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# Biodiesel Production From the Microalgae N*annochloropsis* by Microwave Using CaO and MgO Catalysts

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**ABSTRACT:** The needs of world petroleum are increased; in contrast, the fuel productions are getting decreased. Therefore, it has lead to the search for bio-fuel as an alternative energy. There are several different types of biofuel, such as biodiesel, ethanol, bioalcohol, and biogas. Biodiesel is typically made by chemically reacting lipids from a vegetable oil or animal fat with an alcohol producing fatty acid esters, such as methyl or ethyl ester. The present study aimed to study the effect of temperature (50, 60 and 65°C), reaction time (1 to 5 minutes) dan types of catalyst (CaO dan MgO of 1 and 3 %) in the production of biodiesel from microalgae by the transesterification process using microwave methods. It also studied the characteristics of biodiesel which had the greatest yield in the present study, i.e. flash point, cetane number, density, viscosity, and FAME. The greatest yield was 99.35% and obtained with combination of 3% MgO catalyst quantity at temperature of 60°C, in 3 minutes reaction time. At this process conditions, the biodiesel has a flash point of 122°C, cetane number of 55, density of 0.89, viscosity of 5 cP and FAME of 75.12 %.

**Keywords***:* biodiesel, microalgal oil, microwave, transesterification

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## 1. Introduction

Indonesia is a rich natural-resource country, includes renewable and non-renewable resources. Petroleum is one of the non-renewable resources and the world needs a lot of petroleum. According to Abbas and Purwanti (2011) and Sudrajat *et al*. (2005), in year 2000 Indonesia required 1,150,000 barrels/day and 1,300,000 barrels/day of petroleum. The need of petroleum in Indonesia has increased by 13.04 % annually. Highly need of petroleum has to be balanced with awareness of its production which is getting less and less. Petroleum takes thousands of years to form naturally and cannot be replaced as fast as it is being consumed.

To achieve the need of petroleum that will always increase; it has to search an alternative energy. Much attention has been paid to biofuel production from vegetable oils, such as algal oils. Algae are very good source of biodiesel. In the same area, the yield of oil from algae is over 200 times the yield from other vegetable oils, such as palm oil, physic-nut oil, soybean oil, *etc*.

The extraction of algal oils is very simple. Most research on oil extraction are focused on microalgae to produce biodiesel from algal oil. According to Demirbas (2011), Chisti (2007), Hu, *et al.* (2008), microalgae are organism in 4-500 µm-diameter which have high-photosynthetic efficiency. Microalgae have several advantages compared to macroalgae; such as microalgae produce more oils and grow faster than macroalgae.

Microalgae have good-ability to adapt, so they can compete an entire growing cycle every few days. The growing condition influences the metabolism of

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adaptation and the production of algal oils. In normal conditions, algal oil contains 5-20% of dry biomass and increases up to 20-50% of dry biomass in unsuitable conditions (Hu *et al*. 2008). Several factors influence the production of algal oils, such as intensity of light, temperature, salinity, pH and conditions of cultivation growth. Microalgae cells contain protein, carbohydrate, fatty acids and nucleic acid, which their compositions differ depending on the algae strains. Oil contents of some microalgae is presented in Table 1 (Demirbas 2011).

**Table 1**
Oil content of several microalgae

| Species | Oil content, % dry weight |
|---|---|
| *Botryococcus braunii* | 25-75 |
| *Chlorella sp.** | 28 32 |
| *Crypthecodinium cohnii* | 20 |
| *Cylindrotheca sp.* | 16-37 |
| *Dunaliella primolecta* | 23 |
| *Isochrysis sp.* | 25-33 |
| *Monallanthus salina* | >20 |
| *Nannochloris sp.* | 20-35 |
| *Nannochloropsis sp* | 31-68 |
| *Neochloris oleoabundans* | 35-54 |
| *Nitzschia sp.* | 45-47 |
| *Phaeodactylum tricornutum* | 20-30 |
| *Schizochytrium sp.* | 50-77 |
| *Spirulina platensis** | 4-9 |
| *Spirulina maxima** | 6-7 |
| *Tetraselmis sueica* | 15-23 |

Table 1 shows that several algae contain more than 40% fatty acids, which can be extracted and reacted into biodiesel. The oil contents of algae are similar to the oil contents of other vegetable oils, such as palm oil, physic-nut oil, soybean oil, *etc*., which are usually used as biodiesel source. In common, biodiesels are produced from triglyceride of vegetable and algal oils (Demirbas 2011, Koberg *et al.* 2010, Miao and Wu 2006).

