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## The Development of Heterogeneous Catalyst C/CaO/NaOH from Waste of Green Mussel Shell (*Perna varidis*) for Biodiesel Synthesis

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### Abstract

This study was aimed to use green mussel shell (*Perna viridis*) as raw materials for CaO heterogeneous catalyst in the transesterification process of palm oil into biodiesel. Green mussel shell was calcined for 3 hours at a temperature of 900°C to become CaO catalyst, then mixed by activated carbon with the ratio of C : CaO = 2 : 3 and impregnated with a solution of NaOH. The catalyst was used in biodiesel production at constant reaction temperature of 65°C for 3 hours and methanol to oil ratio of 0.5 : 1 (% wt). The optimum yield biodiesel was 95.12%, which was achieved at NaOH concentration at impregnation process of 30% and the catalyst load of 7.5%.

The obtained biodiesel properties were in agreement with national standard (SNI) of biodiesel.

## Keywords

Mussel shells; heterogeneous catalysts; CaO; biodiesel; Transesterification; palm oil.

## 1. Introduction

Biodiesel is an alternative energy as replacement of diesel fuel in the form of alkyl esters of fatty acids. The advantages of biodiesel include as it is a renewable energy, biodegradable, non-toxic, has low emissions of CO and CO<sub>2</sub>, reduces dependence on imported fuel, as well as free of sulfur [1]. The esterification of oil to biodiesel mostly use homogenous catalyst such as NaOH or H<sub>2</sub>SO<sub>4</sub>. However, the use of conventional homogenous catalyst such as basic or acid catalyst in biodiesel production led to lower yield and inefficiency of product separation. Therefore, the heterogeneous catalyst was introduced to overcome these problems. The CaO based heterogeneous catalyst has been intensively studied to increase the yield of biodiesel production. To increase the activity, CaO catalyst must be supported by other compounds such as activated carbon, fly ash or impregnated in basic solution [2,3].

Various studies have been conducted in developments of heterogeneous catalyst from waste in the form of shells, bones or skin of marine animals because of their rich CaCO<sub>3</sub> to be decomposed into CaO catalyst through calcination[2]. The previous work showed that *Anadara granosa* and *Paphia undulata* shell could be utilized for heterogeneous catalyst and improved the yield of biodiesel up to 96% [2,3]. In biodiesel production from soybean oil using 2% activated carbon supported CaO catalysts (C/CaO optimum = 4:6) which was impregnated with 25% KOH and calcinated at a temperature of 500°C for 5 hours, mole ratio of the oil with methanol was 1:10, the optimum biodiesel yield was 98% [4]. Production of biodiesel from palm oil using

waste scallop shells with optimum calcination conditions of 1000°C, 10 wt% catalyst C/CaO/KOH, in which mole ratio of oil to methanol was 1:9 for 3 hours calcination resulted a yield of 95.44% [5].

The disadvantages of heterogenous catalyst such as CaO are low surface area, sensitive to the presence of water, deterioration of active sites due to glycerol and disturbing by soap forming side reactions. Therefore, CaO catalyst must be supported by carbon materials such as activated carbon, nanotubes or nanoporous carbon[4]. The activated carbon has proved to be highly effective as a catalyst support in transesterification reaction due to its advantages features of large surface area which allows the catalyst to disperse over it largely and effectively, higher intensity after calcination and easy to separate from the product[4][5] and it can be produced from a variety of raw material[4]. In this study, waste of green mussels shell (*Perna viridis*) which was supported with activated carbon and then impregnated with NaOH was used. The use of activated carbon was aimed to facilitate the process of separation of the product, increase the intensity after the calcination process, and enlarged the surface area of the catalyst. The catalyst was impregnated with basic solution NaOH to increase the activity of the catalyst. The NaOH was selected based its high activity and inexpensive[6]. The success of the decomposition process of CaCO<sub>3</sub> was characterized by the formation CaO which was then analyzed by XRD and SEM.

## **2. Material and Methods**

### **a. Material**

In this study, palm oil branded Sovia and methanol (Merck 99.9%) were used as raw material of biodiesel synthesis. Raw material of CaO catalyst was green mussels shell (*Perna viridis*), and they were obtained from waste of Momow Leker and Kerang cafe in Banyumanik, Semarang. The supporting catalyst was activated carbon and NaOH solution (Merck).

