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THE UTILIZATION OF DOLOMITE AS CATALYST IN BIODIESEL PRODUCTION

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ABSTRACT

Biodiesel as a renewable fuel has much of public concern to reduce the human's dependence on fossil fuels. A catalyst is necessary for increasing the rate of biodiesel production. The progress of biodiesel synthesis is focused on the efficiency of production and reduction of its negative impact to the environment. In this study, dolomite was used as a heterogeneous catalyst which was environmentally friendly in biodiesel manufacturing. The mixed CaO.MgO oxide was resulted through the calcinations stage of dolomite mineral on optimum temperature (900^0C). Before being applied as catalyst, mixed oxide was characterized by XRF, XRD, SEM and BET. The CaO.MgO oxide was applied as a catalyst in trans-esterification reaction of palm oil and methanol to form biodiesel. The reaction yielded 78.09% biodiesel with 15% catalyst ratio to oil for 60 minutes reaction under temperature of 60^0C. Dolomite can be used as a catalyst in the production of biodiesel from palm oil and methanol.

Keywords: characterization, dolomite, catalyst, biodiesel, palm oil

INTRODUCTION

Nowadays, many researcher's concerns are studying a renewable energy sources namely vegetable oils or animal fats. This material is transformed into Fatty Acid Methyl Ester known as FAME by using NaOH and KOH as homogenous catalyst. In general, some researchers have studied a method of making fatty acid methyl ester from palm oil through trans-esterification process by using NaOH and KOH as catalyst. NaOH and KOH catalysts have drawbacks such as high corrosive properties that can give negative impacts on machine tools. The catalyst may not be reused in the methyl ester and then it is released as waste of NaOH solution that's harmful for environment[1]. Many efforts have been made to reduce the negative impact of homogeneous catalyst and one of them is by using heterogeneous catalyst.

Biodiesel is a renewable fuel that can be obtained from the esterification reaction between vegetable oils or animal fats and methanol using a homogeneous catalyst or a heterogeneous catalyst[2-7]. Research on biodiesel is focused on production efficiency and efforts to minimize the environmental impact. The use of heterogeneous catalyst can minimize environmental impact because the catalyst can be reused[8-10]. One of heterogeneous catalysts that can be used is dolomite. Dolomite is a natural mineral containing compounds namely $Ca.Mg(CO_3)_2$ and several other compounds in small quantities[11]. The use of dolomite as a catalyst in various processes has gained wide attention because it's cheap and environmental friendly[12].

This research was conducted to use the advantage of dolomite as a heterogeneous catalyst that's environmentally friendly. Dolomite performance as catalyst applied to the trans-esterification reaction between palm oil and methanol yielded biodiesel with various ratios of catalyst to oil, duration and temperature of reactions.

EXPERIMENTAL

Material and Method

The materials used in the research are dolomite mineral originating in Kamang - Agam district, cooking oil, methanol and aquadest.

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Catalyst Preparation

Dolomite was crushed by a crusher to 45μ fineness size and its composition was characterized by using XRF instrument. The dolomite powder was calcinated for 3 hours at four various temperatures respectively namely 700°C, 800°C, 900°C and 1000°C. Each calcinated powder composition was characterized by XRF instrument.

Characterization of Dolomite Catalyst

The crystal structure and size of catalyst were analyzed by XRD. The morphology of catalyst surface was characterized by SEM and specific surface area was observed by BET. All characterization processed were applied to original dolomite powder and calcinated dolomite powder in optimum temperature (which has the highest composition of MgO).

Optimization of Catalytic Activity of Catalysts Dolomite (CaO.MgO)

The catalytic activity of catalyst dolomite (CaO.MgO) was tested with three parameters namely: the concentration of catalyst to oils, stirring duration and temperature of the trans-esterification reaction.

Applications of Catalyst Dolomite (CaO.MgO) Performed on Biodiesel Manufacture

Pour 60 grams of methanol into a three – neck flask to suspend 10 grams of catalyst dolomite (CaO.MgO) while stirring them with a magnetic stirrer. Pour 100 grams of palm oil to the mixture and heat it at 60°C for 1 hour with constant stirring speed. Let the reaction mixture be for few minutes until it forms separated solid and liquid phase. The liquid phase is suspected to be methyl ester (biodiesel) and the solid phase is catalyst dolomite (CaO.MgO). Let the liquid phase be for several minutes until it forms two layers, the bottom layer is glycerol and the top layer is suspected as biodiesel. Biodiesel is tested by using gas chromatography to determine the chemical composition. The biodiesel physical properties are characterized by determining the viscosity, calorific value, and density.

The same treatment is applied to various amounts of catalyst (5%, 10%, 15% and 20% b/b) to palm oil, various times (30, 60, 120 and 150 minutes), and various reaction temperatures (40°C, 50°C, 60°C and 70°C).

