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Utilization of Limestone as Catalyst in Biodiesel Production

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Abstract:

Developments efforts to find renewable energy sources that are more environmentally friendly is to create alternative energy sources such as biodiesel. Biodiesel can be extracted from the esterification of free fatty acid with alcohol through using acid catalyst or transesterification from triglyceride and alcohol using a basic catalyst. catalyst CaO is a more active catalyst and has long been researched for transesterification reaction because it is inexpensive and has high strong of base. In this study, the authors have synthesized calcium oxide (CaO) from limestone which used as a catalyst in the esterification of palm oil which converted into biodiesel. The synthesis was carried out by limestone calcination at temperature variations 700, 800, 900 and 1000°C. Calcination of limestone at 900°C showed the highest amount of CaO used as a catalyst in biodiesel production.

Key words: limestone; biodiesel; catalyst; palm oil

INTRODUCTION

The evolution of the industry in the world has made an increase in energy needs. Most of today's energy needs are still being supplied from non-renewable natural resources such as petroleum, natural gas, and coal which will soon run out. One of the developments efforts to find renewable energy sources that are more environmentally friendly is to create alternative energy sources such as biodiesel[1]. Vegetable oil can be used as a precursor for biodiesel production because it is a renewable energy source, can be mass-produced and environmentally friendly[2].

Biodiesel can be extracted from the esterification of free fatty acid with alcohol through using acid catalyst or transesterification from triglyceride and alcohol using a basic catalyst[3]. Examples of the commonly used catalyst are NaOH and KOH. These homogeneous catalysts have disadvantages such as highly corrosive that can impact on the machine causing damage and less eco-friendly[4]. One of the efforts to handle these disadvantages is by using a heterogeneous catalyst..

Heterogeneous catalyst is a catalyst that has different phases with reactants and products, The usage of heterogeneous catalyst in biodiesel production has been done like the usage of MgO/SiO_2 catalyst in biodiesel production[5], CaO-ZnO catalysts in biodiesel production[6], biodiesel production using metal oxide[7] and the application of calcium oxide and magnesium oxide from natural dolomitic rock for biodiesel[8]. The result of the researches suggests that heterogeneous catalyst has an impact on the esterification reaction process and can increase biodiesel production.

The reaction of an alkaline-based solution with methanol will produce methoxide compound, so this property can also occur in group II A compound, like CaO and MgO. Using these oxide compounds as catalyst give advantages where CaO and MgO have low solubility in water. Besides that, catalyst CaO is a more active catalyst and has long been researched for transesterification reaction because it is inexpensive has high strong of base[9]and hardly soluble in methanol compared with oxide compounds or earth alkali hydroxide compounds such as SrO and $Ba(OH)_2$ that are fully soluble in reaction[10]. These advantages push us to use group II A oxide compounds like CaO as a catalyst in biodiesel production from palm oil.

In this research, the synthesis of calcium oxide (CaO) from limestone will be used as a catalyst in the transesterification reaction of palm oil to produce biodiesel. The synthesis was carried out by limestone calcination at variations of 700, 800, 900 and 1000°C. The results of calcination of limestone at 900°C showed the highest CaO element to be used as a catalyst in biodiesel production.

MATERIAL AND METHODS

The main tools and instruments used in this research are a set of crusher, Hot plate, and magnetic stirrer, furnace, glassware (like three-necked Erlenmeyer, beaker glass, separating funnel, stirring rod) condenser, thermometer, GC-MS (Gas Chromatography-Mass Spectrometer). The material we used is limestone, methanol, palm oil.

Preparation of CaO catalyst from limestone

After all the limestone has been collected, it is cleaned from the ground, then crushed using a crusher until its smoothness is 45 µ. Then the composition is measured using the XRF instrument.

The Limestone powder is calcined in 4 temperature variations, that is 700, 800, 900 and 1000°C for 3 hours to get calcium in the form of an oxide (CaO). Then the

composition is measured again with the XRF, XRD, SEM and BET instruments.

Biodiesel production using CaO catalyst

The calcium oxide that is produced then used as a catalyst in biodiesel production with precursors of palm oil and methanol. CaO catalyst with a ratio of CaO/Palm Oil (6/100; 8/100; 10/100; 12/100) (%w/w) is mixed with 60 g of methanol while being stirred with a magnetic stirrer. In the mixture, 100 g palm oil is added. The solution then poured into three-necked Erlenmeyer coupled with a stirrer, thermometer, and condenser. The variation of time reaction is 30, 60, 90 and 120 minutes with temperature variations of 40, 50, 60, 70^{o}C.

