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Siti Jamilatun:

Thank you for submitting the manuscript, "In-Situ Catalytic Pyrolysis Spirulina platensis residue (SPR): Effect of Temperature and Amount of Catalyst C12-4 on Product Yield" to [Jurnal Rekayasa Proses](#). With the online [journal](#) management system that we are using, you will be able to track its progress through the editorial process by logging in to the [journal](#) web site:

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Home | About | User Home | Search | Current | Archives | Announcements | Statistics | Indexing and Abstracting | Editorial Team | Peer Reviewer

Home > User > Author > Submissions > #60477 > Review

## #60477 Review


SUMMARY REVIEW EDITING

### Submission

Authors Siti Jamilatun, Ratih Mahardhika, Imelda Eka Nurshinta, Lukhi Mulia Sithopyta 

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

Section Articles

Editor Dr.-Ing. Teguh Ariyanto, S.T., M.Eng. 

### Peer Review

#### Round 1

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Initiated 2020-11-09

Last modified 2021-03-09

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### Editor Decision

Decision Accept Submission 2021-01-16

Notify Editor  Editor/Author Email Record  2021-01-16

Editor Version None

Author Version [60477-199293-3-ED.DOCX](#) 2021-01-11 [DELETE](#)

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- Email Header:** [jrekpros] Editor Decision (Kotak Masuk), Dr.-Ing. Teguh Ariyanto, S.T., M.Eng. <teguh.ariyanto@ugm.ac.id> kepada saya, Kam, 10 Des 2020 08.21
- Email Body:**

Siti Jamilatun:

Thanks for choosing [Jurnal Rekayasa Proses](#) for publishing your nice work. We have completed the reviewing process of your submission titled "In-Situ Catalytic Pyrolysis Spirulina platensis residue (SPR): Effect of Temperature and Amount of Catalyst C12-4 on Product Yield"

to [Jurnal Rekayasa Proses](#), and reached a decision that revisions are required before your article can be reconsidered for publication. You can find the reviewers' comments at the end of this email.

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Please note that we expect to receive your revised manuscript within 4 weeks from the decision date (the deadline: 07.01.2021). Manuscripts submitted beyond this time may be treated as new submissions. Please inform us in advance if more time is required to revise your manuscript.

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Dr.-Ing. Teguh Ariyanto, S.T., M.Eng.  
Chemical Engineering Department, Universitas Gadjah Mada
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Managing Editors,  
Dr.-Ing. Teguh Ariyanto, S.T., M.Eng.  
Chemical Engineering Department, Universitas Gadjah Mada  
[teguh.ariyanto@ugm.ac.id](mailto:teguh.ariyanto@ugm.ac.id)

Reviewer A:

This paper describes the influence of catalyst C12-4 to the pyrolysis of SPR to obtain bio oil with insitu technique. The experiments were conducted from 300-600°C. In addition to bio oil, they also present the yield of water phase, char and gas product. Overall, the quality of presentation is low and the english needs to be improved. In addition, exploration as well as discussion of their result is very limited. Based on my review, I would suggest major revision for this manuscript to be considered again for acceptance in **Rekayasa Proses**. The detail comments are as follows:

- The english needs to be improved. I provide some examples here:
  - The use of fossil energy hurts the environment...
  - One solution is to find alternative energy sources that are friendly to the ground, renewable and sustainable.
  - In-situ catalytic pyrolysis is between biomass and catalyst mixed in one reactor, while ex-situ catalytic pyrolysis is biomass, and the catalyst is separated in reactors 1 and 2
  - SEM-EDX analyzed the catalysts at the Laboratorium Pengujian dan Penelitian Terpadu (LPPT), UGM. Based on Figure 1 and 2, can see the results of SEM-EDX analysis in the form of percentage by weight of catalyst constituent.
  - This sentence is not needed: The results and discussion of the topic of In-situ catalytic pyrolysis SPR with the influence of temperature and the amount of catalyst C12-4 with SPR 100 mesh grain size on product yield are (1) the characteristics of the pyrolysis apparatus and (2) the effect of

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📄 Meeting Prodi Teknik Ki...

✖ Rapat

1. Fixed-bed reactor carried out catalytic pyrolysis Spirulina platensis residue (SPR) grain size of 100 mesh using .....etc.

2. The author needs to provide reasoning why it is important to use the C12-4 catalyst? What is special about this catalyst and what positive impact that you expect when you use this catalyst. It would be better if there is a plot showing the bio oil yield without catalyst for comparison.

3. Figure 5 presents the influence of temperature and catalyst loading to bio oil yield. I have computed with two way ANOVA based on the presented data and it turned out that the influence of catalyst and temperature are not significant. Thus, it is hard to conclude that the 500°C is the optimum temp to obtain maximum yield of bio oil.

4. The explanation or discussion of figure 5 is too general and shallow.

The greater the amount of catalyst used, the greater the number of active surfaces for the reaction to occur, so the conversion is greater. The use of a catalyst can also reduce the activation energy, the greater the reaction rate constant, which causes even greater products (Jamilatun et al., 2019d)

At this level, the explanation should be more detail focusing on your result. In addition, try to connect with your catalyst properties or with other data from literature. Thus, readers can get benefit from reading this article. If the authors want to discuss about  $E_a$  without catalyst and  $E_a$  with catalyst and prove your statement that  $E_a$  with catalyst is lower than without catalyst.

5. It seems like there is no need to discuss or present the results from water phase, char and gas product as they are not the focus of this work. The discussion from this results is limited and nearly meaningless to the readers. This is because the authors does not elaborate or provide any consequences of this result to the current process of microalgae or residue pyrolysis.

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- Shinta Amelia
- Aous Aktawan

**Ruang**

- Meeting Prodi Teknik Ki...

**Rapat**

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Reviewer B:  
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General:  
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This manuscript is quite interesting as the fundamental investigation on catalytic pyrolysis of Spirulina platensis residue (SPR). However, a major revision must be needed prior to publishing. Here are the reviewer's comments.  
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Major comments:  
-----  
1) The proximate analysis (e.g., fixed carbon, volatile matter, ash, and total moisture contents) of the SPR sample is strongly needed to help the reader understand the initial characteristic of the raw material of SPR. I think it can be done in a thermogravimetric analysis method.  
-----  
2) Figures 1 and 2, as well as those discussions, should be moved to the discussion section. Also, the specification of SEM-EDX equipment is needed. A contextual discussion regarding the comparison between the grain morphology of the C12-4 and the other similar catalyst is needed. An EDX-mapping of the catalyst may be needed to discuss its atomic distribution  
-----  
3) Pyrolysis conditions are not well described in the research methodology section. It is difficult to understand the heating method of the process. Was the same holding time applied for each temperature selection? Please report how long the real-time was taken for each experimental condition, instead of mentioning, "The experiment is stopped if no more liquid is dripping."  
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4) The author mentioned, "The combustion product in the form of gas condensed into condensate is accommodated in the accumulator and measured by weight." I think there would be no combustion in this process.

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Main content area:

section. in my understanding, to separate the non-condensable gas product (i.e., H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>), the condenser temperature should be strictly -73 oC.

6) How did the author distinguish the liquid product into bio-oil and water phases? It should be clear to be mentioned in the method section.

7) The discussion on the effect of temperature and the amount of the catalyst must be split into different subsections to avoid an overlay interpretation between both effects. I think a comparison between the pyrolysis with and without a catalyst is strongly needed to distinguish the significances between the effect of temperatures and catalyst amounts on the pyrolysis product yields. Finally, a straightforward suggestion should be delivered, which one of the effects (temperature or catalyst) has a significant contribution to the pyrolysis process in this study.

8) The author mentioned, "This condition is due to the secondary reaction." The authors should discuss what mechanism occurs in the primary and secondary (pyrolysis) reaction corresponding to the study's findings.

