Optimization of Synthesis of Biodiesel from *Jatropha curcas* L. with Heterogeneous Catalyst of CaO and MgO by Trans-esterification Reaction Using Microwave

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Abstract. The purpose of this study was to find the optimum conditions in synthesis of Biodiesel from *Jatropha Curcas* with heterogeneous catalyst of CaO and MgO by transesterification reaction using microwave. The research was conducted in five stages, that is determining acid number of *Jatropha* oil; esterification process; preparation of CaO and MgO catalysts; synthesis of biodiesel via transesterification reaction in various catalyst concentration and various times; identification and characterization of biodiesel involves the synthesis, testing TLC, GC-MS analysis, the index test bias, the density test, test the viscosity and acid number test. The results showed that optimum conditions the synthesis of biodiesel from *Jatropha* oil through transesterification reaction using microwaves produce yield 92.39% ± 0.04, with a catalyst concentration of 7.5% CaO-MgO. Furthermore, identification of compounds contained in biodiesel using GC-MS showed that biodiesel contains palmitoleic methyl compound (2.40%), methyl palmitate (21.20%), methyl oleate (62.40%), and methyl stearate (14.00%). We found also that the refractive index of the biodiesel is 1.465, the density of 0.888 g/mL, viscosity 4.23 cSt, and acid number is 0.58 mg KOH/g.

Keywords: Biodiesel, *Jatropha curcas*, heterogen catalyst, microwave.

1. Introduction
Petroleum fuels are one of the most important sources of energy for human life. Fuel needs continue to increase, along with the development of industry in various fields. Sustainable petroleum exploration (nonrenewable resources) on an ongoing basis will lead to an energy crisis in the world. Utilization of renewable alternative fuels has great importance for the sustainability of a nation [1,2]. The superiority of renewable energy is that it can be produced in quick time, availability (a lot or renewable source), does not produce harmful, cheap and easy to get emissions.

Alternative fuels, one of which is biodiesel that can be made from raw materials of palm oil, non-edible *Jatropha* and used as fuel for diesel engines [3,4]. Vegetable oils are triglycerides and can be used as raw materials for biodiesel, such as *nyamplung* seed oil, palm oil, and castor oil fence. The use of palm oil as a raw material for biodiesel production collides with the needs of community food production. The selection of biodiesel feedstock is very important to prevent competition between food needs and production needs. Indonesian people recognize *Jatropha curcas* as a bush fence plant that has not been fully utilized, whereas *Jatropha curcas* L. is one of the oil producing plants that can...
be used as raw material for biodiesel production. *Jatropha curcas* has developed as a raw material in the manufacture of biodiesel [4], [5] by pressing oil from *Jatropha* seeds.

Biodiesel from vegetable oils is made by converting triglycerides to fatty acid alkyl esters by utilizing the catalyst through a transesterification reaction [1,2]. Transesterification reaction is generally done conventionally, so it requires a long reaction time. The biodiesel synthesis time of *Jatropha* oil [1] was 2 hours, using a heterogeneous CaO catalyst of 1.5%. The catalyst was activated by immersing the CaO in an ammonium carbonate solution then dried in an oven at 1100 °C and calcined at 9000 °C for 1.5 hours. Comparison of oil mol: methanol used is 1:12. The castor oil converted to biodiesel was refluxed at 700 °C and a yield of 95% was obtained. The conventional method of biodiesel synthesis of rapeseed oil [6] takes 3.5 hours at 64.50 °C, and the ratio of mole oil to methanol is 1:18. The catalyst used was CaO and MgO by 10%. CaO and MgO catalysts were each calcined at 7000 °C for 2 hours then mixed and stirred. The yield of biodiesel produced is 92%.

Long reaction time on conventional methods can be overcome by utilizing microwaves, so the reaction time goes faster. Utilization of microwaves in the synthesis of biodiesel from fish oil ever done [6]. The ratio of oil and methanol ratio is 1:18, the catalyst used is NaOH, the optimum reaction time required is 10 minutes and yields the yield of 84.5% biodiesel. Synthesis of biodiesel using microwave has also been done [6,7]. The raw material used is kapok seed oil, reaction time required is 5 minutes. The catalyst used is KOH with ratio of oil and methanol that is 1: 7, and yield of biodiesel produced is 98.52%.

