Microwave-assisted Pyrolysis of Microalgae in Producing Bio-oil using CaO catalyst and Charcoal as heat Absorber

L Qadariyah¹, V Aswie¹, H V Widjaya¹, K H Aditya¹, M Mahfud¹, *
¹Chemical Engineering Department, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia
*
E-mail: mahfud@chem-eng.its.ac.id

Abstract. In the microwave-assisted pyrolysis process the solid material to be cracked requires an absorber material to capture microwaves to be converted into heat as a heat source and a catalyst to accelerate the pyrolysis process. This research is focused on studying the use of a potential heat absorber, namely coconut shell charcoal and CaO as catalyst in the microwave-assisted pyrolysis process in converting microalgae (dry Chlorella sp) into bio-oil. The round boiling flask as a reactor is placed in a microwave oven, equipped with a condenser and a vacuum pump. The operating variables were microwave power, pyrolysis time and catalyst ratio to microalgae. The products obtained consisted of 3 phases, namely solid residue (char), liquid product (bio-oil) and gas products. The results show that microwave power, pyrolysis time, and ratio of catalyst to microalgae using shell charcoal absorbent can provide an increase in product yield. The optimum yield is 20.57% of bio-oil obtained when the microwave power is 600 watts, 20 minutes, and CaO catalyst of 1 gram and ratio absorber to microalgae 1/6. The use of a mixture of catalyst and absorber improve the performance of pyrolysis in producing bio-oil from microalgae using microwave-assisted pyrolysis technology.

1. Introduction
Microalgae are believed to be one of the most promising alternative sources for producing third generation biofuels [1]. This is because the source does not have the shortcomings of previous generations of biofuels. This source is a potential alternative raw material for large scale biofuel production without disturbing the environment. So, they can overcome the weaknesses presented by the first and second generations [2]. The growth rate is much higher than that of other resource biofuels, thus affecting greater production [3]. In fact, their growth does not even require land areas with fertile soil, and does not overlap with the food sector [2]. The production costs and the final cost efficiency of this product are high and low, respectively [4]. Hence the use of microalgae has developed into biofuels through the conversion methods as reported by several reports.

One such conversion method is a thermochemical conversion. Thermochemical routes to convert biomass can be categorized into combustion [5,6], gasification [7,8], liquefaction [9,10] and pyrolysis [11–14]. Based on all of these conversions, pyrolysis (thermal degradation of the material without oxygen during process) can take place at a temperature range of 400 to 600°C and followed by direct condensation of the formed steam is a promising and cost-effective method, which plays an important role in biomass conversion [1]. In addition, pyrolysis (a method of thermochemical conversion) is a relatively new approach to conversion of biofuels. Although it still requires more steps to become a fuel, this approach is easy, fast and efficient to be applied in producing bio-oil (the main ingredient of biofuel). Biomass products from pyrolysis conversion can produce solid (char), liquid (bio-oil) and gaseous fuel [15].
As a heating medium, the currently developing and promising heating technology is microwave technology. This is because it can increase and speed up chemical reactions. When compared with conventional pyrolysis, microwave-assisted pyrolysis has several advantages including high heating efficiency, reduced residence time, and easy control of the pyrolysis process [8]. Zainan et al. (2018) reported the effect of catalysts and non-catalysts on the bio-oil production from microalgae *Chlorella vulgaris* through a pyrolysis process using a fixed bed reactor at a temperature of 300-600°C and variations in the ratio of catalysts to algae 5:1.2; 1.1; 1. The results of catalytic pyrolysis are more promising for converting microalgae into bio-oil. The optimal pyrolysis temperature for catalytic and non-catalytic pyrolysis is 500°C [16]. Pan et al. (2010) also reported that the pyrolysis of the residues of *Nannochloropsis sp.* with and without the HZSM-5 catalyst to produce bio-oil. Based on the data, it shows that the use of a catalyst provides more aromatic hydrocarbons than noncatalytic pyrolysis [13]. Although it can produce bio-oil, some reports claim that biomass (especially microalgae) is a bad absorber of microwaves, mixing it with a microwave absorption enhancer will increase biomass heating. Therefore, mixing raw material with a heat absorber can increase the material’s ability to absorb effectively [8,17,18]. Thus, further investigation into the effectiveness of mixing heat absorber with catalysts in producing bio-oil as a raw material in the production of biofuels is needed.

