Bio-oil synthesis from *Botryococcus braunii* by microwave-assisted pyrolysis

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OBJECTIVES Microalgae have proven to be a promising resource in renewable energy search; Products such as bio-oils could contribute to the replacement of petroleum. The objective of this investigation is to determine the decomposition mechanism, obtain the kinetic reaction, as well as evaluate the potential to obtain microalgae bio-oil through microwave-assisted pyrolysis (MAP). MAP is a new thermochemical conversion from biomass to bio-oil that is faster, efficient, controllable, and flexible, compared to conventional pyrolysis, rapid pyrolysis, or instant pyrolysis. As raw material in this experiment, Indonesian microalgae, *Botryococcus braunii* was used.

METHODS The investigation focused on the temperature effect (100–300 °C) and the residence time (10-30 min); a modified microwave oven was used with a power of 900 W. Hexane was used for the extraction of bio-oil. The bio-oil composition was measured with gas chromatography of mass spectrometry (GC-MS) and then this data was used to evaluate a kinetic model and calculate the constant kinetic reaction of the pyrolysis process.

RESULTS The results indicated that bio-oil production begins from 100 °C, however, temperatures between 200–250 °C favor the production of bio-oil, while temperatures above 250 °C and the long residence time prioritize the production of bio-gas. Regarding the kinetic evaluation, the reactions seem to show from third to sixth order with an activation energy (E) of around 30 kJ/mol and a pre-exponential factor (lnA) of around 9 s⁻¹.

CONCLUSIONS Based on GC-MS Analysis, the bio-oil contains short chain alkanes, cycloalkanes, organic acids as well as aromatic, phenol, benzene compounds. On the other hand, although small amounts of oil were achieved, the decomposition of biomass was up to 50% favoring gas production, these results indicate that MAP has potential in the obtaining of biofuels such as bio-gas and bio-oil.

KEYWORDS biofuel; bio-oil; microalgae; microwave; pyrolysis

1. INTRODUCTION

The cultivation of microalgae presents an alternative to the future, the development of new technologies will allow the reduction of costs in the production of biofuels, it should be noted that microalgae are the main CO₂ capacity to convert it into biomass, as well as composition of the microalgae allows the choice not only of microalgae but also of other products of interest, such as pigments and proteins (Demirbas 2010). The main constituents of microalgae remain carbohydrates, proteins, and lipids but their proportion varies greatly with the type of microalgae, nutrients, and culture conditions such as light, salinity, pH, aeration, and temperature. *Botryococcus braunii* (*B. braunii*), a green microalgae, is a rich source of renewable hydrocarbons. It has attracted much attention for its potential to generate biofuels (Ali et al. 2018). *B. braunii* is characterized by unusually high hydrocarbon content, reported to reach up to 75% of the dry weight of the cell (Banerjee et al. 2002). Hydrocarbons obtained from microalgae by extraction are converted to hydrocarbons with lower degrees of unsaturation and shorter chain lengths, due to their suitability as a liquid fuel. This process is normally carried out by pyrolysis; A thermochemical process by which hydrocarbons are converted into oil more easily extractable by thermal cracking. Pyrolysis is receiving a lot of attention as a process of choice to convert algae biomass to biofuels. It is a complex conversion process that is highly influenced by composition, properties, and operating conditions. Pyrolysis is a promising and inexpensive way to extract energy from microalgae because it is difficult to recover all the oil from its intracellular structure. This process involves the thermochemical decomposition of organic structures in an inert atmosphere, in non-condensable gases, condensable liquids and solid residues, which may be in the presence or absence of a catalyst. Pyrolysis generally involves three important steps including (a) removal of moisture, (b) organic decomposition structures, (c) and slow disintegration of residual solids (Ali

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et al. 2018).

