A PYROLYSIS OF 80 MESH *Spirulina platensis RESIDUE* (SPR) WITH Fe_3O_4 CATALYST

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Received : February 12, 2021   Accepted : May 5, 2021   Published : December 31, 2021

Abstract: *Spirulina platensis* Residue (SPR) is obtained from the solid residue of *Spirulina platensis* extraction, which has high carbohydrate and protein content. Pyrolysis technology will convert SPR into a bio-oil, water phase, char, and gas (CO, CO_2, H_2, CH_4) product with the potential as an environmentally friendly and sustainable fuel. This study aims to obtain data on the optimum conditions and product yield composition of SPR catalytic pyrolysis using the in-situ method. Pyrolysis occurs in a fixed-bed reactor with SPR 50 g feed and Fe_3O_4 catalyst (2.5 g and 5 g) at temperature variations of 300-600 °C with an average heating rate of 14.07 °C/min. The higher the pyrolysis temperature, the more bio-oil yield, the optimum at a temperature of 500 ºC. The use of 2.5 and 5 gram catalysts obtained bio-oil yields of 25.01 and 17.67 %. The yield of biochar will be lower with increasing pyrolysis temperature. The optimum condition for the gas production was achieved at 300 °C, using a catalyst of 2.5 and 5 grams, the yield of gas was 23.59, and 19.74 %. Moreover, the smaller the specific gravity and the higher the bio-oils pH, the better it is as a vehicle fuel.
Keywords: *Spirulina platensis* residue; Pyrolysis; Fixed-bed reactor; Bio-oil; Fe_3O_4

Abstrak: *Spirulina platensis* Residu (SPR) diperoleh dari residu padat ekstraksi *Spirulina platensis* yang memiliki kandungan karbohidrat dan protein tinggi. Teknologi pirolisis akan mengubah SPR menjadi produk bio-oil yang berpotensi sebagai bahan bakar ramah lingkungan dan berkelanjutan. Penelitian ini bertujuan untuk mendapatkan data kondisi optimum dan komposisi *yield* produk dari pirolisis katalitik SPR dengan metode in-situ. Pirolisis SPR akan menghasilkan produk berupa bio-oil, *water phase*, char dan gas (CO, CO_2, H_2, CH_4). Pirolisis berlangsung dalam reaktor *fixed-bed* dengan umpan SPR 50 g serta katalis Fe_3O_4 (2.5 g dan 5 g) pada variasi suhu 300-600°C dengan *heating rate* rata-rata 14,07 °C/min. Semakin tinggi suhu pirolisis semakin banyak *yield* bio-oil, optimum pada suhu 500 ºC. Pemakaian katalis 2,5 dan 5 gram diperoleh *yield* bio-oil sebanyak 25,01 dan 17,67 %. *Yield* biochar akan semakin rendah dengan kenaikan suhu pirolisis. Kondisi optimum produk gas dicapai pada 300 °C dengan katalis 2,5 dan 5 gram diperoleh *yield* gas sebesar 23,59 dan 19,74 %. Tambahan lagi, semakin kecil berat jenis dan semakin tinggi pH bio-oil maka semakin baik sebagai bahan bakar kendaraan.
Kata kunci: *Spirulina platensis residue*; Pirolisis; Reaktor *fixed-bed*; Bio-oil; Fe_3O_4

Recommended APA Citation :
Jamilatun, S., Shitophyta, L. M., Nisa, H. O., & Nurhidayah, M. E. (2021). A Pyrolysis of 80 Mesh *Spirulina platensis* Residue (SPR) With Fe_3O_4 Catalyst. *Elkawnie*, *7*(2), 252-262. https://doi.org/10.22373/ekw.v7i2.8950

