IOP Conf. Series: Journal of Physics: Conf. Series **877** (2017) 012037 doi:10.1088/1742-6596/877/1/012037

Biodiesel Production by Using CaO Catalyst and Ultrasonic Assisted

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Abstract. Biodiesel is an alternative energy and sustainable products. Biodiesel can be produced from vegetable oil by using homogenous and heterogenous catalyst. In this research, biodiesel was produced by using CaO catalyst from limestone and assisted by ultrasonic wave. CaO catalyst was used 1- 4.4% of oil weight. Ultrasonic wave was generated by using ultrasonic cleaner at 28 and 42 kHz of frequency. Cooking oil was preparated by esterification process by using sulphuric acid as catalyst until amount of free fatty acid (FFA) is under 0.5%. The results shown yield of methyl ester obtained highest 89.98% on the reaction carried on mole ratio methanol to oil, 9: 1 and frequency of 40 kHz. Increasing frequency of ultrasonic wave cause increasing of yield of biodiesel.

1. Introduction

Biodiesel is a diesel engine fuel made from biological sources or biomass. Meanwhile, according to today's understanding of the industry, biodiesel is a fuel for diesel engines consisting of alkyl esters of fatty acids **Error! Reference source not found.**. Ester is a chemistry term that means a compound formed from condensation of alcohol with acid. The process of making biodiesel by reacting alcohol with fatty acids can be done in two ways, namely esterification and transesterification [5]. In making the ester biodiesel can be made from vegetable oils by esterification or transesterification reaction or a combination of both reactions. The esterification reaction is a reaction between free fatty acid with an alcohol to form an ester and water. The reaction that occurs is an endothermic reaction and temperature reaction at 55-60^{o}C [1-2].

Commonly, biodiesel was produced with homogenous catalyst[1-2,5], like sulphuric acid for esterification and potasium hydroxide for transesterification reaction. Heterogenous catalyst was also used in biodiesel production like as KI/KIO_3/H-zeolite[6], calcium oxide[7-12]. Widayat et.al (2016) were used KI or KIO_3 that loading on H-zeolite for catalyst on biodiesel production from palm oil. H-zeolite was prepared from natural zeolite with chemical and physical treatment[6]. Hadiyanto et.al (2016) were used calcium oxide as catalyst on biodiesel production. Calcium oxide catalyst was prepared from mollusk shell and combining with fly ash from coal combustion[7,8]. Waste of animal bone was also used as catalyst in biodiesel production and physical treatment was used for preparation of CaO catalyst[9]. Calcium oxide has potential catalyst in biodiesel production[10- 12].

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Catalysts are compounds that speed up reactions by lowering the activation energy without participate in reaction[13]. The advantages of heterogenous catalyst are separation from products were quite simple, namely by using filtering. One sources of CaO in natural resources is limestone. Limestone is a sedimentary rock composed largely of the minerals calcite and aragonite, which are different crystal forms of calcium carbonate ($CaCO_3$). CaO catalyst was used in transesterification reaction .

Biodiesel or Fatty Acid Methyl Ester (FAME) can produced with esterification and transesterification[1-2,14].The esterification reaction is done before the transesterification reaction if the used oil containing high free fatty acid (> 0.5%)[1,14]. In esterification reaction, free fatty acid convert to FAME with adding of methanol and acid catalyst. Transesterification reaction also called alcoholysis reaction, reaction between triglycerides with alcohol and alkaline catalyst to produce an methyl ester /FAME and glycerol. Alcohols that used transesterification reaction were methanol, ethanol and isopropanol. FAME and glycerol are easily separate with decantation processing [13].

The objective of this research is to study effect of mole ration methanol to triglycerides and CaO catalyst concentration on transesterification reaction.

2. Methods

2.1. *Material*

Palm oil was purchased from local market. Limestone was bought from material store. Methanol has industrial specification and sulphuric acid obtained from Merck Ltd. In biodiesel production was used reactor that require with mechanical mixing and ultrasonic assisted. Ultrasonic wave was generated in ultrasonic cleaner with 200 watt of power and 28, 40 kHz of frequency. This equipment like presented in Figure 1.