In this study used *Jatropha* oil as the raw material of biodiesel production because *Jatropha* oil does not compete with the food needs of the community. The transesterification reaction of *Jatropha* oil and methanol is supported by heterogeneous catalysts of CaO and MgO and microwaves. The purpose of this research is to find the optimum condition of biodiesel synthesis from *Jatropha* oil using microwave wave through transesterification reaction with time variation and CaO and MgO catalyst concentration. The synthesized biodiesel is identified and characterized as, TLC, GC-MS analysis, refractive index test, type density test, viscosity test and acid number test.

Transesterification is the reaction between triglycerides and alcohols to form a new ester and a new alcohol. Transesterification is usually referred to as an alcoholic reaction, since the ester is reacted with an alcohol with the aid of an acid or base catalyst to a new ester form and a by-product of glycerol [8]. The equation of the transesterification reaction is shown at Figure 1.

![Figure 1](image-url)

**Figure 1.** The transesterification reaction occurring between triglycereides and alcohols with the catalyst

The transesterification reaction is reversible that occurs at room temperature and runs slowly in the absence of a catalyst, so as to push the reaction to the right it can be used excess alcohol. The commonly used alcohol in the transesterification reaction is methanol because it is cheap and more reactive than the longer chain alcohol [2,9]. Transesterification requires the catalyst in its reaction, because in the absence of a catalyst, the resulting conversion is maximum but the reaction proceeds slowly. The catalyst commonly used in the transesterification reaction is an alkaline catalyst [8,10].

One type of heterogeneous catalyst that has been studied by some researchers on the manufacture of biodiesel is a group of heterogeneous alkaline base group catalysts, such as magnesium oxide [8]
and calcium oxide [9]. The use of CaO as an alkaline catalyst has many advantages, due to its high activity, low reaction conditions, long catalyst period, and low catalyst cost [1,11]. For MgO catalysts to have optimum activity, MgO catalysts need to be combined with other catalysts such as in combination with CaO catalysts as in a study conducted by Liang et al. [3], the yield of biodiesel from rapeseed oil obtained was 92%, using a CaO mixed catalyst and MgO.

The biodiesel properties are similar to those of diesel oil, so biodiesel can be used as diesel fuel. Conversion of triglycerides into methyl esters through a transesterification reaction reduces the molecular weight of triglycerides by one-third, reduces viscosity by one-eighth, and slightly increases the flash point [4,15]. The use of the Microwave oven itself works so quickly and efficiently because the electromagnetic waves penetrate the food and excite the water and fat molecules evenly (not just the surface) [7]. Waves at a frequency of 2.5 GHz is absorbed by water, fat, and sugar. When absorbed, the atoms are excited and generate heat. This process does not require a heat conduction like an ordinary oven, because that's how the process can be done very quickly.

2. Materials and Methods
This research was a laboratory experimental study that aims to obtain optimum conditions of biodiesel synthesis utilizing microwave. The alcohol used for the transesterification reaction is methanol, the catalyst used is heterogeneous CaO and MgO catalysts. The study consisted of 5 stages including determination of Jatropha oil number, esterification process, CaO and MgO catalyst preparation, optimization of biodiesel synthesis through transesterification reaction of Jatropha oil of esterification using microwaves with variation of time and concentration of CaO and MgO, identification and characterization of synthesis biodiesel includes, TLC test, GC-MS analysis, refractive index test, type density test, viscosity test and acid number test.

2.1 Determination of Jatropha Oil Number
Determination of Jatropha oil number is by weighing ± 1 gram of oil and put into Erlenmeyer. Then plus 20 mL of n-hexane and 20 mL of alcohol. Added 3 drops indicator pp then titrated with 0.1 N KOH solution until the color of the solution turns into pink.

