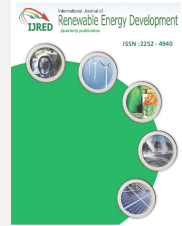




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Research Article

# Biodiesel Production through Catalytic Microwave In-Situ Transesterification of Microalgae (*Chlorella sp.*)

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**ABSTRACT.** Aim of this research are to study and develop research related to the potential of *Chlorella sp.* into biodiesel with the help of microwaves in-situ transesterification by characterizing parameters such as microwave power (300; 450; 600 W) and reaction time (10; 30; 50 minutes) with catalyst concentration of KOH and molar ratio of microalga : methanol are 2% and 1:12 respectively and optimized by response surface methodology with Face Centered Central Composite Design (FCCCD). The study was carried out by dissolving the catalyst into methanol according to the variable which was then put into a reactor containing microalgae powder in the microwave and turned on according to the predetermined variable. After the reaction process is complete, the mixture is filtered and resuspended with methanol for 10 minutes to remove the remaining FAME and then the obtained filtrate is cooled. Water is added to the filtrate solution to facilitate the separation of hydrophilic components before being separated and pushed apart until 3 layers are formed. Amount of FAMES in the first layer formed were extracted with n-hexane solution and washed with water and the FAME product obtained was then distilled to remove the remaining n hexane and then weighed. The results indicated that yield increased with increasing reaction time and microwave power with the best conditions of 50 minutes each and 440.53 watts with the highest yield reaching 35.72% (dry basis) through using of KOH catalysts with low concentrations, 2%. ©2020. CBIORÉ-IJRED. All rights reserved

**Keywords:** Biodiesel, *Chlorella sp.*, In-situ Transesterification, Microalgae, Microwave

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## 1. Introduction

Data from the National Energy Council (DEN) shows that between 2006 and 2030 the world's energy demand increased by 45% and this was not offset by the availability of increasingly depleted fossil fuels coupled with developing crisis issues on environmental and energy issues which resulted in many researchers have developed sustainable renewable energy (Bahadar and Bilal Khan, 2013). The effort that has been made by Indonesia is to increase the development of new renewable energy such as biofuel. Regarding the development of biomass technology, BPPT has succeeded in developing first and second generation biodiesel derived from vegetable oils such as palm oil (first generation) and agricultural and forestry processing wastes such as oil palm empty fruit bunches and rice husk (second generation). Biodiesel is chosen because it is a new alternative to replace fuel that is more environmentally friendly.

However, the development of first generation biodiesel is less effective because the prices are relatively cheaper than the raw materials and raw materials based on food ingredients will result in competition between energy and food needs which causes large land requirements. While

the second generation has a weakness because it requires a long time in preparing the raw material.

Therefore, it is necessary to develop fuels that weigh the concept of environmentally sustainable development. Microalgae is a third generation biodiesel feedstock (there is no competition between the food and energy sectors) which is now being researched because of the potential to be developed. Approximately, 1.46 x 10<sup>11</sup> tons of biomass is produced throughout the world through photosynthesis, including 40% for microalgae photosynthesis. The quantum efficiency of microalgae in converting solar energy into biomass ranges from 2-10% compared to terrestrial plants which are less than 1%. Plus, the growth rate is very high up to 1-3 times per day (Ananyev, Carrieri and Dismukes, 2008). and the oil productivity of microalgae is much higher when compared to palm oil for the same land area which can reach 20 times (Khan *et al.*, 2009).

One type of microalgae that can produce lipid products is *Chlorella sp.* Compared to other types of microalgae, the lipid content of *Chlorella sp.* quite high at 10-58% of the dry weight (Chisti, 2007). The two main fatty acid content is palmitic acid (C16: 0) which reaches 8.09% and

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palmitoleic acid (C16: 1) of 2.15% (Prartono *et al.*, 2010). Biodiesel consists of C12-C22 fatty acids, so that the fatty acid content of *Chlorella sp.* which is dominated by palmitic acid (C16: 0) and palmitoleic acid (C16: 1) has the potential to produce biodiesel with high yield.