Emphasizing the pyrolysis process, microalgae biomass can be converted to biofuel by taking advantage of its full composition without using expensive equipment and technologies. Pyrolysis is the decomposition of organic matter to more basic components through high temperatures in the absence of oxygen (Lee et al. 2019). The pyrolysis typically refers to a process by which the biomass is thermally degraded at moderate temperatures (350–700 °C in absence of oxygen. It produces solid, liquid, and gaseous products. These products are interesting, as they are likely alternate sources of energy and/or chemicals. Therefore, the study of pyrolysis has been gaining increasing importance. (Marcilla et al. 2013).

Microwave-assisted pyrolysis (MAP) is a relatively new technique that has been developed and investigated in recent decades. This process offers several advantages over traditional processes, including uniform internal heating of large biomass particles, ease control, and no need for agitation or fluidization, and hence less particles (ashes) in the bio-oil. Investigated the microwave-assisted pyrolysis of Chlorella vulgaris under different microwave power levels, catalysts and contents of activated carbon and solid residue. In this study, the microwave power of 1500 W and 2250 W were found to be optimal for obtaining the maximum bio-oil yield of 35.83% and the maximum bio-fuel yield of 74.93%, respectively. The research indicated that the maximum temperature rising rate and pyrolysis temperature became higher as the microwave power increased. Furthermore, it has been shown that the pyrolysis reaction can be handed by mixing C. vulgaris with catalysts. Under this study, activated carbon exhibited the best catalysis action followed by the solid residue (Marcilla et al. 2013).

In pyrolysis the main objective is to decompose matter through thermal energy, the difference of microwave-assisted pyrolysis compared to conventional pyrolysis is that microwave heating occurs through the transfer of electromagnetic energy to thermal energy. In addition of some advantages that are presented is the ability of the electromagnetic waves to penetrate the material and store it in the volume of the sample, which eventually results in the generation of heat throughout the volume. Due to this the distribution of heat is uniform and faster compared to conventional pyrolysis. This presents another pair of advantages such as requiring a shorter residence time, lower temperatures and greater selectivity since a uniform heat distribution prioritizes the main decomposition reaction, preventing secondary reactions, which means greater control in the process (Zhao et al. 2012). Microwaves have been applied to various pyrolytic biomass materials in recent years and the results showed that microwave pyrolysis could generate higher quality products compared to conventional heating (Dong and Xiong 2014).

Microwaves are electromagnetic waves with frequencies between 300 MHz and 300 GHz, and therefore the corresponding wave lengths are between 1 mm and 1 m. Microwave heating includes two mechanisms: one is dipole rotation, and the other is migration ion. Both can heat materials quickly and evenly. Microwave heating is also selective and energetic (Huang et al. 2013). Regarding the mechanism of action, the sample is placed inside the microwave where after a short time (about one minute) it begins to heat up (Huang et al. 2013). This is since at first the material of the sample absorbs the radiation and after that it absorbs enough radiation. It is converted into thermal energy, which translates into an increase in the temperature of the sample. Variables to be considered are the maximum temperature and the maximum heating speed which depend on the microwave power level, which will be detailed later.

Finally, regarding the reaction mechanism, the Brodoo-Shafizadeh model (Bradbury et al. 1979) can be considered. There are 2 main stages, the first one is where the volatile non-condensable, volatile condensable and intermediate solids are generated, and the second one is where the intermediate solids are decomposed into volatile non-condensable and solid residues. The microwave power levels are generally 200–500 W. Power levels of the 200 W type favor the production of liquids by decreasing gasification in the first stage, while at higher microwave power levels of the 500 W type, the intermediate solid would undergo gasification to produce more gases. Regarding the kinetic analysis, the thermogravimetric analysis (TGA) and the use of the Arrhenius equation are necessary.

