Kinetics and Characterization of Microalgae Biofuel by Microwave-assisted Pyrolysis Using Activated Carbon

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Highlights:

- Kinetics analysis of microwave-assisted pyrolysis (MAP) of microalgae *Chlorella* sp. with activated carbon without the presence of nitrogen in producing biofuels.
- The use of vacuum pumps as a substitute for carrier gas in the MAP process.
- Characterization of biofuel from microalgae *Chlorella* sp. using MAP.

Abstract. The reaction kinetics and the effect of power on microwave-assisted pyrolysis (MAP) in converting microalgae to biofuel were investigated to determine the decomposition mechanism and then characterize the best product. The resulting product consisted of three phases, namely liquid phase (bio-oil), solid residue (char), and uncondensable gas products. The results showed that the optimal increase in microwave power obtained was 20.57% with a 600-watt microwave power condition, a reaction time of 20 minutes, a microwave absorber to microalgae ratio of 1:6, and a heating rate of 25.96 K/min (600 watts). The reaction kinetics evaluated in the best condition showed a second-order reaction with activition energy (Ea) and pre-exponential factor (A) at 35.5971 kJ/moles and 2,606.75/minute, respectively. The characteristics of the biofuel product obtained were 1.01 gr/mL density, viscosity 10.97 cP, and pH 9.30. In addition, based on GC-MS analysis, the bio-oil contained aliphatic, aromatic, phenol, FAME, and polycyclic aromatic hydrocarbon (PAH) organic compounds. These results indicate that MAP has the potential to be developed as an alternative production process for biofuels.

Keywords: *activated carbon; biofuel; Chlorella sp.; kinetics; microwave; pyrolysis.*

1 Introduction

Microalgae have attracted a lot of attention in recent years as biomass that can be converted into biodiesel because it can replace fossil fuels, which have bad effects on the environment and human health [1,2]. This is because, (1) biomass can bind and capture CO_2 emissions in the environment [3]; (2) the productivity of biomass

is higher than that of other oil crops up to 5-30 times on the same area of land [4]; (3) 50% of the weight of dry cells can be converted into high-quality biofuel [5]; (4) biofuel has better quality than oil from lignocellulosic plants in terms of viscosity, density, and heating value [6]. Biomass can be converted through biochemical and thermochemical conversion [3]. Carlos, *et al.* (2019) compared these two methods in producing bioenergy. Thermochemical conversion gave better results in reducing CO_2 emissions in producing biofuel by up to 35.50% [7]. Gong, *et al.* (2019) reported that pyrolysis as one of the thermochemical conversion methods can efficiently recover most of the available energy in biomass and improve the performance of the process [8]. However, conventional heating requires a long time and a large amount of energy, so the study did not run effectively and efficiently [9].

Using microwave technology is a promising approach because it can enhance chemical reactions [10]. However, in practice, although it can produce bio-oil, some reports have stated that biomass (especially microalgae) is a bad absorber of microwaves. Mixing it with a microwave absorption enhancer will increase biomass heating [11]. Hu, *et al.* (2012) converted *Chlorella vulgaris* using MAP with the addition of activated carbon, CaO, SiC, and solid residue (biochar). The highest biofuel yield was obtained at 87.47% when using 5% of activated carbon [12]. Moreover, Du, *et al.* (2011) reported that the conversion of *Chlorella* sp. using MAP for 20 minutes and 750 watts of power with the help of N_2 as the carrier gas produced the best yield at 28.6% [2]. Based on these studies, the selection of activated carbon as a microwave absorber is quite effective in maximizing the product because it has a high dielectric loss tangent (tan δ) of 1.71 [13]. A material with tan δ > 0.2 can potentially be a good microwave absorber [14].

The nitrogen present in the study by Du, *et al.* (2011) could be eliminated by adding a vacuum pump to remove oxygen during the process. The presence of nitrogen during the process can produce toxic gases such as NO_x and HCN [15]. Research must be carried out effectively and efficiently and consider the concept of environmentally friendly sustainable development. Therefore, this study aimed to produce biofuel from microalgae *Chlorella* sp. assisted activated carbon as microwave absorber. The MAP technique was used without the presence of nitrogen to be able to make the research more economical and obtain a more optimal product. In addition, kinetics analysis was carried out to understand the decomposition mechanism of biomass using MAP.