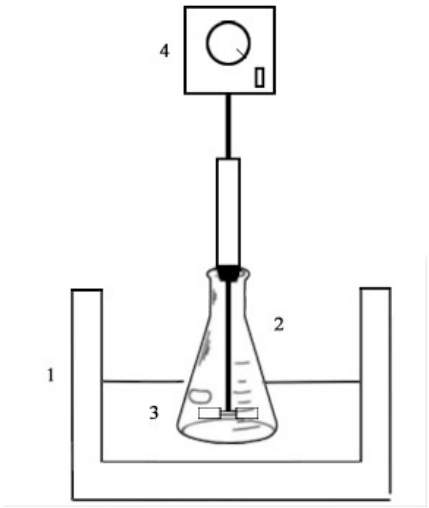


Figure 1. Apparatus for biodiesel production (1.ultrasonic cleaner; 2. Erlenmeyer as reactor; 3. Water as transmition medium; 4. Mechanical stirer)

2.2. *Catalyst preparation*

100 grams of limestone were washed by deionized water to remove dust and impurities, and then dried overnight in an oven at 105^{o}C. The acquired limestone as well as commercial $CaCO_3$ were crushed and sieved, and then calcined at 900^{o}C for 1 ½ hours. The characterization of the limestone and catalyst were analyzed by The X-ray diffractometer (XRD) for knowing the composition and Scanning Electron Microscopy (SEM) to discover the size of crystals formed.

2.3. Cooking oil preparation

Cooking oil first is tested free fatty acid (FFA) composition. The FFA value must be under 0.5%. If the certain condition did not achieve, the esterification had to be done in order to decrease the FFA value until reached under 0.5%[1,14]. The esterification reaction was carried out in a three-neck glass batch reactor equipped with a condenser and a thermometer. 800 ml cooking oil was mixed with 10 ml sulfuric acid and methanol by mole ratio to FFA 40:1, which all of the material had already been heated to 60^{o}C. The reactor was placed in a water bath and heated on a hotplate. The agitating speed was kept at 600 rpm to ensure the efficient mixing. The reaction kept going for 2 hours.

2.4 *Biodiesel production*

The transesterification reaction was carried out in a batch reactor equipped with a propeller. The reactions were performed using Branson (USA) ultrasonic processor (28 kHz and 42 kHz) with a full power of 200 W. 100 ml of triglycerides were filled in reactor. Methanol was added in reactor at mole ratio 3:1 -15:1. Amount of CaO catalyst was loaded in reactor with concentation 1 -4.4% (w/w). A mixture was heated until 60^{o}C. Ultrasonic radiation was setted in reaction time 45 minutes. After the transesterification reaction, the catalyst was removed from the mixture by filtration. The filtrate was kept in the filter paper for 24 h or more in 70^{o}C oven. The filtrate was decanted until glycerol (lower layer) and methyl ester (upper layer) by using separation column. FAME product was analyzed with Gas chromatography (GCMS) for composition of methyl ester.

