Biodiesel Production from Microalgae with Trans-esterification Method Using Microwave

L Qadariyah, F Mujaddid, D S Bhuana and M Mahfud
Department of Chemical Engineering, Sepuluh Nopember Institute of Technology Surabaya.
Email: lailatul_2008@yahoo.com

Abstract. Microalgae has a highly potential to be biodiesel fuel due to its high lipid content. The research used Nannochloropsis oculata microalgae refer to high lipid content (approximately 68%). The objectives of this research are to study edible oil extraction process from Nannochloropsis oculata, to study the effect of microwave on biodiesel yield using KOH catalyst, time reaction as well as catalyst percentage. The trans-esterification process was carried out on microwave with lipid molar-methanol comparison of 1:10, microwave power, reaction time and catalyst composition were also varied. It was found that the addition of co-solvent (addition n-hexane) seems to give the best result in terms of yield, i.e. 54.19%, which was obtained at a 600-watt microwave power, reaction time of 40 min, and 2.5% catalyst concentration. The fatty acid consists of several major constituents, such as palmitic acid 84.81%, oleic acid 12.41% stearic acid 1.87% and linoleate 0.88%. It can be concluded from the study that the in-situ trans-esterification process is such an efficient method due to the short reaction time, less energy consumption and relatively efficient owing to the combined extraction and trans-esterification steps.

1. Introduction

Biodiesel has several generations, the first generation of edible generation (food), among others, including palm oil and soybeans. The second generation is a non-edible biodiesel, among others, jatropha and nyamplung are some widely known examples. The third generation is microalgae. Harvesting of microalgae can be done daily. Microalgae are the fastest organisms in photosynthesis and contain high lipid content. This can produce up to 200 times more yields than other plants [1]. Microalgae have recently become promising candidates as alternative third generation biotechnology to produce large amount of biomass energy [2]. The triglycerides contained in the microalgae can easily be extracted and esterified to obtain biodiesel. This research uses Nannochloropsis oculata microalgae as the main ingredient. Nannochloropsis oculata contains 68% fat on dry weight. Nannochloropsis oculata has more lipid than Chlorella and Dunaliella. Chlorella has 32% fat compared to Dunaliella's 23% [3]. The conventional process of biodiesel making, the transesterification process is carried out after the extraction and purification process of the oil [4]. Therefore, it is necessary to develop biodiesel manufacturing process that is simple, efficient, energy efficient and can produce high quality biodiesel through in situ transesterification process. In situ method is one of the methods applied in the process of making biodiesel by doing direct extraction on the source of raw materials containing oil or fat. In the in situ process the raw material used is a solid material containing oil. This process is known as transesterification in situ. Microwave irradiation is one of the new technologies in extracting lipid microalgae. It has been reported that microwave is a simple and effective technology for extracting lipid microalgae. Warming up with a microwave can help speed up the extraction and simultaneously turn it into FAME. Other experiments confirmed that the addition of co-solvent is also considered as a way to increase the yield on in situ transesterification because co-solvent can increase the solubility of alcohol and speed up the in situ transesterification [5]. Therefore, the aim of this research is to produce a high yield of biodiesel from microalgae as potential resource of biodiesel using microwave as source energy by in situ transesterification method.
2. Methods

2.1. Materials
The materials used include powder of microalgae *Nannochloropsis oculata*, which was collected from BBAP Jepara. Another material such as Methanol 96%, KOH and ethyl acetate 96 % was used from MERCK products meanwhile for n-hexane 96 % was used from FULLTIME products).

2.2. Apparatus
In situ transesterification was performed in EMM2308X Electrolux microwave unit. The apparatus of biodiesel from microalgae comprised of a vacuum pump, a condenser, magnetic stirrer and reactor pyrex. The temperature is controlled using a thermocouple.

2.3. Extraction of microalgae oil using soxhlet
The experiment was carried out in round neck flask. The loaded amount of microalgae powder was 5 gram for microalgae oil extraction with methanol were 50 ml. Microalgae powder and solvent were mixed in round neck flask. The extraction process was done at the soxhlet. the reaction time of 12 hours. After the extraction was completed, the product was cooled down and separated by filter vacuum. the filtrate and residu were obtained. The residu was dissolved in the mixture of hexane and methanol to get the remaining oil. The filtrate was put into a separatory funnel and washed using 40 °C of aquadest. After that, the filtrate was distilled to separate the solvent and microalgae oil. The microalgae oil was analyzed by gas chromatography (GC).