2 Materials and Methods

2.1 Materials

Microalgae *Chlorella* sp. (dry weight) and activated carbon in granule form were obtained from Balai Budi Daya Air Payau (BBAP) Situbondo, Indonesia. Proximate analysis of the raw materials is provided in Table 1.

Table 1 Proximate composition of microalgae *Chlorella* sp. (dry weight).

Component	Analysis result %
Ash	53.0780
Protein	12.1290
Lipid	12.4140
Rough fiber	0.1410
Carbohydrate	19.4950
Calorie (Kcal/kg)	1398.9820
Water content	3.6147

2.2 Experimental Device

The experiment was conducted using an Electrolux, EMM2007X, type MM820AYC-PA0C microwave oven with frequency, power, and microwave heating rate at 2,450 Hz, 1,250 watt, and 2.3584 °C/min respectively.
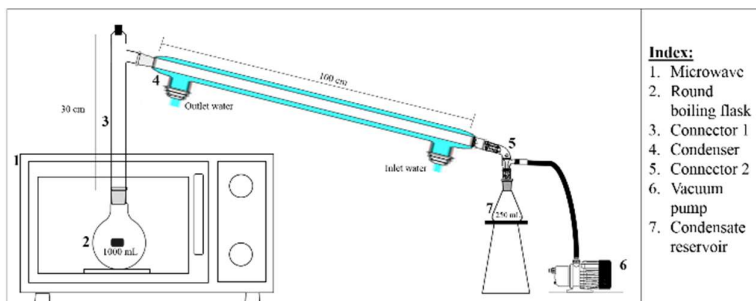

Figure 1 Schematic diagram of MAP setup.

2.3 Experimental Procedure

This study used the MAP technique without the presence of air with the help of a vacuum pump. The first step was to arrange the MAP setup according to the diagram in Figure 1. The second step was to mix the activated carbon with 30 gr. of microalgae *Chlorella* sp. at a ratio of 1:6 (w/w) and put it into a round boiling flask and shake it for 1 min. Then, the flask was adjusted into the device circuit and the vacuum pump was turned on for 10 min to ensure the device circuit was free of oxygen. After that, the microwave was turned on and the pyrolysis process

was carried out by adjusting the power at 400; 600; and 800 watts for 20 min each. During the process, gas was formed and condensed into liquid product until the pyrolysis time was reached. All products (bio-oil (wet basis), gas, and char (pyrolysis solid residues)) were then analyzed.

2.4   Yield Analysis

The mass percentage of the product (liquid, gas, and char) can be calculated to obtain the conversion percentage.

1. Liquid product (bio-oil)

$$\%yield\ bio-oil = \frac{Liquid\ mass}{Microalgae\ mass}\ x\ 100\% \tag{1}$$

2. Solid product (char)

$$\%Yield\ char = \frac{Char\ mass\ (solid\ residue)}{Microalgae\ mass}\ x\ 100\% \tag{2}$$

3. Gas product

$$\%Yield\ gas = 100\% - (\%yield\ bio-oil + \%yield\ char) \tag{3}$$

2.5   Product Characteristic Analysis of Bio-Oil

The analysis consisted of three parts, i.e., physicochemical (density, viscosity, pH, and higher heating value (HHV)), GC-MS, and FTIR analysis.

2.5.1   Physicochemical Characteristic Analysis

The physicochemical analysis included analysis of density, viscosity, pH, and higher heating value (HHV) of bio-oil (wet basis).

1. Density (ρ)

$$\rho = \frac{mass\ (gr)}{volume\ (mL)} \tag{4}$$

2. Viscosity (η)

This analysis was carried out using an Ostwald viscometer guided by the ASTM D-7279 standard.

2.5.1.1   Power of Hydrogen (pH)

The measurement of pH was carried out at a temperature of 25 °C using an OHAUS Starter300 pH meter, which was started by calibrating the pH with a

buffer solution. Next, the pH rod was inserted into the bio-oil sample by pressing the Read button and waiting for the pH results to be constant.

2.5.1.2   Higher Heating Value (HHV)

A 5E-C5500 (serial number 0261311295) bomb calorimeter was used to determine the high heating value (HHV) of the bio-oil produced in accordance with the ASTM D-4809 standard. It should be noted that the bio-oil analyzed was produced from microwave-assisted pyrolysis with a microwave power of 600 watts, a pyrolysis time of 20 minutes, and a catalyst to microalgae ratio of 1:6.