It is important to study the effectiveness of this mixture because a higher ratio of absorber, catalyst and biomass will lead to higher consumption of microwave energy which makes this method inefficient. Therefore, this study focuses on investigating the ratio of the amount of heat absorber with a mixture of catalysts and microalgae biomass to the pyrolysis time and microwave power used in producing bio-oil as a feedstock for biofuel production through the microwave-assisted pyrolysis method.

### 2. Materials and Methods

#### 2.1. Materials

*Chlorella sp.* (dry microalgae) was obtained from the Centre for Brackish Water Cultivation Situbondo regency, East Java. Based on the proximate analysis carried out (Analyzed by the Forage Laboratory, Department Animal Husbandry, Faculty of Veterinary Medicine, Airlangga University Surabaya) the results of the content analysis of the microalgae *Chlorella sp.* as follows.

| Component      | Analysis result % |
|----------------|-------------------|
| Ash            | 53.078            |
| Protein        | 12.129            |
| Lipid          | 12.414            |
| Rough fiber    | 0.141             |
| Carbohydrate   | 19.495            |
| Calorie (Kcal/Kg) | 1398.982       |
| Water content  | 3.614             |

In addition, the catalyst and heat absorber used in this study were solid calcium oxide (CaO) and charcoal in the form of granules, respectively.

#### 2.2. Experimental device

Microwave-assisted pyrolysis was conducted using a microwave with the Electrolux Model brand, EMM2007X, type MM820AYC-PA0C with a frequency and power of 2450 Hz and 1,250 Watt, respectively. The microwave heating rate is 2.3584°C/minute and categorized as slow pyrolysis.

#### 2.3. Experimental procedure

In producing biofuel from the microalgae *Chlorella sp.* using microwave-assisted pyrolysis process, the first step taken is assembling a microwave-assisted pyrolysis device. The second, 30 grams of
microalgae are mixed with an absorber (1/8; 1/6 and ¼ of Chlorella sp. mass) and CaO catalyst (0 and 1 gram) into a round bottom flask and the mixture was homogenized by shaking it for 1 minute. Then, the round bottom flask is installed into the microwave making sure there is no airflow. After that, the vacuum pump was turned on for 10 minutes so that there was no oxygen in the assembly during the process. After the time was reached and the water flow has been flowed to the condenser, then the microwave was turned on by adjusting the power and pyrolysis time of 600 watts and 20 minutes, respectively. During the process, 3 products will be formed, namely liquid product (bio-oil), solid product (char), and non-condensed gas (gas fuel). All products were weighed and the results calculated. Finally, all procedures were repeated with other variables until the best results were obtained.

2.4. Yield analysis
The mass percentage of the composition of the product formed can be calculated to obtain% conversion (liquid, gas and char) according to the following formula.

2.4.1. Liquid product (bio-oil)*

\[
\% \text{Yield char} = \frac{\text{Char mass (solid residue)}}{\text{Microalgae mass}} \times 100\%
\]  

*(The bio-oil yield calculation still contains water from the pyrolysis process (wet basis)

2.4.2. Solid product (char)

\[
\% \text{Yield char} = \frac{\text{Char mass (solid residue)}}{\text{Microalgae mass}} \times 100\%
\]

2.4.3. Gas product

\[
\% \text{Yield gas} = 100\% - (\% \text{Yield bio-oil} + \% \text{Yield char})
\]

2.5. Physicochemical characteristic analysis
Physicochemical analysis includes analysis of density, viscosity, pH and higher heating value (HHV) of bio-oil (wet basis) was according to:

2.5.1. Density

\[
\rho = \frac{\text{mass (gr)}}{\text{volume (ml)}}
\]

2.5.2. Viscosity
The viscosity was analyzed using Ostwald viscometer guided by ASTM D-7279 by immersing the viscometer in a water bath at 40°C and the bio-oil sample inserted into it. This experiment was carried out 3 times. The viscometer equation was given as follows :

\[
\eta = t \times k
\]

where: \( \eta \) = viscosity (cSt)  
\( t \) = Time required sample from a to b (seconds)  
\( k \) = The multiplier of used viscometer (2.5)

Conversion the unit from cSt to cP, can be formulated :

\[
\mu \ (cP) = \eta \ (cSt) \times \rho \ (\frac{gr}{ml})
\]
2.5.3. Power of H (pH)
PH measurements were carried out at 25°C using a pH meter OHAUS Starter300 which begins by calibrating the pH with a buffer solution. Then the pH bar inserted into the bio-oil sample by simultaneously pressing the "read" button and waiting for the pH results to be constant.