In pyrolysis and roasting, maximum temperature, residence time, and biomass composition (biomass type) are the most varied parameters in an experimental montage. However, when using microwave (MW) heating other parameters such as MW power, reaction time, heating rate and type of absorber must be considered. The MW power is important because the general performance (solids, liquids, and non-condensing gases) and the maximum temperature depend on it. According to roasting studies using wood biomass, a fixed temperature (200 °C) and various MW power levels (600, 900, 1200 W). They discovered that the MW power level influences the product yields, the characteristics of the roasted solid biomass, the biofuel compounds, and the composition of the derived gas. Likewise, the MW power level is directly proportional to the heating rate. Furthermore, it was observed that the coal yield decreased with an increase in the MW power level. Methane (CH₄) was obtained at a low reaction temperature and a high level of MW power. An increase in MW power level caused a decrease in both C / H and C / O ratios (Wu et al. 2014).

According to other studies on the influence of the MW power level on the heating rate and the maximum temperature. Regardless of biomass type, higher MW power levels resulted in higher heating rates, which led to higher maximum temperatures, higher temperatures can be counter-productive to biomass properties by generating secondary cracks (pyrolysis). Due to this, several authors recommend MW power levels between 150 and 300 W, which generates a low heating rate, which takes a heating rate of less than 50 °C / min (Huang et al. 2012; Satpathy et al. 2014; Wang et al. 2012).

Microwave-assisted pyrolysis applies electromagnetic waves to interact with matters (Lin et al. 2017). Which is volumetric and instantaneous. Therefore, biomass can be instantaneously heated to the desired temperature, with more energy efficient and less secondary reaction than conventional heating and fast microwave-assisted pyrolysis technology has been applied to produce biofuels successfully (Bundhoo 2018). Figure 1 shows the process flowchart of the microwave pyrolysis.

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In this work, the pyrolysis kinetics of B. braunii subjected to microwaves were studied considering the influence of the heating rate and temperature. The kinetic parameters of *Botryococcus b* pyrolysis were determined. Based on the dominant reaction region, including activation energy, reaction order, and frequency factor. These data can be useful both for the design and optimization of reactors and for a greater utilization of the biomass resources of microalgae *Botryococcus b*. The use of MAP is a recent process, so there is little research on it compared to other pyrolysis processes. Likewise, the use of microalgae is also recent compared to other biomasses.

### 2. RESEARCH-METHODOLOGY

#### 2.1 Materials

Microalgae flour with *Botryococcus braunii* species. Obtained from BPBAP (Balai Brackish Aquaculture and Fisheries) Situbondo, East Java. Was used as biomass feedstock in this experiment, the biomass contained 17% of moisture. A thermal gravimetric analysis was used to determine the proximate and ultimate analysis of the biomass. Nitrogen gas (N$_2$) obtained from PT. Industrial gas Samator, Yogyakarta. Granular activated carbon as absorber from CV Progo Mulyo Store. N-hexane with 99.8% content produced by Merck.

#### 2.2 Experimental apparatus and procedures

The pyrolysis experiments were conducted in Electrolux type microwave with an output power of 900 watts and a capacity of 2.5 liters, in the microwave there is a reactor that measures a liter, and a ball cooler of 3 cm in diameter and 50 cm of height, magnetic stirrer and controller to control the temperature and speed of agitation. The equipment is shown in Figure 2. The test was carried under N$_2$ atmosphere with a flow rate of 200 ml/min. About 10 g of biomass was used in each experiment. The sample was mixed in a ratio 1:3 with activate carbon, the activated carbon was previously heated to 200 °C per 20 min to eliminate the moisture present on it.

The temperature is a key parameter used in kinetic analysis to calculate activation energy. However, accurate temperature measurement is very difficult under microwave field because of the non-uniform distribution of electric field intensity. In this study, the sample was heated from room temperature to 100, 150, 200, 250 and 300 °C for a heating time about 10, 20 and 30 min. The temperature and weight data are automatically collected and recorded by the data acquisition system during the experiments. All experiments were carried out in triplicate.

To extract the bio-oil it is necessary to use a solvent to separate the solid waste from the bio-oil, for this purpose it is mixed with hexane in a certain proportion (3:1), mixed by means of a magnetic stirrer and a temperature of about 40 °C, for about 1 hour. After mixing with the n-hexane, the hexane together with the bio-oil is in the upper layer of the mixture and is separated from the mixture with the help of a volume pipette. From this process, bio-oil will be extracted in n-hexane.