Several methods have been applied in converting biomass to biofuels including biochemical methods (fermentation, transesterification and anaerobic digestion) and thermochemistry (combustion, gasification, liquefaction and pyrolysis). Among several methods of production, transesterification is a popular and more commercial method for producing biodiesel. In addition, this method has been proven successful for several types of feedstock (Akubude, Nwaigwe and Dintwa, 2018). Moreover, its application from microalgae produced by transesterification algal oil and methanol using base or acid catalyst (Kalsum *et al.*, 2018). Dai *et al.* (2014) conducted a study to compare treatment methods using conventional, ultrasonic and microwave assistance in extracting microalgae lipids. Based on the results of his research, microwave assisted methods have more effective results of up to 18% compared to conventional and ultrasonic methods which each obtain 14% and 5% by weight (Dai *et al.*, 2014). This is because microwave energy can increase temperature optimally, causing cells to be damaged because the internal pressure exceeds the pressure around the cell wall (Mahfud *et al.*, 2018).

Therefore, microwave transesterification needs to be applied. In order to be an effective and efficient method, this research will develop a catalytic microwave in situ transesterification method because the extraction and transesterification process occurs simultaneously so that it can save time and energy. Thus, the purpose of this study was to determine the potential of in situ transesterification with the help of microwaves in generating biodiesel from *Chlorella sp.*, find out the effects of the parameters used as variables and optimize condition of this research using Face Centered Central Composite Design (FCCCD)

Development of the use of energy sources in the in situ transesterification process is carried out by the use of microwave irradiation which is applied to help penetrate the cell wall and supply the energy needed during the transesterification process. Microwave waves can accelerate heating, generate temperature and pressure gradients, help remodel cell walls, increase transfer mass and reaction speed so that the process runs more efficiently and effectively because it can save time and energy.

## 2. Materials and Methods

### 2.1 Materials

The microalgae used is *Chlorella sp.* powder which is the raw material for making biodiesel and obtained from the Brackish Aquaculture Center (BBAP) in Jepara, Central Java. The catalyst in this study is potassium hydroxide (KOH). In addition, the reagent for transesterification is used methanol obtained from the chemical supplier PROLAB-UN 1230 Brataco Chem brand Made In France with 99% content and assisted with n-hexane solution (96%) as a solvent and co-solvent in the process.

### 2.2 Microwave Apparatus

The main equipment used in this study was an Electrolux microwave EMM2007X model with a frequency of 2.45 GHz and a maximum power of 800 Watts. The transesterification reaction was carried out in a three neck pumpkin glass reactor equipped with a condenser.

### 2.3 Microwave Apparatus

Parameters in this study included microwave power (300; 450; 600 watts), and reaction time (10; 30; 50 minutes) with molar ratio of *Chlorella sp.* : methanol and KOH catalyst as control parameters are 1:12 and 2%, respectively in atmospheric pressure conditions. On the other hand, this research was optimized by Design Expert 12 with the design type is Face Centered Central Composite Design (FCCCD) with 3 level for each factor and 3 replications at the center points.

**Table 1.**  
Factor in the experimental design

Factor	Unit	Level		
		Low	Middle	High
		-1	0	+1
A: Power	W	300	450	600
B: Time	min	10	30	50

### 2.4 Yield

Yield is a measurement that is defined as the ratio of the amount of product (biodiesel) produced to the maximum amount of product produced by raw materials. In conventional biodiesel manufacturing, the yield can be expressed as a comparison of the total amount of biodiesel produced with the amount of lipids / oil processed during the reaction.

$$\text{Yield} = \frac{\text{crude product mass} \times \text{purity}}{\text{lipid mass}} \times 100\% \quad (1)$$

### 2.5 Experiment Procedure

The research was carried out by dissolving the catalyst into methanol according to the specified variable and stirring it with a magnetic stirrer. The methanol and catalyst mixture is inserted into the reactor containing 10 gr. of microalgae powder in the microwave and turned on according to the predetermined variable. This process is carried out on all variables of the microalgae-methanol ratio, catalyst concentration and microwave power. After the reaction process is complete, the mixture is filtered using a vacuum filter to separate the filtrate. The mixture was resuspended with methanol for 10 minutes to remove the remaining Free Acid Methyl Ester (FAME) and then the obtained filtrate was cooled. Water is added to the filtrate solution to facilitate the separation of the hydrophilic components before being separated, pushed apart for 3 to 3 layers formed. The number of FAMES in the first layer formed were extracted 3 times with n-hexane solution and washed with water to remove the remaining catalyst and methanol. The FAME product obtained was then distilled to remove the remaining hexane and then weighed. The methyl ester product obtained was then determined by the yield and analyzed by Gas Chromatography-Mass Spectroscopy (GC MS).