### **b. Catalyst preparation**

Waste of green mussels' shell was cleaned by using warm water for several times. After the cleaning process, the shell waste were dried in an oven at 100 °C for 4 hrs and crushed with a mortar and then sieved to 80 mesh size before calcination process.

### **c. Catalyst calcination**

The sieved shell was calcinated in furnace at 900°C for 3 hours in an atmospheric pressure. After calcination process, green mussels shell was decomposed to CaO and it was stored in silica gel desiccator. The XRD analysis was conducted to determine the characteristic of heterogeneous catalyst particularly for CaO content in the catalyst.

### **d. Impregnation process**

The CaO catalyst was supplemented with activated carbon as carrier or catalyst support. The ratio of activated carbon and CaO was varied in order to determine the optimum weight ratio for biodiesel production experiment. The mixture was immersed in a solution of NaOH with variable of 25%, 30%, 35% (w/w) and it was stored for overnight. The catalysts mixture was dried in an oven temperature of 100 °C for 5 hours. After dried, the calcination process was conducted again at temperature of 500°C for 5 hours. Supported catalyst that had been formed was kept in a desiccator. The SEM analysis was conducted to assume the compounds contained in the supported catalyst, the particle sizes and morphology.

### **e. Biodiesel Production**

The esterification process was conducted in a batch reactor. The shell catalyst and methanol was combined in the reactor for 30 minutes. The cooking oil that had been warmed at 60°C, was fed to the reactor and stirred at 600 rpm. The mixture was warmed at 65°C for 3 hours. The mole

ratio of methanol and cooking oil was 1:2 (w/w) for both heterogeneous and homogeneous catalysts. The independent variables in this study were the concentration of NaOH solution during the process of impregnation (25%, 30%, 35%) and the amount of heterogeneous catalysts (supporting catalyst) which was 1.5%, 2.5%, 5%, and 7.5%.

#### **f. Biodiesel purification**

The heterogeneous catalyst was separated from a mixture of methanol, biodiesel, remaining cooking oil and glycerol using centrifugation with a speed of 6000 rpm for 10 minutes. The supernatant was precipitated for 3 hours in a decanter to separate methanol, glycerol, biodiesel, and unreacted oil from the previous process. The obtained biodiesel mixture at the top of layer was washed using warm water. The washing process was intended to dissolve the remaining methanol. The water in biodiesel was removed by heating in the oven at 110°C for 1 hour. The product was analysed according to ISO 7182-2012.

For homogenous catalyst experiment, the product of the trans-esterification was immersed for 3 hours in a funnel to separate NaOH, methanol, glycerol, unreacted oil from biodiesel mixture. After decantation, there were remaining two layers: biodiesel at the top and glycerol in the bottom. Biodiesel was then washed using warm distilled water. After 15 minutes, then biodiesel was separated from the washing water. To remove the remaining water, biodiesel was dried in an oven with a temperature of 110°C for 1 hour. The biodiesel was then analyzed according to ISO 7182-2012 method.

### **3. Result and Discussions**

#### **a. Characterization of catalysts**

The content of CaCO<sub>3</sub> in mussel shells was in the range of 95% - 99% [2]. In this study, the XRD analysis of the CaO catalyst was conducted after calcination at 900°C for 3 hours in a furnace.

This XRD analysis was aimed to determine the composition of CaO in the catalyst. The result of XRD analysis of heterogenous catalyst derived from mussel shell is depicted in Fig.1.

### Figure 1

The CaO formed is indicated by diffraction peaks at  $2\theta = 31.64^\circ$ ;  $36.6^\circ$ ;  $52.9^\circ$ ;  $66.36^\circ$ ;  $78.38^\circ$ ; and  $88.62^\circ$ . The diffraction patterns were verified and consistent according to JCPDS file number 00-037-1497 as well as with published reports by Chen et al. [7]. The catalyst contained Calcite ( $\text{CaCO}_3$ ) at  $2\theta$  of  $26.72^\circ$ ;  $43.36^\circ$ ;  $46.36^\circ$  which indicated that the decomposition of  $\text{CaCO}_3$  to CaO was not fully completed. This is probably due to the hard physical structure of mussel shell that is difficult to decompose even at high temperature. In this catalyst, some minerals are also present such as tricalcium silicate,  $\text{AlBr}_4\text{Cu}$  and  $\text{Ag}_9\text{In}_4$ .

