In-Situ Catalytic Pyrolysis of *Spirulina platensis residue* (SPR): Effect of Temperature and Amount of C12-4 Catalyst on Product Yield

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ABSTRACT

Currently, dependence on fossil energy, especially petroleum, is still high at 96% of the total consumption. One solution to overcome fossil energy consumption is processing alternative energy sources derived from microalgae biomass. This study aims to study the pyrolysis of microalgae with the addition of the C12-4 ($Cr_2O_3+Fe_2O_3+C+CuO+$promoter) catalyst. The biomass used in this study was *Spirulina platensis residue* (SPR). This study used a fixed bed reactor with an outer diameter of 44 mm, an inner diameter of 40 mm, and a total reactor height of 600 mm. The C12-4 was mixed fifty grams of SPR with a particle size of 100 mesh with a ratio variation of 5, 10, and 15 wt.%. The feed mixture was placed in the reactor (in-situ), and the reactor was tightly closed. The nickel-wire heater wrapped around the reactor wall was employed. The pyrolysis heating rate was 24.33 °C/min on average, and the temperatures were varied as 300, 400, 500, 550, and 600 °C. The research found that the optimum temperature conditions without and with the catalyst to produce bio-oil were different. The pyrolysis without any catalyst (500 $^{\circ}$C), with a catalyst of 5 wt.% (500 $^{\circ}$C), 10 wt.% (400 $^{\circ}$C), and 15 wt.% (550 $^{\circ}$C) produced the bio-oil yield of 15.00, 17.92, 16.78 and 16.54, respectively. The use of 5, 10, and 15 wt.% catalysts increased the water phase yield. The char yield was influenced by the amount of catalyst only at 300 $^{\circ}$C; i.e., the more catalysts, the less char yield. The pyrolysis without any catalysts produced the highest gas product. A catalyst significantly increased the pyrolysis conversion from 48.69 (without catalyst) to 62.46% (15. wt.% catalyst) at a temperature of 300 $^{\circ}$C. The optimum conditions for producing the best bio-oil were at 600 °C and 10 wt.% of catalysts, which resulted in an O/C ratio of 0.14.

Keywords: C12-4 catalyst, in-situ catalytic pyrolysis, *Spirulina platensis residue*, yield bio-oil

ABSTRAK

Ketergantungan terhadap energi fosil khususnya minyak bumi, saat ini masih tinggi yaitu mencapai 96% dari total konsumsi. Salah satu solusi untuk mengatasi ketergantungan energi

fosil adalah dengan mengolah sumber energi yang berasal dari biomassa mikroalga. Penelitian ini bertujuan untuk pirolisis mikroalga dengan penambahan katalis C12-4 (Cr_2O_3 + Fe_2O_3 + C + CuO + promotor). Sampel yang digunakan adalah residu Spirulina platensis (SPR). Penelitian ini menggunakan reaktor unggun tetap dengan diameter luar 44 mm, diameter dalam 40 mm, dan tinggi reaktor 600 mm. Spirulina platensis dengan ukuran partikel 100 mesh sebanyak 50 gram dicampur dengan katalis C12-4 dengan variasi 5, 10, dan 15 wt.%. Campuran umpan (in-situ) dimasukkan ke dalam reaktor dan ditutup rapat. Pemanas menggunakan arus listrik melalui kawat nikel yang dililitkan pada dinding reaktor. Laju pemanasan pirolisis rata-rata 24,33 °C/menit, variasi suhu 300, 400, 500, 550, dan 600 °C. Kondisi optimum tanpa dan dengan katalis untuk menghasilkan bio-oil memiliki nilai yang berbeda yaitu pirolisis tanpa katalis (500 ^{0}C), dengan katalis 5 wt.% (500 ^{0}C), 10 wt.% (400 ^{0}C) dan 15 wt.% (550 ^{0}C) menghasilkan bio-oil 15,00; 17,92; 16,78; dan 16,54. Penggunaan katalis 5, 10, dan 15 wt.% berat dapat meningkatkan fasa air hasil. Yield char dipengaruhi oleh jumlah katalis hanya pada 300 ^{0}C, semakin banyak katalis maka yield char semakin menurun. Pirolisis tanpa katalis menghasilkan produk gas tertinggi. Penggunaan katalis sangat signifikan dalam meningkatkan konversi pirolisis dari 48,69 (tanpa katalis) menjadi 62,46% (katalis 15 wt.%) pada suhu 300 ^{0}C. Kondisi optimum untuk menghasilkan minyak nabati terbaik adalah pada 600 °C dengan katalis 10% berat, menghasilkan rasio O/C sebesar 0,14.

Kata kunci: C12-4 catalyst, in-situ catalytic pyrolysis, Spirulina platensis residue, yield bio-oil

1. Introduction

Dependence on fossil energy, especially petroleum in Indonesia, is still high, reaching 96% of the total consumption (BPPT–OEI, 2019). Fossil energy is detrimental to the environment because the waste from combustion produces harmful substances such as NO_x, CO, SO_x, and particulates that pollute the environment (Yang et al., 2019). One solution is to find alternative energy sources environmentally friendly, renewable, and sustainable, i.e., from microalgae biomass. Microalgae are photosynthetic oil-producing microorganisms with lipid content of 30% and can produce 200 times more oil than other vegetable sources or as much as 58,700 L/ha. Moreover, it can have high efficiency in photosynthesis so that growth is faster than other plants and can absorb carbon dioxide to reduce the greenhouse effect (Suganya et al., 2016).