Minor comments:

1) The specific purpose corresponding to the result of this study is not easy to follow. Please state more straightforward in the introduction section.

2) The composition of the materials is better to be presented in a table.

3) The sample pictures of the raw material SPR, the C12-4 catalyst, and the mixtures under different catalyst weight percentages are necessary to put in the research methodology section to improve the reader's understanding.

4) English editing should be needed to improve readability.

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

## ABSTRACT

Currently, dependence on fossil energy, especially petroleum, is still high at 96 % of total consumption. One solution to overcome reliance on fossil energy is processing energy sources derived from microalgae biomass. This study aims to pyrolysis microalgae with the addition of the C12-4 ( $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{C} + \text{CuO} + \text{promoted}$ ) catalyst. The sample used was *Spirulina platensis* residue (SPR). The study used a fixed-bed reactor with an outer diameter of 44 mm, an inner diameter of 40 mm, and a reactor height of 600 mm. SPR with a particle size of 100 mesh of 50 grams mixed with C12-4 catalyst with a variation of 5, 10, and 15 wt.%. The feed mixture (In-Situ) is inserted into the reactor and tightly closed. The heater uses electric current through a Nickel wire wrapped around the outside of the reactor. The heating rate of pyrolysis on an average of 24.33 °C/min, temperature variations of 300, 400, 500, 550, and 600 °C. The optimum conditions without and with a catalyst to produce bio-oil have different values, pyrolysis without a catalyst (500 °C), with a catalyst of 5 wt.% (500 °C), 10 wt.% (400 °C) and 15 wt.% (550 °C) produces bio-oil 15.00, 17.92, 16.78 and 16.54, respectively. The use of 5, 10, and 15 wt.% catalysts can increase the yield water phase. Yield char is influenced by the amount of catalyst only at 300 °C; the more catalysts, the char yield decreases. Pyrolysis without a catalyst produces the highest gas product. The use of catalysts is very significant in increasing the conversion from 48.69 to 62.46 % at a temperature of 300 °C. The optimum conditions for producing the best bio-oil are at 600 °C with 10 wt.% catalysts, resulting in an O/C ratio of 0.14.

Keywords: *Spirulina platensis* residue, In-situ catalytic pyrolysis, C12-4 catalyst, 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 ( $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{C} + \text{CuO} + \text{promotor}$ ). 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. SPR 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 di luar 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 °C), dengan katalis 5 wt.% (500 °C), 10 wt.% (400 °C) dan 15 wt.% (550 °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 °C, semakin banyak katalis maka yield char semakin menurun. Pirolisis tanpa katalis menghasilkan produk gas tertinggi. Penggunaan katalis sangat signifikan dalam meningkatkan konversi dari 48,69 menjadi 62,46 % pada suhu 300 °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: *Spirulina platensis* residue, In-situ catalytic pyrolysis, C12-4 catalyst, yield bio-oil

## 1. Introduction

Dependence on fossil energy, especially petroleum in Indonesia, is still high, reaching 96 % of total consumption (BPPT-OEI, 2019). The use of fossil energy is detrimental to the environment because the waste from combustion produces harmful substances such as NO<sub>x</sub>, CO, SO<sub>x</sub>, and particulates that

pollute the environment (Yang et al., 2019). One solution is to find alternative energy sources that are environmentally friendly, renewable, and sustainable, resulting from microalgae biomass. Microalgae are photosynthetic oil-producing microorganisms with a 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 done 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 a large amount of 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 to produce bio-oil, bio-char, and gas (Hu and Gholizadeh, 2019). Pyrolysis products are very dependent on several parameters, namely biomass composition, heating rate, pyrolysis temperature, residence time, biomass grain size, and usage 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, slightly lower calorific value than diesel oil and other fuel oils. Bio-oil still contains many oxygenate compounds that can cause corrosion in machines if used. Catalytic pyrolysis is one way to improve the quality (upgrading) of bio-oil by reducing the O 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, namely discussing the effect of catalysts on the 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 a decrease in 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). Moreover, magnetite ( $\text{Fe}_3\text{O}_4$ ) (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.  $\alpha\text{-Fe}_2\text{O}_3$  (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.  $\text{Fe}_2\text{O}_3$  is useful for CO oxidation, photocatalytic water oxidation, reduction of  $\text{NO}_x$  to  $\text{NH}_3$  in diesel exhaust (Baimoldina et al., 2019). The Fe catalyst in ZSM-5 showed a significant improvement in pyrolysis products' quality compared to the 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 dominated by Fe around 56 % can increase bio-oil products' conversion and quality. Metal modified catalysts increased monocyclic aromatic hydrocarbons (MAHs) while reducing the formation of polycyclic aromatic hydrocarbons (PAHs). Moreover, most effective at increasing the formation of MAHs and holding 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) (Lou 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-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 ( $\text{Cr}_2\text{O}_3+\text{Fe}_2\text{O}_3+\text{C}+\text{CuO}$ +promoted) 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 °C and using a catalyst 5, 10, and 15 wt.%. Ultimate, proximate, and higher heating value (HHV) analyze SPR raw materials. The C12-4 catalyst was analyzed by SEM-EDX (Scanning Electron Microscope – Energy Dispersive X-ray). Analysis of bio-oil products with GC-MS 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. SPR was obtained from the Laboratory of Chemical Engineering UGM Eco Mini Plant and analyzed proximate, ultimate, and HHV 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.

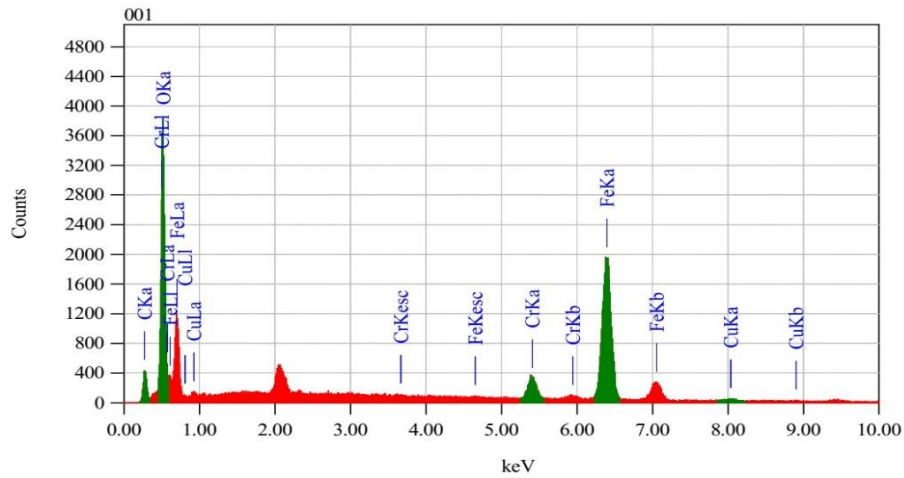
**Table 1. *Spirulina platensis residue* (SPR) characteristic (Jamilatun et al., 2019)**

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

#### 2.1.2. C12-4 Catalyst

The catalyst with the trade name C12-4 ( $\text{Cr}_2\text{O}_3+\text{Fe}_2\text{O}_3+\text{C}+\text{CuO}$ +promoted) in the form of pellets is obtained from PT. Clariant Kujang Catalyst, Kujang Industrial Estate, Jl. Jend. A. Yani No. 39 Cikampek Indonesia. C12-4 has a specific gravity of 0.98-1.25 kg/L and a melting point of more than 650 °C. Based on the Material Safety Data Sheet (MSDS: No. 7011, 2016) and SEM-EDX, it can see the composition and concentration of the catalyst. SEM-EDX was analyzed at the Laboratorium Pengujian dan Penelitian Terpadu (LPPT) Universitas Gadjah Mada (UGM); the results can be seen Figure 1 and Table 2.