2.5.2   Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis

GC-MS analysis was performed by injecting 2 µL of the solution inside the inlet sample into the injection site with the following specifications:

Brand   : Agilent Technologies 7890B/5977B MSD
Sample injection volume   : 2 µL
Run time   : 51 min
Post run time   : 0 min
Temperature (Initial)-GC   : 60 °C
Hold Time   : 2 min
Post Run   : 110 °C
Thermal Aux 2 (MSD Transfer Line) Temperature
Setpoint   : 280 °C
Post Run   : 0 °C.

2.5.3   Fourier Transform Infrared (FTIR) Analysis

The infrared spectrum was used to qualitatively determine the functional groups of the bio-oil using a Nicolet IS 10 FTIR Spectrometer with a spectral range of 7800-350 cm-1. One drop of the bio-oil sample was dropped onto the plate of the device and was then pressed using a mechanical device. This pressure was maintained for several minutes, after which the plate was placed in the FTIR sample holder.

2.6   Reaction Kinetics

Reaction kinetics analysis was carried out using the Coats & Redfern equation (1964). This is used to determine the solid degradation rate, which may be written as follows [16]:

$$\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) = \ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT} \qquad \text{(for n = 1)} \qquad (1)$$

$$\ln\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right) = \ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT} \qquad \text{(for } n \neq 1\text{)} \tag{2}$$

Next, the plot relation between $\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right)$ to $\frac{1}{T}$ when n = 1, or $\ln\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right)$ to $\frac{1}{T}$ when n $\neq$ 1, hence forming a straight line with the slope $\frac{-E_a}{R}$ and intercept $\ln\left[\frac{AR}{\beta E_a}\right]$ for correction of n (order). Furthermore, the kinetics can be determined from $k(T) = A.\exp(\frac{-E_a}{RT}))$ [17].

3　　Result and Discussion

3.1　　Microwave Power Effect on the Product Yield

As shown in Figure 2, all temperature curves increased under the various power levels, where the final temperature was 538.15 K, 785.15 K, and 974.15 K at 400 watts, 600 watts, and 800 watts respectively. When the microwave power increased, the heating section had a greater degree of temperature increase. This was due to the higher microwave strength, which makes the interaction between the microwave field and the water molecules of the material more intensive and accelerates the dehydration of the material [18].
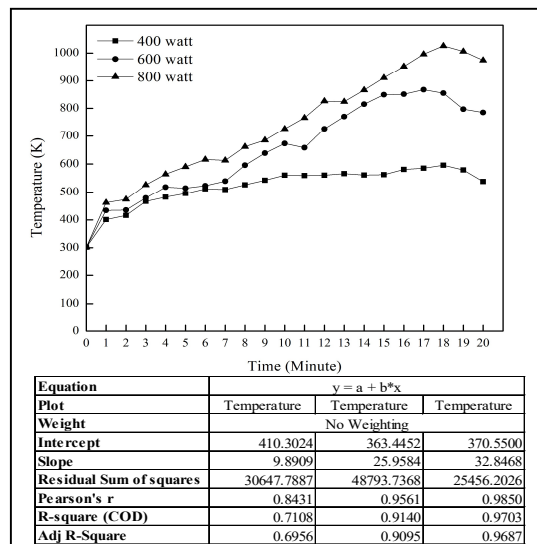

Equation	y = a + b*x		
Plot	Temperature	Temperature	Temperature
Weight	No Weighting		
Intercept	410.3024	363.4452	370.5500
Slope	9.8909	25.9584	32.8468
Residual Sum of squares	30647.7887	48793.7368	25456.2026
Pearson's r	0.8431	0.9561	0.9850
R-square (COD)	0.7108	0.9140	0.9703
Adj R-Square	0.6956	0.9095	0.9687

Figure 2　Temperature profile from various microwave power settings with linear fit analysis.

323

The heating rate for each power setting was obtained from the regression of each line. The heating rate can be defined as $\beta = \frac{dT}{dt}$. The heating rate at each power setting is shown in Table 2.

Table 2 Effect of various microwave power settings on heating rate.