The chemical composition of catalyst has been determined by using XRF analysis (Table 1). The CaO content in this catalyst is 35.5%, which make mussel shell is potential for biodiesel catalyst. Other CaO was in the form of tricalcium silicate (13.8%), which may contribute in supporting the catalyst.

### Table 1

The image of SEM analysis of catalysts C/CaO/NaOH is shown in Figure 2. This analysis is important to determine the morphology profile of the surface of objects[8]. The morphology of catalyst with magnification of 3000x show un-even structure and shape. The particle sizes have been identified in the range of 5 to 10  $\mu\text{m}$ .

### Figure 2

#### b. Determination of optimum C: CaO ratio

The C/CaO ratio was determined by conducting preliminary experiment. The experiment was done by varying C/CaO mass ratio and then impregnated at room temperature for 8 hrs in 30% NaOH solution followed by calcination process at  $800^\circ\text{C}$  for 3 hrs. Figure 3 shows the effect of variation of C/CaO weight ratio to biodiesel yield and it can be concluded that optimum ratio of

C/CaO was achieved at 2:3. At low C/CaO ratio, the catalyst has less active components while excessive C/CaO ratio leads to lower catalytic activity[6]

### Figure 3

#### c. The effect of NaOH concentration to biodiesel yield

Biodiesel yield shows an increase when the concentration of NaOH solution in impregnation process was increased from 25% to 30%, but then it decreased after addition of NaOH to 35% (Figure 4). There was no significant improvement of yield observed after addition of 35% NaOH in impregnation process. The highest yield was obtained when the catalyst added at 7.5% (w/w) with a NaOH concentration of 30%. The addition of 35% NaOH had disturbing effect to the active sites and there was uneven NaOH distribution in the catalyst, which resulted in partial dissolution of the carrier. However, if the concentration of NaOH were too small, amount of the active site or active centers would reduce and weaken the activity of the catalyst [5][6].

### Figure 4

#### d. The effect of catalyst load to biodiesel yield

The optimum yield was obtained at the amount of the catalyst loading of 7.5% with 30% NaOH added to impregnation process. Increasing the amount of catalyst would increase the yield of biodiesel (Figure 4). From Figure 4, it is observed that the increase in catalyst dosage from 1.5 to 7.5 wt% resulted in corresponding increase in biodiesel yield from 82 to 96% at impregnation with 30% NaOH. At low catalyst loading, it is insufficient to drive the direction for completion the esterification [3][9]. The increase in biodiesel yield by increase of amount of catalyst was attributed to the sufficient number of active sites available for reaction. However, the amount of NaOH at high catalyst load (7.5%) had deterioration effect to biodiesel yield, and therefore the yield decreased from 96 to 84% [10, 11].



#### e. Analysis of biodiesel products

The biodiesel was analyzed referring to the ISO Biodiesel including yield, acid number, numbers soap, iodine number, cetane number. The results of product analysis is shown in Table 2. The yield obtained from heterogonous catalyst (yield=95.12%) has higher value as compared to homogenous catalyst (77%). The yield of biodiesel prepared by using heterogamous C/CaO/NaOH catalyst was higher than homogenous NaOH catalyst.

Yield of biodiesel was affected by catalyst activation from impregnation result that produced larger surface area and larger amount of active site. The use of homogenous NaOH catalyst eventually produced a lower yield due to the saponification reaction occurring during reaction and there was possible loss of biodiesel because of the washing processes.

No significant differences in density were observed between biodiesels obtained from heterogeneous catalyst and those obtained from homogenous catalyst. Moreover, the density of both experiment meet the density value specified by ISO biodiesel standard (0.85-0.89 g/cm<sup>3</sup>).

#### Table 2

Other biodiesel physical parameters such as kinematic viscosity, saponification number, cetane number, and iodine numbers in this study are also already fulfilled the quality standards of ISO Biodiesel except for acid value, which is higher than 0.6 mg KOH/g (Table 2). This is probably due to quality of raw materials, oil-refining level, the influence of the type of catalyst and the hydrolysis of the ester bond when biodiesel was stored in a long time. Acid number or free fatty acids that were too high indicates biodiesel was corrosive and able to cause slag in diesel engine injector [12].