2.2 Esterification
A total of 200 g of oil was introduced into a three-necked flask, heated to the temperature of 70 ºC, carefully added 12 g of methanol and 1.7 mL of concentrated H$_2$SO$_4$, then the mixture was refluxed for 2 hours at temperature of 69 to 71 ºC while stirring. Added 6 g of methanol and 0.8 mL of concentrated H$_2$SO$_4$, continued reflux for 1 hour at temperature of 69 to 71 ºC with stirring, cooled and then separated in separating funnel. The top layer was washed with a little water and heated with a hotplate at a temperature of 90 to 100 ºC.

2.3 Preparation of CaO and MgO Catalyst
CaO powder is calcined for 2 hours at temperature of 700 ºC with the aim of activating the active side of the catalyst. Similarly, the calcined MgO powder for 2 hours at temperature of 700 ºC for the purpose of activating the active side of the catalyst, then stored in a desiccator 24 hours. After CaO and MgO are obtained, the CaO and MgO catalysts are prepared by mixing CaO and MgO with a ratio of 1: 1.

2.4 Biodiesel Synthesis Optimization Through Transesterification Reactions Using Microwaves
A total of 25 g of esterified oil was introduced into the beaker, then carefully added CaO and MgO catalysts with appropriate concentrations (5%, 7.5% and 10%) and the mole oil ratio: methanol 1:18 was then stirred with mechanical stirrer with a speed of 200 rpm. The mixture was introduced into the microwave with time variation (5; 7.5; 10; 12.5; 15) minutes, then centrifuged for 20 minutes at a speed of 3000 rpm. The mixture is then poured into the separating funnel and left for ± 24 hours. The esters in the top layer are separated from the glycerol on the bottom layer by opening the separating
funnel valve. The top layer is then washed to remove residual catalyst, water and glycerol with warm water until neutral pH and heated at temperature of 90 to 100 °C to remove water leftover laundry.

3. Results and Discussion

3.1. Determination of Figures of Jatropha Oil

Jatropha oil which will be converted into biodiesel must be determined its acid number first. The determination of Jatropha oil is important because it can affect the amount of biodiesel product. The maximum acceptable acid number in a system using an alkaline catalyst is less than 2.5%. The transesterification reaction of a vegetable oil containing high levels of fatty acids and using an alkaline catalyst will lead to the formation of soap. Soaps will decrease the yield of biodiesel and will complicate the separation of biodiesel by glycerol [5]. The free fatty acid saving reaction is as follows:

$$R_1\text{-COOH} + \text{NaOH} \rightarrow R_1\text{-COONa} + \text{H}_2\text{O}$$

Free fatty acid sodium hydroxide fatty acid salls water

The number of Jatropha oil acids after analyzed is 14.39% ± 0.07. The acid number is still high and has not met the standard acid number less than 2.5% [2], this will cause the reaction of saponification. Jatropha oil must be lowered by acidification by esterification process. Jatropha oil must be esterified in advance for transesterification reaction to produce maximum biodiesel product. The reaction occurring in Jatropha oil which is esterified using methanol and concentrated sulfuric acid catalyst is as follows.

$$\begin{align*}
O & \quad \text{O} \\
R - \text{C} - \text{OH} & \quad \text{CH}_3 - \text{OH} \quad \overset{\text{H}^+}{\longrightarrow} \quad R - \text{C} - \text{OCH}_3 + \text{H}_2\text{O}
\end{align*}$$

The esterification result is then separated in a separating funnel. The result of esterification reaction is formed two layers as shown in Figure 2.

![Figure 2. Esterification Reaction Generate Two Layers](image)

The esterification process takes place twice because in the first esterification, the acid number is still above 2.5% so that the esterification is done again to decrease the acid number to <2.5%. The second esterification resulted in an acid number of 2.26% ± 0.

3.2. Biodiesel Synthesized from Jatropha Oil

The process of activating CaO and MgO catalysts refers to [4,6] study, ie by heating the catalyst in the furnace (calcination) at temperature of 700 °C for 2 hours. After CaO and MgO are obtained, the CaO and MgO catalysts are prepared by mixing CaO and MgO with a ratio of 1:1.