Processing biomass into energy can be performed in several ways, namely by biochemical (fermentation) or thermochemical processes. The biochemical process is more selective and requires a long reaction time but does not require much external energy. On the other hand, the thermochemical process requires a large amount of external energy, but the reaction time is not long. Several thermochemical techniques include combustion, pyrolysis, gasification, and liquefaction (Basu, 2010). Biomass pyrolysis is carried out by heating in oxygen-free conditions and produces liquid (bio-oil), solid (biochar), and gas products (Hu and Gholizadeh, 2019). Pyrolysis products are very dependent on several parameters, such as biomass composition, heating rate, pyrolysis temperature, residence time, biomass grain size, and catalyst (Jamilatun et al., 2018; Jamilatun et al., 2019).

Microalgae bio-oil is a dark-colored liquid fuel that smells like smoke and has a more excellent heating value than bio-oil from lignocellulosic biomass (Maity et al., 2014). Still, it has a slightly lower calorific value than diesel oil and other fuel oils. In addition, Bio-oil still contains many oxygenate compounds that can cause corrosion in machines if directly used. Catalytic pyrolysis is one way to improve the quality (upgrading) of bio-oil by reducing the oxygen content. The lower the oxygenate content or O/C ratio, the better the bio-oil quality (Hu et al., 2018). In general, the use of catalysts in biomass pyrolysis can lower pyrolysis temperature, reduce equipment and energy costs, increase biomass conversion, and change product distribution (Zang et al., 2018).

Several studies have been conducted, for examples, discussing the effect of catalysts on the pyrolysis of microalgae *Nannochloropsis sp.* (Pan et al., 2010); *Chlorella* (Babich et al., 2011), lignocellulosic biomass (Kabir and Hameed, 2017), and plant biomass (Chisti, 2008). Pyrolysis with catalysts was carried out by Pan et al. (2010), with Nannochloropsis sp. The bio-oil analysis results showed decreased oxygen content from 30.09 to 19.5 wt.%, and a higher heating value (HHV) increased from 24.4 to 32.7 MJ/kg when compared without a catalyst. Several pyrolysis studies with catalysts include HZSM-5 (Guo et al., 2018; Tan et al., 2018), hybrid composites (hexagonal mesoporous silicate (HMS), and ZSM-5 with impregnation of Ni, Fe, or Ce (10 % metal loading) (Jafarian and Tavasoli, 2018). Other catalysts are magnetite (Fe_3O_4) (Yu et al., 2018), silica-alumina (Tan et al., 2018), and reuse alumina-silica (Tan et al., 2019).

Iron oxide is considered a promising catalytic material due to its high efficiency, environmental friendliness, and low cost. The α-Fe_2O_3 (hematite) is one of the most stable polymorphs of iron oxide under ambient conditions and is used in various catalysis fields, especially in reduction/oxidation and acid/base reactions. The Fe_2O_3 is useful for CO oxidation, photocatalytic water oxidation, reduction of NO_x to NH_3 in diesel exhaust (Baimoldina et al., 2019). The Fe catalyst in ZSM-5 showed a significant improvement in pyrolysis products' quality than non-catalytic experiments. The catalyst can enhance the removal of oxygen from the organic phase of the bio-oil and further promote desired products such as phenolics and aromatic compounds. The composition of the C12-4 catalyst which is dominated by Fe around 56 % can increase bio-oil products' conversion and quality. Metal-modified catalysts increased monocyclic aromatic hydrocarbons (MAHs) and reducing the formation of polycyclic aromatic hydrocarbons (PAHs). Moreover, metal-modified catalysts most effectively increase the formation of MAHs and hold the formation of PAHs up to 10 % (Zang et al., 2018).

Mixing biomass can be carried out by catalytic pyrolysis with a catalyst (in-situ catalytic pyrolysis) (Aysu et al., 2016; Zabeti et al., 2012) or by separating biomass and catalyst (ex-situ catalytic pyrolysis) (Luo and Resende, 2016), which are carried out simultaneously in a one-step process. In-situ catalytic pyrolysis, biomass, and catalyst are mixed in one reactor, while biomass and catalyst are separated and placed in reactors 1 and 2, called ex-situ catalytic pyrolysis (Jamilatun et al., 2019). The increase in the product by in-situ was strongly influenced by the catalyst to biomass ratio, while the temperature influenced ex-situ in reactor 2. In

addition, in-situ enhancement had higher selectivity against xylene and aromatics (C9), and ex-situ showed higher selectivity against benzene and toluene (Shafaghat et al., 2017).

The opportunity to utilize solid residue from SP microalgae extraction for the manufacture of liquid fuels is auspicious. In this study, the pyrolysis of *Spirulina platensis residue* (SPR) was studied using a solid C12-4 (Cr_2O_3+Fe_2O_3+C+CuO+promoter) catalyst. Pyrolysis was carried out using a fixed bed reactor by mixing SPR without and with a catalyst (in-situ pyrolysis) at a temperature variation of 300-600 ^{0}C and using a catalyst 5, 10, and 15 wt.%. Ultimate, proximate, and higher heating value (HHV) analysis was performed to characterize SPR raw materials. The C12-4 catalyst was analyzed by SEM-EDX (Scanning Electron Microscope−Energy Dispersive X-ray) with type JED-2300, instrument: 6510 (LA), volt: 15.00 kv, pixel: 1024 x 768. Analysis of bio-oil products with Shimadzu GCMS type [GCMS-QP2010 SE] Rastek Rxi-5MS column length 30 m, ID 0.25 mm with Helium carrier gas, 200 °C injector temperature, total flow 128 mL/min, column flow 0.85 mL/min. GCMS data to determine the effect of using a catalyst on the C/O ratio without using a C12-4 catalyst.