The saponification number indicates the amount of acyl groups per unit weight of oil. A low saponification number indicates a lower proportion of low molecular weight fatty acids in the oil

or vice versa [13] and therefore it can be used to measure the average molecular weight of oil and expressed in mg of KOH per gr of oil ( $\text{mg KOH g}^{-1}$  oil). In this experiment, the saponification number for both homogenous and heterogenous catalyst has the same magnitude, 248.24 mg KOH/g oil and 255.25 mg KOH/g oil, respectively.

The iodine number is the indicator of amount of unsaturated oil. The iodine number is normally used for identification of chemical stability of oil or biodiesel and overall degree of oil saturation which is important for viscosity and cloud points[12]. Therefore, the lower iodine number will give better performance as biodiesel. In this study, biodiesel obtained from the heterogenous catalyst has lower iodine number (34.01 mg  $\text{I}_2/\text{g}$  oil) than homogenous catalyst (41.62 mg  $\text{I}_2/\text{g}$  oil).

In general, the iodine number has conversely correlation with cetane number [12]. The amount of unsaturated fatty acid chain is the most significant cause of lower cetane number. The higher cetane number may result in decreased engine life, however it gives better viscosity characteristic in cooler condition [14]. It is also supported by our findings as tabulated in Table 2.

In GC-MS analysis (Figure 5), the largest content of methyl esters in biodiesel was methyl linoleate (61.39%) followed by methyl oleate (30.94%), methyl palmitate (6.02%), methyl stearate (1.67%) and methyl linoleate (1.1%) (Table 3).

Overall, the biodiesel product obtained from this experiment was qualified as a substitute fuel for diesel engines, and the catalyst showed good performances to replace the homogenous catalyst.

### **Table 3**

### **Figure 5**

#### **f. Comparison of homogeneous and heterogeneous catalyst**

The comparison of FTIR result of biodiesel using conventional NaOH catalyst and heterogeneous C/CaO/NaOH is shown in Figure 6. Both biodiesel showed the similar trend of spectra which may due to high chemical similarities that exist among triglycerides and methyl ester. The peaks of typical of esters, C=O and C-O stretching are clearly observed at region of 1700-1800  $\text{cm}^{-1}$  and 1170-1200  $\text{cm}^{-1}$ , respectively. Other peaks that indicate the characteristic of C-H bond and asymmetric stretching of  $-\text{CH}_3$  group in the methyl ester are observed at 2922  $\text{cm}^{-1}$  and 1446  $\text{cm}^{-1}$ , respectively.

#### **Figure 6**

#### **4. Conclusion**

The results showed that mussel shells contains 90%  $\text{CaCO}_3$  and decomposed to 35%  $\text{CaO}$ . The optimum FAME yield was 95.12%, which was achieved at NaOH concentration of 30% and the catalyst load of 7.5%. The biodiesel produced with C/CaO/NaOH catalyst fulfilled the national standards and had a better quality compared to homogenous basic catalyst (NaOH). The GC-MS analysis showed that the biodiesel contained methyl ester whose largest component was methyl linoleate (61.39%).