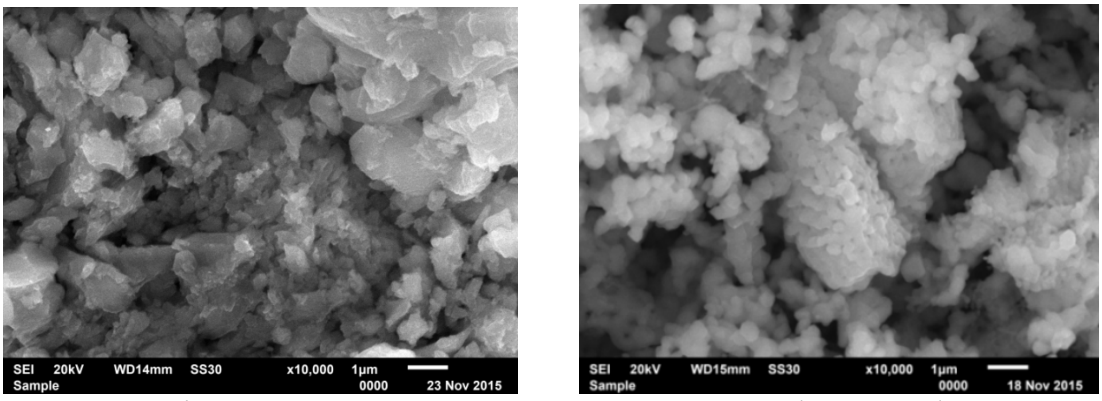
2.5. Catalyst characteristic

The CaO catalyst products were analyzed of characterization of morphology and crystallite. The analysis of crystallography was used x-ray diffractometer, XRD-7000S model Shimadzu brand with X-ray tube target Cu, voltage 30 kV, current 30 mA, and Kα radiation. XRD data was analyzed with PCXRD software. Morphology of catalyst was analyzed with JEOL PC Scanning Electron Microscope (PCSEM) model JSM-6510LA with magnification x5000. The analysis process was conducted in Center of Research and Service Diponegoro University (CORES DU).

3. Result and discussions

3.1 *Characterization of CaO catalysts*

The characterization of CaO catalysts and limestone about morphology like presented in Figure 2. Figure 2.a. is a photograph a limestone that a fragile material. Limestone was calcinied in 900^{o}C temperature at 1.5 hours. This process affected in structure and morphology, because compounds was convert from $CaCO_3$ to CaO and $Ca(OH)_2$ convert to CaO and H_2O[11-12]. Morphology of CaO like presented in Figure 2.b. CaO catalyst has more crystaline than limestone. Cao catalyst was not rigid and had surface area more than limestone.



a. Limestone b. CaO catalyst

Figure.2. Photographs of limestone and CaO catalyst through Scanning Microscope

XRD results of limestone and CaO catalyst was presented Figure 3. The color of catalyst products commonly has white. The calcination processing don't cause change of color Figure 3. also indicate that physical treatment influence in preparation of CaO catalyst. XRD patterns have peaks as similar in 2 theta degree 18. Intensity of limestone pattern has peak lower than CaO catalyst. This indicates Caocatalyst has crystallinity more than limestone. Physical treatment with calcination process affected appearance of peak in 2 theta degree 32,38, 68 and 80. This peak shwon an new compunds likes calcium oxide (CaO). CaO was form calcination calcium carbonate and calcium hydroxide[7,11-12]. The circle signs in Figure 3 as indicate CaO.