Microwave power (watt)	Line equation	Heating rate, β (K/min)
400	y = 9.8909x + 410.3028	9.8909
600	y = 25.9558x + 389.4010	25.9558
800	y = 32.8468 + 370.5500	32.8458

The relation between pyrolysis power and heating rate is shown in Table 2. This shows that the strength of the microwave can increase the heating rate of the pyrolysis process. However, there was a significant difference in the heating rate between the high-power segment (600 to 800 watts) and the low-power segment (400 to 600 watts), where the increase in heating rate decreased by 83.66%. This is due to the chemical composition and physical structure of *Chlorella* sp. contrary to microwave absorption after pyrolysis at higher microwave power [19]. Similar results were obtained in the study of Li, *et al.* [18], who found that the average heating between the high-power segment (1500 to 2250 watts) and the low-power segment (750 to 1500 watts) decreased by 74.03%. Thus, the range of pyrolysis temperature level increase decreased, which is represented by the heating rate. This shows that increasing the microwave power is not an effective method for achieving ideal pyrolysis temperature levels. The correlation of this statement can be seen in Figure 3, which shows the relationship between microwave power and yield.
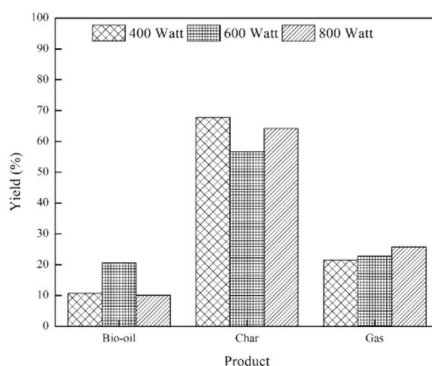

Figure 3 Comparison of all products to yield for various microwave power settings.

Figure 3 shows that an increase in bio-oil yield (wet basis) of 92.24% occurred from 400 to 600 watts with the acquisition of a bio-oil yield (wet basis) of 20.57% at 600 watts. This increase occurs by following the terms mentioned in Li, *et al.* [18], i.e. an *in-situ upgrading* reaction, which causes the steam to decompose the material. The decrease in bio-oil yield (wet basis) that occurred from 600 to 800 watts was 50.75%. Following the previous explanation, with the heating rate increase from 600 watts to 800 watts, the heating rate decreased by 83.66%, which caused the heating of the material to not be optimal. Another reason that can be indicated is that the cracking reaction rate is greater than the rate of polymerization, so the secondary decomposition reaction occurs in the material which causes more uncondensable gas to be produced. However, the char products having fluctuating results is because bio-oil products (wet basis) also go through an increase in the low-power segment while decreasing in the high-power segment, whereas gas products always experience an increase from 400 to 800 watts of power. Menendez, *et al.* (2007) state that higher microwave power easily produces smaller molecules and is advantageous for producing gas [11].

3.1. Reaction kinetics

A second-order reaction was conducted in this study because the R^2 value was higher than zero in the first-order reaction. The model used the Coats & Redfern (1964) method [20-22].
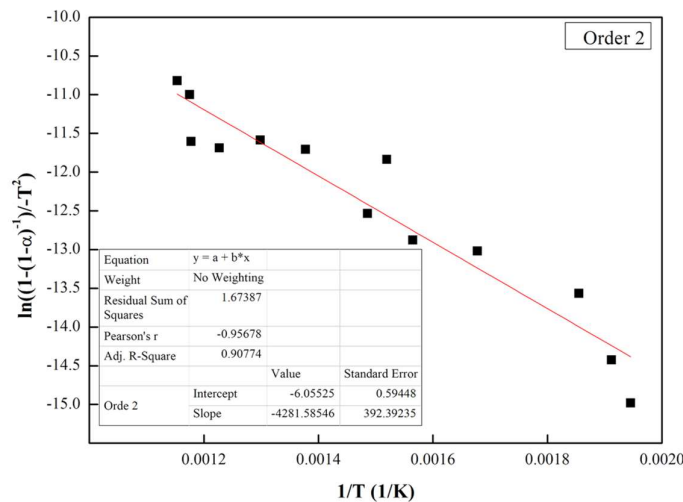

Figure 4 Prediction graph of second-order reaction.

Based on Figure 4, the linear equation with R^2 close to 1 was equal to 0.9077, so the microalgae degradation reaction with the MAP process had a second-order kinetics model. The straight line equation from Figure 4 is y = -4281.5854x – 6.0552, where the slope value can be expressed as $\frac{-E_a}{R}$ and the intercept as $\ln\left[\frac{AR}{\beta E_a}\right]$ to obtain the value of A, the pre-exponential factor, the activation energy (Ea) by using a heating rate, β, of 25.96 K/min and a gas constant, R, of 8.314 J/mol.K. The MAP kinetics model for microalgae *Chlorella* sp. is shown in Table 3.