2. Research Methodology

2.1 Materials

2.1.1 Spirulina platensis residue (SPR)

The research material used was SPR, a solid residue from the extraction of *Spirulina platensis* with methanol. The SPR was obtained from the Laboratory of Chemical Engineering UGM Eco Mini Plant. It was characterized by proximate, ultimate, and HHV analysis at the Laboratorium Pangan dan Hasil Pertanian, Departemen Teknologi Pertanian dan Lab Pangan dan Gizi, Pusat Antar Universitas (PAU) UGM. The analysis results are shown in Table 1.

Table 1. *Spirulina platensis residue* (SPR) characteristics (Jamilatun *et al.*, 2019)

Component	SPR
Composition analysis (wt.%)	
Lipid	0.09
Carbohydrate	38.51
Protein	49.60
Ultimate analysis (wt.%)	
Sulfur	0.55
Carbon	41.36
Hydrogen	6.60
Nitrogen	7.17
Oxygen	35.33
Higher heating value (MJ/kg)	18.21

Table 2. MSDS data (No. 7011, 2016) and SEM-EDX analysis of the C12-4 catalyst

Chemical Name (MSDS)	Concentration, %	Element (SEM-EDX)	Mass, %
Fe_2O_3	80-95	C	8.04
CrO_3	5-10	O	28.75
CuO	1-5	Cr	4.93
C	1-5	Fe	56.64
Cr_2O_3	<5	Cu	1.64

2.1.2 C12-4 Catalyst

The catalyst with the trade name C12-4 (Cr_2O_3+Fe_2O_3+C+CuO+promoter) was obtained from PT in the form of pellets. Clariant Kujang Catalyst, Kujang Industrial Estate, Jl. Jend. A. Yani No. 39 Cikampek Indonesia. The C12-4 catalyst has a specific gravity of 0.98-1.25 kg/L and a melting point of more than 650 ^{0}C. Based on the Material Safety Data Sheet (MSDS: No. 7011, 2016) and
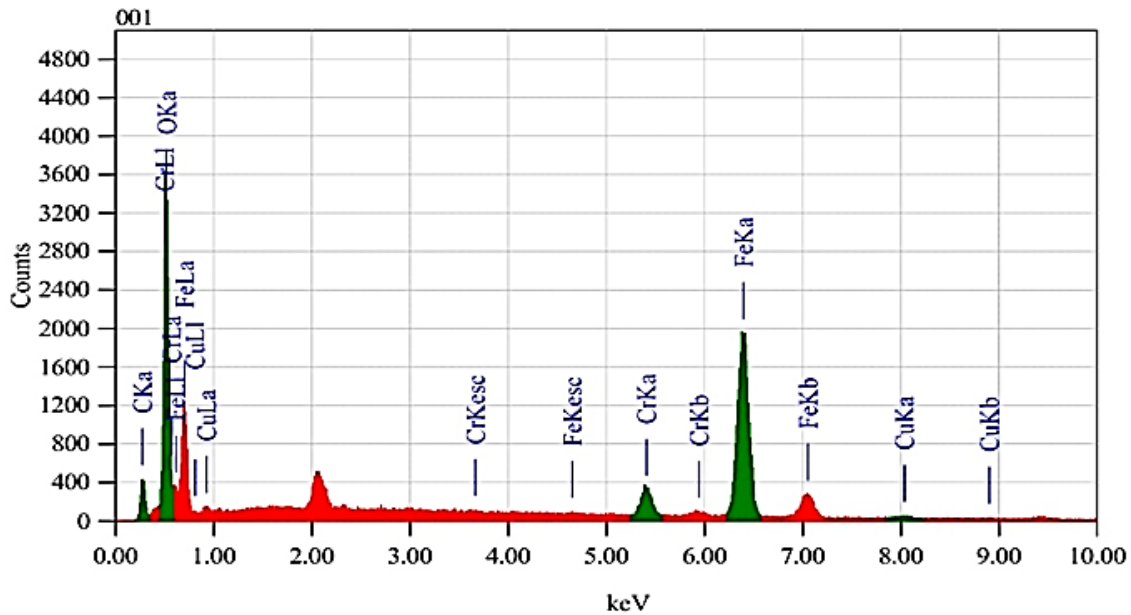
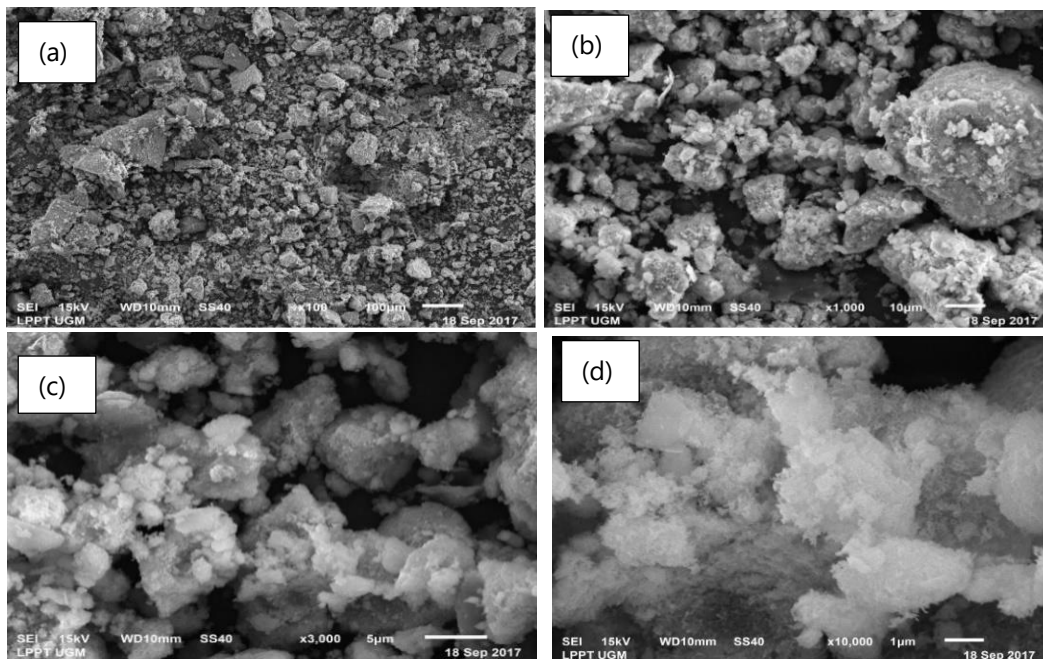Figure 1. SEM-EDX C12-4 catalyst analysis results