Introduction

Biomass is a renewable energy source that is abundant throughout the world. One of the potential biomass alternatives to substitute for fossil fuels is microalgae (Budiardi et al., 2010; Gultom et al., 2014; Jamilatun et al., 2020). Some of the benefits of microalgae development have been summarized by Verma et al. (2010) are (i) having a simple cell structure, (ii) the ability to control cells without reducing their productivity, (iii) converting about 3-8 % of sunlight into energy (other plants are only about 0.5 %), (iv) a short microalgae life cycle of 1-10 days, (v) very high-fat synthesis (± 40-86 % dry weight of biomass), (vi) the ability to survive microalgae in extreme environmental conditions (high salinity or polluted environment) is perfect, (vii) requires low nutrients and fertilizers, (viii) does not compete with foodstuffs, and (ix) reduces CO_2 in the air due to photosynthesis of microalgae.

Many studies have converted biomass from microalgae into biodiesel energy (Scott et al., 2010), biofuels, and biogas (Debowski et al., 2014). However, the solid residue from microalgae extraction has not been utilized properly. Based on various reliable biomass characterization studies, the study results state that this residue can be used as raw material for pyrolysis, which will produce products in the form of bio-oil, water phase, charcoal, and gas. The addition of product value to bio-oil and gas is estimated to support the world's energy supply by ± 14 % (Shen et al., 2013).

Spirulina platensis residue (SPR) is a solid residue from the *Spirulina platensis* algae extraction (Jamilatun et al., 2019a). The fat content at low SPR is around 0.01 wt.% with high carbohydrate (38.51 wt.%) and protein (49.60 wt.%) content. The composition is feasible as a raw material for pyrolysis; the high carbohydrate content is very beneficial because it can optimize bio-oil products' yield (Chen et al., 2015; Jamilatun et al., 2019b). SPR processing by pyrolysis is considered more economical because it can carry out the process at atmospheric pressure and does not require other additives. Biofuel produced from the pyrolysis process consists of bio-oil, water phase, char, and gas. According to Jamilatun et al., 2019d, SPR has a low nitrogen compound content, making it easier for bio-oil to achieve stability in its use (Jamilatun et al., 2019c).

Bio-oil produced from SPR pyrolysis still contains high oxygenate compounds; one solution to this is the use of catalysts in pyrolysis. The use of a silica-alumina catalyst can reduce oxygenated compounds by as much as 65.8 % (Jamilatun et al., 2019c). The use of Fe catalyst in ZSM-5 improves the quality of pyrolysis products compared to non-catalytic pyrolysis. The catalyst can increase oxygen reduction, further promoting the desired products such as phenolics and aromatic compounds. The catalyst composition, which Fe dominates around 56 %, can improve bio-oil products' conversion and quality. Metal-modified catalysts can increase monocyclic aromatic hydrocarbon (MAH) products. In comparison, they reduce the formation of polycyclic aromatic hydrocarbons (PAH) (Zang et al., 2018).

This study carried out pyrolysis with Fe_3O_4 catalyst to determine the product yield with a 2.5 and 5 grams catalyst, SPR 50 grams. The explanation above is necessary to use SPR using pyrolysis technology to increase its economic value. This research will conduct characterization of product yield and obtain the optimum conditions for bio-oil production from SPR.

Materials and Methods

Materials

Spirulina platensis residue solid with the enrichment of 80 mesh in this study obtained from waste extraction *Spirulina platensis* (SP) and catalyst Fe_3O_4 with the number of variations is 2.5 and 5 grams.

Tools

Dry *Spirulina platensis* residue (SPR) was pyrolyzed in a fixed-bed reactor made from stainless steel equipped with a heater outside the reactor; the pyrolysis unit can see in figure 1 (Jamilatun et al., 2019a).