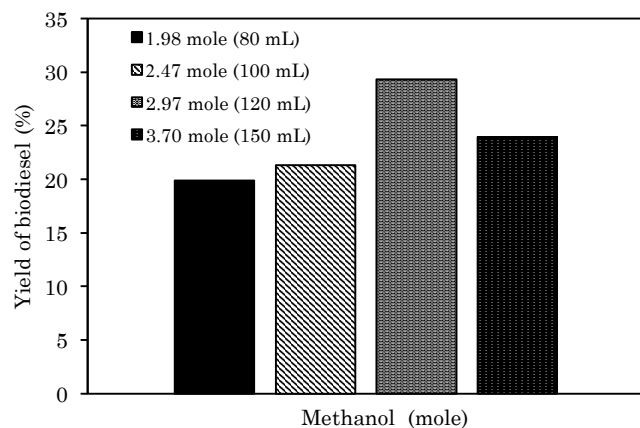
### 3. Result and Discussion

#### 3.1 Catalytic Microwave In-situ Transesterification Optimization

In situ transesterification of microalgae is a transesterification process that occurs directly (direct transesterification) or simultaneously in producing biodiesel. This process is reported to be superior to two-stage transesterification or conventional processes that are more dependent on extraction results with organic solvents with low separation efficiency because of the incomplete extraction process. The ineffective use of solvents, the length of time and the many stages of the process are also things that cause high operational costs and product prices. In this study the transesterification of in situ microalgae in producing biodiesel was studied using a microwave as a reactor and heater. Microwave use is intended to replace ineffective conventional heating systems in terms of energy use and time. Energy efficiency of heating by using microwaves is much smaller when compared to conventional heating (Gude *et al.*, 2013)

#### 3.2 The Effect of Microalgae and Methanol Ratio on Yield

The ratio of the amount of methanol and microalgae used in this study has a very significant effect on the in-situ transesterification reaction. In this reaction methanol functions as a solvent to extract lipids / microalgae oil (Al-Ameri and Al-Zuhair, 2019) and also as a reactant during the transesterification process. The use of large amounts of methanol causes contact between methanol and microalgae to be greater and optimal so that the yield produced is also greater.



**Fig. 1** Yield of Biodiesel on various methanol as a solvent at 450 watt, 30 minutes with KOH 2%

Figure 1. shows the use of a 2% KOH catalyst at a reaction time of 30 minutes at various methanol to microalgae ratios at 600 watts power. The increase in yield occurred significantly in the use of the ratio of methanol and microalgae 1:8; 1:10, 1:12 and 1:15 (w/v). The optimum yield is obtained at a ratio of 1:12 which shows that the greater the ratio of methanol and microalgae will increase the yield amount. On the use of methanol with a larger volume the methyl ester yield has decreased (the ratio of methanol and microalgae (w/v) 1:15). This was also reported by Martinez-Guerra *et. al.* (2014) which stated that the use of a molar ratio above 1: 500 in in-situ transesterification and 2% KOH catalyst with microwave irradiation was ineffective and did not show an increase in

yield. So in this study using a molar ratio of microalgae to methanol of 1:12.

Transesterification reaction is a reversible reaction that takes place slowly so that the use of excess methanol can accelerate the reaction and shift the reaction right towards the formation of the product. The large amount of methanol causes contact between methanol and microalgae to be greater and the yield produced also becomes larger. The use of excess methanol in the in-situ transesterification reaction causes the capacity of the microwaves absorbed by the material to be greater thereby increasing the excitation of molecules in the material and encouraging an increase in temperature. More volume of methanol can reduce the effect of the catalyst so that microwave irradiation has no effect on microalgae biomass.

