

## Biodiesel synthesis optimization from wet and dry based microalgae *Chlorella vulgaris* by reaction time arrangement

Dianursanti<sup>1</sup>, D N Putri<sup>1</sup>, P Religia<sup>1</sup> and P Anggraini<sup>1</sup>

<sup>1</sup> Chemical Engineering Department, Universitas Indonesia, Kampus Baru UI Depok 16424, Depok, Indonesia

E-mail: dianursanti@yahoo.com

**Abstract.** Microalgae have the potential to be used as the raw material for biodiesel synthesis. One of promising microalgae species to be used is *Chlorella vulgaris*. However, in the process of biodiesel synthesis from microalgae needs to be optimized. In this study, optimization of biodiesel synthesis from wet and dry based microalgae *Chlorella vulgaris* has been studied. Optimization done by arranges the time of transesterification reaction. Transesterification reaction has been done using KOH catalyst. The reaction time was varied at 20, 40, and 60 minutes. From the results, the highest yields of biodiesel are obtained on the 40 minutes reaction time with biodiesel yield is 75% for wet based microalgae and 62.8% for dry based microalgae. Biodiesel from dry based microalgae *Chlorella vulgaris* composed by several types of FAME, including saturated FAME such as methyl myristate (4.48%), methyl palmitate (28.3%), and methyl stearate (17.1%), and also composed by unsaturated FAME such as methyl palmitoleate (11.1%) and methyl oleate (39.1%).

### 1. Introduction

Biodiesel is biofuel composed by monoalkyl esters derived from organic oils from plants or animals through transesterification process [1]. Several feed stocks from plants commonly used to produce biodiesel such as corn, soybean, peanut, canola, rapeseed, castor, karanj (*Pongamia pinnata*), coconut, oil palm, and microalgae. However, microalgae are the highest oil producer compared with other feed stocks. Based on [2], microalgae are able to produce 58.700-136.900 L of oil per hectare area. Moreover, microalgae are also doesn't compete with food needs. Therefore, microalgae will become very potential to be used as the main raw material for biodiesel production. In addition, microalgae are fairly easy to be developed in Indonesia due to its tropical climate. One of microalgae species that exist in Indonesia is *Chlorella vulgaris*. *Chlorella vulgaris* has lipid content about 5-58 wt% [3]. Due to its lipid content, *Chlorella vulgaris* are promising to be used as raw material of biodiesel production.

In the process of biodiesel production from microalgae, initial condition of microalgae is one of the influential factors. All this time, dry based microalgae are usually used to produce biodiesel. However, drying process of microalgae takes a long time and may damage the lipid content of microalgae. Meanwhile, by using wet based microalgae, the water content that remain in the extracted lipid may cause an increase of Free Fatty Acid (FFA) values. This condition will results saponification reaction which able to inhibit transesterification process. However, wet based microalgae can be used for in-situ transesterification methods. By using in-situ transesterification, lipid extraction process can be removed.



Moreover, in conducting biodiesel synthesis from microalgae through transesterification process, there are several important factors that affect, such as reaction temperature, reaction time, type of catalyst, catalyst concentration, and mole ratio between oil and methanol. These factors mostly affect to the yield of biodiesel produced. In order to optimize biodiesel synthesis from microalgae through transesterification process, arrangement of reaction time and temperature should be done to obtain the best yield of biodiesel. Therefore, this present study will analyze the effect of initial condition of microalgae to the character and amount of biodiesel produced. The synthesis will be conducted by arrange the reaction time, in order to optimize the operating condition of transesterification process to obtain the highest yield of biodiesel.

## 2. Materials and Methods

### 2.1. Microalgae Preparation

Microalgae *Chlorella vulgaris* were cultivated in a photobioreactor at Bioprocess Engineering Laboratory, Department of Chemical Engineering, Universitas Indonesia using Walne medium. Microalgae were then separated from the medium to obtain wet base biomass of *Chlorella vulgaris*. In order to obtain dried biomass, wet biomass of *Chlorella vulgaris* was then dried by drying process to decrease the water content.