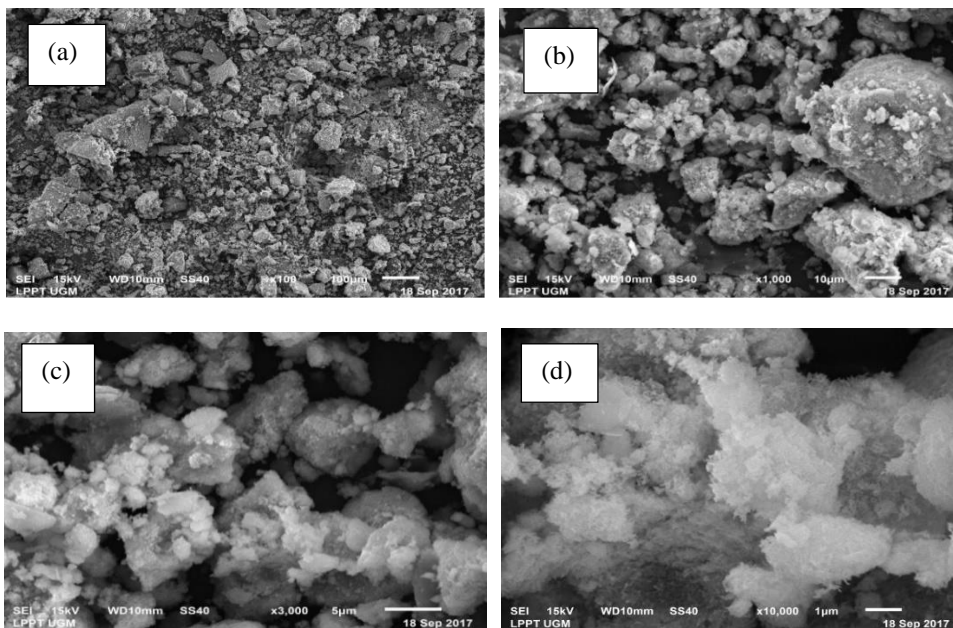
Figure 1 shows the magnitude of the voltage (keV) used and the total counts of each catalyst constituent (C, O, Cr, Fe, and Cu), for Fe obtained at a voltage of 6,398 keV with a total counting of 1900 counts, while O is received at a voltage of 0.525 keV with 3800 counts.



**Figure 1. SEM-EDX C12-4 catalyst analysis results**

**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 <sub>2</sub> O <sub>3</sub>	80-95	C	8.04
CrO <sub>3</sub>	5-10	O	28.75
CuO	1-5	Cr	4.93
C	1-5	Fe	56.64
Cr <sub>2</sub> O <sub>3</sub>	<5	Cu	1.64



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

Based on Table 2, the catalyst's composition consists of  $\text{Fe}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $\text{CuO}$ ,  $\text{C}$ , and  $\text{Cr}_2\text{O}_3$  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, which are 56.64, 28.75, 4.93, 1.64, and 8.04 %, respectively. The largest composition is Fe (56.64 %) and O (28.75 %), which are composed of  $\text{Fe}_2\text{O}_3$  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  $\text{Fe}_2\text{O}_3$  oxide is black iron to steel gray mixed with reddish  $\text{CrO}_3$  and  $\text{CuO}$ .

## 2.2 Procedures

The research goes through several stages of the process: (1) preparation of materials, (2) Preparation of pyrolysis equipment, and (3) pyrolysis process.

### (1) Preparation of materials.

*Spirulina platensis residue* (SPR) was crushed, then sieved with a size of -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) Preparation of Pyrolysis Equipment

The pyrolysis reactor is a fixed-bed reactor in the form of a vertical cylinder with an inner diameter of 40 mm, an outer diameter of 44 mm, a height of 600 mm, a series of pyrolysis equipment as shown in Figure 3. The tool's performance is necessary to study the device's characteristics, namely temperature and time on the heating rate.

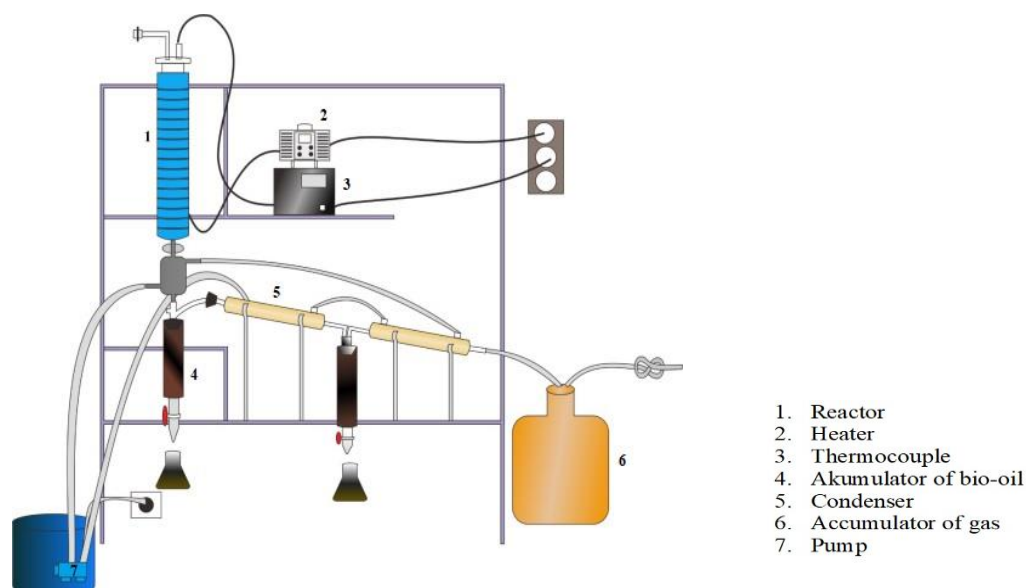


Figure 3. The In-situ catalytic pyrolysis equipment (Jamilatun *et al.*, 2019)

### (1) Pyrolysis Process

Pyrolysis was started by mixing 50 grams of SPR with catalyst C12-4 with variations of 0, 5, 10, and 15 wt.% until homogeneous, then 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 °C/minute. Pyrolysis was carried out with temperature variations of 300, 400, 500, 550, and 600 °C; a thermocouple measured the temperature increase. Condensable gas is condensed into condensate; the results are accommodated in the accumulator and calculated by weight. The non-condensable gas is flowed into the water tank to be absorbed, while the charcoal formed is 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 is about 40 minutes. The yield of bio-oil, water phase, charcoal, gas, and conversion can be calculated using equations (1) - (7). The mixture of bio-oil and water phase is called tar or liquid product.

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

$$Y_L = \frac{W_L}{W_M} \times 100 \% \dots\dots\dots(1)$$

$$Y_B = \frac{W_B}{W_M} \times 100 \% \dots\dots\dots(2)$$

$$Y_{WP} = \frac{W_{WP}}{W_M} \times 100 \% \dots\dots\dots(3)$$

$$Y_C = \frac{W_C}{W_M} \times 100 \% \dots\dots\dots(4)$$

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

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

$$X = \frac{(W_B+W_{WP}+W_G)}{W_M} \times 100 \% \dots\dots\dots(7)$$

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

### 3. Results and Discussion

#### 3.1. Characteristics of the pyrolysis apparatus

The reactor uses a heating medium from the electric current, which is controlled by a voltmeter. The pyrolysis device's characteristic test is crucial for initial research and ensures that the minute and temperature must raise the voltage. 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.