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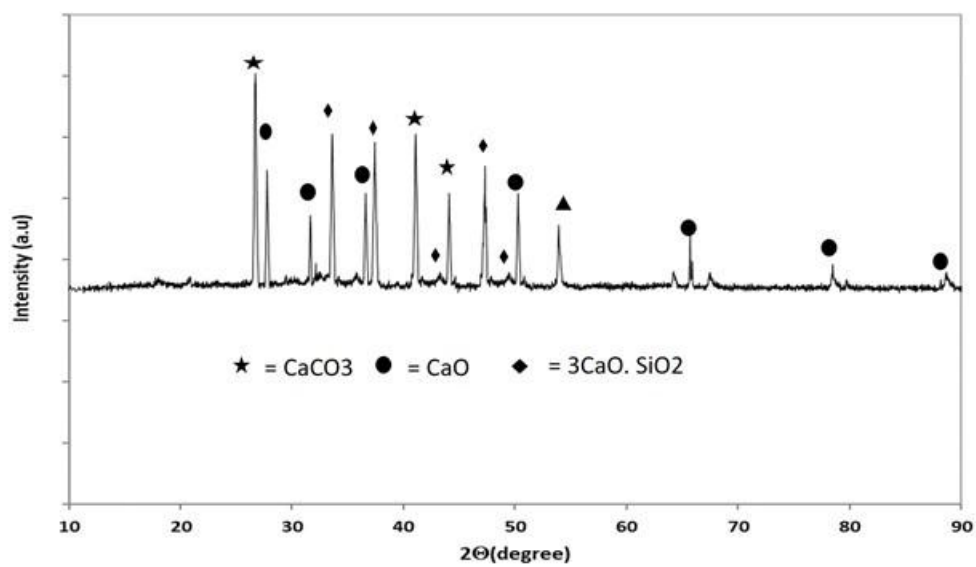