The optimum condition of biodiesel synthesis from Jatropha oil through transesterification by inhomogeneous catalyst [4,9] using microwaves based on the highest yield is shown in Figure 3.
Figure 3. The Yield of Biodiesel Product

Figure 4 shows that the yield of biodiesel increases with increasing catalyst concentration and reaction time, reaching maximum at 7.5% concentration at 10 minutes with a yield of 92.39% ± 0.04. The yield increases as the catalyst concentration increases and the duration of the reaction. This indicates that the longer the reaction time and the greater the concentration of the catalyst, it will increase the yield of biodiesel, but if the reaction has reached equilibrium then the reaction time and the magnitude of the catalyst concentration will not increase the yield of the catalyst. The results showed that at 10% CaO and MgO catalyst concentration, the yield of biodiesel began to decrease. This happens because the long reaction of biodiesel synthesis causes the biodiesel product to react with the soap produced from the transesterification reaction, so the product becomes reduced resulting in reduced biodiesel yield.

The optimum condition of biodiesel synthesis from *Jatropha* oil through transesterification reaction using microwave was at 10 minutes with CaO and MgO concentration of 7.5%. The highest yield (92.39% ± 0.04) obtained from *Jatropha* oil synthesis with CaO and MgO catalysts using microwaves has a yield value that is not much different from that of [1,4] that is 92%.

3.3. Identification of Biodiesel Components from *Jatropha* Oil

Transesterification biodiesel from *Jatropha* oil is a mixture of methyl esters which can be analyzed using GC-MS. The purpose of the analysis is to know the composition of the compounds that make up the biodiesel. The analysis is based on structural approaches, compositions and molecular weights of biodiesel or methyl esters which will produce chromatograms of typical peaks. The GC-MS biodiesel chromatogram is shown in Figure 4.

Figure 4. Chromatogram of Biodiesel from *Jatropha* oil
According to Figure 4 is shown that Methylesters or biodiesel from *Jatropha* oil contain four major constituent components. Retention time and the peak area of the chromatogram of the four main components of the biodiesel constituent of *Jatropha* oil is shown in Table 1.

### Table 1. Time Retention (tR) and of Four Major Components of Biodiesel from *Jatropha* Oil

| Peaks | Retention (minutes) | Time Area (a. u.) | Percent Area (%) |
|-------|---------------------|-------------------|-----------------|
| 4     | 18.502              | 7798897           | 2.40            |
| 5     | 18.759              | 68252263          | 21.20           |
| 9     | 20.908              | 201368020         | 62.40           |
| 10    | 21.058              | 45192916          | 14.00           |

The chromatogram peaks of mass spectrum of biodiesel at retention time of 18.502 minutes is shown in Figure 5.

![Figure 5. Peaks of Chromatogram of Biodiesel from *Jatropha* oil at tR of 18.759 Minutes.](image)

The mass spectrum obtained is then compared to the mass spectrum found in the WILEY7.LIB library and searched for peaks of relatively equal position. Based on the observation, the peaks are positioned relatively similar to those contained in the library WILEY7.LIB entry number 178119, it is suspected that the compound is methyl palmitoleate. The possibility of the methyl ester compound is methyl palmitoleate, it is reinforced by a possible fragmentation pattern, particularly the major peaks with m/z of 41, 55, 97, 123, 152, and 236.

Peak with m/z 55 are thought to be obtained from the peak with m/z 268 with carbon-carbon and hydrogen bond (I) termination bonds as follows:
Based on the analysis of peak fragmentation pattern of biodiesel chromatogram with retention time of 18.502 min with m/z of 41, 55, 97, 123, 152, and 236, it can be concluded that the compound is methyl palmitoleate with C\textsubscript{17}H\textsubscript{32}O\textsubscript{2} molecular formula and structure formula as follows:

\[
\text{CH}_3\text{(CH}_2\text{)}_7\text{CH}==\text{CH}\text{(CH}_2\text{)}_4\text{CH}_2\text{C}=\text{O} \quad \text{Methyl palmitoleate}
\]