#### 3.3 Analysis of Variance (ANOVA)

Analysis of variance (ANOVA) of Face Centered Central Composite Design (FCCCD) for response surface quadratic model for the yield of biodiesel is shown in Table 2. ANOVA data shows that the model of this experiment has a significant value which is indicated by p-value 0.15% (below 5%). This is supported by a large conversion coefficient value,  $R^2$  is 0.9619. In addition The Predicted  $R^2$  of 0.7409 is in reasonable agreement with the Adjusted  $R^2$  of 0.9239; i.e. the difference is less than 0.2. Adeq. precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 15.726 indicates an adequate signal. This model can be used to navigate the design space.

**Table 2.**

Analysis of variance (ANOVA) for Quadratic Model of Face Centered Central Composite Design (FCCCD)

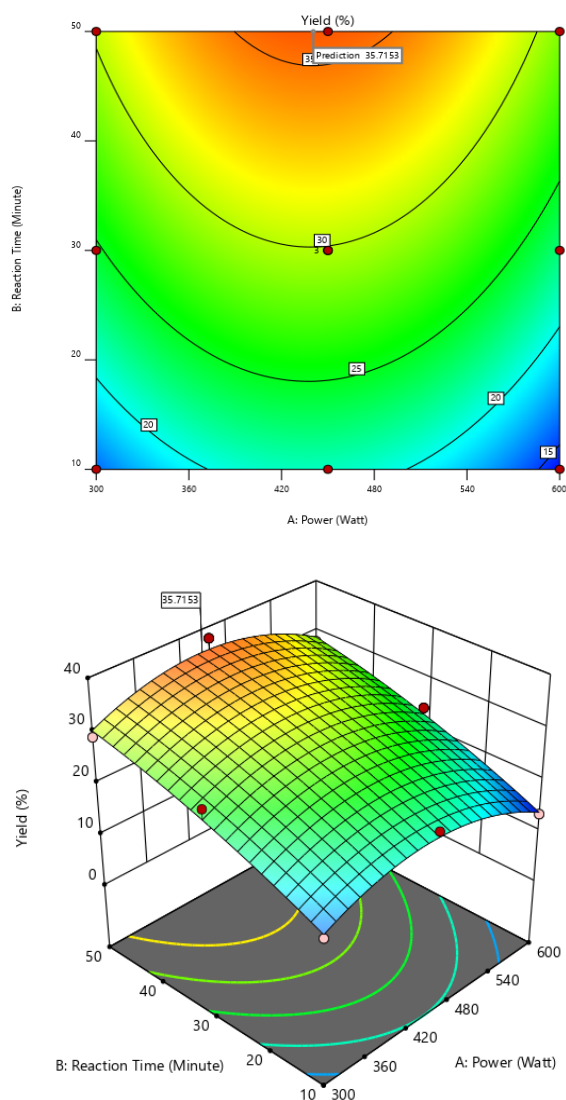
Source	Sum of Squares	df	Mean Square	F-value	P-value
Model	447.18	5	89.44	25.27	0.0015
A-Power	5.28	1	5.28	1.49	0.2762
B-Time	320.32	1	320.32	90.52	0.0005
AB	0.1089	1	0.1089	0.0308	0.8676
A <sup>2</sup>	95.24	1	95.24	26.91	0.0035
B <sup>2</sup>	5.45	1	5.45	1.54	0.2698
Residual	17.69	5	3.54		
Lack of Fit	17.00	3	5.67	16.27	0.0585
Pure Error	0.6966	2	0.3483		
Cor Total	464.88	10			

$R^2 = 96.19\%$ ,  $R^2(\text{pred}) = 74.09\%$ ,  $R^2(\text{adj}) = 92.39\%$ , Adeq precision (15.726) (df = degree of freedom; F-value = value of probability distribution; p-value = value of probability > F).

#### 3.4 The Effect of Microwave Power and Reaction Time on Yield Biodiesel

The effect of various microwave power on the catalytic microwave in situ transesterification process of microalgae *Chlorella sp* was studied at 2% of KOH catalysts concentration with varying reaction times of 10, 30, 50 minutes and microalgae ratio: methanol 1:12 (w/v). The influence of different uses of microwave power in the process of making biodiesel in situ is shown in Figure 2.