Fig 1. XRD analysis of heterogeneous catalyst C/CaO/NaOH

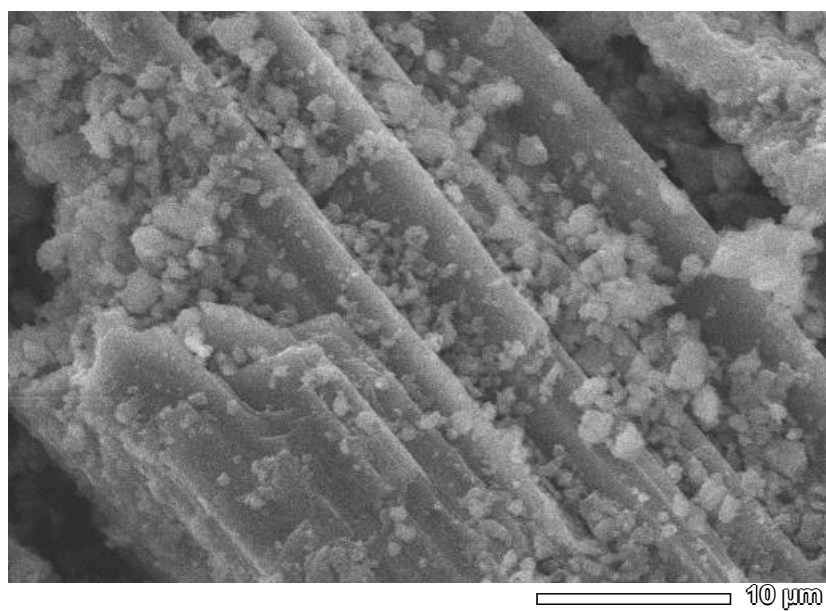


Figure 2. SEM Image of Catalyst C/CaO/NaOH

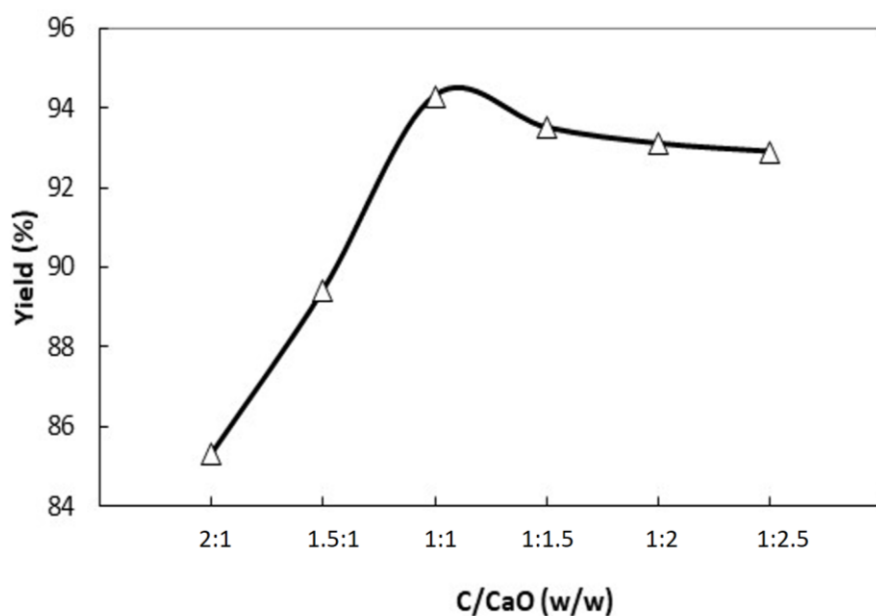


Figure 3. The effect of activated carbon: CaO weight ratio to biodiesel yield

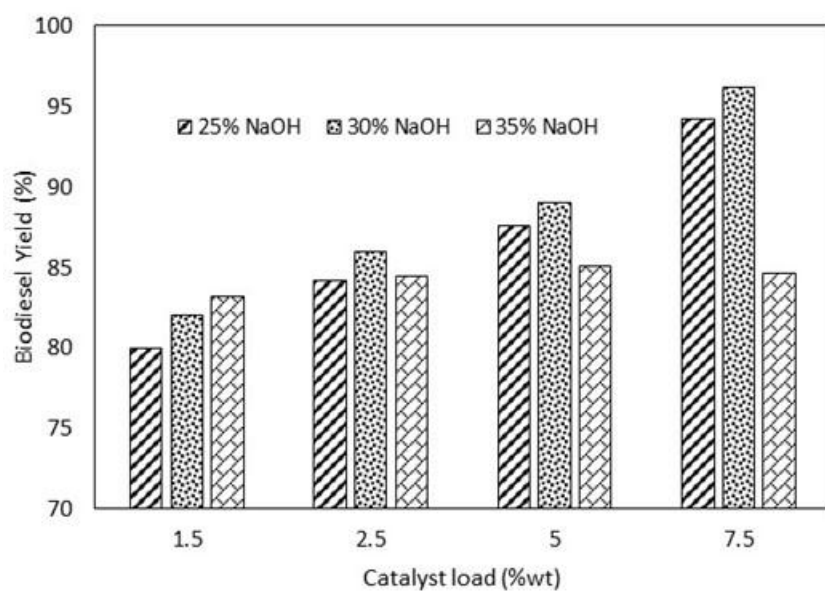


Figure 4. Effect of catalyst and NaOH concentration in impregnation process to biodiesel yield

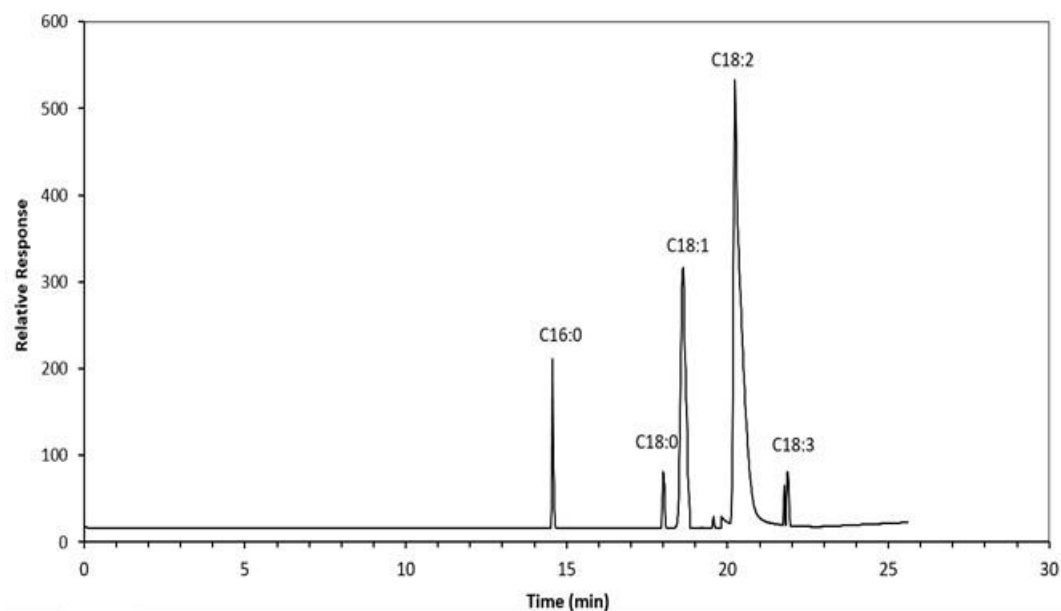


Figure 5. The GC-MS spectra of biodiesel obtained from heterogeneous catalyst C/CaO/NaOH