The biodiesel production from vegetable oils is poor in a low-temperature. The polyunsaturated of microalgae oils has lower freezing point than the monosaturated of other vegetable oils (Chisti 2007, Hu *et al.* 2008, Knothe *et al*. 2005, Xiao *et al*. 2010). High levels of polyunsaturated in algae biodiesel are suitable for cold weather climates.

Biodiesel is an alternative fuel from vegetable oils, animal fats, or algal oils, to substitute petro-diesel. Biodiesel has similar combustion characteristics to petro-diesel Biodiesel has been suggested as a very good candidate for fossil-fuels in transportation (Chew and Bhatia 2008, Dizge *et al*. 2009).

In the present study, the productions of biodiesel from microalgal oils were carried out using transesterification process in liquid phase and base-catalyst, such as KOH, NaOH and combination of both types of base. Biodiesel produced were then analyzed according to SNI parameter.

The aim of this study was to study the influence of temperature, types of catalyst, and the amount of catalyst, on the yield and characteristics of biodiesel products.

## 2. Methods

This study was carried out into four-stages; such as: (1) extraction of microalgae *Nannochloropsis* to produce microalgal oil using n-hexsana as solvent; (2) analysis of microalgae as raw materials, such as density, viscosity, and free fatty acids (FFA); (3) transesterification in microwave oven, using methanol as reactan methanol and CaO and MgO as catalyst; (4) calculation of biodiesel yield. Biodiesel product which had the greatest yield, was then analyzed using *American Society for Testing and Materials (ASTM) and* Standar Nasional Indonesia (SNI) for biodiesel (SNI 04-7182-2006), i.e., viscosity, density cetana number, flash point, dan Fatty Acid Methyl Ester (FAME).

### *2.1 Catalyst*

Catalyst were used : CaO dan MgO for 1 dan 3 % of dry white microalgal oils.

### *2.2 Extraction Conditions*

Extraction of dry microalgae *Nannochloropsis* was firstly done to produce microalgal oil. Experiments were carried out using n-hexane as solvent at the ratio of dried microalgal to n-hexane solvents of 1 : 4 (w:v), temperature of 65°C dan time of 5 hours. The extracted lipids was separated from the solvent by rotavapor distillations to purify the microalgal oils.

### *2.3 Free Fatty Acids (FFA) Analysis*

Ten grams of dried microalga was mixed with 25mL neutral-alcohol and heated in waterbath (100°C). After reaching the room temperature, the extracted liquid were then given phenolphtalein indicator for FFA titration .

### *2.4 Transesterifications Process*

Transesterification process was carried by adding CaO and MgO catalyst. The ratio of methanol and microalgal oils were 6:1 and the catalyst was 1 to 3% of microalgal oil. Microalgal 50mL was mixed with methanol, heated at 50, 60 dan 65°C for 30 seconds, and then stirred for 1 to 5 minutes. After reaction completed, the biodiesel was separated from microalgal oils and the greatest yield of biodiesel was further analyzed.

## 3 Results and Discussion

### *3.1 Microalgae Oils*

Table 2 presents the characteristics of *Nannochloropsis* microalgal oil for biodiesel production.

**Table 2**
Characteristics of Microalgal Oil

| Characteristics | Units | Amount |
|---|---|---|
| Yield | % | 31.7 |
| Density | g/cm$^3$ | 0.9278 |
| Kinematics Viscosity | cP (at25°C) | 5 |
| Free Fatty Acids (FFA) | (%) | 0.76 |

Table 2 shows that microalgal oil had met the characteristics of biodiesel raw material, which has low free fatty acid content (less than 2%). Sudradjat *et al*. (2005) mentioned that the free fatty acid content in raw material of biodiesel must not exceed than 2%.

Other fatty acids in microalgal oil were also analyzed using gas chromatography. It was measured that the algal oil contains 77,16% of fatty acids, details are shown in Table 3.