After the extraction process, a mixture of hexane and bio-oil is obtained, the hexane being more volatile allows the separation of the mixture by distillation, the mixture is heated and the hexane evaporates from of the mixture, resulting in the bio-oil, hexane is collected to be reused.

After the extraction of the bio-oil, there is a mixture between solid residues and an organic polar and insoluble aqueous phase in hexane. To separate them it is necessary to filter the aqueous phase by means of filter paper assisted by a vacuum pump.

The resulting residual solids are wet, so it is required to dry them in an oven at a temperature of 105 °C to obtain the dry weight of the residual solids. To measure the ash content it is necessary to burn the dry solid in an oven to more than 700 °C. The resulting ash is weighed after cooling in a desiccator.

#### 2.3 Kinetics model of microwave pyrolysis

Pyrolysis of biomass can be modeled according to Arrhenius equation for solid state described as:

![Flowchart microwave-assisted biomass pyrolysis process.](image1)

![Microwave assisted extraction device.](image2)
\[
\frac{da}{dt} = k(T) \cdot f(\alpha) = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (1)
\]

Where A was pre-exponential factor(s⁻¹). E was the activation energy (J mol⁻¹). R was the universal gas constant (8.314 J mol⁻¹ K⁻¹). t was the duration time of reaction (min). \(T\) was absolute temperature; and \(\alpha\) was conversion degree, which can be identified by:

\[
\alpha = \frac{m_0 - m_f}{m_0 - m_e} \quad (2)
\]

Where: \(m_0\) and \(m_e\) was the initial and final mass of the sample respectively. \(m_f\) was the mass of sample at a given time.

Considering heating rate \(\beta\) as:

\[
\beta = \frac{dT}{dt} \quad (3)
\]

Combining the heating rate Eq. 3 with the rate of reaction Eq 1 we can get:

\[
\beta \frac{da}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (4)
\]

Now it is necessary determine the function of conversion degree \(f(\alpha)\) this is normally expressed as:

\[
f(\alpha) = (1 - \alpha)^n \quad (5)
\]

Where \(n\) is the reaction order

Replacing the function of conversion Eq. 5 degree in the Eq. 4

\[
\frac{da}{dt} = \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1 - \alpha)^n \quad (6)
\]

Eq. 6 is the elementary expression for calculating kinetic parameter based on the TGA data, integrating the Eq. 6 as follow

\[
f_0^{a} \frac{da}{1 - \alpha)^n} = \int_{T_0}^{T} \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) \quad (7)
\]

Using as integration limits the conversion degree and initial time and the corresponding temperature, also the conversion degree in determinate time and a determinate Temperature for that time. Integrating both sides we can get a logarithmic expression as follow:

\[
\ln\left[-\ln\left(1 - \frac{a}{T^2}\right)\right] = \ln\left[A \cdot \frac{R}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}; \text{for } n = 1 \quad (8)
\]

And

\[
\ln\left[\frac{1 - \left(1 - \frac{a}{T^2}\right)^n}{T(1 - \frac{a}{T^2})}\right] = \ln\left[A \cdot \frac{R}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}; \text{for } n \neq 1 \quad (9)
\]

Because 2RT/E ≪ 1, Eq 7 and Eq 8 can be simplify as:

\[
\ln\left[-\ln\left(1 - \frac{a}{T^2}\right)\right] = \ln\left[A \cdot \frac{R}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}; \text{for } n = 1 \quad (10)
\]

And

\[
\ln\left[\frac{1 - \left(1 - \frac{a}{T^2}\right)^n}{T(1 - \frac{a}{T^2})}\right] = \ln\left[A \cdot \frac{R}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}; \text{for } n \neq 1 \quad (11)
\]

Considering the left term as \(y\) and 1/T as \(x\) and making a plot of \(y\) against \(x\), should result in a straight line with slope (-E/R) and intercept \(\ln(AR/\beta E)\) for the correct value of \(n\). The kinetic parameters were determined by combining iterative and the least squares method.