### 2.2. Lipid Extraction

1 gram of microalgae *Chlorella vulgaris* both wet and dried based was extracted each using 50 mL n-hexane solvent. The extraction was done by ultrasonication method for 60 minutes, at a temperature of 60°C. Lipid extracted was then separated and evaporated to remove solvent content and obtain crude lipid of microalgae.

### 2.3. Calculation of FFA values

Lipid extracted from microalgae was then calculated by FFA value. FFA value of the extracted lipids can be calculated using the following equation:

$$FFA = \frac{56,1 \times N_{KOH} \times V_{KOH}}{10 \times w} \times 100\% \quad (1)$$

where,

56.1 = FFA calculation constant

NKOH = Normality of KOH standardized

VKOH = volume of KOH used during titration (mL)

w = mass of the test sample (g)

### 2.4. Transesterification

Lipid from microalgae *Chlorella vulgaris* were reacted with 200 mL methanol to carry out transesterification reaction at 60°C. In this transesterification reaction, 1 gram of KOH was added as the catalyst used. Transesterification was done by varying the reaction time at 20, 40, and 60 minutes. Biodiesel produced were then purified to remove the remaining solvent and catalysts. The biodiesel yield was calculated using the following equation:

$$Y = \frac{m_B}{m_L} \times 100\% \quad (2)$$

where:

Y = yield of biodiesel (%)

mB = mass of biodiesel (g)

mL = mass of lipid extracted (g)

### 2.5. Product Analysis

Biodiesel from microalgae were analyzed its Fatty Acid Methyl Esters (FAME) content. Analysis was done by using GC-MS. This analysis will show the composition of FAME on biodiesel product from microalgae.

## 3. Results and Discussions

### 3.1. Effect of Microalgae Condition to Total Lipid Extracted

The amount of lipid extracted from different microalgae base can be seen in table 1.

**Table 1.** The Number of Lipid Extracted

Condition	Lipid (%)
Wet based microalgae	0,238
Dry based microalgae	1,57

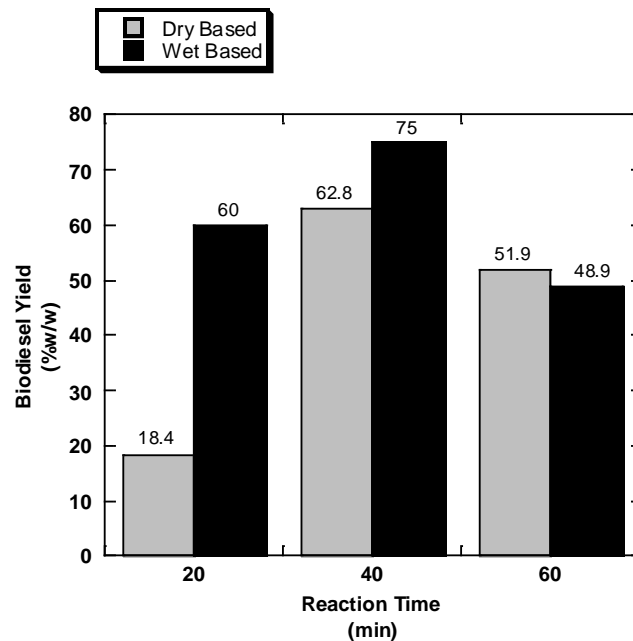
Based on Table 1, it can be seen that dry based microalgae produce more lipids. This is because on wet based microalgae, there is remained water in microalgae biomass. In the extraction process, n-hexane as a solvent is non-polar whereas water is polar. This difference, causing n-hexane is not able to contact the biomass maximally. Therefore the lipids extracted from the wet based microalgae were also not optimal. Meanwhile, on dry based microalgae, the water content in microalgae biomass has been relatively small. This condition causes the non-polar n-hexane are able to contact with microalgae biomass maximally. Therefore the lipids extracted from dry based microalgae can be optimized.

### 3.2. Effect of Time Reaction on the Number of Biodiesel Produced

In order to observe the effect of reaction time to the yield of biodiesel, temperature reaction is kept constant at 60°C. This temperature is chosen according to the transesterification of *Chlorella vulgaris* microalgae lipid by [4] that produce the highest yield of biodiesel with the amount is 36.79%.