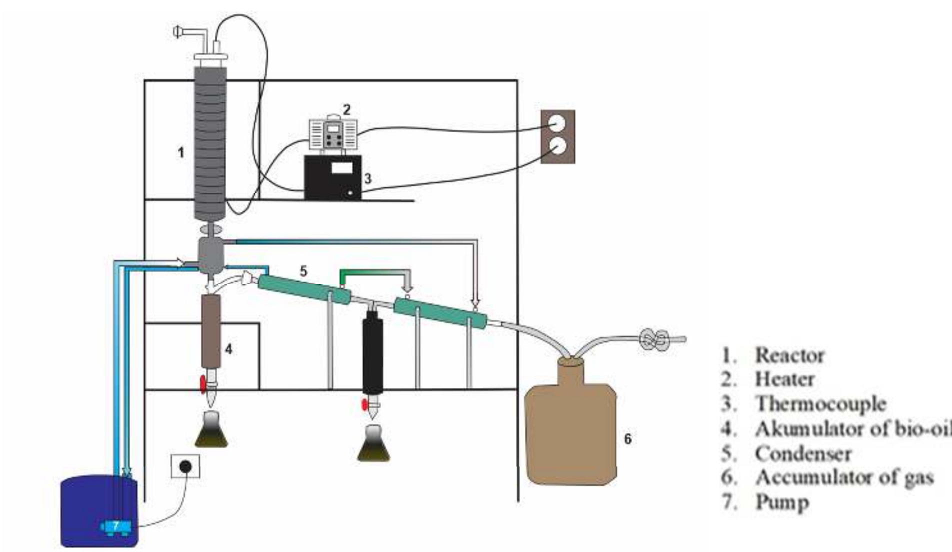


Figure 1. The catalytic pyrolysis equipment (Jamilatun et al., 2019d).

Methods

The material used is dry *Spirulina platensis* residue (SPR) with a size of 80 mesh. The first step to obtaining SPR 80 mesh size is dry SPR cleaned of dirt and mashed, then sieved using a sieving machine and taking SPR with 80 mesh size. Each experiment used a sample of 50 grams with variations of the catalyst Fe_3O_4

as much as 2.5 and 5 grams. Pyrolysis is carried out in-situ, mixing the catalyst with SPR in the sample container until it is homogeneous and then put into the reactor. The fixed-bed reactor is a cylindrical tube containing a mixture of 50 grams of *Spirulina platensis* residue (SPR) and Fe_3O_4 catalyst with variations of 2.5 and 5 grams.

Pyrolysis begins by inserting the reactor tube into the fixed-bed reactor, fixing the reactor cover until it is tightly closed, and ensuring that the screw is tightly attached. The heating comes from the electricity flow, the electric cables wrapped around the outside of the reactor tube. Heating starts from room temperature to the desired temperature, namely 300-600 ^{o}C, with a heating rate of around 14.07 °C/minute, controlled by adjusting the voltage connected to the thermocouple. The pyrolysis steam formed is condensed and then collected as a liquid product (bio-oil and water phase), and the volume is measured every specific time. The final product of the liquid product in the bio-oil and water phase is measured in total volume. The char can be taken and weighed after the pyrolysis is complete and the reactor has cooled, while the weight of the gas is the difference in weight of the SPR minus the weight of liquid and char.

The equation calculates total liquid products, bio-oil weight, and gas weight (Jamilatun et al., 2019a-2019d):

$$Y_L = \left(\frac{W_L}{W_M}\right) \times 100\ \% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$Y_A = \left(\frac{W_A}{W_M}\right) \times 100\ \% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$Y_{Ai} = \left(\frac{W_{Ai}}{W_M}\right) \times 100\% = Y_L - Y_A \quad \ldots\ldots\ldots\ldots(3)$$

$$Y_C = \left(\frac{W_C}{W_M}\right) \times 100\ \% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$Y_G = 1-(Y_L + Y_C)\ x\ 100\ \% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Remark:
Y_L: liquid product yield
Y_A: yield of water phase products
Y_{Ai}: bio-oil yield
Y_C: charcoal yield
Y_G: gas yield

In this case, W_L is the weight of liquid products; W_M is the weight of the sample; W_A is a heavy water phase product; W_{Ai} is a heavy bio-oil, and W_C is heavy charcoal.