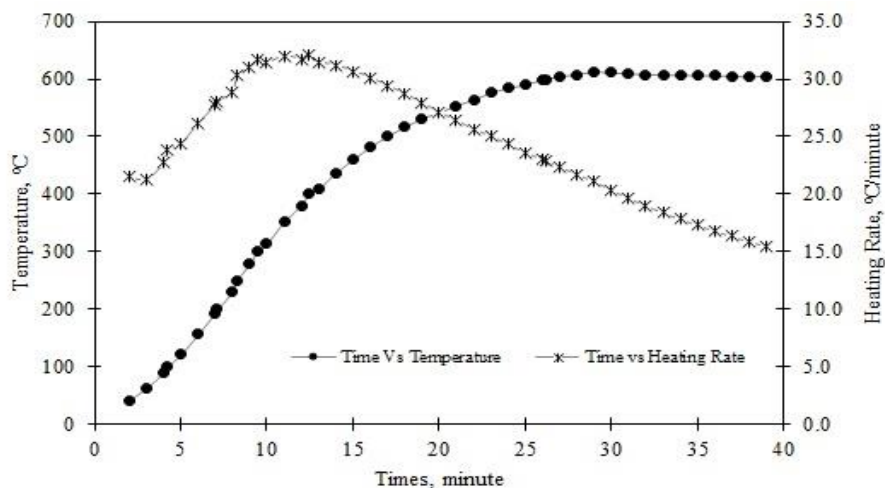


Figure 4. The relationship between time, temperature, and heating rate

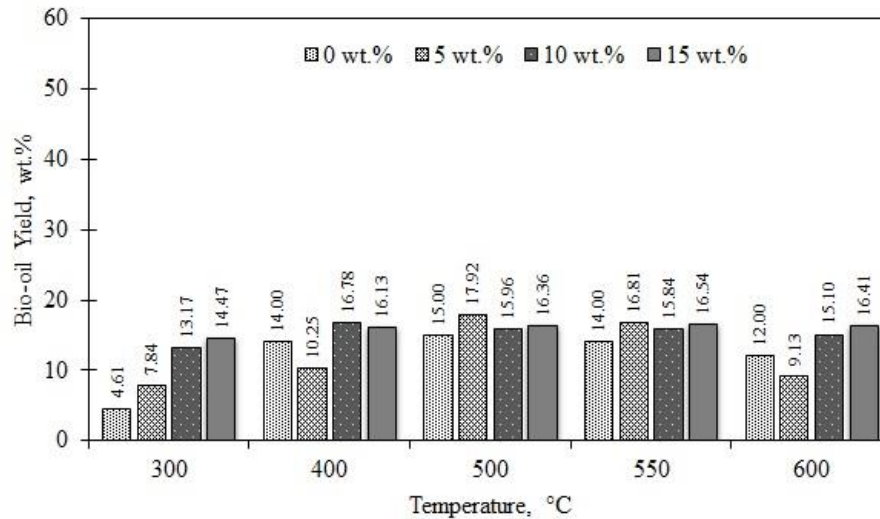
Jamilatun et al. (2017) have examined the pyrolysis of SPR with a Thermogravimetry Analyzer (TGA); the heating rate affects the time required for pyrolysis from 30 to 1000 °C. The greater the heating rate, the shorter the pyrolysis time, respectively, the time needed for SPR pyrolysis at heating

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 SPR pyrolysis's heat is always the same for all variables. This is 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 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. Effect of temperature and the amount of catalyst C12-4 on bio-oil yield**

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 increase, on the other hand, the bio-oil yield will decrease. The formation of char in secondary cracking is minimal so that it does not affect the formation of char (Jamilatun et al., 2018). The optimum conditions for pyrolysis without and with a catalyst have different values. Pyrolysis without a catalyst at 500 °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 °C with bio-oil yields of 17.92, 16.78, and 16.54 %, respectively.

#### 3.2.2. Yield Water Phase

The effect of temperature and the amount of catalyst C12-4 is presented in Figure 6; the calculation follows Equation 3. Based on the figure, the effect of temperature on the yield water phase fluctuates and the amount of catalyst. Overall, in the temperature range of 300-600 °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 yield water phase value 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 and the use of 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 its different phases, the upper phase (oil phase) in the form of bio-oil and the lower phase (water phase) in the form of the water phase. This liquid product is generally referred to as tar.

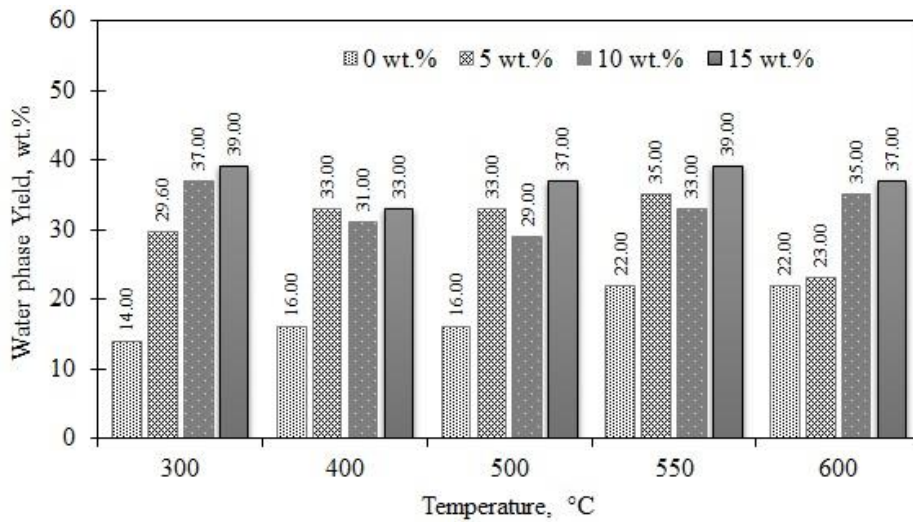


Figure 6. Effect of temperature and the amount of catalyst C12-4 on water phase yield

### 3.2.3. Char Yield

Figure 7 presents the effect of temperature and the amount of catalyst on char yield; the calculation follows Equation 4.

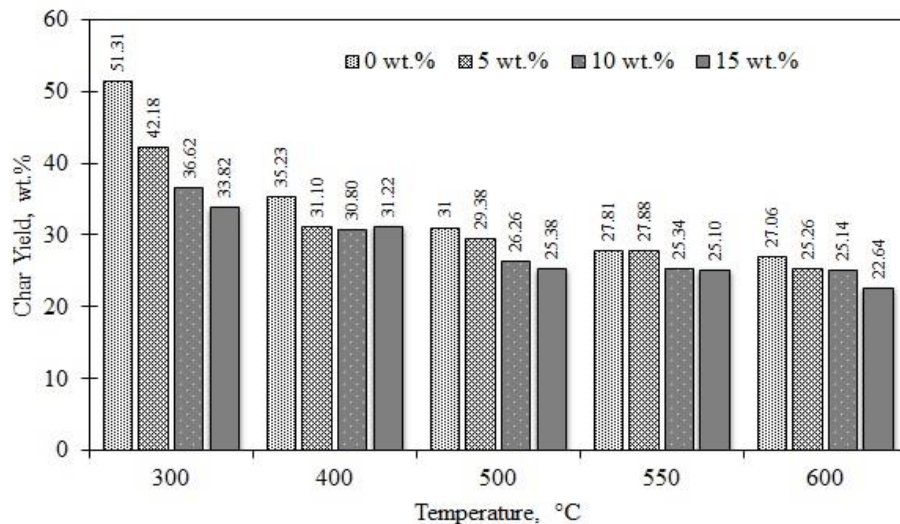


Figure 7. Effect of temperature and the amount of catalyst C12-4 on char yield

Based on Figure 7, it can be seen that the higher the pyrolysis temperature, the lower the char weight. Using catalysts is very influential on yield char only at 300 °C; the more catalysts, the lower the yield. However, at a 400-600 °C temperature, the amount of catalyst has relatively little effect on reducing



char yield. Pyrolysis at a low temperature of less 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 be more active so that the char yield will drop (Jafarian et al., 2018).