Effect of reaction time on the number of biodiesel produced can be seen in figure 1. Based on figure 1, it is clear that the reaction time is very influential to the amount of biodiesel produced. On wet based microalgae, biodiesel yield are 60%, 75%, and 48.9% respectively for the reaction time of 20, 40, and 60 minutes. As well as for dry based microalgae, the difference of reaction time also poses a considerable difference in biodiesel produced. Yield of biodiesel obtained are 18.4%, 62.8%, and 51.9% for the reaction time of 20, 40, and 60 minutes.

Based on these results, the highest biodiesel yield obtained at 40 minutes of reaction time, both on wet and dry based microalgae. At 20 minutes, biodiesel yield is lower than at 40 minutes. This is due to the formation of biodiesel is not completed yet. The amount of reactant is more than the amount of product. Therefore, due to transesterification is reversible reaction, the equilibrium is shifted toward the formation of the product. Meanwhile, at 60 minutes, production of biodiesel decreased as compared to the 40 minutes. This is due to the amount of the product is much more than the reactant. Therefore the equilibrium shifts towards to the reactants resulting in a reduced number of products that have been formed. This result is in line with a study on *Nannochloropsis* sp. microalgae direct transesterification by [5]. Yield of biodiesel is increase when the reaction time up to 4 hours. However, the yield is decrease when the reaction time up to 6 hours. The decrease of biodiesel yield is also able to occur because the catalysts used are fewer after long time reaction [6].



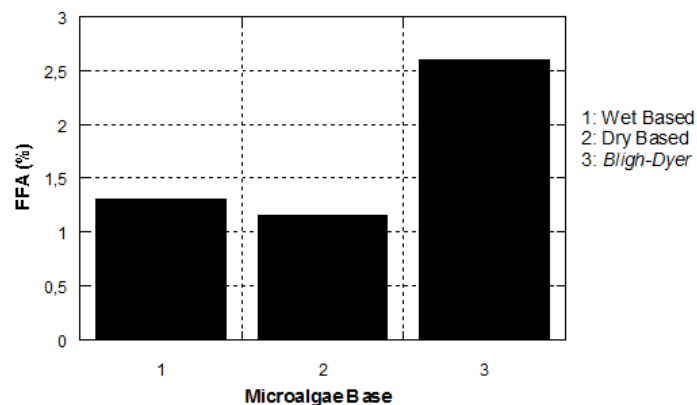
**Figure 1.** Effect of Time Reaction on the Number of Biodiesel Produced at 60°C

Based on the results, it is also known that the highest biodiesel yield is obtained from wet based microalgae. However, this is due to wet based microalgae done without any drying process. Therefore, lipid quality and quantity of microalgae are avoided from damage caused by drying using heating process. Therefore, biodiesel produced from wet based microalgae are higher than dry based microalgae.

### 3.3. Effect of FFA Value on the Number of Biodiesel Produced

Free Fatty Acid (FFA) value is a value that plays role in the selection of catalyst on biodiesel synthesis. If the FFA content less than 2.00%, alkaline catalyst can be used in the reaction. If the FFA value more than 2.00%, acid catalyst have to be used before the alkaline catalyst.

figure 2 shows the FFA value from wet base, dry base, and Bligh-Dyer method. Effect of FFA value on the number of biodiesel produced can be seen in Table 2, where the operation condition is 60°C and 40 minutes.



**Figure 2.** FFA Value (1) Wet Based, (2) Dry Based, (3) Bligh-Dyer

Based on figure 2, it appears that microalgae lipid extracted by the Bligh-Dyer method has higher FFA levels than others. FFA level is influenced by the amount of water from the source. On wet based, the water does not react on microalgae due to the solvent used was non-polar n-hexane. While the Bligh-Dyer method, the solvent used is chloroform which is slightly polar. Slightly polar nature of chloroform causing water levels of lipids from microalgae becomes larger.