Figure 2. SEM analysis of C12-4 at magnification, (a) 100 times, (b) 1000 times, (c) 5000 times and (d) 10,000

SEM-EDX, the composition and concentration of the catalyst can be observed. SEM-EDX was performed at the Laboratorium Pengujian dan Penelitian Terpadu (LPPT) Universitas Gadjah Mada (UGM) and was shown in Figure 1 and Table 2.

Figure 1 shows the magnitude of the voltage (keV) used and the total counts of each catalyst constituent (C, O, Cr, Fe, and Cu), for Fe obtained at a voltage of 6,398 keV with a total counting of 1900 counts, while O is received at a voltage of 0.525 keV with 3800 counts.

Based on Table 2, the catalyst's composition consists of Fe_2O_3, CrO_3, CuO, C, and Cr_2O_3 with concentrations of 80-95, 5-10, 1-5, 1-5, and <5%, respectively. Furthermore, the composition of Fe, O, Cr, Cu, and C mass percent are 56.64, 28.75, 4.93, 1.64, and 8.04 %, respectively. Therefore, the largest composition is Fe (56.64%) and O (28.75 %), which are composed of Fe_2O_3 compounds (80-95%).

The microstructure test with SEM at magnifications of 100, 1000, 5000, and 10,000 times is presented in Figure 2. Figure 2d shows that Fe_2O_3 oxide is black iron to steel gray mixed with reddish CrO_3 and CuO.

2.2 Procedures

The research was conducted in several stages of the process: (1) preparation of materials, (2) preparation of pyrolysis equipment, and (3) pyrolysis process.

2.2.1 Preparation of materials

Spirulina platensis residue (SPR) was crushed, then sieved with -80 + 100 mesh and -100 mesh. SPR used a grain size of -100 mesh. SPR was sun-dried for ten (10) days to reduce moisture content.

2.2.2 Preparation of Pyrolysis Equipment

The pyrolysis reactor is a vertical cylinder operated as a fixed bed reactor with an inner diameter of 40 mm, an outer diameter of 44 mm, and 600 mm. The complete setup of the pyrolysis equipment is shown in Figure 3. In addition, the reactor was equipped with the instruments necessary to study the reactor characteristics, namely temperature and time on the heating rate.
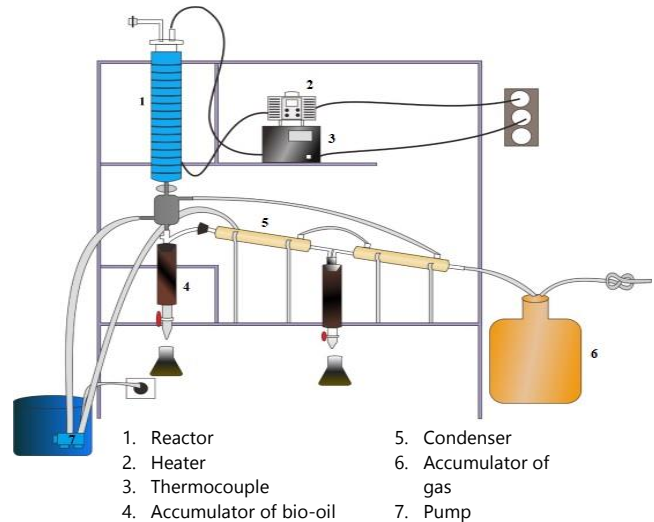

1. Reactor	5. Condenser
2. Heater	6. Accumulator of
3. Thermocouple	gas
4. Accumulator of bio-oil	7. Pump

Figure 3. The In-situ catalytic pyrolysis equipment (Jamilatun *et al.*, 2019)