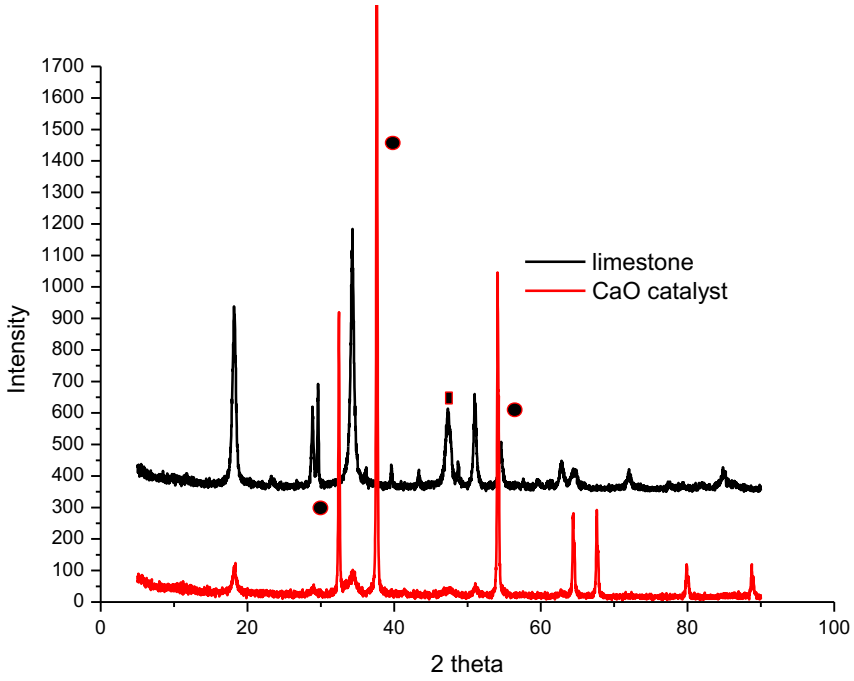


Figure 3. XRD pattern of limestone and catalyst product

3.2. Effect of ultrasonic frequency

The results of the frequency effect like presented in Fgure 4. Ultrasonic frequency has a significant effect in biodiesel forming. Biodiesel processing that use of a greater frequency of 42 kHz produces methyl ester conversion of 89.98 % and 28 kHz frequency jusat 64.68 %. This is due to the influence of ultrasound on the reaction can be described by the Arrhenius equation. Frequency influnce in power that generate ultasonic wave. So, power can affected in activation energy on transesterification reaction. Widayat et.al (2015) describe that activation energy as ultrasonic power function (P). Effect of ultrasonic can be described by quadratic equations [5] as follows:

$$Ea = a.P^{0.9} + c \quad (1)$$

In this equation Ea is activation energy, P as ultrasonic power and a,c as constante

The activation energy is the minimum energy needed for certain chemical reactions can occur. Increasing the ultrasonic frequency is proportional to the increase in power , where the greater power of ultrasonic cavitation bubbles can form more. The existence of cavitation bubbles may affect the particles that damage the walls will decrease the value of the activation energy [5].

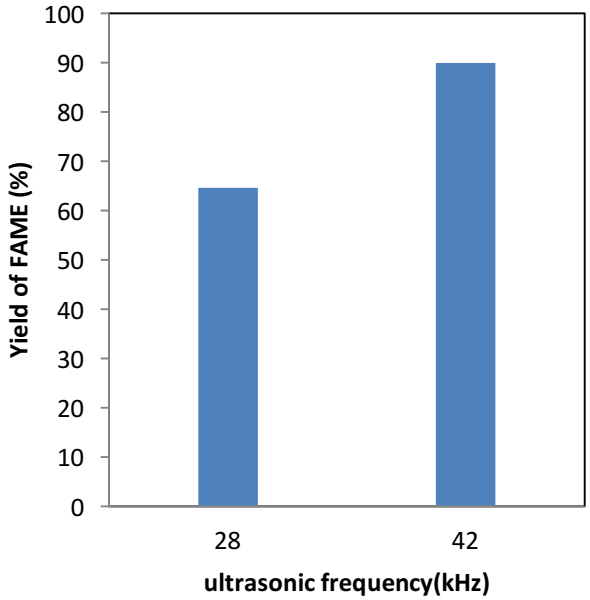


Figure 4. effect of difference frequency on transesterification on cooking oil

3.3. Effect of mole ratio methanol to triglyceride

The influence of mole ratio methanol to triglyceride in biodiesel production with resphonse variable yield of biodiesel was presented in Figure 5. Increasing moles of methanol occurs on the ratio 3: 1 to 9 : 1, and the higher obtained yield of biodiesel 89.98 %. After that, yield of biodiesel was decrease. However, the addition of further methanol does not increase yield biodiesel, Yield of biodiesel has tends to decrease when mole ratio of methanol to oil change to 12: 1 and 15: 1. This is can be occur because by-product of glycerol formed largely will react with methanol excess. Furthermore, it hinder reaction of methanol with catalyst. In mechanism of biodiesel production methanol was react with catalyst and formed methoxyde compounds (catalyst). In this research methanol react with CaO catalyst form Camethoxide ($Ca(CH_3O)_2$) [7-8]. Thereby disrupting separation of glycerine is then lowered conversion to shift the equilibrium towards the opposite (reactants) [9]. In this research We obtain the best ratio of methanol to oil is 9:1. Widayat et.al reported biodiesel production can obtained maximum at ratio methanol to oil 10:1[1;2]. So this research more better than previous research, because can save methanol as reactant.