2.5.4. Higher heating value (HHV)
The bomb calorimeter model used is 5E-C5500 serial number 0261311295 in accordance with ASTM D-4809 which is used to determine the high heating value (HHV) of the bio-oil produced.

3. Result and Discussion
3.1. Effect of heat absorber on yield product
Heat absorber has a very significant effect in this study. It is proven that the initial experiment was carried out without adding a heat absorber at 400, 600 and 800 watts of power for 20-35 minutes. The results obtained were not profitable, because no gas or bio-oil (wet basis) products were produced due to no addition of heat absorber. In addition, the microalgae (solid) product does not have a color change (the solid color before and after the process is the same). This is because the material used is dry microalgae with a moisture content of only 3.6147%. In fact, during the heating process that occurs in a microwave oven, electromagnetic waves can only heat polar materials (e.g. water). In addition, if the water content is too little in a material, there will be little or no heating.

In connection with the heating process of microwave-assisted pyrolysis as described in the previous section, the efficiency of materials to convert electromagnetic radiation into heat energy depends on electrical properties, including dielectric loss tangent (tan δ), which is the ratio between the efficiency of converting microwave energy to thermal energy (dielectric loss factor - ε″) with the ability of material molecules to be polarized (dielectric constant - ε′)[19]. Seeing that microalgae cannot produce products without the help of a heat absorber in this study and most of the biomass cannot be heated in the microwave field and therefore needs to be mixed with high-grade materials which have a tan δ> 0.2 which can potentially be a good heat absorber [17]. Antunes, et al (2017) reported that charcoal has tan δ, ε″, ε′ respectively 1.71; 27.50; and 16.12 so that charcoal can be said to be an excellent heat absorber [20].

![Figure 1](image)

**Figure 1.** Comparison of product on yield at various of heat absorber ratio

Figure 1. shows that when using 600 watts of power and 20 minutes of pyrolysis time, the best ratio of heat absorber to microalgae to obtain bio-oil is obtained at the use of a ratio of 1/6 of 20.57% with an increase in bio-oil yield (wet basis) of 1 8 to 1/6 ratio of 28.80%. Meanwhile, the decrease in bio-oil
yield (wet basis) occurred in the use of heat absorber from a ratio of 1/6 to 1/4 ratio at various times of pyrolysis with a decrease of 19.30%.

This is because the absorption effect on charcoal occurs on the entire surface of the carbon. So that the decomposition of the molecules during the degradation process can produce large vapour because the increase in heat absorption occurs almost all over the surface of the material so that it is able to transfer heat to the larger material. The greater the amount of heat absorber used, the greater the area of contact that occurs in the pyrolysis process so that the degradation of the molecules will take place optimally. In addition, Antunes, et al (2018) stated that charcoal has a large surface area, up to 134.7 m²/g so that the contact between the raw material and the heat absorber is getting bigger, which results in the material getting a greater heating as well and the presence of charcoal can improve process performance well [20].

The use of a ratio of 1/8 to the amount of charcoal does not get the best results for each reaction time, because the small amount of charcoal as a heat absorber will provide suboptimal heating of the biomass due to insufficient heat during pyrolysis process. Therefore, most of the biomass is not hydrolyzed. Conversely, for a higher number in the case of this study of 1/4, heat absorber will cause local heating on char only [21]. Therefore, it can be seen that the use of a heat absorber to microalgae ratio from 1/6 to 1/4 at various times of pyrolysis has decreased by 19.30% which has been previously mentioned.

This decrease can also be explained according to Zainan et al. (2018) that when the amount of heat absorber is used more, it causes the layer thickness of the material to increase, which results in more volatile substances trapped in the carbon pores. In addition, it also causes secondary reactions which are supported by a longer residence time so that it can produce more gas products [16]. Based on this study, it can be proven that the gas produced from the use of a heat absorber on mass of microalgae (w / w) 1/4 > 1/6 > 1/8.