Pyrolysis variables in the form of 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. Gas Yield

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 °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 produces higher gas than pyrolysis with a catalyst because the catalyst causes more active hydrogenation and hydrodeoxygenation 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 °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.

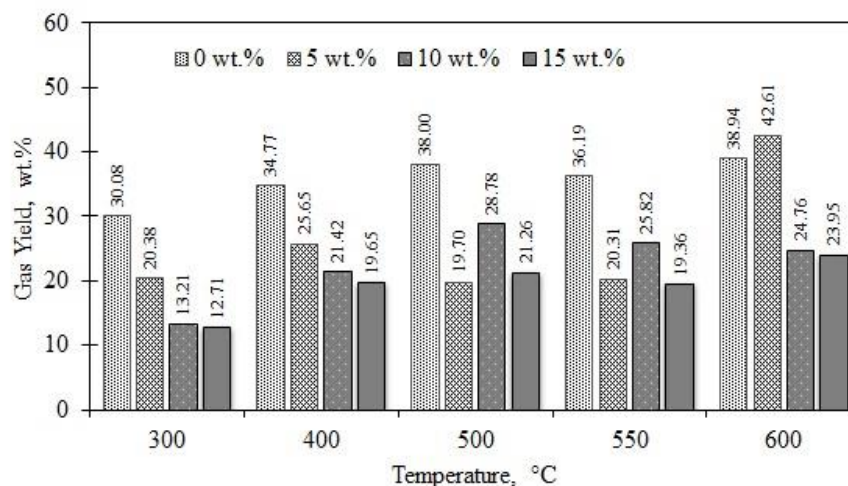


Figure 8. Effect of temperature and the amount of catalyst C12-4 on gas yield

### 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 °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 °C, the use of 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 °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.

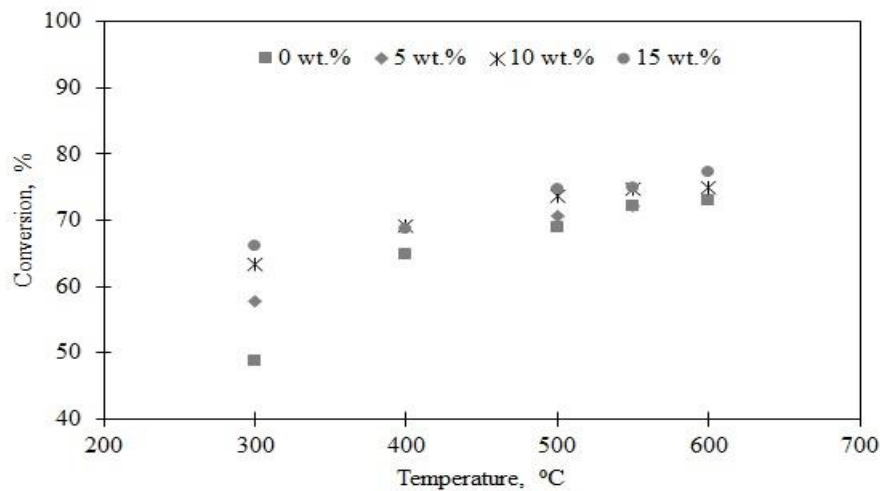


Figure 9. Effect of temperature on various amounts of catalyst on conversion

### 3.2.6. Upgrading Bio-oil

Based on GC-MS data obtained, the O and C components in bio-oil. 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 °C and amount of catalyst 5, 10, 15 wt.% on the O/C ratio compared to bio-oil products without a catalyst, the results are presented in Figure 10.

Figure 10 shows without catalyst at a temperature variation of 300-600 °C. The O/C ratio is in the range of 0.47-0.74 and with a 10 wt.% in the range of 0.14-0.44. The average O/C drop from 300-600 °C without and with the catalyst is from 0.48 to 0.26, reduced 84.62 %. The optimum condition is reached at a temperature of 600 °C with a 10 wt.% produce O/C ratio of 0.14.

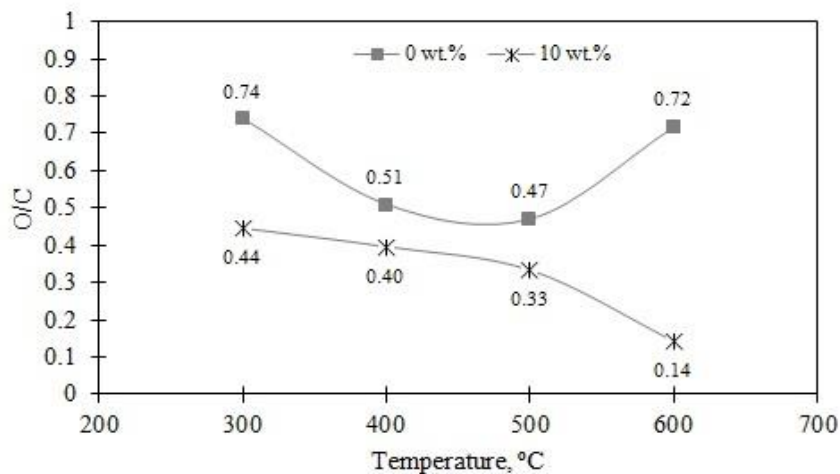


Figure 9. Effect of temperature on various amounts of catalyst on O/C ratio

## 4. Conclusions

Catalytic pyrolysis of residual *Spirulina platensis* (SPR) with a grain size of 100 mesh was carried out in a fixed-bed reactor from a temperature of 300-600 °C. C12-4 catalysts ( $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{C} + \text{CuO} + \text{promoter}$ ) were used at 5, 10, and 15 wt.% with an average heating rate of 24.33 °C/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 °C with bio-oil yields 15.00, 17.92, 16.78, and 16.54 %, respectively. The temperature range of 300-600 °C 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 %. The effect of using catalysts on yield char is only at 300 °C, the more catalyst the yield of char decreases. However, at a temperature of 400-600 °C, the amount of catalyst does not significantly affect char yield reduction. 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. A catalyst is very significant in increasing the conversion, from 48.69 to 62.46 % at 300 °C. The average O/C ratio drop from 300 to 600 °C 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.

### Acknowledgments

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## Respon untuk Reviewer

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

REVIEWER A

No.	Review comments	Tanggapan/ Perbaikan penulis
1	<p>The English need to be improved. I provide some examples here:</p> <ol style="list-style-type: none"> <li>a. The use of fossil energy hurts the environment.</li> <li>b. One solution is to find alternative energy sources that are friendly to the ground, renewable, and sustainable.</li> <li>c. In-situ catalytic pyrolysis is between biomass and catalyst mixed in one reactor, while ex-situ catalytic pyrolysis is biomass, and the catalyst is separated in reactors 1 and 2</li> <li>d. SEM-EDX analyzed the catalysts at the Laboratorium Pengujian dan Penelitian Terpadu (LPPT), UGM. Based on Figure 1 and 2, can see the results of SEM-EDX analysis in the form of percentage by weight of catalyst constituent.</li> <li>e. This sentence is not needed: The results and discussion of the topic of In-situ catalytic pyrolysis SPR with the influence of temperature and the amount of catalyst C12-4 with SPR 100 mesh grain size on product yield are (1) the characteristics of the pyrolysis apparatus and (2) the effect of temperature and the amount of catalyst.</li> <li>f. Fixed-bed reactor carried out catalytic pyrolysis Spirulina platensis residue (SPR) grain size of 100 mesh using etc.</li> </ol>	<p>Perbaikan yang telah dilakukan</p> <ol style="list-style-type: none"> <li>a. The use of fossil energy is detrimental to the environment because the waste from combustion produces harmful substances such as NO<sub>x</sub>, CO, SO<sub>x</sub>, and particulates that can pollute the environment.</li> <li>b. One solution is to find alternative energy sources that are environmentally friendly, renewable, and sustainable, resulting 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.</li> <li>c. 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.</li> <li>d. SEM-EDX analyzed the C12-4 catalyst at the UGM Integrated Testing and Research Laboratory (LPPT). The results can be seen in Figures 1 and 2.</li> <li>e. Sudah dihapus</li> <li>f. Catalytic pyrolysis of residual Spirulina platensis (SPR) with a grain size of 100 mesh was carried out in a fixed-bed reactor from a temperature of 300-600 °C. C12-4 catalysts (Cr<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> + C + CuO + promoter) were used at 5, 10, and 15 wt.% with an average heating rate of 24.33 °C / minute.</li> </ol>
2	<p>The author needs to provide reasoning on why it is important to use the C12-4 catalyst? What is special about this catalyst, and what positive impact that you expect when you use this catalyst. It would be better if there is a plot showing the bio-oil yield without a catalyst for comparison.</p>	<p>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).</p> <p>The bio-oil yield decreased with the addition of a catalyst to pyrolysis. The Fe catalyst in ZSM-5 showed a significant improvement in pyrolysis</p>