2.4. Biodiesel Production from Microalgae *Nannochloropsis oculata* by In-Situ Microwave-Assisted Transesterification
The in-situ transesterification takes place in a round neck flask, insert a 5 gram microalgae powder and methanol is 50 ml for all experiments. Microalgae and methanol powder were mixed in a round neck flask. In situ transesterification was carried out at 300, 450, 600 watt microwave power, with reaction time of 10,20,30,40 minutes and catalyst concentration of 1%, 1.5%, 2%, and 2.5%, respectively. The reactant was then cooled to room temperature and separated with a vacuum filter so that the filtrate and the residue were formed. The residue was dissolved in a hexane and methanol mixture to obtain the remaining FAME. Ethyl acetate was added to the filtrate to form three layers. The upper layer was heated to a temperature of 77.1 °C. The crude biodiesel was then analyzed by mass-gas chromatography (GC).

3. Results and discussion

3.1. Characterization of Microalgae Oil
The experiments were performed inside a round neck flask under microwave irradiation. In-situ transesterification was carried out with and without the addition of co-solvent (n-hexane) using KOH as an alkaline catalyst. The use of KOH in this process will provide some more reactive advantages than acid catalysts. The biodiesel yield is defined as the mass of crude biodiesel divided by the mass of the microalgae oil. Based on the experiment, the yield of microalgae oil extraction was 12.934 % (based on its dry weight). The lipid composition of *Nannochloropsis oculata* is shown by Table 1. *Nannochloropsis oculata* contains 16.43% FFA and 5.7302 % triglycerides makes *Nannochloropsis oculata* potentially become biodiesel.
Table 1. Lipid composition from *Nannochloropsis oculata*

| Lipid          | Composition (%) |
|----------------|-----------------|
| Free fatty acid| 16.43           |
| monoglycerides | 2.69            |
| diglycerides   | 11.49           |
| triglycerides  | 5.73            |
| Total          | 36.34           |

3.2. The Effect of Reaction Time and Microwave Power Without Solvent and Co-Solvent

The co-solvent method gave the highest yield of 54.19% at 40 minutes on 2.5% catalyst. Figure 1 shows the effect of reaction time on biodiesel yield on various catalysts in solution without solvent and co-solvent. At 10 minutes, 20 minutes, 30 minutes, and 40 minutes, the biodiesel yield gradually increases with increasing reaction time. In this condition, the longer the reaction time the contact between the reacting substances will be greater so that the results obtained will also be greater. The use of microwaves that provide a large heat effect so that time will increase the temperature on the media and one of the high solubility factors is the increase in temperature so that the reaction time is longer. The temperature will increase so that the contact time will increase the yield of biodiesel. The results of this study are supported by previous research which states that time variables affect the resulting results [6].

![Figure 1. The effect of reaction time on yield at 600 watt without solvent (a) co-solvent (b)](image)

Figure 1 shows the effect of power on biodiesel yield at various reaction time. At power of 300, 450 and 600 watt biodiesel yield gradually increased with power. The highest yield of biodiesel were 54.19 % at

![Figure 2. The effect of power on yield at 600 watt without solvent (a) co-solvent (b)](image)
40 minutes at catalyst 2.5%. This is mainly because high temperatures can help break down cell walls and make contact between methanol and lipids more easily and produce higher yields [7].

### 3.3 The Effect of Catalyst Concentration Without Solvent and Co-Solvent

The co-solvent method gave the highest yield of 54.19% at 40 minutes on 2.5% catalyst and 600 watt. Figure 3 shows the effect of catalyst on biodiesel yield at various reaction time. The yield increases with the increase of catalyst concentration in the range 1.0 - 2.5%. The catalyst will react with methanol to form methoxide ions. This ion will react with lipids to produce methyl esters (biodiesel). The more catalysts used the greater percentage of yield product. This happens because the function of the catalyst is to decrease the activation energy. In accordance with Arrhenius law which states that the addition of catalysts can activate the reagents so that the activation energy (Ea) becomes smaller and the value of the reaction rate constant becomes greater, so as to increase the rate of reaction because the reaction rate constant is directly proportional to the reaction rate causing the formed product more abundant so that the yield percentage of the product becomes greater [8].