Results and Discussions

Spirulina platensis residue (SPR) Characteristic

The pyrolysis process is carried out with a fixed bed with the addition of power at each constant temperature shown in figure 2.

Figure 2 shows that the longer the time used to perform the pyrolysis process, the higher its temperature. So, the relationship between time is directly proportional to temperature. The method of retrieving temperature data is every interval of 5 minutes until it reaches the desired temperature.

The effect of time and temperature on the heating rate is shown in figure 3. The heating rate decreased over time, with an average heating rate of 14.07 °C/min.

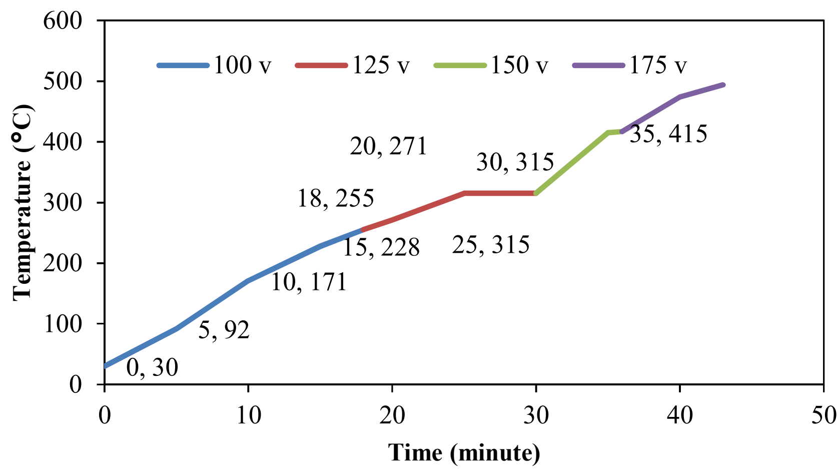


Figure 2. Effect of time on the pyrolysis temperature

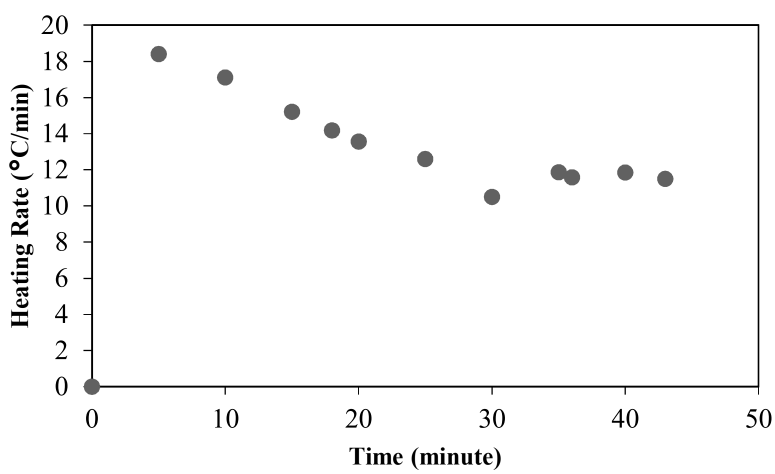


Figure 3. Effect of time on pyrolysis heating rate

Based on figure 3, the longer the time used in the pyrolysis process, the heating rate will decrease because the heating rate is obtained from comparing temperature and time. However, from the data got there is an increase in the heating rate at the time to 35 minutes; this is due to the administration of voltmeter power that is too high so that from 30 minutes to 35 minutes, there is a high-temperature surge that can lead to unstable heating rate.

Pyrolysis Product

The experiment results with various catalysts (2.5 grams and 5 grams) and temperature variations (300, 400, 500, 550, and 600 °C) are presented in figure 4.

