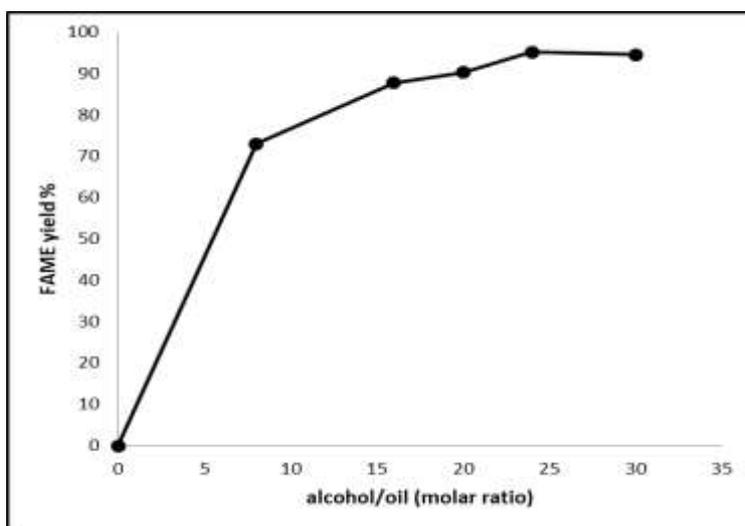


Fig. 12: Effect of alcohol/oil molar ratio on FAME yield

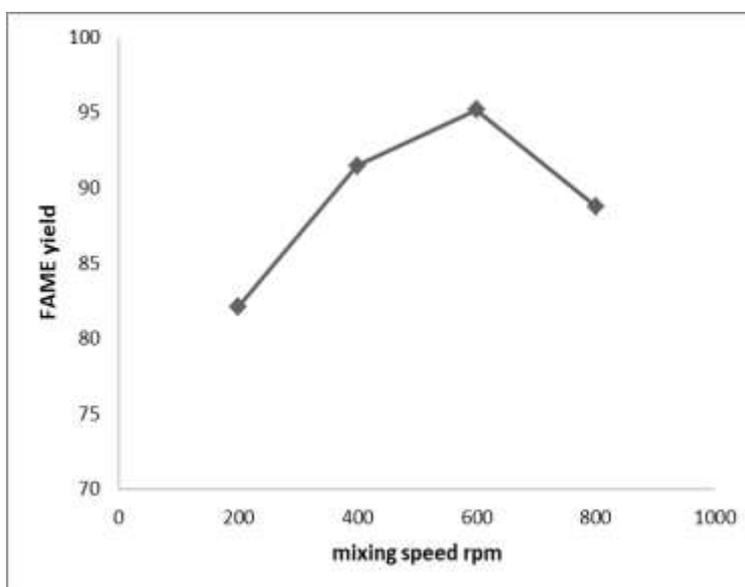


Fig. 13: Effect of agitation speed on FAME yield

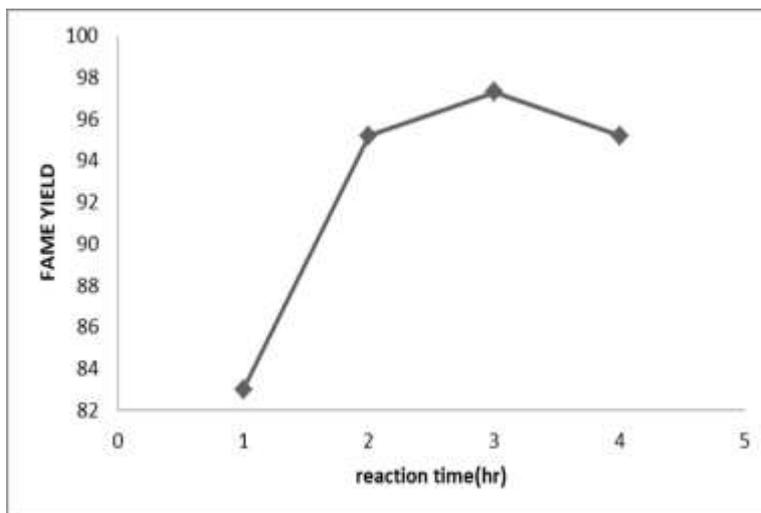


Fig. 14: Effect of reaction time on FAME yield

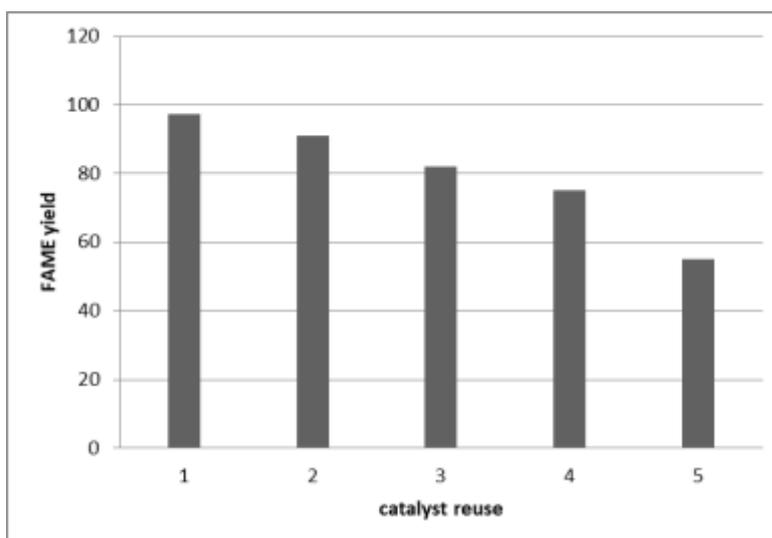


Fig. 15: Catalyst reusability

Table 1  
Produced biodiesel properties

Property	Test method	Min. limit	Max. limit	The value obtained from the current study	units
Viscosity at 40°C	EN ISO 3104	3.5	5	4.48-4.64	mm <sup>2</sup> /s
Flash point	EN ISO 3679	120	-	125	°C
Acid number	D664	-	0.5	0-0.1	mg KOH/gh
Cetane	D613	47	-	43	-
Color	ASTM			0.4-0.5	-
Density at 15°C	EN ISO 3675	860	900	860-880	Kg/m <sup>3</sup>

The synthesized catalyst showed good reusability with 5 cycles of transesterification processes; this advantage leads to reduce the overall biodiesel production cost. Synthesized calcium oxide showed good results in the transesterification of WVO even with high free fatty acid.

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