![Figure 3. The effect of catalyst on yield at 600 watt without solvent (a) and co-solvent (b)](image)

### 3.4. The Effect of Co-Solvent Addition to the Yield of Biodiesel Products

In in-situ transesterification, other than as a reactant, methanol also acts as a solvent in extracting oil. But methanol is not a good solvent for extraction, whereas hexane is. Thus, hexane was used as co-solvent in this study to assist the extraction process in in-situ transesterification. As can be seen on Figure 4, the transesterification process with the addition of co-solvent can increase the yield of crude biodiesel when compared to the transesterification process without co-solvent. The highest yield obtained in the transesterification process with co-solvent at 40 minutes was 54.19%. In this study, the in-situ transesterification process with the addition of 40 ml of co-solvent (hexane) produced a one-phase solution. Basically, hexane and methanol will not coalesce, however, with a considerable volume of methanol a one-phase solution is produced. As a co-solvent, hexane can increase the solubility of the oil in methanol. With the addition of co-solvent, the interfacial surface tension of the oil and methanol will decrease and the liquid will form one phase. In other words, the reaction will increase because the contact between the reactants is better. It is in the presence of this one-phase solution which causes the in situ transesterification process with the addition of co-solvent to increase the yield of crude biodiesel. In the in situ transesterification process, the ongoing reaction can occur in two possibilities. First, the process occurs simultaneously (extraction and transesterification take place at the same time) [9]. Second, the process begins with lipid extraction and is then simultaneously converted to FAME. Based on this research, it can be concluded that the in-situ transesterification process begins with lipid / oil extraction and then followed by the production of fatty acid methyl ester (FAME) from the lipid/oil. This statement is supported by the results of the research provided that transesterification with the addition of co-solvent (hexane) will increase the yield of crude biodiesel. it was supported by another research the addition of n-hexane give high oil extraction from microalgae. The addition of the co-solvent itself provides an important role in the initial process of extraction in in situ transesterification so that the resulting yield also increases [10]. The results obtained maintains that the addition of hexane as a co-solvent in in situ transesterification might increase the yield of biodiesel [5].
3.5 FAME compounds of Nannochloropsis oculata

From Table 2, the main compounds of methyl ester of biodiesel were palmitic acid, stearic acid, oleic acid and linoleic acid. The results obtained are in accordance with the GC yield of raw materials with lipid composition Nannochloropsis oculata where the dominant fatty acids in the lipid is palmitic acid of 84.8173%. This analysis fits reporting that all plants oil which is used for biodiesel production must contain palmitic and linoleic of fatty acids. From the investigated methyl ester compounds tested with the GC, it can be concluded that the production of biodiesel from Nannochloropsis oculata microalgae using in situ transesterification method with microwave wave was successfully carried out.

Table 2. Methyl Ester Biodiesel Composition From Nannochloropsis oculata

| Methyl Ester     | Composition (%) |
|-----------------|----------------|
| Palmitic acid   | 84.8173        |
| Oleic acid      | 12.4169        |
| Linoleic acid   | 0.8869         |
| Stearic acid    | 1.8787         |

4. Conclusion

The in-situ transesterification was studied by microwave irradiation at microwave power of 300, 450, and 600 watt, reaction time of 10, 20, 30 and 40 minutes, and KOH catalyst concentration of 1%, 1.5%, 2% and 2.5%, respectively. Whereas the in-situ transesterification with co solvent (addition of n-hexane) was studied by microwave irradiation at microwave power of 300, 450, 600 watt, reaction time of 10, 20, 30 and 40 minutes, KOH catalyst concentration of 1%, 1.5%, 2% and 2.5%. The most effective method in terms of the biodiesel amount was the one by using co-solvent (addition of n-hexane), i.e. with the highest yield of 54.19% which was obtained at 600 watt microwave power, reaction time of 40 min, and 2.5% catalyst concentration. Biodiesel yield is found to be affected by microwave power, reaction time, acid catalyst concentration. The longer the reaction times would give higher biodiesel yields.

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