**Table 3**
Composition of Fatty Acids in Microalgal Oil

| Fatty Acids | Compound | Weight % |
|---|---|---|
| Miristic Acid | C14:0 | 0.25 |
| PalmiticAcid | C16:0 | 35.12 |
| Palmitolenoic | C16:1 | 6.76 |
| Oleic Acid | C18:1 | 3.17 |
| Linoleic Acid | C18:2 | 15.41 |
| $\gamma$ -linoleic Acid | C18:3 | 16.22 |
| Eicosadienoic Acid | C20:2 | 0.23 |

*3.2 Characterization of Catalyst*

CaO and MgO catalyst were activated by heating at 550°C for 5 hours. Characterization of both catalysts were analyzed by XRD, SEM and EDX at the Laboratory of Energy, Institut Teknologi Sepuluh Nopember Surabaya. SEM and XRD results of CaO and MgO are presented in Figure 1 to Figure 4. Figure 1 and 2 show the micrographs of selected MgO and CaO. From the micrographs, the difference in porosity of particle can be seen obviously. The particle size of CaO is wider than MgO and the pores decreas apparently. Typical x-ray diffraction pattern of MgO and CaO are shown in Figure 3 and 4. Several peaks are less occurred in the x-ray diffraction patterns of MgO, compared to CaO. The highest intensity of MgO and CaO are found at 2θ of 42.94$^o$C and 34.38$^o$C.

*The Infuence of Temperature Reaction on the Yield of Biodiesel Product*

This present study investigated the influence of temperature transesterification reaction on the yield of biodiesel product. Experiments were carried out at 50, 60 and 65°C. Theoritically, temperature is an important parameter in transesterification process. Increasing temperature causes in increasing the reaction rate; therefore, the conversion achieved is higher and the reaction time required is short. Transesterification is a reversible-endothermic reaction. As temperature is increases the yield of product is also increased (Xiao *et al.* 2010).

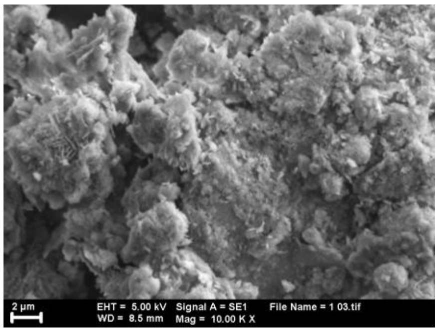

**Fig. 1** SEM of MgO

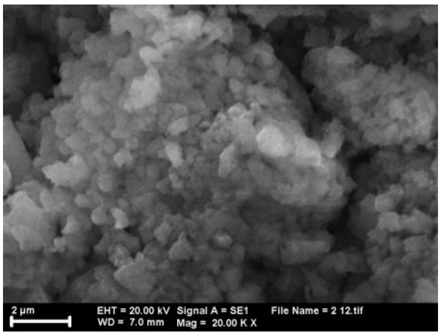

**Fig. 2** SEM of CaO

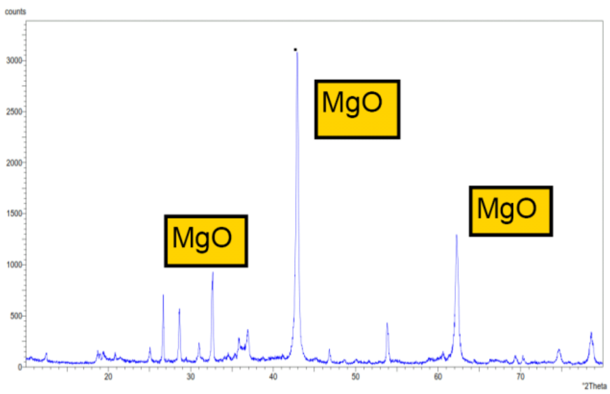

**Fig. 3** XRD of MgO

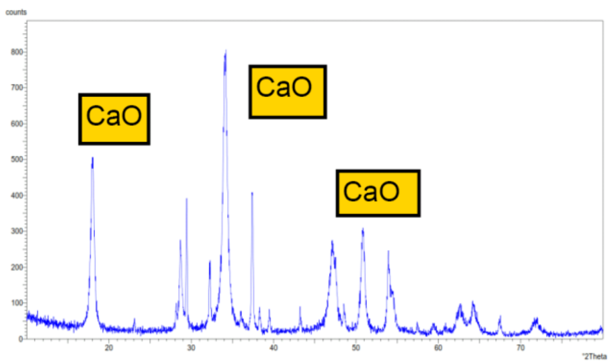

**Fig. 4** EDX results gave the composition of MgO and CaO were 70.62% and 79.07 % respectively.

At a constant reaction time, the yield of biodiesel increases as the temperature increases. The temperature used has to be below the alcohol boiling points. Increasing temperature results more frequent of interaction among particles, means that the reactan is faster to achieve the balance reaction.

