The Use of Co-solvent for In-situ Transesterification of Microalgae with Base Catalyst under Microwave Irradiation

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Abstract. The utilization of co-solvent was considered as one of several methods to improve yield of methyl ester on in situ transesterification of microalgae. The research aims to study the effect of co-solvent in the in situ transesterification of Chlorella Sp using base catalyst under microwave irradiation. The in situ transesterification reaction carried out in a microwave reactor using 1% of base catalyst with an addition 30 ml of n-hexane as a co-solvent. The microwave was equipped with a reflux condenser and the reactor was a round bottom flask equipped with magnetic stirrer. The reaction study was performed by varying the reaction time (10, 20, 30, 40, 50) min at 450 W of microwave power. Based on the experiment result obtained that the optimal yield of methyl ester was 30.08% at 40 min. The analysis result obtained that the component of Fatty Acid Methyl Ester (FAME) from Chlorella Sp was a medium chain methyl ester (C₁₂−C₂₀) with Saturated Fatty Acid (SAFA)s as the dominant component.

1. Introduction
The increasing of energy consumption in the transportation sector has the big impact in the decreasing of fossil fuel energy stock and the increasing of environment pollution. The most effect contributes global warming and the Green House Gas (GHG) emission. The global warming is a serious problem which impacts to the human life and environment and needs a huge solution to solve it.

Microalgae is an autotrophs microorganism has high lipid content which prospective to develop into biodiesel. Biodiesel from microalgae is one of renewable energy sources that has potential to replace fossil fuel energy and decrease the green house gas emission. The economical production of biodiesel from microalgae mainly depends on the energy for process and type of lipid extraction process used. Lipid extraction method of microalgae is divided into mechanical and chemical methods. The mechanical methods involve microwave-assisted extraction, ultrasonic assisted extraction and press; while chemical methods imply soxhlet extraction, ionic liquid extraction and supercritical extraction [1]. In situ transesterification is a method to eliminate the extraction process and improve the conversion performance [2]. It is reported that in the in situ trans esterification oils in the material directly contact with alcohol alkalized or alcohol acidified and the process acts as a pre-extraction reaction with alcohol [3]. The in situ transesterification method has the potential to simplify the conversion process, reducing the number of unit operation and the process cost for biodiesel production [4]. However, an optimization of reaction condition still required on the process extraction and tran esterification which occur simultaneously [5]. The usage of co-solvent is one of several methods to accelerate reaction and improve yield in the in situ tran esterification process. In situ
transesterification process from wet microalgae using chloroform-methanol solvent and sulfuric acid has been researched with conversion yields as high as 91% [6]. In order to reduce the reacting methanol volume and increase in situ transesterification process, several co-solvents have been used to enhance yield of lipid to methyl ester [7]. In this study, the effect of microwave on in situ transesterification of microalgae using base catalyst and addition of n-hexane as co-solvent in the reaction were evaluated. This work optimized the experimental parameters on conversion of yields for in situ transesterification of microalgae.

2. Methods

2.1 Materials
Dry microalgae powders (Chlorella Sp) were supplied from Balai Budi Daya Air Payau Takalar, South Sulawesi. Sodium hydroxide, methanol and n-hexane were purchased from Brataco Chem.

2.2 Experimental Procedures

2.2.1 Extraction Microalgae Lipids. Extraction lipid of microalgae aims to determine the fatty acid component contained in microalgae lipids. The extraction process carried out using mixture of methanol - n-hexane solvent and a microwave as a heating source. Ten grams of dried Chlorella vulgaris were mixed with 100 ml of methanol-hexane solution. The mixture was subjected to the microwave for 50 min with 450 W of microwave power for extraction process. After filtration, the filtrate was then destilled to evaporate remains solvent and lipids were weight and analysis by GC MS.

2.2.2 In situ Transesterification and In Situ Transesterification with Co-Solvent. In situ transesterification experiments were carried out in a microwave reactor. The microwave reactor equipped with a reflux condenser to provide condensation of evaporation from solvent mixture. A magnetic stirrer was used to assure a uniform mixture with a constant mixing speed. Ten grams of dry microalgae powder were mixed with solution of methanol and sodium hydroxide catalyst. The mixture was then expose to microwave irradiation with power of 450 W, reaction time 20-50 min; catalyst concentration 1% and dry algae to methanol (w/v) 1:12 and n-hexane volume 30 ml. The samples were cooled and filtered before the separation steps. The same experiment was carried out with an addition 30 ml of n-hexane in the reaction mixture to observe the effect of co-solvent in the in-situ transesterification reaction. After filtration, the samples were separated in a separating funnel before purification stage and analysis by GC MS.

3. Result and Discussion

3.1 Characterization of Microalgae Lipids
The analysis of Chlorella Sp 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 and C18: 1 oleic acid. Both components of these fatty acids and some of the various fatty acids in microalgae have the potential to be developed into biodiesel. The raw materials for diesel fuels are hydrocarbons containing 8-10 per molecular carbon atoms. The number of carbon atoms found in vegetable oil is around 16-20 carbon atoms per molecule. Therefore, microalgae oil must be transesterified before being used as fuel.