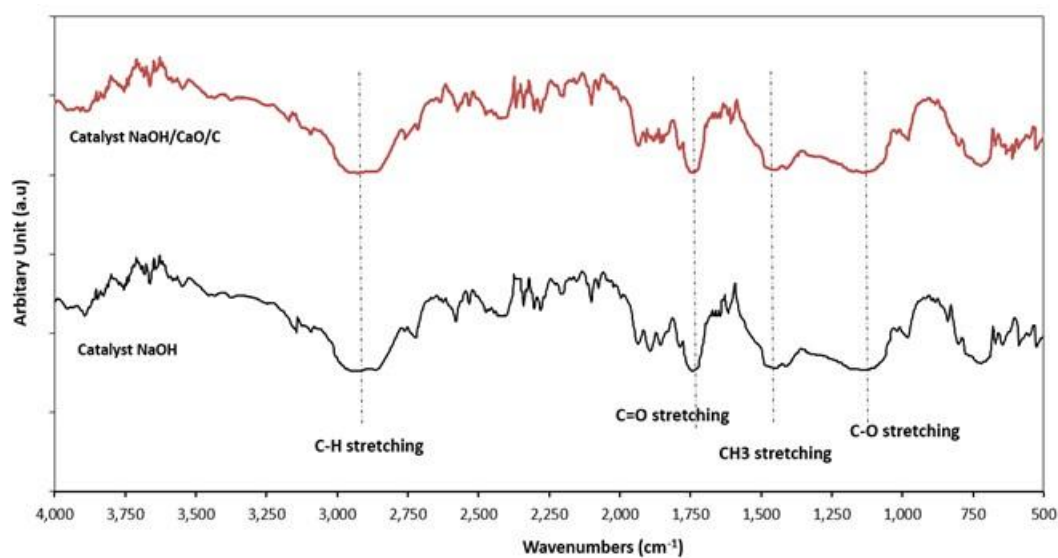


Figure 6. The FTIR analysis of biodiesel products produced from heterogeneous catalyst (C/CaO/NaOH) and homogenous catalyst (NaOH)



**Table 1.** The result of XRD diffraction and concentration of each component in the catalyst

Compound	2 $\theta$ [°]	Total (%)
CaCO <sub>3</sub>	26.72; 43.36; 46.36	38.6
3CaO.SiO <sub>2</sub>	26.72; 27.76; 33.6; 36.6; 37.86; 38.36; 39.06; 41.76; 43.36; 46.36; 48.86; 50.7	13.8
CaO	31.64; 36.6; 52.9; 66.36; 78.38; 88.62	35.5
AlBr <sub>4</sub> Cu	27.76; 33.6; 39.06; 43.36; 46.36; 50.7; 53.54; 56.8	6.3
Ag <sub>9</sub> In <sub>4</sub>	26.72; 33.6; 38.36; 41.76; 46.36; 52.9	5.9

**Table 2.** The physical properties of biodiesel obtained from heterogonous (C/CaO/NaOH) and homogenous (NaOH) catalyst

Physical properties of biodiesel	Type of Catalyst		ISO standard
	C/CaO/NaOH	NaOH	
Yield (%)	95.12	77.8	
$\rho$ (g/cm <sup>3</sup> )	0.88	0.87	0.85 – 0.89
$\eta$ (cSt)	2.33	2.02	2,3 – 6,0
Acid number (mg KOH/g oil)	1.66	1.795	max. 0,6
Saponification number (mg KOH/g oil)	248.24	255.25	max.312
Iodine number (mg I <sub>2</sub> /g oil)	34.01	41.62	max. 115
Cetane number	59.61	57.07	min. 51

**Table 3.** Composition of methyl ester in biodiesel analyzed using by GC-MS

Components Methyl Ester	Concentration (%)
Methyl palmitate (C16:0)	6.02
Methyl stearate (C18:0)	1.67
Methyl oleate (C18:1)	30.94
Methyl linoleate (C18:2)	61.39
Methyl linoleate (C18:3)	1.1