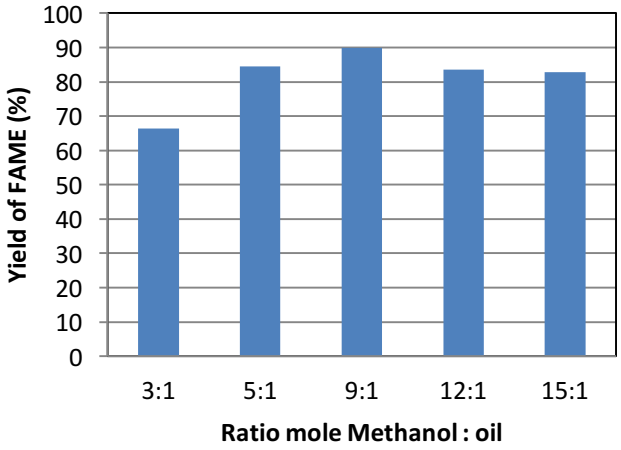
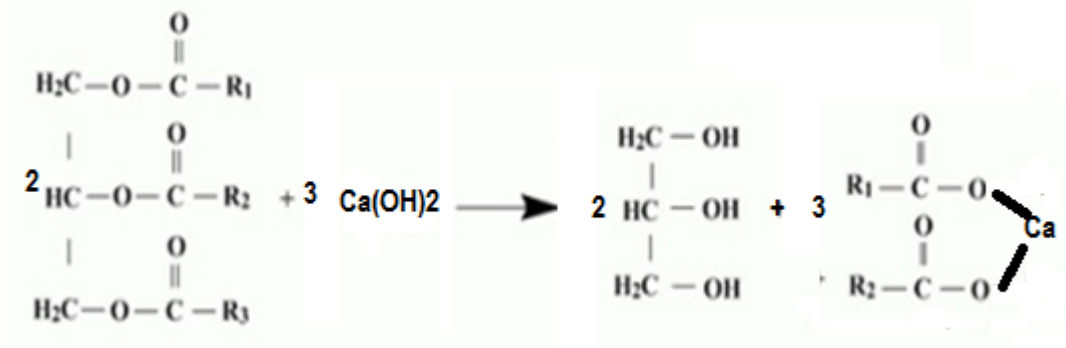


Figure 5. effect of mole ratio on transesterification on cooking oil

3.4. *Effect of catalyst concentration*

The effect of the catalyst concentration presented in Figure 6. Yield of FAME could be analysed by varying catalyst concentration of 1- 4.4% wt. The study was conducted with the help of ultrasonic systems while stirring using a propeller. Figure 6 shown yield of FAME was increase along with the increased amount of catalyst loading. This experiments similar with Chen et.al (2014) [15]. Concentration of catalyst was increased from 1% wt. to 2.6% wt., yield of FAME produced gradually increased and reached the best results at 2.6% wt with yield of 89.98%. However, excess addition of a catalyst in the sample (above 2.6 wt%) will reduce the yield produced. This is due to the addition of the catalyst will occur the saponification reaction. Saponification reaction is caused by $Ca(OH)_2$ which has base properties[7-8].The following is the reaction of the saponification:



Due to the formation of soap (saponification), it made the solution too viscous so that it would be difficult to dissolve and reacting [15].