3.2 The Effect of N-Hexane Addition on in Situ Transesterification of Microalgae Under Microwave Irradiation
In situ transesterification with co-solvent addition as co-solvent into the reaction mixture were studied at 450 W of microwave power, 1:12 (w/v) microalgae biomass to methanol, 1% of KOH and
difference reaction time (10 to 50) min. Co solvent volume was investigated by study the effect of n-hexane use during in situ transesterification with microwave and compare the results with direct transesterification in the absence of co-solvent.

Figure 1. Yield of FAME from in situ transesterification with 1% of KOH, 30 ml of n-hexane and 450 W of power

Figure 1 shows yield of FAME obtained by in situ transesterification with KOH under microwave irradiation and in situ transesterification with co-solvent. As shown in fig 1, Yield of microalgae FAME increased significantly with the increase in reaction time for both reactions. The significant increase in yield starts from 10 min to 50 min of reaction. The influence of reaction time on the increase in yield of methyl ester under microwave irradiation caused by the longer contact time that induces more disrupted cell walls and faster triglycerides are released into the reaction mixture, therefore there is sufficient time for reactant mixture to form biodiesel [8]. The influence of microwave use as a heater in this process was also presented by Guerra et al., 2013 which states that microwaves can accelerate organic synthesis with a short reaction time due to an increase in reaction rate. Microwave energy produces electromagnetic waves, wherein the amount of wave energy per unit of time is reflected as the strength. Heating process with microwaves can take place very quickly because the absorption capacity of microwave energy from polar molecules is very high, and the presence of heat transfer in microwaves which rapidly leads to molecular material cause an increase in yield of product. Based on the nature of polarization, the homogeneity between alcohol and oil occurs rapidly due to the movement of the dipole molecule without changing the molecular structure of the material. Therefore, the addition of supplied power leads to the heating at the molecular level that takes place very quickly and affects the speed of the reaction rate [8, 9, 12]. As stated by Arrhenius law that with the longer reaction time the contact between reactant molecules is also increased and yield of product is likely to increase. But if there has been an equilibrium, the increasing time will not affect the yield of product.

The effect of n-hexane addition in the in situ transesterification also displayed in figure 1. From the graph can be seen that yields obtained from reaction with hexane were higher than yield by reaction with the absence of hexane. At the end of the reaction, the highest yield with hexane addition was 30.08%, which was 1.84% higher than yield resulted by in situ transesterification without n-hexane. The effect of n-hexane as co-solvent on the increase in yield FAME caused by the ability of hexane to increase the solubility of alcohol in the lipid and the power of extraction before reacting with alcohol. The role of n-hexane as co-solvent was a mediator during the reaction under microwave which can increase the mass transfer between catalyst and methanol. In addition, n-hexane is a non-polar solvent which transparent and able to pass through the microwave irradiation without receiving a heating process. Meanwhile, the polarity nature of methanol can absorb microwave energy strongly due to the
permanent moment dipole. As a result, an extractive transesterification in this study can be provided by the combination of polar and non-polar solvent use.

3.3 Analysis of Fatty Acid Methyl Ester (FAME)

The analysis to Chlorella Sp Fatty acid methyl ester showed the composition of methyl ester from Chlorella Sp. The fatty acid compound was a medium chain methyl ester, MCFA with (C\textsubscript{12}-C\textsubscript{20}) which consist of esters from lauric acid (C12:0), myristic acid (C14:0), palmitic acid C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1n9), vaccenic acid (C18:1n7), linoleic acid (C18:2), arachidonic acid(C20:4) and eicosapentanoic acid (C20:5).

| Compounds              | Formula          | Mass (%) |
|------------------------|------------------|----------|
| Palmitic acid ME       | C\textsubscript{16}H\textsubscript{32}O\textsubscript{2}  | 26.93    |
| Myristic acid ME       | C\textsubscript{14}H\textsubscript{28}O\textsubscript{2}  | 0.76     |
| Palmitoleic acid ME    | C\textsubscript{16}H\textsubscript{30}O\textsubscript{2}  | 2.25     |
| Eicosapentanoic ME     | C\textsubscript{22}H\textsubscript{44}O\textsubscript{2}  | 1.66     |
| Linoleic MEcatalyst    | C\textsubscript{18}H\textsubscript{32}O\textsubscript{2}  | 3.95     |
| Linolenic ME           | C\textsubscript{18}H\textsubscript{30}O\textsubscript{2}  | 1.04     |
| Oleic ME               | C\textsubscript{18}H\textsubscript{32}O\textsubscript{2}  | 14.55    |
| 7.10 Hexadecadienoic ME| C\textsubscript{17}H\textsubscript{30}O\textsubscript{2}  | 0.76     |
| 10-Heptadecen-8-yenoic acid | C\textsubscript{18}H\textsubscript{30}O\textsubscript{2} | 1.08    |
| Octadecanoic acid ME   | C\textsubscript{18}H\textsubscript{36}O\textsubscript{2}  | 3.96     |
| Others                 |                  | 36.47    |

4. Conclusion

Base in situ transesterification with co-solvent was performed for biodiesel production from microalgae. The evaluated the process parameters required to produce biodiesel using microwave as a heating source. From the parameters evaluated (methanol volumes, reaction time and microwave powers) the highest yield was obtained at 50 min with biomass to methanol ratio, 1:12 and power of 450 W. It was represented that 30.08% of yield can be obtained from base catalyzed in situ transesterification with c-hexane addition. From analysis, FAMEs profile was identified and the majority of FAME produced from palmitic acid, stearic acid and oleic acid.

5. References

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