		products' quality compared to the 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. Also, metal modified catalysts increased the production of monocyclic aromatic hydrocarbons (MAHs) while reducing the formation of polycyclic aromatic hydrocarbons (PAHs), were most effective at increasing the formation of MAHs and holding the formation of PAHs up to 10% (Zang et al., 2018).
3	Figure 5 presents the influence of temperature and catalyst loading on the bio-oil yield. I have computed with two way ANOVA based on the presented data, and it turned out that the effect of catalyst and temperature is not significant. Thus, it is hard to conclude that the 500°C is the optimum temp to obtain the maximum bio-oil yield.	Based on data processing using ANOVA, it can be concluded that $F_{crit} > F$ ; $H_0$ is accepted, meaning that there is a significant difference/change in the interaction of catalyst weight and temperature on yield
4	<p>The explanation or discussion of figure 5 is too general and shallow:</p> <p>The greater the amount of catalyst used, the greater the number of active surfaces for the reaction to occur, so the conversion is more significant. The use of a catalyst can also reduce the activation energy, the greater the reaction rate constant, which causes even greater products (Jamilatun et al., 2019d)</p> <p>At this level, the explanation should be more detailed, focusing on your result. Besides, try to connect with your catalyst properties or with other data from the literature. Thus, readers can get benefit from reading this article. If the authors want to discuss <math>E_a</math>, then calculate the <math>E_a</math> without catalyst and <math>E_a</math> with catalyst and prove your statement that <math>E_a</math> with the catalyst is lower than without catalyst.</p>	<p>The greater the amount of catalyst used, the greater the number of active surfaces for the reaction to occur; the catalyst can reduce the activation energy (<math>E_a</math>). The <math>E_a</math> value without a catalyst in SPR pyrolysis with a heating rate of 20 °C / min is 41.10 KJ / mole (Jamilatun et al., 2017), while with the same 50% heating rate catalyst obtained <math>E_a</math> 39.46 KJ / mole (Jamilatun et al., 2020).</p>
	It seems like there is no need to discuss or present the results from the water phase, char, and gas product as they are not the focus of this work. The discussion from these results is limited and nearly meaningless to the	Pyrolysis variables in the form of 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,

	<p>readers. This is because the authors do not elaborate or provide any consequences of this result to the current process of microalgae or residue pyrolysis.</p>	<p>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.</p> <p>The formation of gaseous products is strongly influenced by temperature; the higher it is, the higher it is. At temperatures above 300 °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.</p>
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REVIEWER B

No.	Review comments	Tanggapan/ Perbaikan penulis																								
1	<p>The proximate analysis (e.g., fixed carbon, volatile matter, ash, and total moisture contents) of the SPR sample is strongly needed to help the reader understand the initial characteristic of the raw material of SPR. I think it can be done in a thermogravimetric analysis method.</p>	<p>Done</p> <p>Table 2. The composition of the C12-4 catalyst was based on concentration data from MSDS (No. 7011, 2016) and mass percent from SEM-EDX analysis</p> <table border="1" data-bbox="774 913 1353 1153"> <thead> <tr> <th>Chemical Name (MSDS)</th> <th>Concentration, %</th> <th>Element (SEM-EDX)</th> <th>Mass, %</th> </tr> </thead> <tbody> <tr> <td>Fe<sub>2</sub>O<sub>3</sub></td> <td>80-95</td> <td>C</td> <td>8.04</td> </tr> <tr> <td>CrO<sub>3</sub></td> <td>5-10</td> <td>O</td> <td>28.75</td> </tr> <tr> <td>CuO</td> <td>1-5</td> <td>Cr</td> <td>4.93</td> </tr> <tr> <td>C</td> <td>1-5</td> <td>Fe</td> <td>56.64</td> </tr> <tr> <td>Cr<sub>2</sub>O<sub>3</sub></td> <td>&lt;5</td> <td>Cu</td> <td>1.64</td> </tr> </tbody> </table>	Chemical Name (MSDS)	Concentration, %	Element (SEM-EDX)	Mass, %	Fe <sub>2</sub> O <sub>3</sub>	80-95	C	8.04	CrO <sub>3</sub>	5-10	O	28.75	CuO	1-5	Cr	4.93	C	1-5	Fe	56.64	Cr <sub>2</sub> O <sub>3</sub>	<5	Cu	1.64
Chemical Name (MSDS)	Concentration, %	Element (SEM-EDX)	Mass, %																							
Fe <sub>2</sub> O <sub>3</sub>	80-95	C	8.04																							
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C	1-5	Fe	56.64																							
Cr <sub>2</sub> O <sub>3</sub>	<5	Cu	1.64																							
2	<p>Figures 1 and 2, as well as those discussions, should be moved to the discussion section. Also, the specification of SEM-EDX equipment is needed. A contextual discussion regarding the comparison between the grain morphology of the C12-4 and the other similar catalyst is required. An EDX-mapping of the catalyst may be needed to discuss its atomic distribution</p>	<p>Done</p>																								
3	<p>Pyrolysis conditions are not well described in the research methodology section. It is difficult to understand the heating method of the process. Was the same holding time applied for each temperature selection? Please report how long the real-time was taken for each experimental condition, instead of mentioning, "The experiment is stopped if no more the liquid is dripping."</p>	<p>The experiment is stopped if no more liquid is dripping; each pyrolysis's average time is about 40 minutes.</p>																								

