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The effect of n-hexane as co-solvent in direct trans esterification of *Spirulina platensis* using microwave

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Abstract

The addition of co-solvent on in situ trans esterification was considered as one of method to improve the extractive process and increase in yield of biodiesel from microalgae. In this study, in situ trans esterification with co-solvent using microwave was studied for improving performance of in situ trans esterification from microalgae. The biodiesel produced from this method was compared with the in situ trans esterification without co-solvent addition. In the optimal reaction conditions (ratio of microalgae to methanol 1:15 w /v; 30 ml of co-solvent and 30 % of H2SO4) at 50 min of reaction time, yield of Fatty Acid Methyl Ester (FAME) produced was 81.04 % compared to only 75,246 % methyl ester produced by in situ trans esterification without co-solvents. The Fatty Acid Methyl Ester Analysis showed the methyl ester profile was a Medium Chain Fatty Acid, MCFA and the largest fatty acid component was dominated by Saturated Fatty Acid, SAFA.

Keywords: Co-solvent; Biodiesel; Microwave; *Spirulina platensis*

1. Introduction

Along with the increasing growth of human population and the rapid development of the world economy, energy consumption from all sectors of energy users nationally also increased rapidly. The rapid increase in the amount of energy consumption in the transport sector has led to a decrease in fossil fuel stocks and an increase in environmental pollution. In Indonesia, the use of fossil energy still dominates the use of energy in various sectors, so that it requires a solution based on an energy management paradigm that promotes energy diversification and energy conservation. The energy diversification and energy conservation program is considered to increase in the role of new and renewable energy optimally and expected to be the main support for future national energy supply. Biofuel is a renewable energy generated from renewable resources which is expected to contribute to replace fossil energy use, reduce greenhouse gas emissions and increase protection from energy supplies. One kind of renewable and non edible oil source that can be developed into biodiesel feedstock is microalgae.

Microalgae declared as the thirdgeneration biofuel feedstock which higher photoshyntetic efficiency and biomass productivity than other energy crops [1]. It does not interfere with the stability of the food chain and the land use as other plants. Microalgae have high oil contents around 1-75% of dry weight and can be harvested more than once a year [2], so that microalgae is stated as a potential source to be developed into biodiesel for the higher scale of production [3].

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Generally, biodiesel from microalgae can be performed by three methods:

- Two step procedure which consist of extraction step using organic solvent and then trans esterified into biodiesel using catalyst;
- One step procedure or direct transesterification of algal biomass using catalyst at atmospheric pressure and ambient temperature and
- One step biodiesel production at high temperature in absence of a catalyst [4].

In situ transestrerification will be an effective process if the combination of extraction and trans esterification steps can provide economic value in the overall biodiesel production process and has the potential to simplify the process and reduce the operation cost of the process [5, 6].

Many researchers have studied in situ trans esterification for biodiesel production from different kind of raw materials and catalysts. For examples, evaluated in situ trans esterification from microalgae *Schizochytrium limacinum* using different solvents (e.g. methanol, chloroform, hexane and petroleum ether) and reached 66% of maximum yield with chloroform as a co-solvent [7]. Tested sunflower seed on in situ trans esterification using excess methanol and sulfuric acid catalyst [8]. Their study showed yield was 20% higher than the results of two steps of trans esterification. Biodiesel production from *Chlorella Sp* was studied and obtained that a maximum lipid to FAME conversion was around 88% after 2 hours at 90^{o} of temperature using 0,04 moles of sulfuric acid and 500:1 of methanol to biomass ratio [9].

Biodiesel production from microalgae mainly depends on energy for the process and type of lipid extraction process used. Alternatively, co-solvent can be added to in the situ transesterification reaction to increase yield of biodiesel. The effects of co-solvent addition on in situ transesterification using a mixture of chloroform-methanol and sulfuric acid as catalyst has been studied and yield obtained with the process was around 91%. A study with the addition of co-solvent in direct transesterification reaction using hexane and 75% ethanol has also been carried out in order to increase biodiesel conversion and reduce the heat consumption during the process and from this research can be produced biodiesel with high conversion around 90 % [10]. The development of heating process to improve biodiesel production efficiently can be done using a microwave. The application of microwave irradiation is beneficial to accelerate the in situ transessterification process due to the short time needed for extraction and transesterification and also low solvent requirements [11].

In this research in the situ transesterification process from *Spirulina platensis* with an addition of hexane as co solvent was evaluated. The effect of microwave during the process was examined as well. The method was compared with the in the situ transesterification without an addition of n-hexane.

2. Material and methods

2.1. Materials

Microalgae used in the present study was dried microalgae powders (*Spirulina platensis*) supplied from Balai Budi Daya Air Payau Takalar, South Sulawesi and the chemicals used were methanol and sulphuric acid respectively. Methanol commercial (purity: 96%) was purchased from Brataco Co. Ltd. (Indonesia). Sulphuric acid (95: 98%) and n-hexane (95,5%) were obtained from a local chemical supplier (O.V. Chemicals, Co Ltd).