2.2.2 Pyrolysis Process

Pyrolysis was started by mixing 50 grams of SPR and C12-4 catalyst with the ratio variations of 0, 5, 10, and 15 wt.% until homogeneous. Next, the feed was put into the reactor. Heating was carried out with an electric current through a nickel wire wrapped around the outside of the tube—an average heating rate of 24.33 ^{0}C/minute. Pyrolysis was carried out with temperature variations of 300, 400, 500, 550, and 600 ^{0}C and monitored using a thermocouple. Condensable gas is condensed into the accumulator and the liquid was weighted. The non-condensable gas was flowed into the water tank to be absorbed, while the charcoal formed was taken after the pyrolysis is complete, then weighed. The experiment was stopped when the pyrolysis was finished at the desired pyrolysis temperature, i.e., no more liquid was dripping. The average time required for each pyrolysis was about 40 minutes. The yield of bio-oil, water phase, charcoal, gas, and conversion was calculated using equations (1) - (7). The mixture of bio-oil and water phases was called tar or liquid product.

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

$$Y_L = \frac{W_L}{W_M} x\ 100\ \% \qquad (1)$$

$$Y_B = \frac{W_B}{W_M} x\ 100\ \% \qquad (2)$$

$$Y_{WP} = \frac{W_{WP}}{W_M} x\ 100\ \% \qquad (3)$$

$$Y_C = \frac{W_C}{W_M} x\ 100\ \% \qquad (4)$$

$$Y_G = 100\ \% - (Y_B + Y_{WP} + Y_C)\% \qquad (5)$$

$$Y_L = Y_B + Y_{WP} \qquad (6)$$

$$X = \frac{(W_B + W_{WP} + W_G)}{w_M} x100\ \% \qquad (7)$$

In this case, Y_L, Y_B, Y_{WP}, Y_C, and Y_G are the yields of the liquid (wt.%), bio-oil (wt.%), water phase (wt.%), and gas (wt.%), respectively; W_M, W_L, W_B, W_{WP}, and W_C are the weight of the SPR sample (gram), the weight of the liquid product (gram), bio-oil (gram), water phase (gram), and char (gram), respectively whereas X is conversion.

3. Results and Discussion

3.1 Characteristics of the pyrolysis apparatus

The reactor used electrical current for heating, which is controlled by a voltage regulator. The characteristic test of the pyrolysis apparatus is very important for initial research and to ensure that the heating rate at the initial temperature reaches the desired temperature in a certain range. This voltage control is intended to stabilize the heating rate in the temperature range of 300-600 °C. The results were quite good by carrying out the performance test 3 times, namely the heating rate on an average of 24.33 °C/minute. The effect of temperature and time on the heating rate of the appliance is presented in Figure 4.

Jamilatun et al. (2017) have examined the pyrolysis of SPR with a Thermogravimetry Analyzer (TGA); the heating rate affects the time required for pyrolysis from 30 to 1000 °C. The greater the heating rate, the shorter the pyrolysis time, respectively, the time needed for SPR pyrolysis at heating rates of 10, 20, 30, 40, and 50 °C/minute is 36.28; 15.08; 10,15; 7.50 and 5.97 minutes. The heating rate is kept constant so that the heat of SPR pyrolysis is always the same for all variables because the heating rate significantly affects product yield distribution (Jamilatun et al., 2019).

3.2 The effect of temperature and the amount of catalyst

3.2.1 Yield of Bio-oil

The effect of temperature and use of catalyst C12-4 wt.% on bio-oil yield in SPR pyrolysis with 100 mesh grain size is presented in Figure 5; the calculation follows Equation 2.

Figure 5 shows the effect of temperature and the amount of catalyst on the bio-oil yield. Overall pyrolysis of 300-600 °C with catalysts 0, 5, 10, and 15 wt.%, the result is the bio-oil yields in the range of 4.61-15, 7.84-17.92, 13.17-16.78, and 14.47-16.54%, respectively. The use of 15 wt.% catalysts gave the best results, namely the highest amount of bio-oil at a temperature of 300-600 °C. In general, the higher the pyrolysis temperature, the more active the decomposition is so that more bio-oil is formed. However, at 400-600 °C, the effect of secondary cracking is very dominant where the tar produced from primary cracking will decompose into gas and char (Jamilatun et al., 2017), the decomposition will cause the gas yield to
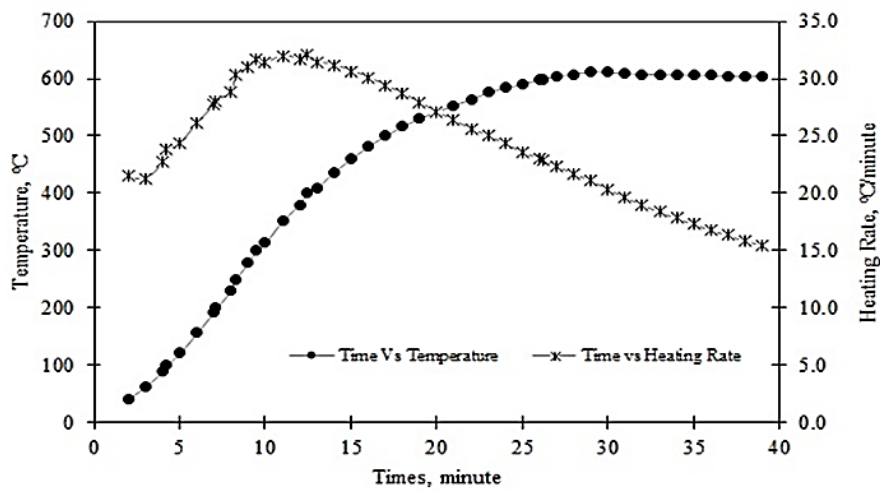
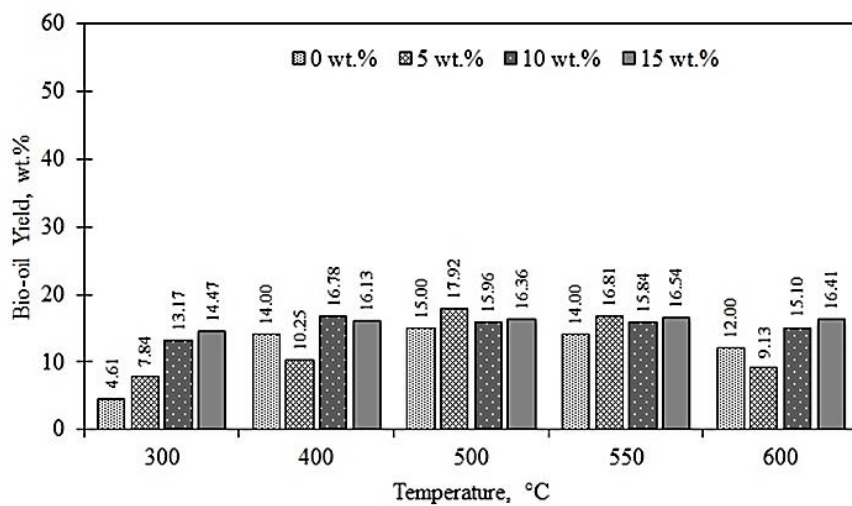**Figure 4.** The relationship between time, temperature, and heating rate