Figure 5 and 6 shows the yield of biodiesel product under different temperature and catalyst type. The yield of biodiesel increased by 5% to 9% when the transesterification was carried out from 50 to 60°C, but it decreased when the temperature increased from 60 to 65°C. Temperature of 60°C gave the highest yield of 96.46 % when using CaO 3% (w) and 99.35 % (w) when using MgO 3% catalysts.

*3.3 The Infuence of Catalyst Types on the Yield of Biodiesel Product*

The yield of biodiesel was affected by the type of catalyst during transesterification process. Properties and characteristics of different type of catalyst affect the reaction process and the yield of biodiesel, as presented in Figure 5 and 6.

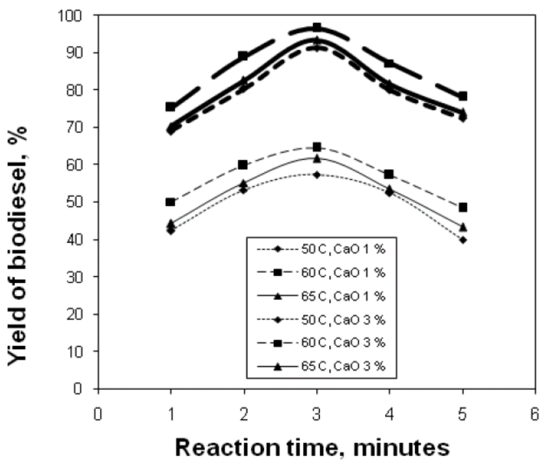


**Fig. 5** The influence of reaction time, temperature using CaO catalyst on the yield production.

At a constant temperature of 60°C, the highest yield of biodiesel product was 99.35 % (w) when using MgO 3% catalysts and 96.46 % when using CaO 3% (w). MgO catalyst gave more influence on the biodiesel yield, compared to CaO catalyst. SEM analysis shows that the morphology of MgO is more porous than CaO and the surface area of MgO (157.4 $m^2/g$) is greater than CaO (90 $m^2/g$) (Tran *et al.* 2010).

*3.4 The Infuence of Catalyst Amount to the Yield of Biodiesel Production*

From Figure 5 and 6, it is showed that the higher amount of catalyst used (3%), gave higher biodiesel yield, compared to a small amount of catalyst used (1%), both using MgO and CaO catalysts. By employing bigger amount of catalyst, microalgal oil and methanol are more frequent contacted each other, so the yield of biodiesel reaction is higher

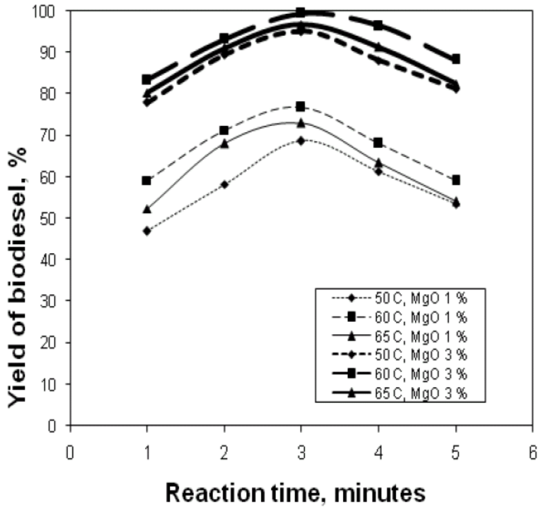


**Fig. 6** The influence of reaction time, temperature using MgO catalyst on the yield production

*3.5 The Infuence of Reaction Time on the Yield of Biodiesel Product*

Figure 5 and 6 shows that the reaction time affected the yield of biodiesel product. As the time of reaction increased from 1 to 3 minutes, the yield of biodiesel also increased, since longer contact time between microalgal oil and methanol results more biodiesel produced. While increasing time from 3 to 5 minutes, resulted a decreasing in biodiesel yield, since the reactant had been reacted into product.