**Table 2.** Effect of FFA Value on the Number of Biodiesel Produced

	FFA (%)	Biodiesel (%)
Wet Base	1.30	75.0
Dry Base	1.15	62.8
<i>Bligh-Dyer</i> Method	2.60	50.0

Based on table 2, the amount of biodiesel produced in the Bligh-Dyer method are smaller because more microalgae lipids react with the catalyst to form soap through a saponification reaction so that the effectiveness of the catalyst decreases due to only a portion of catalyst reacts with the fatty acids. On dry based microalgae, the amount of biodiesel produced is also smaller than the wet based microalgae. This is due to some content of microalgae are damaged as a result of drying process with the use of heat.

#### 3.4. Composition of Fatty Acid Methyl Ester (FAME) from Biodiesel Synthesis Process

FAME compositions of biodiesel were tested using GC-MS. The tested biodiesel were obtained from dry based microalgae lipid which was extracted using Bligh-Dyer method and reacted with methanol at 60°C and 40 minutes. FAME compositions from biodiesel can be seen in the table 3.

From the results, composition of biodiesel produced from *Chlorella vulgaris* microalgae are varied for each method with the fixed component are methyl palmitate and methyl stearate. The most dominant component in both types of FAME composition is methyl palmitate.

Fatty acids in microalgae consisting of saturated fatty acids and unsaturated fatty acids. Based on Table 3, the content of saturated FAME includes methyl myristate, methyl palmitate, and methyl stearate. For biodiesel derived from dry based microalgae, the amount of saturated FAME content was 49.9%. Meanwhile, biodiesel derived from microalgae through Bligh-Dyer extraction process has saturated FAME content of 42.0%.

**Table 3.** Composition of FAME from Dry Base and Bligh-Dyer Method

Type of FAME	FAME (%)	
	Dry Based	<i>Bligh-Dyer</i>
Methyl Myristate <sup>(Sat)</sup>	4,48	-
Methyl Palmitoleate	11,1	-
Methyl Palmitate <sup>(Sat)</sup>	28,3	30,9
Methyl 9-Octadecanoate	-	34,8
Methyl Linolenate	-	23,3
Methyl Oleate	39,1	-
Methyl Stearate <sup>(Sat)</sup>	17,1	11,0

#### 4. Conclusion

The highest yields of biodiesel are obtained on the 40 minutes reaction time with biodiesel yield is 75.0% for wet based microalgae and 62.8% for dry based microalgae. Based on the initial condition of microalgae, wet based microalgae produced higher yield of biodiesel than dry based microalgae. From the results, biodiesel from dry based microalgae *Chlorella vulgaris* composed by several types of FAME, including saturated FAME such as methyl myristate (4.48%), methyl palmitate (28.3%), and methyl stearate (17.1%), and also composed by unsaturated FAME such as methyl palmitoleate (11.1%) and methyl oleate (39.1%).

#### 5. Acknowledgement

The authors would like to thank the financial support provided by Universitas Indonesia through the Publikasi Internasional Terindeks Tugas Akhir (PITTA) 2017 funding scheme under grant no. 762/UN2.R3.1/HKP.05.00/2017 managed by the Directorate for Research and Public Services (DRPM) Universitas Indonesia.

#### 6. References

- [1] Demirbas A 2007 Importance of biodiesel as transportation fuel *Energy Policy* **35** 4661-4670
- [2] Gouveia L and Oliveira AC 2009 Microalgae as Raw Material for Biofuels Production *J. Ind. Microbiol Biotechnol.* **36**:269-274
- [3] Mata TMM, António A, Caetano, and Nidia S 2010 Microalgae for biodiesel production and other applications: A review *Renewable and Sustainable Energy Reviews* **14**(1):217-32
- [4] Dianursanti, Delaamira M, Bismo S, and Muharam Y 2017 Effect of reaction temperature on biodiesel production from *Chlorella vulgaris* using CuO/zeolite as heterogeneous catalyst *IOP Conf. Series: Earth and Environmental Science* **55** 012033
- [5] Dianursanti, Religia P, and Wijanarko A 2015 Utilization of n-Hexane as co-solvent to increase biodiesel yield on direct transesterification reaction from marine microalgae *Procedia Environmental Sciences* **23**:412-20
- [6] Ma X 2012 Biodiesel production from algae through in situ transesterification technology *University of Minnesota*