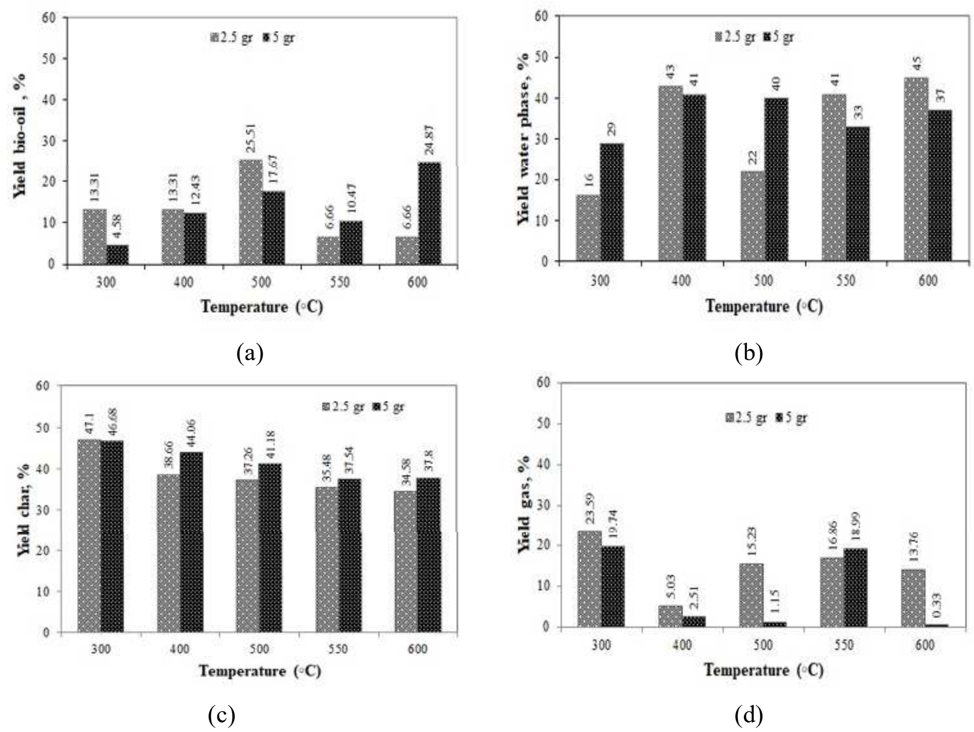


Figure 4. Effect of temperature and number of catalysts on (a) Bio-oil yield (b) Yield bio-char (c) Yield water phase (d) Yield gas.

Based on figure 4 (a), Bio-oil yield with an average heating rate of 14.07 °C/min at catalyst usage of 2.5 gram and temperature set (300, 400, 500, 550, and 600°C) is 13.31, 13.31, 25.51, 6.66, and 6.66 %, and for the use of catalysts 5 gram and the same set of temperatures in a row are 4.58, 12.43, 17.67, 10.47 and 24.87 %. The peak yield of bio-oil produced at 500 °C is 25.01 % with a catalyst of 2.5 grams and at 600°C is 24.87 % for catalysts of 5 grams. The study with a temperature of 600°C got a bio-oil yield of 24.87 % because the biomass used is different from the previous biomass. This biomass may contain more protein, so the bio-oil produced is pretty much equivalent to a bio-oil yield at 500 °C with a catalyst of 2.5 grams. If drawn conclusions based on the same bait, then the maximum bio-oil acquisition at the temperature set of 500 °C for the use of 5 grams of Fe_3O_4 catalyst with the addition of bio-oil yield is 17.67 %. This bio-oil

DOI: 10.22373/ekw.v7i2.8950

yield data is similar to Chaiwong's, 2015, pyrolysis *Spirulina sp*. and *Spirogyra sp*. at 500 °C with fixed-bed reactor obtained bio-oil yield 29 and 13 wt.%.

Based on experimental data, there is a tendency to increase bio-oil yield and increase the temperature from 300-500 °C, but at a temperature of 500 to 600 °C, there is a decrease in bio-oil yield. The reduction of bio-oil due to secondary cracking starts at 500 °C, where the tar (a mixture of bio-oil and water phase) formed in the primary cracking will decompose into gas and char so that the weight of the bio-oil will decrease. This study follows Yu et al., 2018, the more the amount of catalyst used, the lower the vegetable oil yield. The secondary cracking phenomenon at high temperatures causes the thermal decomposition speed to be faster so that the bio-oil tends to turn into a gas product.