*3.6 Characterization of Biodiesel*

The highest yield biodiesel or methyl ester product (99.35%) was achieved by using 3% MgO catalyst at temperature reaction of 60°C for 3 minutes in reaction time. The biodiesel product in the optimum conditions was then analyzed to meet the SNI criteria (SNI 04-7182-2006) for biodiesel (Abbas dan Purwanti 2011), such as density, viscosity, flash point, cetane number, and FAME content.

*3.6.1 Density*

The density of biodiesel was measured to meet the SNI standard. The viscosity of current biodiesel was 0.89 $g/cm^3$ (890 $kg/m^3$), which is in the range of 850-890 $kg/m^3$ as mentioned in SNI standard.

*3.6.2 Viscosity*

The viscosity of biodiesel was also analyzed to compare the biodiesel product to the SNI standard. The viscosity influences the flow profilem atomization, and the effectivity of lubricant. Biodiesel product had a viscosity of 5.0 $mm^2/s$ (at 30˚C), which is in the range of 2.3-6.0 $mm^2/s$ as in SNI criteria.

*3.6.3 Cetane Number*

Cetane number is one of fuel properties to indicate the spontanity of fuel imidiately after injected in the ignition room (Knothe *et al.* 2005). The cetane number of current biodiesel study was 55, which is above the SNI standard (minimum of 51).

*3.6.4 Fatty Acid Methyl Ester (FAME)*

FAME was analyzed by gas chromatography. It indicates the percentage of fatty acid which is converted into methyl ester. Results in Table 4 showed that total FAME of 75.12% in microalgal oil.

**Table 4**
FAME Contents of Biodiesel (at optimum conditions)

| FAME contents | % Weight |
|---|---|
| Methyl Palmetic (C 16:0) | 35.31 |
| Methyl Palmitoolenoic(C 16:1) | 6.37 |
| Methyl Olenoic (C 18:1) | 2.94 |
| Methyl Linolenoic (C 18:2) | 14.52 |
| Methyl $\gamma$ -linolenoic (C 18:3) | 15.98 |
| **Total** | **75.12** |

*3.6.5 Flash Point*

Flash point of biodiesel is needed to know the ignition point when it is used as fuels. High flash point make the fuel is easier during storage at room temperature (Abbas and Purwanti 2011).

**Table 5**
Characteristics of biodiesel from microalgal oil compared to SNI standard for biodiesel (SNI 04-7182-2006)

| No. | Characteristics of Biodiesel | Current work | SNI |
|---|---|---|---|
| 1 | Flash Point | 122 °C | Min 100°C |
| 2 | Viscosity | 5.0 $mm^2/s$ | 2.3 – 6,0 $mm^2/s$ |
| 3 | Density | 890 $kg/m^3$ | 850 – 890 $kg/m^3$ |
| 4 | Cetane number | 55 | Min 51 |

The flash point of biodiesel on the present study gave flash point of 122˚C, which is above the minimal standard of biodiesel flash point given by SNI (100˚C). Details of biodiesel characteristics compared to SNI standards are given in Table 5.

## 4 Conclusion

In summary, the current study reports on the influence of temperature reaction on the yield of biodiesel product, by transesterification process using microwave oven. The yield of biodiesel increasedwhen the temperature increased from 50 to 60°C and decreased when the temperature increases from 60 to 65°C. MgO catalyst gave higher biodiesel yield than CaO catalyst. The greater amount of catalyst (3%) resulted in higher biodiesel yield (1%). The reaction time also affected the biodiesel yield. In between 1 and 3 minutes, the yield increased; in between 3 and 5 minutes, the yield decreased. The optimum conditions were achieved by using 3% MgO catalyst at temperature of 60°C for 3 minutes reaction, gave the biodiesel yield of 99.35%. Characteristics of biodiesel from microalgal oils has achieved the criteria given by SNI standard for biodiesel (SNI 04-7182-2006).

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