4	<p>The author mentioned, "The combustion product in the form of gas condensed into condensate is accommodated in the accumulator and measured by weight." I think there would be no combustion in this process.</p>	<p>In the form of gas condensed into condensate, the pyrolysis product is accommodated in the accumulator and measured by weight.</p>
5	<p>Besides, what temperature of the condenser condition, and on what consideration of it? It should be mentioned clearly in the method section. In my understanding, to separate the non-condensable gas product (i.e., H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>), the condenser temperature should be strictly -73 C.</p>	<p>At room temperature, the non-condensable gas will be a gas, while the condensable gas will condense</p>
6	<p>How did the author distinguish the liquid product into bio-oil and water phases? It should be clear to be mentioned in the method section.</p>	<p>Liquid pyrolysis products are in the form of bio-oil and water phases. Furthermore, it can be separated because of its different phases, the upper phase (oil phase) in the form of bio-oil and the lower phase (water phase) in the form of the water phase. This liquid product is generally referred to as tar</p>
7	<p>The discussion on the effect of temperature and the amount of the catalyst must be split into different subsections to avoid an overlay interpretation between both results. I think a comparison between the pyrolysis with and without a catalyst is strongly needed to distinguish the significances between the effect of temperatures and catalyst amounts on the pyrolysis product yields. Finally, a straightforward suggestion should be delivered, which one of the impacts (temperature or catalyst) has a significant contribution to the pyrolysis process in this study.</p>	<p>In pyrolysis 500-550 °C, the amount of catalyst does not affect the bio-oil yield. This condition is due to the secondary reaction, while the tar will decompose in the secondary reaction into gas and a little char (Jamilatun et al., 2018; Jamilatun et al., 2019). The greater the amount of catalyst used, the greater the number of active surfaces for the reaction to occur; the catalyst can reduce the activation energy (E<sub>a</sub>). The E<sub>a</sub> value without a catalyst in SPR pyrolysis with a heating rate of 20 °C / min is 41.10 KJ / mole. In contrast, silica-alumina catalytic pyrolysis with the same heating rate obtained E<sub>a</sub> 39.46 KJ / mole (Jamilatun et al., 2017).</p>
8	<p>The author mentioned, "This condition is due to the secondary reaction." The authors should discuss what mechanism occurs in the primary and secondary (pyrolysis) reaction corresponding to the study's findings.</p>	<p>In general, primary pyrolysis and secondary pyrolysis occur. Primary pyrolysis produces tar (bio-oil and water phase), char and gas, while secondary pyrolysis converts the tar from primary pyrolysis into gas and char. At a temperature of 300 °C, the use of 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</p>



		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 °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.
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	<p>Minor comments:</p> <ol style="list-style-type: none"> <li>1) The specific purpose corresponding to the result of this study is not easy to follow. Please state more straightforward in the introduction section.</li> <li>2) The composition of the materials is better to be presented in a table.</li> <li>3) The sample pictures of the raw material SPR, the C12-4 catalyst and the mixtures under different catalyst weight percentages are necessary to put in the research methodology section to improve the reader's understanding.</li> <li>4) English editing should be needed to improve readability.</li> </ol>	Done

## LAMPIRAN 6. ACCEPTED

The screenshot shows a Gmail interface with the following elements:

- Browser Tabs:** [jrekpros] Editor Decision - sitjar, REVIEW DOKUMEN-Biochar from, (278) WhatsApp, Sistem Informasi Manajemen PA, Download file | iLovePDF, #60477 Review.
- Address Bar:** mail.google.com/mail/u/0/#search/jurnal+rekayasa+proses/FMfcgxxKkbdjNMDCxrIbDbVFRwwBKtlb
- Gmail Header:** Search for "jurnal rekayasa proses", user profile "AHMAD DAHLAN", and status "Aktif".
- Left Sidebar:** Navigation menu including "Email" (Kotak Masuk: 9,570, Berbintang, Ditunda, Penting, Terkirim, Draf: 198, Kategori, Unwanted), "Chat" (Rachma Tia Evitasari, maryudi maryudi, Melia Dian, Heni Anggorowati, Shinta Amelia, Aaus Aktawan), and "Ruang" (Meeting Prodi Teknik Ki...).
- Email Content:**
  - From:** [jrekpros] Editor Decision (Kotak Masuk)
  - To:** Dr.-Ing. Teguh Ariyanto, S.T., M.Eng. <teguh.ariyanto@ugm.ac.id>
  - Subject:** Siti Jamilaton:
  - Body:**

We are pleased to inform you that your recent submission titled, "In-Situ Catalytic Pyrolysis Spirulina platensis residue (SPR): Effect of Temperature and Amount of Catalyst C12-4 on Product Yield", has been accepted for publication in [Jurnal Rekayasa Proses](#).

Please complete the statement of originality as attached and send the filled form to [jurnal\\_rekpros@ugm.ac.id](mailto:jurnal_rekpros@ugm.ac.id) as soon as possible. For publication process, we will contact you again when your proof is ready for you to check before its publication.

You are also requested to pay publication fee  
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Thank you for your interest in [Jurnal Rekayasa Proses](#). We look forward to publishing your future article.

Managing Editors,  
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Chemical Engineering Department, Universitas Gadjah Mada  
[teguh.ariyanto@ugm.ac.id](mailto:teguh.ariyanto@ugm.ac.id)

[Jurnal Rekayasa Proses](#)  
<http://journal.ugm.ac.id/index.php/jrekpros>
- Taskbar:** Windows taskbar with search bar, taskbar icons (File Explorer, Edge, etc.), and system tray showing 77°F Clear, 18:41, 06/07/2022.

## LAMPIRAN 7. COPYEDITING

The screenshot shows a Gmail interface with a search bar containing "jurnal rekayasa proses". The email being viewed is titled "[jrekpros] Copyediting Review Request" and is marked as "Eksternal" and "Kotak Masuk". The sender is Dr.-Ing. Teguh Ariyanto, S.T., M.Eng. (teguh.ariyanto@ugm.ac.id), dated "Sen, 7 Jun 2021 15.58".

**Siti Jamilatur:**

Your submission "In-Situ Catalytic Pyrolysis Spirulina platensis residue (SPR): Effect of Temperature and Amount of Catalyst C12-4 on Product Yield" for **Jurnal Rekayasa Proses** has been through the first step of copyediting, and is available for you to review by following these steps.

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This is the last opportunity to make substantial copyediting changes to the submission. The proofreading stage, that follows the preparation of the galley, is restricted to correcting typographical and layout errors.

The deadline for copy-editing is 1x24 h.

If you are unable to undertake this work at this time or have any questions, please contact me. Thank you for your contribution to this **journal**.

The left sidebar shows the Gmail navigation menu with categories like "Kotak Masuk" (9,570), "Draf" (198), "Chat", "Ruang", and "Rapat". The bottom of the image shows a Windows taskbar with various application icons and a system tray displaying "77°F Clear" and the date "06/07/2022".



## SURAT PERNYATAAN KEASLIAN NASKAH

Saya yang bertanda tangan di bawah ini:

Nama : 1) Siti jamilatun  
2) Ratih Mahardika  
3) Imelda Eka Nurshinta

Institusi\* : Universitas Ahmad Dahlan

Email\* : sitijamilatun@che.uad.ac.id / phone:081933096313.

Tempat, tgl lahir\* : Klaten, 12 Agustus 1966

Alamat\* : Jalan Barokah Gang Nuri 361 Cebongan Kasihan Bantul DIY

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

Artikel diterima : tanggal 16 bulan Januari tahun 2021

Saya menyatakan bahwa artikel tersebut di atas merupakan naskah asli, hasil pemikiran sendiri, bukan saduran/terjemahan, dan belum pernah dipublikasikan di media apapun. Saya bersedia bertanggung jawab jika kelak terdapat pihak tertentu yang merasa dirugikan secara pribadi atau tuntutan hukum atas diterbitkannya artikel ini.

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Yogyakarta, 16 Januari 2021

Penulis,

(Siti Jamilatun)

\* Tuliskan data penulis utama

**Pernyataan ini dikirimkan kembali via e-mail: [jurnal.rekpros@ugm.ac.id](mailto:jurnal.rekpros@ugm.ac.id)**

## LAMPIRAN 8. PROOFREADING

The screenshot shows a Gmail interface on a desktop browser. The browser's address bar displays the URL: mail.google.com/mail/u/0/#search/jurnal+rekayasa+proses/FMfcgzGkXwFWFvHRkzqWmKXKWhJmDXnF. The Gmail search bar contains the text "jurnal rekayasa proses". The email list on the left includes folders like "Kotak Masuk" (9,570), "Berbintang", "Draf" (198), "Kategori", "Unwanted", "Chat", and "Ruang". The selected email is from "Dr.-Ing. Teguh Ariyanto, S.T., M.Eng." with the subject "[jrekpros] Proofreading Acknowledgement (Author)". The email body contains the following text:

Siti Jamilatur:

Thank you for proofreading the galley for your manuscript, "In-Situ Catalytic Pyrolysis Spirulina platensis residue (SPR): Effect of Temperature and Amount of Catalyst C12-4 on Product Yield," in [Jurnal Rekayasa Proses](#). We are looking forward to publishing your work shortly.