2.4 Products analysis

The weight of the bio-oil obtained, the chart and the aqueous phase is measured, characteristics of the bio-oil were analyzed by Gas chromatography – mass spectrometry (GC-MC).

3. RESULT AND DISCUSSION

3.1 Performance of microwave heating

The activated carbon as absorbent was efficiently heated by the microwave radiation, the biomass mixed with activated carbon can easily reach the targeted temperature. On the other hand, carrying the experiment without material absorbed isn’t a good option because the biomass of microalgae did not absorb enough microwave, so in the target time it does not reach the desired temperatures. Low temperature pyrolysis is considered, so the samples will only be heated from 100 to 300 °C, after determining the heating rate, the pre-exponential factor \(A\) and the activation energy \(E\) can be calculated. Figure 3 Shows the heating rate in the microwave pyrolysis, It can be seen that the heating rate is not uniform, in the figure it reaches about 150 °C in the first 2 minutes, which would be mathematically equivalent to about 60 °C/min, then it maintains a uniform heating rate for 14 minutes reaching 290 °C, which is equivalent to a heating rate of 10 °C/min, and finally reaches almost uniform behavior, reaching 300 °C in the following 4 minutes. It can be concluded that the heating rate is variable, however the heating rate depends on the dielectric properties of the sample, the average electric field value in the oven and the surface cooling rate. After heating, the humidity decreases and the pyrolysis changes the composition of the sample, so the heating rate varies throughout the time that the pyrolysis lasts, however, for purposes of calculating the kinetics, a constant heating rate can be considered. Although the predominant heating rate is around 10 °C/min, considering that it takes 15 minutes to reach 280 °C, the heating rate could be considered approximately 15 °C/min

3.2 Microwave pyrolysis biomass from Botryococcus braunii

The efficiency of biomass pyrolysis under microwave irradiation depends mainly on its dielectric property, this is determined according to its chemical composition (Fernandez et al. 2011). Generally, biomass material has poor dielectric properties, therefore an absorbent material is necessary
to carry out the experiment (Adam 2017). In this study microwave pyrolysis of biomass of Botryococcus was carried out at an input power of 900 W and an approximate heating rate of 15 °C/min. Accordingly, the pyrolysis of B. braunii underwent a moisture evaporation process below about 100 °C, and a quick thermal decomposition process was observed in the first 5 minutes with an average heating rate of about 40 °C/min, followed by a slow weight loss process until the end of the heating. The differences created were probably due to the thermal effects of microwaves. Hotspot is a thermal effect in heterogeneous reactions that can be generated by the non-uniform distribution of the electromagnetic field or the selective heating of microwaves for the conversion of solid to vapor (de la Hoz et al. 2005). Considering the high ash content, at temperatures greater than 200 °C and times between 10 and 20 min, a thermal decomposition between 70 and 80% is achieved.

3.3 Product distribution

After microwave pyrolysis of B. braunii, the distribution of product was shown in the Table 2. Was consider the distribution for a residence time of 30 min. The yield of biochar continuous decrease with temperature to 50%, also considering that the minimum yield of biochar is determined by the high content of ash, for that biochar would be always high of around 50% for this kind of biomass. Although certain components were extracted in the liquid phase, the water evaporated and escaped in the form of gas, likewise possibly a better condensation system would better recover the liquid phase and the oily phase, the proposed experimental setup then fails in the recovery of water and condensable volatile compounds, apparently the exchanger used is not efficient enough to recover these compounds, hence the bio-oil obtained is less than 1% and the gas phase ranges from 25 to 50%. However, despite this, the thermal decomposition can be estimated so that the kinetics of the pyrolysis can be determined. It can also be seen that high temperatures are not needed to achieve thermal decomposition and bio-oil and gas phase can be obtained from 100 °C, even at 300 °C, the process is optimal, achieving a decomposition of almost 90%.