Meanwhile, if it is discussed from the resulting gas product, the gas increases with an increase in the ratio of the number of heat absorbers from 1/8 to 1/6 and 1/6 to 1/4 to microalgae by 52.07% and 70.93%, respectively. Zeng et al. (2013) found that the yield of bio-oil (wet basis) decreased while the amount of gas increased and the amount of char did not vary significantly with the increase in the number of heat absorbers [22].

3.2. Effect of catalyst on yield product

![Figure 2. The effect of adding CaO catalyst on yield at 20 minutes,600 watts.](image-url)
Figure 2 shows the effect of adding CaO catalyst on the best use of heat absorber at 600 watts of power and 20 minutes of pyrolysis time. The addition of 1 gram of CaO catalyst had an effect on the addition of bio-oil yield by 18.62% with bio-oil yield of 24.40%. This is due to the catalytic effect on the CaO catalyst so that the decomposition of the molecules during the degradation process can produce large vapor due to the increase in activation energy by the catalyst. The greater the amount of catalyst used, the greater the area of contact that occurs in the pyrolysis process so that molecular degradation will take place optimally. In addition, using a portion of the catalyst amount will provide a larger catalyst contact area in the microalgae degradation process, which can reduce the activation energy so that the conversion of reactants into products is greater [23]. On the other hand, the char and gas formed, respectively decreased and increased by 8.98% and 5.59%. This can be explained that when using a catalyst, during the process there will be an increase in the thickening of the catalyst layer. Hence, more volatiles trapped in the pores of the catalyst and causes a secondary reaction with a longer residence time to produce more product gas. [13].

3.3. Physicochemical characteristics analysis

Bio-oil is obtained from the process at 1/6 ratio of heat absorber and microalgae, 600 watts power and 20 minutes pyrolysis time, then a physicochemical analysis is carried out and compared with some report using pyrolysis (conventional and microwave) processes and different biomass- different (microalgae and lignocellulose).

Table 2. The physicochemical properties of bio-oil (wet basis) from this study and some report.

| Characteristic          | This work | Chlorella sp. [3] | Microalgae bio-oil (wet basis) [24] | Lignocellulose biomass [15] | Conventional pyrolysis of bio-oil (wet basis) [15] | 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         |

Based on table 2, the physicochemical properties of bio-oil (wet basis) are shown in this study and compared with some literature. The data shows that the calorific value of the bio-oil (wet basis) in this study was 43 MJ/kg, and this result has a higher value than the bio-oil (wet basis) obtained in the study Du, et al., (2011) by using microalgae with the same type and method, higher than bio-oil (wet basis) obtained from the raw material for cellulose biomass (15–21 MJ/kg), higher when compared to bio-oil (wet basis) obtained with conventional methods and have the same heating value with Diesel fuel. So, this can be said that the bio-oil (wet basis) in this study is better than the data from previous studies if viewed from the heating value (higher heating value). This is advantageous so that combustion from bio-oil (wet base) can run perfectly. The density of bio-oil (wet basis) microalgae is ~ 0.98-1.2 kg/L. 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 79–100 cP. If water is not removed from the pyrolytic liquid, the viscosity is around 6-11 cP [24]. Therefore, it can be concluded that the water content in the bio-oil (wet basis) of this study still exists. The pH of bio-oil (wet basis) microalgae is in the range of 9.3-9.9, which is a significant difference from bio-oil from lignocellulose biomass.

4. Conclusion

Microwave-assisted pyrolysis with catalyst and absorber-assisted is a promising thermochemical conversion method for increasing the yield of bio-oil. The optimal use of charcoal heat absorber is the use of 1/6 of the weight of microalgae with a yield of 20.57% with an increase of 28.80%. While the addition of 1 gram of CaO catalyst to the use of charcoal of 1/6 of the weight of the microalgae, also provides increased bio-oil compared to without use, namely 24.40% bio-oil yield which is carried out.
at 600 watts of power and time. Pyrolysis 20 minutes. This study also shows that the use of a catalyst and heat absorbs work simultaneously and has a positive effect on increasing bio-oil in the microwave-assisted pyrolysis process.

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