Figure 5. Effect of temperature and the amount of catalyst C12-4 on bio-oil yield
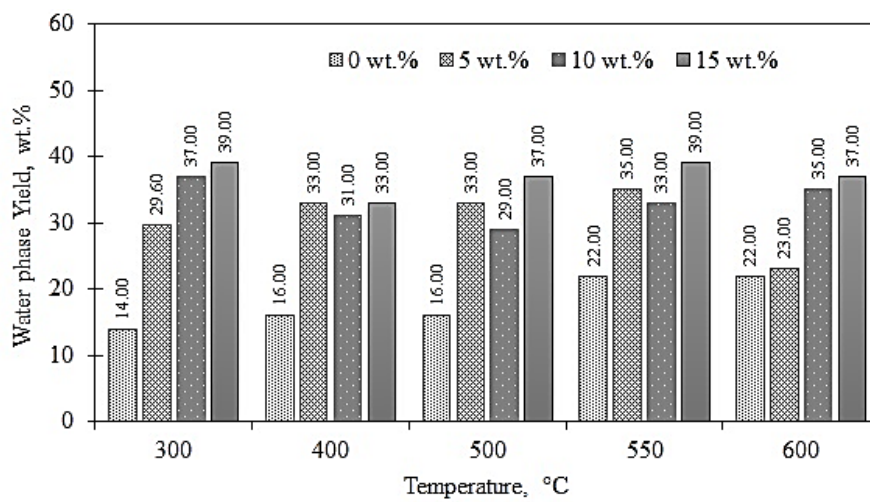

Figure 6. Effect of temperature and the amount of catalyst C12-4 on water phase yield

increase, on the other hand, the bio-oil yield will decrease. This is because the formation of char in secondary cracking is minimal so that it does not affect the formation of char (Jamilatun et al., 2018). Therefore, the optimum conditions for pyrolysis without and with a catalyst have different values. For example, pyrolysis without a catalyst at 500 $^{\circ}$C, the yield of bio-oil is obtained 15.00%. Whereas for 5, 10, 15 wt.%, the optimum conditions were obtained at 500, 400, and 550 $^{\circ}$C with bio-oil yields of 17.92, 16.78, and 16.54%, respectively.

3.2.2 Water Phase Yield

The effect of temperature and the amount of C12-4 catalyst is presented in Figure 6, with the calculation using Equation 3. Based on Figure 6, the effect of temperature on the water phase yield fluctuates and the amount of catalyst. Overall, in the temperature range of 300-600 $^{\circ}$C in the use of catalysts 0, 5, 10, and 15 wt.% in the range 14-22, 23-35, 29-37, and 33-39%. The water phase yield is relatively high due to the SPR microalgae biomass sample's water content. Moreover, the results of the reactions that occur (hydrodeoxygenation and hydrogenation) (Jamilatun et al., 2019). The yield water phase in SPR pyrolysis with 15 wt.% catalysts is higher than without using 5 and 10 wt.%. The higher yield is due to the faster hydrogenation and hydrodeoxygenation reactions water is formed. Another factor is the water content in the microalgae sample, which significantly affects the yield water phase. The microalgae water phase is very potential as a chemical in the pharmaceutical field (Jamilatun et al., 2018). Liquid pyrolysis products are in the form of bio-oil and water phases. Furthermore, it can be separated

because of the different phases, i.e., the upper phase (oil phase) in the form of bio-oil and the lower phase (water phase) in the water phase. This liquid product is generally referred to as tar.