Characterization of Biodiesel

Biodiesel composition was determined by using Gas Chromatography Agilent Technologies supported by software of Agilent Technologies Corporation. Column used was J&W DB-624 with a column length of 30m and a volume of 2μliter. The stationary phase is silica and use detectors Flame Ionization Detector (FID). Biodiesel physical properties were determined by measuring the viscosity, density and calorific value.

RESULTS AND DISCUSSION

The dolomite characterization by using XRF obtained content of oxide[14]. In Table-1, it can be seen that there are MgO 20.17% and CaO 31.25%. XRD analysis shows that dolomite originating from Kamang in Agam District has a chemical structure with formula $CaCO_3.MgCO_3$, shown in Figure-1a. It can be confirmed to the Standard of ICDD 01-083-1766. The results of dolomite analysis by using XRD that are compared to standard dolomite[12], can be seen in Figure-1a.

Figure-1a shows that the dolomite in Kamang have peaks which overlaps with standard ICDD 01-083-1766 and connects to chemical formula $MgCa(CO_3)_2$. Sharp peaks appear on 2θ 30.934° and on 41.108° which is the peak of dolomite with Rhombohedral crystal system. Next, 29.412° is the peak of calcite ($CaCO_3$) that's in accordance with the peak calcite standard of ICDD 01-078-4614[2]. Calcination of dolomite under 4 variations of temperature is obtained from XRF analysis results, shown in Table-2. Table-2 shows that the calcined mineral dolomite will decompose into oxide (CaO, MgO) and CO_2 derived from carbonate compound contained in the mineral[15]. From XRF results, CaO and MgO havea greater percentage than other oxides and they can reach optimum temperature of calcination up to 900°C.

Table-1: The Results of XRF Analysis to dolomite in Kamang

Compound	Content (% weight)
CaO	31,25
MgO	20,17
SiO_2	3,65
Al_2O_3	0,61
Fe_2O_3	0,46
LOI	43,86

LOI: Loss on Ignition

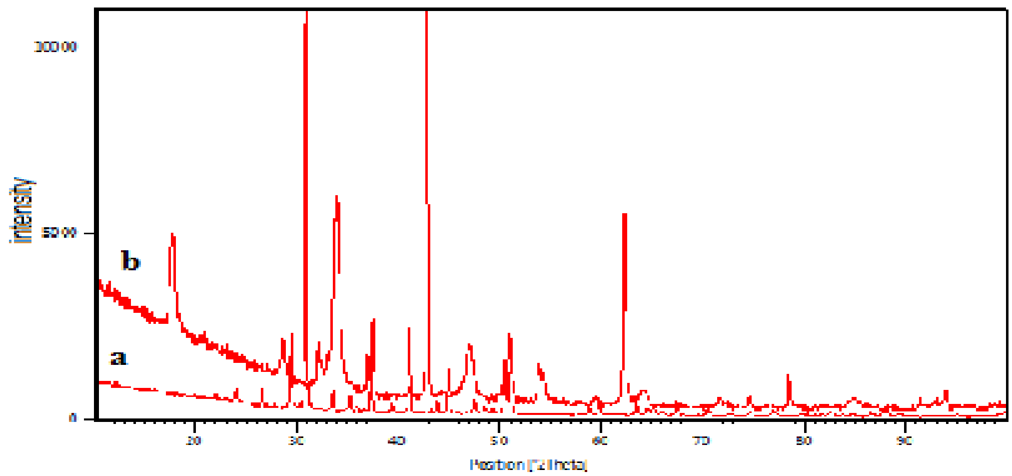

Fig.-1: XRD spectra of the result of (a) dolomite analysis in Kamang (b) dolomite after calcined on temperature $900^{o}C$

Calcination product at the optimum temperature ($900^{o}C$) is analyzed by using XRD. The XRD spectra of the compound as a calcination product of dolomite at optimum temperature can be seen in Figure-1b. Figure-1b shows that the highest peaks are seen in 2θ 42.8708^{o} and 62.253^{o}. By Referring to standard of ICDD 03-065-0476, those peaks are the peaks of MgO compound with a cubic crystal system. Another peak is seen in 2θ 37, 2980^{0} which is the peak of CaO based on standard of ICDD 01-070-5490[14].
Morphology analysis and particle size of dolomite and calcined dolomite (CaO.MgO catalyst) are analyzed by using SEM shown in Figure-2a and 2b. Figure-2a shows that dolomite particles look like heterogeneous lumps form that's colonized and in irregular particle size. Figure 2b shows that particle MgO are colonized so it is difficult to determine the size of its particle. The shapes of the particles resemble cubic. The surface area of dolomite and the catalyst dolomite (CaO.MgO) are analyzed by using BET and their obtained data are shown in Table-3.