Based on the analysis result of biodiesel character from synthesis of \textit{Jatropha} oil, it can be concluded that biodiesel from synthesis has potential as fuel because its character fulfill the standard range of biodiesel quality according to National Standard of Indonesia (SNI). The synthesis biodiesel character of \textit{Jatropha} oil and biodiesel SNI are listed in Table 2. Biodiesel Character Result of Synthesis from \textit{Jatropha} Oil and Biodiesel (SNI)

| Parameter                             | Biodiesel from \textit{Jatropha} Oil | Biodiesel according to SNI |
|---------------------------------------|--------------------------------------|-----------------------------|
| Refractive index                      | 1.46445                              | Max 1.45                    |
| Density (g/mL)                        | 0.888                                | 0.850 – 0.890               |
| Viscosity (cSt)                       | 4.23                                 | 2.30 – 6.00                 |
| Acid number (mg KOH/g biodiesel)      | 0.58                                 | Max 0.80                    |

Biodiesel synthesized from \textit{Jatropha} oil has character similar to the character of biodiesel which has been done by Shah \textit{et al.} [12]. The values of the density, viscosity, and acid number of the previous research are 0.88 g/mL, 3.89 cSt, and 0.48 mg KOH/g biodiesel respectively.

4. Conclusion
The optimum condition of biodiesel synthesis from \textit{Jatropha} oil using microwaves was using catalyst of CaO and MgO with concentration of 7.5% during reaction time of 10 minutes. The yield of biodiesel produced was 92.39\% ± 0.04. The synthesized biodiesel from \textit{Jatropha} oil was prepared using CaO and MgO catalysts assisted by microwaves yielded a methyl palmitoleate of 2.40\%, methylpalmitate of 21.20\%, methyloleate of 62.40\%, and methylstearate of 14.00\%. The properties of synthesized methyl ester possess refractive index of 1.465, density of 0.888 g/mL, viscosity of 4.23 cSt, and acid number of 0.58 mg KOH/g in accordance with national standards of Indonesian biodiesel.

References
[1] Hawash S, El Diwani G, Abdel Kader E. Optimization of biodiesel production from \textit{Jatropha} oil by heterogeneous base catalysed transesterification. International Journal of Engineering Science and Technology 2011;3:5242–5251.
[2] Leung DY, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. Applied Energy 2010;87:1083–1095.
[3] Yan S, Lu H, Liang B. Supported CaO Catalysts Used in the Transesterification of Rapeseed Oil for the Purpose of Biodiesel Production. Energy & Fuels 2008;22:646–51. doi:10.1021/ef070105o.
[4] Hwei Voon Lee, Joon Ching Juan, Nurul Fitriyah Binti Abdullah, Rabiah Nizah MF and Yun Hin Taufiq-Yap. Heterogeneous base catalysts for edible palm and non-edible \textit{Jatropha}-based biodiesel production n.d.
[5] Munishwar N Gupta and Smita Raghava,. Relevance of Chemistry to white technology,
Chemistry Central Journal 2007 1:17 n.d.
[6] Quitain, Armando T. Katoh, Shunsaku, Goto, Motonobu. Microwave-assisted synthesis of biofuels. In: Biofuel Production-Recent Developments and Prospects. InTech, 2011.
[7] Sameh M Osman, Mohamed H El-Newehy, Salem S Al-Deyab and Ayman El-Faham. Microwave synthesis and thermal properties of polyacrylate derivatives containing itaconic anhydride moieties, Chemistry Central Journal 120126:85 n.d.
[8] Betiku E, Adepoju TF. Methanlysis optimization of sesame (Sesamum indicum) oil to biodiesel and fuel quality characterization. International Journal of Energy and Environmental Engineering 2013;4:9.
[9] Inkollu Sreedhar and Yandapalli Kirti Kishan,. Process standardization and kinetics of ethanol driven biodiesel production by transesterification of rice bran oil, International Journal of Industrial Chemistry 2016 7:74 n.d.
[10] Cantrell DG, Gillie LJ, Lee AF, Wilson K. Structure-reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis. Applied Catalysis A: General 2005;287:183–190.
[11] Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S, Hidaka J. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. Fuel 2008;87:2798–2806.
[12] Shah, Shweta, Sharma. Shweta. Gupta, M. N. Biodiesel preparation by lipase-catalyzed transesterification of Jatropha oil. Energy & Fuels, 2004, 18.1: 154-159.