2.2. Procedures

Biodiesel was produced in a microwave assisted batch reactor. The reactor is a round bottom flask made from Pyrex glass equipped with magnetic stirrer. The reaction study was performed by varying reaction time and microwave. The type of microwave is Electrolux Microwave EMM2007X with a frequency of 2.45 GHz, power output of 100 to 800 W. The microwave assisted batch reactor design is shown in Fig. 1.

2.3. Experimental Procedure

2.3.1. Extraction Microalgae Lipids.

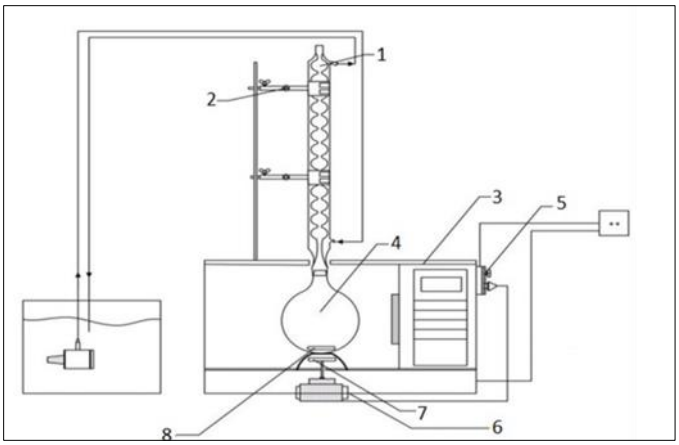
Lipid extraction of microalgae aims to determine the fatty acid components contained in microalgae lipids. The extraction process carried out using a mixture of methanol-hexane solvents with a microwave as a heating source. Ten grams of dried *Spirulina platensis* were mixed with 100 ml of methanol-hexane solution. The mixture was put into the microwave for 50 minutes with 450 W of microwave power to extract the microalgae lipids. After the filtration process,

filtrate was then distilled to evaporate the remaining solvents and lipids obtained were weighted and analyzed by GC MS.

2.3.2. In situ Trans esterification and In situ trans esterification with co-solvent

In situ trans esterification reaction carried out in a batch reactor and controlled by microwave irradiation at different reaction time (Process condition: 10 g dry; 450 W of microwave power; 30% of H_2SO_4 and 1:15 of dry microalgae to methanol ratio, wt/v).

Ten grams of *Spirulina platensis* powder were mixed with a homogeneous solution which was a mixture of methanol and sulfuric acid catalyst. The mixture was then exposed to microwave irradiation with 450 W of power: reaction time of 10 to 50 min. The same experiment was carried out with an addition 20 ml of n-hexane to observe the effect of co-solvent in the in situ trans esterification reaction. After the filtration process, samples were separated from the separating funnel before the purification stage and then analyzed by Gas Chromatography-Mass Spectrometry.



1. Reflux condenser; 2. Stative clamp; 3. Microwave; 4. Reactor; 5. Power setting; 6. Stirrer Motor; 7. Magnetic stirrer; 8. Bar Stirrer

Figure 1 Microwave reactor design for in situ trans esterification

3. Results and discussion

3.1. Characterization of Microalgae Lipids

The analysis of *Spirulina platensis* lipids showed that the fatty acid components produced from the extraction varied from C14-C18 which are saturated fatty acids (SAFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids PUFA). The fatty acids are dominated by palmitic acid C16: 0 that potential to be developed into biodiesel.

3.2. The effect of the addition of co-solvent on yield of Fatty Acid Methyl Ester

The effects of n-hexane on in situ trans esterification were evaluated and Fatty Acid Methyl Ester yield was compared with in situ trans esterification without n-hexane addition. Fig.2 shows the comparison of biodiesel yield produced by in situ trans esterification with and without co-solvent from *Spirulina platensis* using sulphuric acid catalyst under irradiation of microwave.

As can be seen from fig. 2, the presence of n-hexane in the reaction mixture shows an increase in yield of Fatty Acid Methyl Ester during the reaction. The biodiesel yield produced by in situ trans esterification with co-solvent was higher than in situ trans esterification with nonco-solvent. It was around 81.04% of yield produced by in situ transesterification process with the presence of hexane compare to was only 75,746% of methyl ester without an addition of hexane.

In the situ transesterification, n-hexane is useful as a co-solvent or a medium to improve mass transfer of lipid extraction and extractive power of reaction mixture thus increases in yield of biodiesel. The use of n-hexane in this experiment is based on the concept that n-hexane and methanol are the miscible solutions and n-hexane can increase the solubility of lipid in methanol, hence it can produce a mixture of homogeneous catalysts [10. 11]. In its role as a co-solvent, n-hexane is also able to extract the long chain fatty acid in the matrix of microalgae [11]. Further, n-hexane has the ability to

dissolve free fatty acids by increasing extractive ability of reaction mixture and reduce the amount of fatty acids lost during the process.