Figure 4 (b) The water-phase yield on the use of catalysts 2.5 gram and temperature sets (300, 400, 500, 550, and 600°C) are 16, 43, 22, 41, and 45 % in a row. The use of catalysts 5 gram and the same temperature set in a row are 29, 41, 40, 33, and 37 %. Based on figure 4(b), the water phase obtained varies greatly. The yield water phase relies heavily on the material's water content and water formation during the pyrolysis process.

In figure 4 (c), the amount of char yield on the use of catalyst 2.5 gram with temperature set (300, 400, 500, 550, and 600 °C) were 47.1, 38.66, 37.26, 35.48, and 34.58 % while in the use of catalysts 5 gram was 46.68, 44.06, 41.18, 37.54 and 37.8 %. Most of the char is changed at a temperature setting of 300 °C to reach ± 40% of the total product. At a temperature of 300 °C, this is the final dehydration phase in the pyrolysis process, producing a more durable material. It has large amounts of charcoal products (Yang et al., 2019). Based on the results obtained, the optimum conditions for char production are at a temperature of 300 °C with 2.5 grams of catalyst. As the temperature increases, the char yields decrease; according to Chutia et al., 2014 caused by the loss of volatile material or significant secondary decomposition at high temperatures. This secondary decomposition produces a gas that is not condensed, contributing to an increase in gas production. Therefore, at 600 °C, there is very little charcoal product.

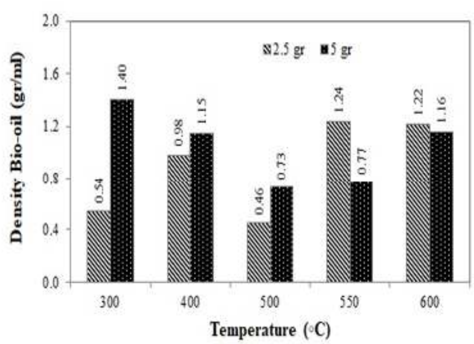
Based on figure 4 (d), the amount of syngas yield on the use of catalysts 2.5 gram with temperature sets (300, 400, 500, 550 and 600 °C) were 23.59, 5.03, 15.23, 16.86 and 13.76 and 13.76 % while in the use of catalysts 5 gram was 19.74, 2.51, 1.15, 18.99 and 0.33 %. According to the literature, syngas yields increase with increasing temperatures; this is not the case in this study because the results tend to be volatile. The influence of bio-char weight and bio-oil also plays a role in these varied results. Based on pyrolysis, the obtained yield of syngas at 300 °C with a catalyst of 2.5 gram was 23.59 %, and at the catalyst, it was 5 gram of 19.74 %. From observations on the gas yield curve with catalyst variations of 2.5 gram and 5 gram at temperatures of 300, 400, 500, 550, and 600 °C irregular gas yield because that affects the yield value of gas is liquid and char weight. Increasing the number of catalysts from 2.5 to 5 grams increases the amount of

CO_2 and H_2 formed by the decomposition reaction of oxygenate compounds. The addition of catalysts to the reaction also affects the formation of methane gas (CH_4). Methane gas is formed through a CO_2 or CO reaction with H_2 (Payormhorm, 2013). However, in this study, the results of gas yield obtained from catalysts are 2.5 gram and 5-gram irregular, so it does not correspond to the literature.