**Fig. 2** 2D Contour and 3D Graph presenting the effects of microwave power (A) and Reaction Time (B) on the methyl ester of microalgae using catalytic microwave in situ transesterification with FCCCD

Based on the results of research conducted on the in-situ transesterification of microalgae with 2% KOH, the 1:12 w/v ratio with different reaction times shows that the increase in power is very influential in the in situ transesterification process. At 300 watts the yield increase significantly occurs from the beginning of the reaction to the reaction time of 50 minutes. In the first 10 minutes the yield FAME obtained was 15.33% which then increased significantly to 29.09% in the 50th minute. This indicates that the use of low power in this process produces maximum interaction in the mixture, so the solvent that evaporates is less. At higher power usage, yield increases occurred until the 40th minute, but decreased after a reaction time of 50 minutes. The optimization with FCCCD shows that maximum yield of 35.72% at reaction time of 50 minutes on the power at 440.53 Watt and it doesn't happen above 450 watts. In the use of microwaves as heaters, increasing microwave power can cause temperatures to rise and produce high yields or decrease with increasing reaction time. The decrease in the number of yields in the increase in microwave power is caused by

the formation of by products of other compounds in microalgae biomass such as di, mono glyceride and glycerol (Martinez-Guerra *et al.*, 2014).

Microwave power and temperature are closely related to in situ transesterification reactions. The incoming power in the microwave affects the amplitude of the wave where the greater the power the greater the electric field produced and the amplitude of the generated microwave will also be greater (Boldor, 2012). The rotational speed of the polar molecule has a linear relationship to the amplitude of the microwave so that the greater the amplitude the faster the polar molecule rotates and the greater the heat generated.

Moreover, the effect of time on the transesterification reaction in situ *Chlorella sp.* with KOH catalyst in producing methyl ester can be seen in Fig 2. In the graph, it can be seen that the transesterification process lasts for 50 minutes. In this process, yield of methyl esters increased significantly to 50 minutes. The effect of the length of reaction time on the increase in yield of methyl esters by using microwave heating is due to the longer contact time causing more damaged cell walls and faster microalgae triglycerides to release enough contact time for the mixture of reactants to form biodiesel (Patil *et al.*, 2011).

The influence of microwave use as a heater in this process was also suggested by Guerra *et al.* (2013) (Martinez-Guerra and Gude, 2016) which states that microwaves can accelerate organic synthesis with a short reaction time due to an increase in reaction speed as expressed through Arrhenius's law that with increasing reaction time the contact between reactant molecules is increasingly large and product yield formation is likely to increase. But if there has been an equilibrium, increasing time will not affect the product yield.

Catalytic microwave in situ transesterification with 2% KOH catalyst, the highest yield of 35.72% was obtained in the reaction using 2% KOH which lasted 50 minutes and microwave power 440.5 W. Trend is shown at 300 watts and 600 watts of power which does not show an increase in yield with increasing reaction time so that it can be stated that the longer reaction time causes the production of biodiesel to be inefficient. Even this is supported by Patil *et al.* (2011) which states that the reaction time is too long resulting in overheating of the reaction resulting in loss of large quantities of solvents, formation by product, and loss of energy in the process.

### 3.5 GCMS Analysis for Biodiesel

Biodiesel is the main product of the microwave using *Chlorella sp.* Biodiesel yield is in the range of 13.51 - 35.08% of its dry weight. Knowing the composition of biodiesel will help better understand the reactions that occur during the transesterification process and explore its potential use.

The main content of biodiesel from *Chlorella sp.* is methyl ester palmitate as much as 21.04%. The content of methyl ester palmitate is in accordance with the research conducted by Ramesh *et al.* (2018) which states that the weak acid content of saturated *Chlorella sp.* is palmitic acid of 17.12% which is desired to produce and stability of biodiesel (Ramesh *et al.*, 2018).

#### 4. Conclusion

Microwave use in converting biomass *Chlorella sp.* being biodiesel using the in-situ transesterification method provides benefits in terms of time and energy so the process can be more effective and efficient. The yield obtained in this study was in the range of 13.51% -35.08% with the best yield of 35.08% in power usage and reaction time of 450 watts and 40 minutes respectively. After optimization, using the response surface methodology with the type of face-centered central composite design is obtained that yield increased with increasing reaction time and microwave power with the best conditions of 50 minutes each and 440.53 watts with the highest yield reaching 35.72% (dry basis) through using of KOH catalysts with low concentrations, 2%. The results of this study can be concluded that changes in reaction time and microwave power have a linear relationship to yield changes until they reach their optimum point.

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