Table 3 MAP kinetics for *Chlorella* sp.

Slope	Intercept	Ea (kJ/mol)	A (1/min)	K (1/min)
-4281.5854	-6.0552	35.5971	2606.75	$k = 2606.75 exp\dfrac{-4281.5854}{T}$

3.2 Biofuel Characteristic Analysis

3.2.1 Gas Chromatography-Mass Spectroscopy (GC-MS)

Based on GC-MS analysis, the components obtained were categorized as aliphatic compounds (15.66%), aromatics (44.50%), alcohols (7.74%), phenols (5.01%), nitrogenous compounds (8.58%), fatty acid methyl esters (4.34%), polycyclic aromatics hydrocarbons (PAHs) (12.65%), and unidentified (1.52%).

Based on the compounds produced, hydrocarbons are valuable components in bio-oil (wet basis) from the standpoint of fuel application. Broadly speaking, the components contained in the bio-oil (wet basis) based on the GC-MS analysis were in accordance with the postulate pathway reported by Yang, *et al.* [23].

Specifically, the aliphatic compounds formed in this bio-oil (wet basis), both olefins (alkenes), alkanes, ether derivatives, aldehydes as reported in the GC-MS analysis are the result of decarboxylation and deoxygenation and cracking of carbohydrate macromolecules contained, as well as alcohol compounds formed, such as terpineol, which is the result of dehydration from carbohydrates.

In addition, aromatic hydrocarbons that can function as industrial chemicals and can also be used as transportation fuel additives to increase the octane value are formed from the cyclization process of olefin compounds formed. 5.01% phenol compounds can be formed from the lipid content that is hydrolyzed so it splits and forms hydrocarbon compounds. Meanwhile, 4.34% of fatty acid methyl ester (FAME) is formed from lipid rupture, which has a large enough TGA content. Based on reports from Yang, *et al.* [23], the results of the pyrolysis of microalgae will produce fatty acid compounds resulting from the hydrolysis of triglycerides. However, the GC-MS results in this study revealed the production of FAME. This

is because in the bio-oil content (wet basis) there is an alcohol content that when it comes in contact with fatty acids will experience an esterification reaction and form a methyl ester compound.

Compounds resulting from protein cracking and the Maillard reaction were also formed, such as benzenopropanenitrile, indole, and quinoline. Thus, the brown color of the product can be explained by the compound content in connection with the presence of the element nitrogen (N), which is present in microalgae bio-oil (wet basis), mainly derived from amino acids [24]. In addition, 12.65% of PAH was also detected. This is because liquid product compositions are so complex, further enhancements, such as denitrogenation and deoxygenation, are needed to make bio-oil (wet basis) suitable for use as engine fuel [2].

3.2.2 Fourier Transform Infrared (FTIR)

Figure 5 shows the FTIR spectrum of the bio-oil (wet basis) from *Chlorella* sp. With the use of 600 watts of microwave power, the ratio of microwave absorber to microalgae was 1:6 at 10, 15, and 20 minutes of pyrolysis time. It is important to be analyze this at various pyrolysis times so that changes in the spectrum of each pyrolysis time can be seen, so that the pyrolysis process, which includes cracking, deoxygenation, decarboxylation, and deoxygenation [23], can be described by the parameters of this study based on the pyrolysis time used. Based on the figure it can be seen that from the 10th to the 20th minute there was degradation of the microalgae *Chlorella* sp. as evidenced by the difference between the graphs. Based on the FTIR graph, the functional groups formed were as follows.
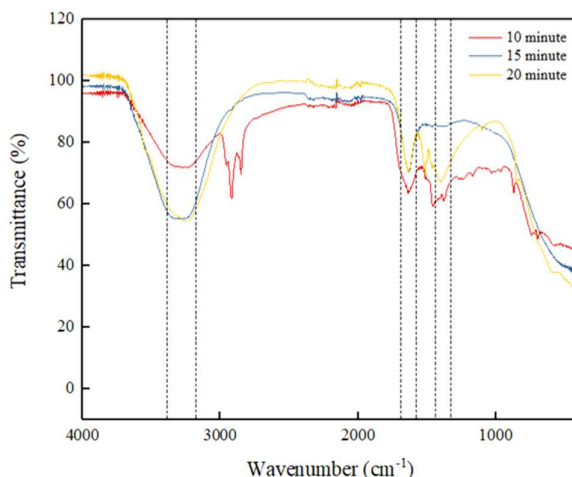

Figure 5 FTIR graph of *Chlorella* sp. bio-oil.