After the reaction time is complete, the reaction will be stopped and the product obtained. The product is allowed to stand so that two layers will form, that is the top layer is biodiesel or methyl ester and the bottom layer is a layer of glycerol consisting of unreacted oil, glycerol, and catalyst. The top layer is separated and weigh as a biodiesel product. Then a density, viscosity and methyl ester composition is analyzed with GC-MS.

RESULT AND DISCUSSION

From the XRF analysis in table 1, it can be seen that the largest element of limestone is CaO, which is 54.11%[11]. Because of that, limestone can be used in synthesis of CaO catalyst. Therefore, limestone can be used in the synthesis of CaO catalysts. Before being used as a catalyst, limestone is calcined to remove water and carbon dioxide[12].

Table 1: XRF test results of limestone

Compounds	Composition (%)
SiO_2	0,59
Al_2O_3	0,22
Fe_2O_3	0,12
CaO	54,11
MgO	0,22
LOL	44,74

The calcination process is carried out at variations in temperature of 700°C, 800°C, 900°C, and 1000°C. The various calcination processes have CaO elements of 78.97%, 82.65%, 90.93%, 90.93%, 88 54% as shown in Figure 1. Figure 1 shows an increase in CaO composition when the calcination temperature is increased to 900^{o}C and decreases at 1000^{o}C. That the catalytic activity of CaO would be maximal if the synthesis had calcined temperatures ranging from 900 to 1000^{o}C[13]. Following previous studies which stated that the calcination temperature increases will cause the oxide content to increase[14].

The results of XRD analysis of limestone and limestone calcination showed similarities with the ICCD standards 01-083-1762 (CaCO3) and ICCD 00-001-1160 (CaO) as shown in Figure 2.

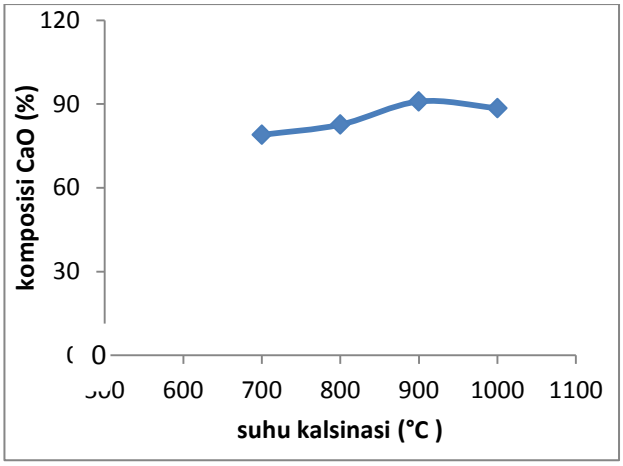

Figure 1: XRF curve result of limestone after being calcinated

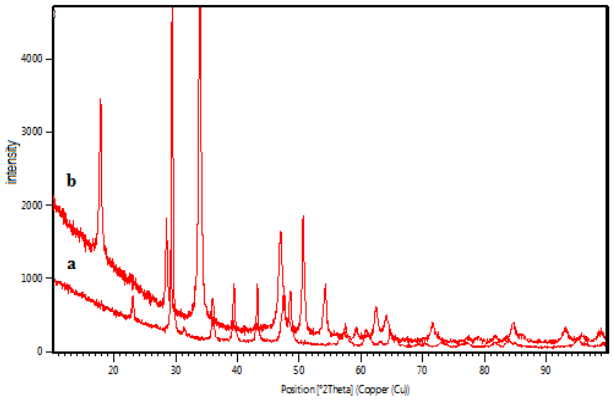

Figure 2: a) XRD Analysis result of limestone catalyst and b)XRD analysis result of CaO catalyst

While the SEM analysis results showed the calcination of limestone made into fine powder still has a large size even though it is in a micrometer size of 6.25 µm, uniform products and surface area based on BET analysis of 6,094 m^2 / g. Calcined limestone has been improved in shape, size and surface area aspects, which is also evidenced by the results of the BET analysis which shows that the surface area is 0.25 µm, SEM analysis has a nearly uniform shape, has a cubic formation and a larger surface area of 17,545 m^2 / g as shown in Figures 3a and 3b.