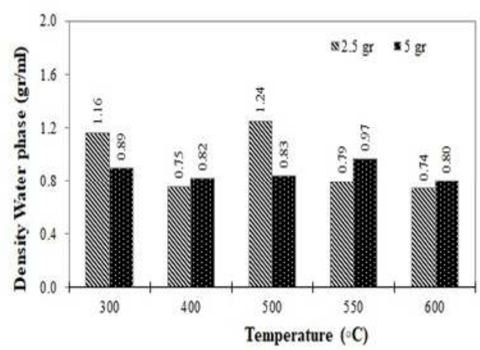
Density and pH testing of bio-oil and water phase

Spirulina platensis residue pyrolysis research aims to determine the effect of the amount of catalyst and temperature variations on product yield distribution. 50 gram of Spirulina platensis and Fe_3O4 catalyst residue were mixed until homogeneous and then put into the reactor tube in-situ. Temperature variations were 300, 400, 500, 550, and 600 °C, while variations of the catalyst used 2.5 and 5 grams.

The bio-oil was tested for density and pH. The density test is carried out by weighing the empty bottle, weighing the bottle containing the bio-oil, and the water phase you want to test. The weight of bio-oil divided by the volume of bio-oil is the specific gravity, then the calculation is carried out according to the formula. The pH test is carried out by diluting the pyrolysis product using (2) two kinds of diluents, namely acetone and water. pH checking using pH paper is then compared with the pH indicator and pH value of bio-oil and the water phase.



(a)



(b)

Figure 5. Effect of temperature and number of catalysts on (a) Bio-oil density (b) Water phase density.

Based on figure 5(a), it is seen the density of bio-oil in the use of the number of catalysts is 2.5 gram with temperatures of 300, 400, 500, 550, and 600 °C are 0.54, 0.98, 0.46, 1.24, and 1.22 gram/ml while for catalyst use 5 gram is 1.40, 1.15, 0.73, 0.77 and 1.16 gram/ml. The density value of bio-oil obtained is higher than in other fuel oil densities with the same volume. It will cause bio-oil to have a thicker texture and inhibit combustion in the engine, so the pressure drop will be more significant and end in engine damage. Based on research can conclude that the best bio-oil is bio-oil with low density.

Based on figure 5(b), density data obtained on the use of catalysts of 2.5 gram with sets of temperatures of 300, 400, 500, 550, and 600 °C in a row are 1.16, 0.75, 1.24, 0.79, and 0.74 gram/ml. The use of catalysts 5 grams with the same temperature set obtained was 0.89, 0.82, and 0.83, and at a rate of 0.97 and 0.80 gram/ml. The water-phase density varies because the water phase is affected by the water content in the bait material used and is also affected by water improvement during the pyrolysis process.

Conclusion

Pyrolysis of *spirulina platensis residue* (SPR) produces bio-oil products that can be environmentally friendly and sustainable fuels. The bio-oil yield from SPR pyrolysis is influenced by grain size, temperature, and the amount of Fe_3O_4 catalyst used. The experiment was carried out with a fixed-bed reactor with an average heating rate of 14.07 °C/minute. Based on the research results at the same temperature, the more catalysts used, the lower the yield of bio-oil and bio-char obtained. The higher the pyrolysis temperature, the higher the bio-oil yield and the optimum at 500 °C, the bio-oil products using 2.5 and 5 grams of catalyst are 25.01 and 17.67 %, respectively. The optimum temperature for the decomposition of SPR into bio-char is 300 °C, with a catalyst of 2.5 and 5 grams, respectively; the yield of biochar is 47.1 and 46.68 %. The optimum conditions for producing gas are obtained at a temperature of 300 °C, with a catalyst of 2.5 and 5 grams; the resulting gas yields are 23.59 and 19.74 %. The smaller the bio-oil density, the better it is used as a vehicle fuel. The pH of the bio-oil and the water phase diluted with water shows a value of 8. As for dilution using acetone, the pH of the water and bio-oil phases is 8 and 7, respectively. The higher the pH of the bio-oil, the lower the acidity, the better bio-oil quality.

Acknowledgements

The author would like to thank for research funding assistance through the Internal Research Fund Scheme through the Universitas Ahmad Dahlan Yogyakarta Lembaga Penelitian dan Pengabdian Kepada Masyarakat (LPPM) with contract number: PD-237/SP3/LPPM-UAD/2020.

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