Table 4 FTIR functional groups of *Chlorella* sp. bio-oil [25].

Wavenumber (cm^{-1})	Functional groups	Compound
3600-3200	O-H stretching	Phenol, Alcohol
3600-3200	N-H stretching	Amine
1680-1575	C=C stretching	Alkenes
1550-1490	C=C stretching	Aromatics
1550-1490	N-H bending	Amide
1470-1325	C-H bending	Alkenes

 Based on Table 4, the functional groups contained in bio-oil (wet basis) included phenols, amine and amide compounds, aromatic compounds, alkenes, alkyne, protein, carbohydrate, etc.

3.3   Physicochemical Characteristics Analysis

The following is a comparative analysis from the physicochemical characteristics analysis of bio-oil (wet basis) from other reports using the same process (MAP).

Table 5   Physicochemical properties of bio-oil.

Characteristic	This work	*Chlorella sp* [2]	Microalgae *bio-oil (wet basis)* [12]	Lignocellulosic biomass [21]	Conventional pyrolysis of *bio-oil (wet basis)* [21]	Diesel Fuel
Density (gr/mL)	1.01	0,98	0.98-1.20	1.15	1.2	0.83
Viscosity 40°C(cP)	10.97	11	6-11	-	-	-
pH	9,30	9,33	9.30-9.90	2.50	2.5	-
HHV (MJ/kg)	43	30,70	26-42	15	16-19	43

In Table 5, the physicochemical properties of bio-oil (wet basis) in this study are shown and compared with values from the literature. The data shows that the HHV of the bio-oil (wet basis) in this study was 43 MJ/kg. This is higher than the bio-oil (wet basis) obtained in the study Du, *et al.* [2], who used microalgae with the same type and method, and higher than bio-oil (wet basis) obtained with conventional methods with the same heating value as diesel fuel. Hence, it can be said that the bio-oil (wet basis) in this study was better than that from previous studies based on the heating value (higher heating value). This is advantageous for making the combustion from the bio-oil (wet base) run perfectly. The viscosity of bio-oil (wet basis) depends on the water content and its chemical composition. If pyrolytic water is separated, the viscosity is around 79 to 100 cP. If water is not removed from the pyrolytic liquid, the viscosity is around 6 to 11 cP [23]. Therefore, it can be concluded that water content was still present in the bio-oil (wet basis) of this study. The pH of bio-oil microalgae is in the range of

9.3 to 9.9, which is significantly different from bio-oil from lignocellulosic biomass.

4   Conclusion

MAP has very significant potential to be developed as a process for producing biofuels from microalgae *Chlorella* sp. (dry weight) with the help of activated carbon as microwave absorber because it can save time and energy. The best bio-oil yield was obtained with the use of 600 watts with a heating rate increase of 20.57% (ratio 1:6 and pyrolysis time 20 min) and a heating rate of 25.96 K/min (600 watts).

The reaction kinetics for the best condition in this study showed a second-order reaction with activation energy (Ea) and pre-exponential factor (A) at 35.5971 kJ/moles and 2,606.75/minute, respectively. The characteristics of the biofuel produced were the characteristics of bio-oil with the following organic compounds contained: aliphatic, aromatic, phenol, FAME, and polycyclic aromatic hydrocarbons (PAHs) compounds. Meanwhile, the physicochemical characteristics of the bio-oil were density, viscosity, and pH of 1.01 gr/mL, 10.97 cP, and 9.30, respectively.

Nomenclature

MAP	Microwave-assisted pyrolysis	β,	Heating rate, K/min
A,	Pre-exponential factor, min^{-1}	α,	Material fraction
W_o,	Initial mass of microalgae, gram	**Ea**	Activation energy, J/mol.K
W_f,	Final mass, gram	**R**	Gas constant, 8.314 J/mol.K
W_t,	Mass after t min, gram	**t**	Pyrolysis time, min
T	Temperature, K	**n**	Order reaction
K	Kinetic model		

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