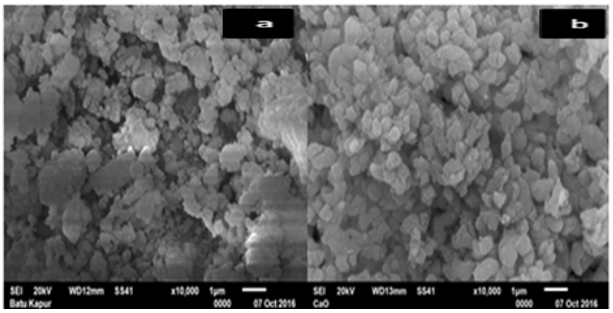

Figure 3: a) SEM analysis result of limestone before calcination and b) SEM analysis result towards CaO (calcination result in temperature 900 °C)

Optimization the Catalytic Activity of Catalysts CaO

The very good catalytic activity of CaO having 95% methyl ester[15]. In this study variations in temperature, reaction time and amount of catalyst were carried out to see the catalytic activity of the catalyst used. The optimal conditions obtained for biodiesel production are at a temperature of 60°C, a reaction time of 60 minutes with the amount of catalyst10%w[16,17]. The results show that the catalyst has an important role in the transesterification reaction. adding the amount of catalyst will increase biodiesel yield. However, increasing the catalyst concentration more than 10% w will reduce the yield of biodiesel. It is caused by the slurry (mixture of methanol, oil, and catalyst) became very viscous, thus demanding higher power consumption for suitable stirring[18].

GC-MS (Gas Chromatography Mass-Spectrometer) analysis

From the results of GC-MS analysis, it can be concluded that the synthesis product obtained is a biodiesel compound, namely methyl ester. The methyl ester compounds obtained are myristic ester, methyl palmitate, methyl linoleic, methyl oleic, methyl stearate, methyl laurate, methyl arachidate as shown in Table 2. The methyl ester compounds obtained following the palm oil content used in this synthesis such as: palmitate acid, myristic acid, stearate acid, linoleic acid, oleic acid[19,20]. Therefore we can conclude that the CaO catalyst can be used as a catalyst in biodiesel production.

Table 2: Retention Time And Peak Area Data Of Gas Chromatography And The Compounds That Are Analyzed In Biodiesel Sample

Peak	Retention time	Peak Area (%)	Methylated Ester
1	12.545	0,20	Methyl Laurate
2	15,406	2,65	Methyl myristate
3	16.597	0.06	Methyl pentadecanoate
4	17.704	2.99	Methyl palmitate
5	18.717	0.35	Methyl Heptadecanoate
6	19.368	12.41	Methyl linoleic
7	19.527	29.49	Methyl oleic
8	19.701	4.66	Methyl stearate
9	20.149	0.53	Methyl linoleic
10	21.210	0.64	Methyl oleic
11	21.443	1.00	Methyl Arachidate

Analysis of Methyl Ester Physical Properties from Transesterification Reaction

Analysis of the physical properties of the Methyl ester product from the transesterification reaction is a test of density, viscosity, and calorific value. Table 3 shows that the methyl ester produced from the transesterification reaction of palm oil with methanol using a CaO catalyst has physical properties that are following SNI 04-7182-2006.

Table 3: Test Results of Methyl Ester Physical Properties

No	Parameters	Units	Value	SNI 04-7182-2006 ranges
1	Viscousity	mm^2/s	5,27	2,3 – 6,0
2	Density	Kg/m^3	860	850 -890
3	Calories value	MJ/Kg	32, 23	-

CONCLUSION

From the research that has been done, we can conclude that CaO catalyst can be made by calcination in temperature 900°C for 3 hours and has largest CaO composition which is 90,93 % and surface area of 17,545 m^2/g. Catalyst CaO of calcination result has almost uniformity and small-sized. The density and viscousity of the biodiesel result are in SNI range, which is 850 – 890 kg/m^3 for density and 2,3 – 6,0 mm^2/s for viscousity. Optimal condition of biodiesel production happened in temperature 60°C, catalyst amount of 10% and reaction period for 1 hour.

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