3.4 Kinetics parameters

The experiment presented linear dependence between the values of ln A and E. Different n values were used to calculate the kinetic values of A and E. The high linearity (R2 over 0.90) suggested the existence of kinetic compensation effect. A heat rate of 15 °C/min were consider. The table 3 showed the calculated kinetic parameter for microwave pyrolysis were rational to a certain extend. Different values of n were used to adjust the equation, values less than 1 do not show linear behavior, values above 2 begin to show linear behavior, after these different values were considered values above 2 where the linear behavior was maintained until those values where the intercept remained negative, since positive intercept values generate exorbitant values of A due to the exponential factor. Therefore, in the end, reaction orders of 6, 5 and 3 were considered for times of 10, 20 and 30 min, respectively. Finally, both the values of E and ln A remain in the same order, with 30 kJ/mol for E and around 9 s⁻¹ for ln A.

3.5 Product analysis

In general, bio-oil is composed of different components depending mainly on the composition of the raw material used, the main compounds that can be found are aliphatic hydrocarbons, aromatic hydrocarbon, phenols, among others. The results of GC-MS are shown in the table 4, an analysis was carried out on the bio-oil obtained at temperatures of 100, 150 and 200 °C, compounds such as alkanes with chains of 6 to 34 carbons with predominance of hydrocarbons from 10 to...
28 carbons, cycloalkanes with a predominance of cyclohexanes, organic acids, fatty alcohols as well as phenolic and benzene compounds. With increasing temperature compounds such as alkanes, fatty acids and benzoic compounds increase, while cycloalkanes and organic acids decrease, this may be since these compounds break down into simpler compounds such as alkanes.

4. CONCLUSION

MAP shows a promising future, in addition to the use of microalgae such as *Botryococcus braunii*. Together with activated carbon as absorbent material, it presents a high degree of degradation, which translates into conversion of biomass into fuels such as bio-oil and bio-gas. In this work, the kinetics of pyrolysis of *B. braunii* were investigated using microwave-assisted pyrolysis. The results indicated that the heating rate had a significant effect on the biomass pyrolysis process, a heating rate of 15 °C/min (900 W) was used, obtaining decomposition values close to 50%.

The reaction kinetics obtained in the investigation showed reactions from order 3 to order 6, with activation energy (E) and pre-exponential factor (ln A) of approximately 30 kJ/mol and 9/sec. respectively. The value of the activation energy also validates the simplifications made in Eq 8 and 9.

The composition of the bio-oil produced includes organic compounds such as: alkanes with chains of 6 to 34 carbons with predominance of hydrocarbons from 10 to 28 carbons, cycloalkanes as cyclohexanes, organic acids, fatty alcohols as well as phenolic and benzene compounds.

The gaseous product increased with increasing temperature, they were obtained at high microwave power levels (900 W) but at moderate temperatures (200-300 °C), it could be considered that microwave-assisted pyrolysis does not require high temperatures or high residence time. However, there is still a need to use an absorbing agent to improve the heat capacities of the sample.

The decomposition of biomass to simpler compounds is appreciable in the GC-MS analysis of bio-oil, where with increasing temperature compounds such as simple alkanes increase their percentage, as well as phenolic compounds, along with organic acids they are decomposed.

5. RECOMMENDATION

In this case the biomass has a high ash concentration so it could affect the expected results, a good option would be to look for a higher quality microalgae biomass with lower ash concentrations, as well as consider other dielectric materials such as silicon carbide (SiC) that although they are more expensive, they guarantee a better distribution and absorption of radiation, in addition, although short residence time are required, the use of a catalyst could help to carry out the experiment in shorter residence time. Another consideration is the use of microwave power less than 900 W, since this value, although it improves biomass decomposition, produces more gaseous products than bio-oil. Finally, improving the experimental setup to better condense the volatile components, including collecting these in addition to other heat exchangers, could increase the amount of bio-oil, or possibly focus the experiment on obtaining biogas could give better results, since the low energy of activation allows easy decomposition of biomass.

REFERENCES