Reaction time has a significant impact on the yield of Fatty Acid Methyl Ester yield for in situ transesterification and in situ transesterification with n-hexane addition under microwave irradiation. As shown in fig.2. Fatty Acid Methyl Ester yield showed significant increases with the increasing reaction time. The increasing reaction time affects the increasing number of damaged cell walls and triglycerides released due to sufficient contact time for the mixture to form biodiesel [12]. Further, microwave can accelerate organic synthesis in a shorter time. However, the length of reaction time can because an overheating, loss of energy and solvent and the formation of by product (Kalsum et al., 2018) [13. 14. 15]

Microwave application as a heating source has a significant influence on in situ transesterification reaction. One of them is the thermal effect caused by the increasing extractive properties of methanol in extracting lipids from microalgae biomass (diffusive extraction). Furthermore, microwave irradiation causes penetration through the cell wall which forces the oils or lipids to exit from the matrix and then enters into the solvent mixture (disruptive extraction).

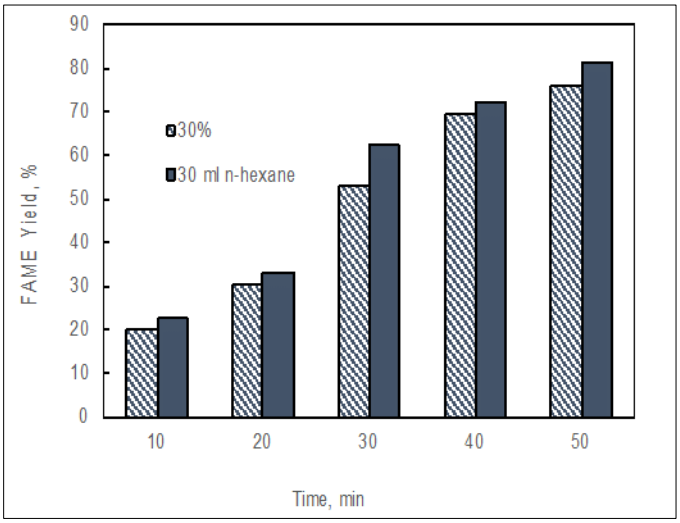


Figure 2 Yield of Fatty Acid Methyl Ester d for in situ transesterification and in situ transesterification with co-solvent using microwave

3.3. Fatty acid Methyl Ester Analysis

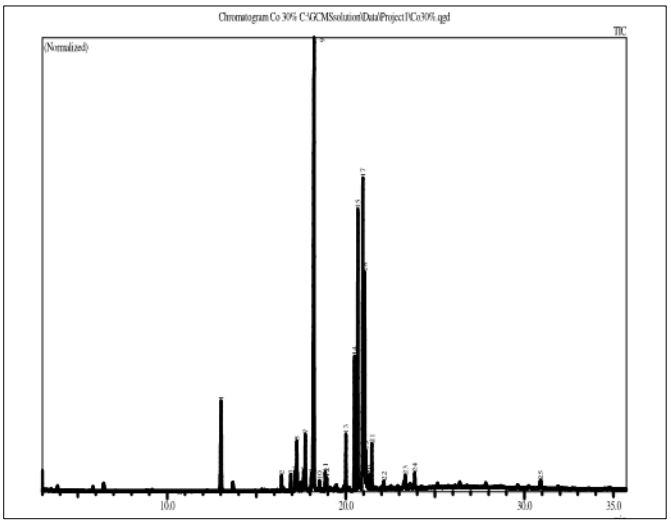


Figure 3 Chromatogram of *Spirulina platensis* Fatty Acid Methyl Ester with co-solvent

Table 1 shows the fatty acids component of *Spirulina platensis* methyl ester which was analyzed by Gas Chromatography Mass Spectrometry Analysis.

As shown in table 1, Gas Chromatography Mass Spectrometry analysis of fatty acid composition showed the fatty acid components of *Spirulina platensis* consist of varied fatty acids from C_{16}-C_{20}. The fatty acids component of *Spirulina platensis* was a medium chain fatty acid (MCFA) which consist of saturated fatty acid, SAFAs and unsaturated fatty acid, MUFAs and PUFAs. ‘

Table 1 The composition of fatty acid methyl ester from *Spirulina platensis*t

Compound Name	Formula	Mass, %
Methyl palmitic	C16:0	31.22
Methyl Palmitoleic	C16:1	4.04
Methyl Linoleic	C18:2	14.06
Methyl Alpha Linoleic	C18:3	12.82
Methyl Stearic	C18:0	1.69
Methyl Oleic	C18:1	13.39
Methyl Gondoic	C20:1	0.57
Methyl Hexadecatrienoic	C16:3	0.83
Others		21.38

4. Conclusion

In situ transesterification with co-solvents under irradiated microwave was carried out for biodiesel production from microalgae. The higher yield of Fatty Acid Metyl Ester obtained through in situ trans esterification with the addition of co-solvents was around 81.41% compared to only 75.246 % yield obtained by in situ trans esterification without co-solvent at 50 minutes. The Fatty Acid Methyl Esters profile was a medium chain fatty, MCFA acids with saturated fatty acids, SAFAs as the largest fatty acid component.

Compliance with ethical standards

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Disclosure of conflict of interest

In writing this scientific article, all authors do not have a conflict of interest

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