Table-2: The Results of XRF Analysis on post calcined dolomite mineral

Temperature Calcination (^{o}C)	Compounds of Calcination Result (%)					
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	LOI
700	58,10	10,65	3,25	0,85	0,72	26,43
800	59,02	26,67	3,05	0,81	0,70	9,75
900	60,46	32,78	3,46	0,98	0,74	1,58
1000	56,17	9,35	3,15	0,81	0,73	29,79

The catalytic activity of catalyst CaO.MgO is tested in the trans-esterification reaction to form methyl ester[15-16]. The optimum condition of the reaction can be reached on temperature $60^{o}C$ for 60 minutes reaction[17-18]. Catalyst concentration of 15% b/v to oil can produce biodiesel up to 78.09%.

GC-MS analysis is conducted to determine quantitatively the compound produced as a result of trans-esterification reaction. The result product is fatty acid methyl ester contained in palm oil. Methyl esters produced are methyl laurate, methyl 9, 15-oktadecadienoat, 14-methyl pentadecanoat, methyl linoleat, methyl oleat, methyl stearat, and methyl 7, 10 hexadecanoat[19-20]. GC-MS analysis of the trans-esterification reaction product is shown in Table-4.

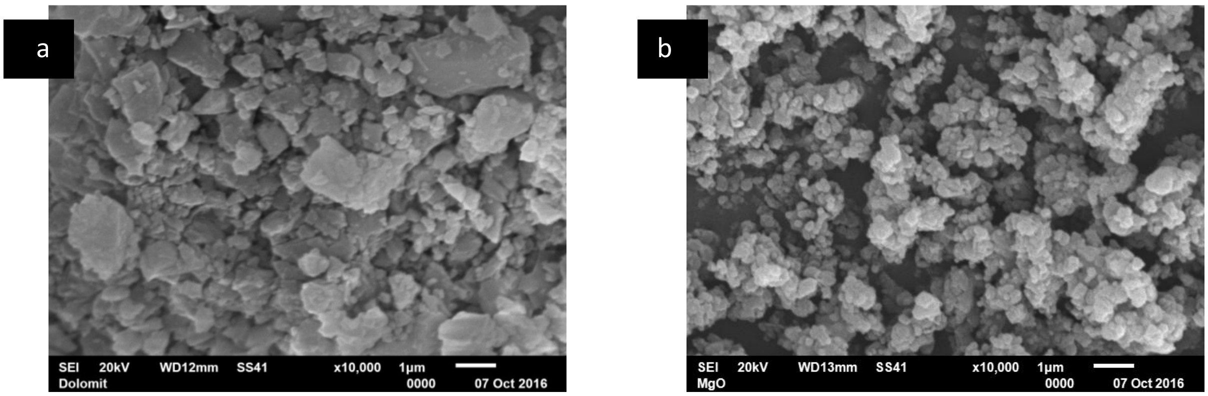

Fig.-2 (a) SEM photograph of dolomite in Kamang after calcinations and (b) before calcinations

Table-3: The surface area of dolomite and catalyst CaO.MgO

Name of Material	Surface Area
Dolomite	0,954 m^2/g
CaO.MgO	6,872 m^2/g

Table-4: GC-MS analysis of Biodiesel compound

Peak	Retention Time	Surface Area (%)	Methyl Ester
1	12.557	0.08	Methyl laurate
2	14.865	0.07	Methyl 9,15-oktadecadienoat
3	17.705	4.10	14-Methyl pentadecanoat
4	19.346	2.81	Methyl linoleat
5	19.440	13.54	Methyl Oleat
6	19.680	1.91	Methyl stearate
7	21.447	0.37	Arachidic acid, methyl ester
8	22.032	0.04	Methyl 7,10-hexadecanoat

The characterization of physical properties of produced biodiesel consists of density test, viscosity and caloric value. Table-5 shows the result of physical properties of biodiesel produced from trans-esterification reaction between oil and methanol and MgO.CaO catalyst in dolomite and then compared to standard biodiesel (ASTM).

Table-5 shows that methyl ester produced by palm oil trans-esterification with methanol and MgO.CaO as catalyst has passed biodiesel standard value (ASTM) such as density, viscosity and caloric value.

Table-5: The result of Physical Test of Biodiesel

No.	Parameter	Result of Analyses	Standard of Biodiesel in Indonesia
1	Density, Kg/m^3	870.5	850– 890
2	Viscosity, mm^2/s	5.36	2.3 – 6
3	Caloric Value, cal/g	9291.06	-

CONCLUSION

Calcination of dolomite at optimum temperature of 900ºC produces oxide CaO.MgO. This oxide can be used as a catalyst in methyl ester (biodiesel) production. The concentration of catalyst has affected trans-esterification reaction wherein the concentration of catalyst produces 15% more methyl ester. Methyl ester (biodiesel) is yielded after 60-minute reaction under 60ºC and up to 78.09%. The values of density, viscosity, and calorie of biodiesel produced by trans-esterification reaction with catalyst dolomite (CaO.MgO) are qualified based on Standard of Biodiesel (ASTM).

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