3.2.3 Yield of Char

Figure 7 presents the effect of temperature and the amount of catalyst on the char yield, with the calculation using Equation 4. Based on Figure 7, it can be seen that the higher the pyrolysis temperature, the lower the char weight. Catalysts are very influential on the char yield at 300 $^{\circ}$C; the more the catalysts, the lower the yield. However, at a 400-600 $^{\circ}$C temperature, the amount of catalyst has relatively little effect on reducing char yield. Pyrolysis at a temperature lower than 400 °C produces higher char. The higher the pyrolysis temperature, the more the decomposition increases so that the liquid and gas products increase; this causes the char yield to decrease. The high heating rate and longer residence time also cause the secondary cracking reaction to being more active so that the char yield will drop (Jafarian et al., 2018).

Pyrolysis variables which are temperature, type and amount of catalyst, heating rate, residence time, and size of biomass grains affect the distribution of product yield composition. These variables will affect the amount of bio-oil yield, water phase, tar (bio-oil and water phase), char, and gas. The amount of char resulting from pyrolysis will decrease with increasing pyrolysis temperature—the rate at which the amount of char decreases is greatly influenced by the heating rate (Hu et al., 2019, Jamilatun et al., 2019).

3.2.4 Yield of Gas

Based on Figure 8, it can be seen that the gas yield of SPR pyrolysis with a catalyst weight of 0, 5, 10, and 15 wt.%, the calculation follows Equation 5. Pyrolysis without and with a catalyst of 5, 10, and 15 wt.% at a temperature of 300-600 ^{0}C yielded a product gas of 30.08-38.94, 20.31-42.61, 13.21-25.82, and 12.71-23.95%, respectively. Figure 8 shows that non-catalytic pyrolysis. Generally, it produces higher gas than pyrolysis with a catalyst because the catalyst causes more active hydrogenation and hydro-deoxygenation reactions. More water is formed. The formation of gaseous products is strongly influenced by temperature; the higher it is, the higher it is. At temperatures above 300 ^{0}C, secondary cracking generally starts to occur, where the tar formed in the primary cracking will decompose into gas and char. For this reason, each pyrolysis variable will affect the distribution of product composition.
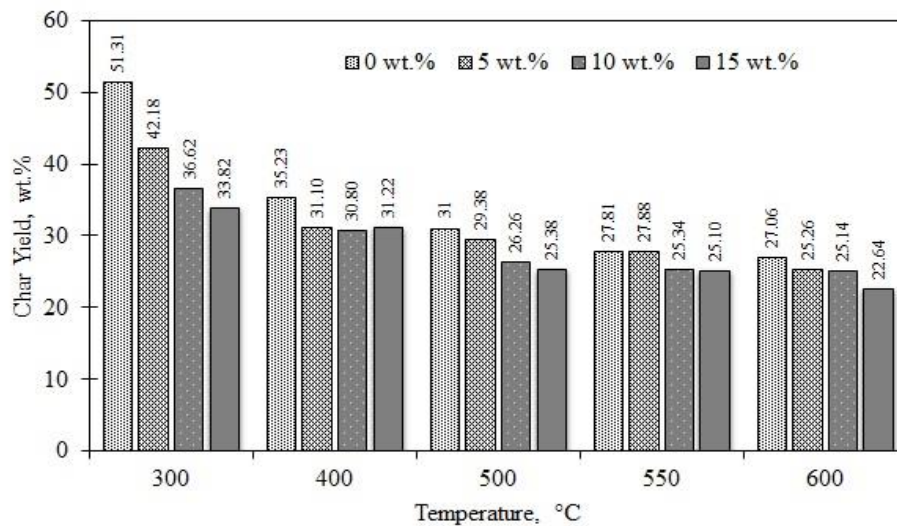

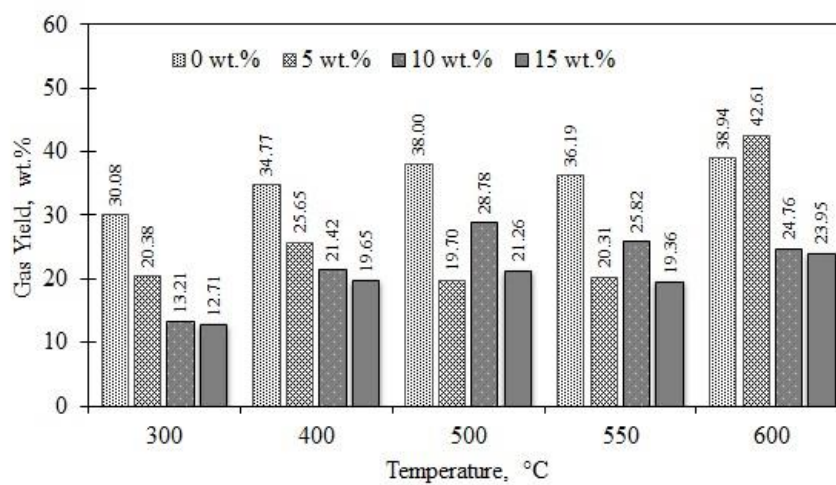**Figure 7.** Effect of temperature and the amount of catalyst C12-4 on char yield

Figure 8. Effect of temperature and the amount of catalyst C12-4 on gas yield

3.2.5 Conversion

Figure 9 shows the effect of temperature on various catalysts on conversion; the calculation follows Equation 7. Based on Figure 9, the higher the pyrolysis temperature and the greater the catalyst used can cause an increased conversion. The average conversion increase before and after using the catalyst at 300, 400, 500, 550, and 600 ^{0}C were 48.69 to 62.46 %, 64.77 to 72.99 %, 69.00 to 72.99 %, 72.19 to 73.89 %, and 72.94 to 75.65 %, respectively. At a temperature of 300 ^{0}C, a catalyst is very significant in increasing the conversion. This phenomenon occurs because the catalyst can accelerate the reaction, and at low temperatures, it has not been affected by secondary cracking; only primary cracking occurs. Tar produced in primary cracking does not react further into gas and char, so the conversion of catalytic pyrolysis is relatively high. Conversely, at a temperature of 400 ^{0}C, secondary cracking begins to occur, which results in the tar formed from primary cracking to form gas and char, so the conversion of catalytic pyrolysis will gradually increase as the temperature increases.