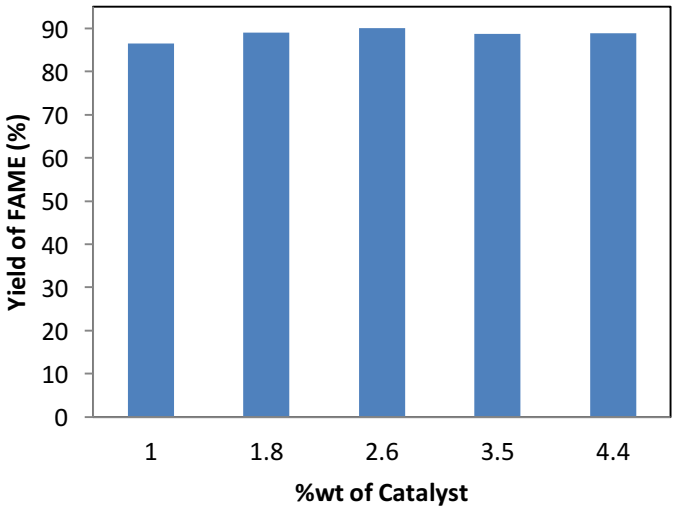


Figure 6. Yield amount of FAME with variation of catalyst concentration (ratio of metanol : oil = 9 : 1)

3.5. Catalyst reusability in biodiesel production

The reusability of CaO catalyst was examined by varying the reaction cycles. Before reuse, the spent catalyst was washed with n-hexane to remove the absorbed materials and dried overnight in an oven at 105°C. Figure 7 shows yield of FAME after reuse of the catalysts in the magnetically stirred system combined ultrasonic system. After the 3th cycle of transesterification, yield of FAME was already 66%. This results of reuseability was diference with Chen et.al (2014) that has 8th cylce of transesterification reaction[16]. The first cycle, yield of FAME reach 89.98%, second cycle yield of FAME is 68.96%, and third cycle yield of FAME is 66.0%. Each experiment generates decreases result in methyl esters composition. This is caused by the formation of $Ca(OH)_2$ and diglyceroxide.

$Ca(OH)_2$ formed by the hydration reaction of CaO that can lower the catalytic activity. Meanwhile diglyceroxide also react with calcium by forming Ca-glyceroxide for their incorporation byproducts are glycerol and CaO catalyst[9]. Ca-glyceroxide can still work as a catalyst for the transesterification, but has a lower catalytic activity than CaO [10]. The decreasing of catalyst activity can also be caused due to sensitivity CaO to CO_2 in any trial process [11] as well as leaching of CaO for reuse [9]

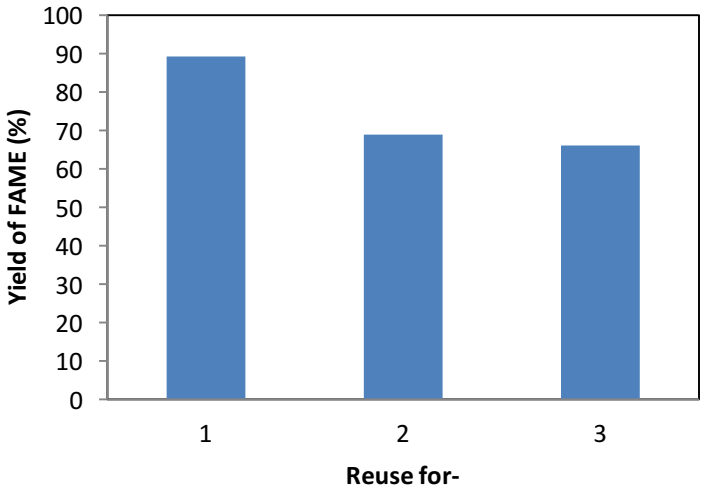


Figure 7. Reuseability of CaO catalyst

4. Conclusions

CaO catalyst was prepared from limestone with calcination process at 900°C and 1.5 hours. Yield of biodiesel /FAME has 98.89% that obtained at mole ratio methanol to oil 9 : 1 and 2.6%w catalyst concentration. The addition of methanol would cause excess methanol reacts with glycerol to inhibit the reaction of methanol and reactants, as well as reversing the direction of the reaction. the best frequency of ultrasonic frequency is 42 kHz.

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