THE UTILIZATION OF DOLOMITE AS CATALYST IN BIODIESEL PRODUCTION

Rita Olivia¹, Novesar Jamarun²*, Syukri Arif² and Yenny Aydiyon Sirin³

¹Vocational High School of Industry Technology, Padang Indonesia.
²Department of Chemistry, Andalas University, Padang, Indonesia.
³Vocational High School of Chemistry Analyst, Padang, Indonesia.

*E-mail: novesar62@yahoo.com

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°C). 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°C. 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 environment¹. 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 catalyst²⁻⁷. 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 reused⁸⁻¹⁰. One of heterogeneous catalysts that can be used is dolomite. Dolomite is a natural mineral containing compounds namely Ca,Mg(CO₃)₂ and several other compounds in small quantities¹¹. The use of dolomite as a catalyst in various processes has gained wide attention because it’s cheap and environmentally friendly¹².

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.
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 calcined 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.

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. 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 CaCO₃.MgCO₃ 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, 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(CO₃)₂. Sharp peaks appear on 20 30.934° and on 41.108° which is the peak of dolomite with Rhombohedral crystal system. Next, 29.412° is the peak of calcite (CaCO₃) that’s in accordance with the peak calcite standard of ICDD 01-078-4614². 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 CO₂ derived from carbonate compound contained in the mineral. From XRF results, CaO and MgO have greater percentage than other oxides and they can reach optimum temperature of calcination up to 900°C.
Calcination product at the optimum temperature (900°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° and 62.253°. 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° which is the peak of CaO based on standard of ICDD 01-070-5490.

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

<table>
<thead>
<tr>
<th>Temperature Calculation (°C)</th>
<th>Compounds of Calcination Result (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
</tr>
<tr>
<td>700</td>
<td>58.10</td>
</tr>
<tr>
<td>800</td>
<td>59.02</td>
</tr>
<tr>
<td>900</td>
<td>60.46</td>
</tr>
<tr>
<td>1000</td>
<td>56.17</td>
</tr>
</tbody>
</table>

The catalytic activity of catalyst CaO.MgO is tested in the trans-esterification reaction to form methyl ester. The optimum condition of the reaction can be reached on temperature 60°C for 60 minutes reaction. 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 transesterification 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 transesterification reaction product is shown in Table-4.

![SEM photograph of dolomite](image)

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

<table>
<thead>
<tr>
<th>Name of Material</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>0.954 m(^2)/g</td>
</tr>
<tr>
<td>CaO.MgO</td>
<td>6.872 m(^2)/g</td>
</tr>
</tbody>
</table>

**Table-4: GC-MS analysis of Biodiesel compound**

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

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 transesterification 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**

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameter</th>
<th>Result of Analyses</th>
<th>Standard of Biodiesel in Indonesia</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density, Kg/m(^3)</td>
<td>870.5</td>
<td>850–890</td>
</tr>
<tr>
<td>2</td>
<td>Viscosity, mm(^2)/s</td>
<td>5.36</td>
<td>2.3 – 6</td>
</tr>
<tr>
<td>3</td>
<td>Caloric Value, cal/g</td>
<td>9291.06</td>
<td>-</td>
</tr>
</tbody>
</table>
CONCLUSION
Calcination of dolomite at optimum temperature of 900°C produces oxide CaO.MgO. This oxide can be used as a catalyst in methyl ester (biodiesel) production. The concentration of catalyst has affected transesterification reaction wherein the concentration of catalyst produces 15% more methyl ester. Methyl ester (biodiesel) is yielded after 60-minute reaction under 60°C 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).

ACKNOWLEDGMENT
The authors are grateful to Faculty of Mathematics and Natural Science, Andalas University (UA) and Ministry of Research, Technology, and Higher Education for the financial support by Hibah Kompetensi Research Grant No.11/UN.16/Kompetensi/LPPM/2016.

REFERENCES

[RJC-1555/2017]