3.2.6 Upgrading the Bio-oil

Based on GC-MS data, the O and C components in bio-oil were evaluated. Upgrading bio-oil with the addition of a catalyst in pyrolysis is intended to reduce the O/C ratio. The effect of temperature 300-600 ^{0}C and amount of catalyst 5, 10, 15 wt.% on the O/C ratio compared to bio-oil products without a catalyst shows the results in Figure 10.
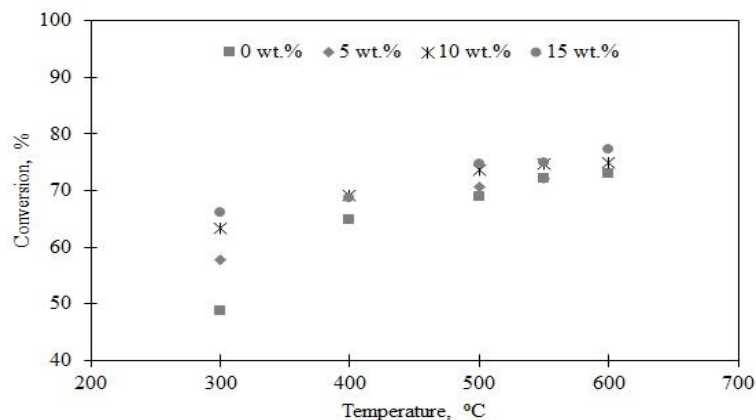

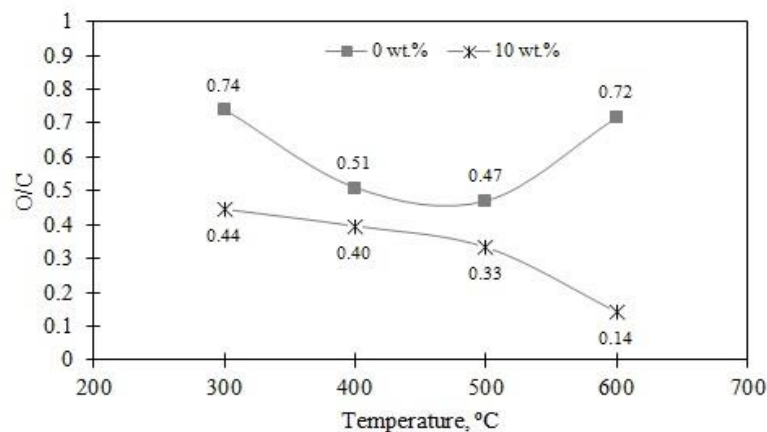**Figure 9.** Effect of temperature on various amounts of catalyst on conversion

Figure 10. Effect of temperature on various amounts of catalyst on O/C ratio

Figure 10 shows the O/C for with and without catalyst at a temperature variation of 300-600 ºC. In case of without catalyst, the O/C ratio is in the range of 0.47-0.74 and with a 10 wt.% is in the range of 0.14-0.44. The average O/C drop from 300-600 °C without and with catalyst was 84.62% (from 0.8 to 0.26). temperature of 600 °C with 10 wt.% catalyst, produced O/C ratio of 0.14.

4. Conclusions

Catalytic pyrolysis of residual Spirulina platensis (SPR) with the particle size of 100 mesh was carried out in a fixed bed reactor at the temperature range of 300-600 ºC. The C12-4 catalysts (Cr_2O_3 + Fe_2O_3 + C + CuO + promoter) were used at 5, 10, and 15 wt.% with an average heating rate of 24.33 ºC/minute. The optimum conditions without and with a catalyst have different values. Without a catalyst, 5, 10, 15 wt.% were obtained at 500, 500, 400, and 550 ºC with bio-oil yields 15.00, 17.92, 16.78, and 16.54 %, respectively. The temperature range of 300-600 ºC in the use of catalysts 0, 5, 10, and 15 wt.% the water phase yield in the range 14-22 % % %, 23-35, 29-37 %, and 33-39 %. Using catalysts on char yield was profound at 300 ºC, i.e., the more catalyst, the less yield of char. However, at 400-600 ºC, the amount of catalyst did not significantly affect the char yield. Pyrolysis without and with 5, 10, 15 wt.% catalysts yielded gas products of 30.08-38.94 and 20.31-42.61, 13.21-25.82, 12.71-23, respectively. The catalyst was very significant in increasing the conversion, from 48.69 to 62.46 % at 300 ºC. The average O/C ratio drop from 300 to 600 ºC without and with the catalyst is from 0.48 to 0.26, reduced by 84.62 %. The optimum condition is reached at a temperature of 600 °C with a 10 wt.% produce O/C ratio of 0.14.

Acknowledgements

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