If you subscribe to our notification service, you will receive an email of the Table of Contents as soon as it is published. If you have any questions, please contact me.

Dr.-Ing. Teguh Ariyanto, S.T., M.Eng.  
Chemical Engineering Department, Universitas Gadjah Mada  
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[Jurnal Rekayasa Proses](#)  
<http://journal.ugm.ac.id/index.php/jrekpros>

At the bottom of the screenshot, the Windows taskbar is visible, showing the system tray with the date 06/07/2022 and time 18:45. The taskbar includes icons for various applications and a search bar.



## 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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(Submission: 8 October 2020; Revision: 11 January 2021; Acceptance: 16 January 2021)

### 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 ( $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{C} + \text{CuO} + \text{promoter}$ ) 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 °C), with a catalyst of 5 wt.% (500 °C), 10 wt.% (400 °C), and 15 wt.% (550 °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 °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 °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 °C), dengan katalis 5 wt.% (500 °C), 10 wt.% (400 °C) dan 15 wt.% (550 °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 °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 °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 ( $\text{Fe}_3\text{O}_4$ ) (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  $\alpha\text{-Fe}_2\text{O}_3$  (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  $\text{Fe}_2\text{O}_3$  is useful for CO oxidation, photocatalytic water oxidation, reduction of  $\text{NO}_x$  to  $\text{NH}_3$  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 ( $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{C} + \text{CuO} + \text{promoter}$ ) 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 °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
<b>Composition analysis (wt.%)</b>	
Lipid	0.09
Carbohydrate	38.51
Protein	49.60
<b>Ultimate analysis (wt.%)</b>	
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, %
$\text{Fe}_2\text{O}_3$	80-95	C	8.04
$\text{CrO}_3$	5-10	O	28.75
$\text{CuO}$	1-5	Cr	4.93
C	1-5	Fe	56.64
$\text{Cr}_2\text{O}_3$	<5	Cu	1.64

#### 2.1.2 C12-4 Catalyst

The catalyst with the trade name C12-4 ( $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{C} + \text{CuO} + \text{promoter}$ ) 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 °C. Based on the Material Safety Data Sheet (MSDS: No. 7011, 2016) and

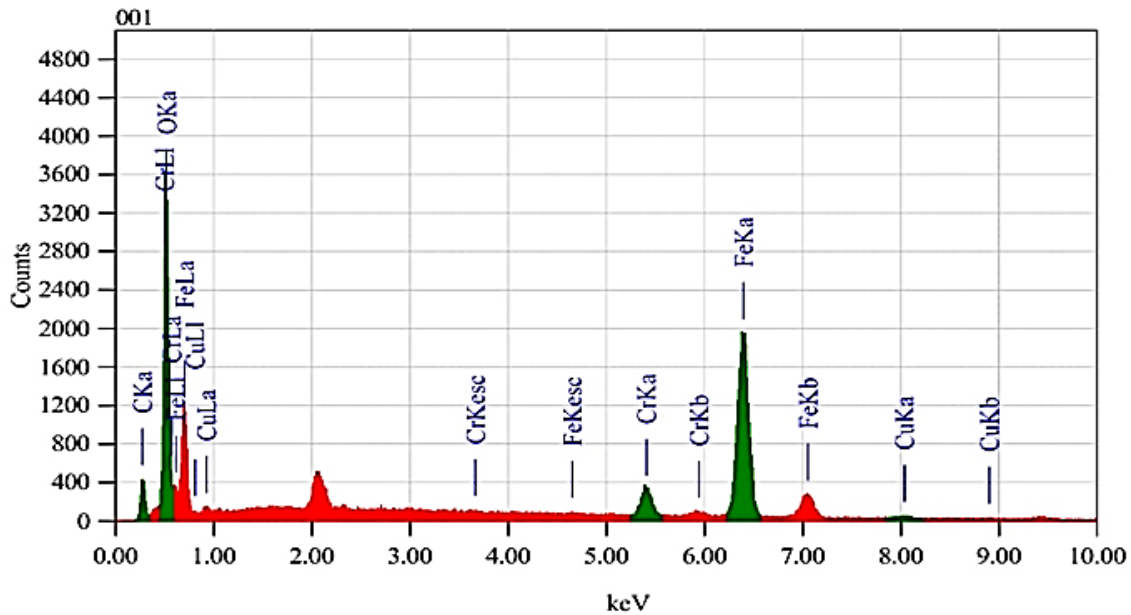


Figure 1. SEM-EDX C12-4 catalyst analysis results

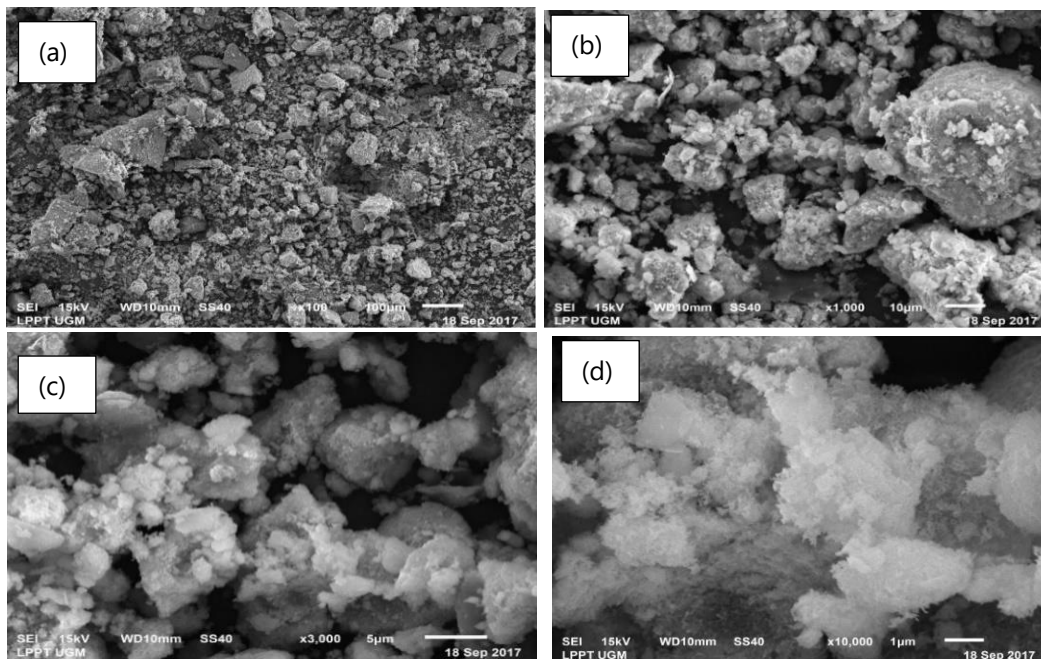


Figure 2. SEM analysis of C12-4 at magnification, (a) 100 times, (b) 1000 times, (c) 5000 times and (d) 10,000

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  $\text{Fe}_2\text{O}_3$ ,  $\text{CrO}_3$ ,  $\text{CuO}$ , C, and  $\text{Cr}_2\text{O}_3$  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  $\text{Fe}_2\text{O}_3$  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  $\text{Fe}_2\text{O}_3$  oxide is black iron to steel gray mixed with reddish  $\text{CrO}_3$  and  $\text{CuO}$ .

## 2.2 Procedures

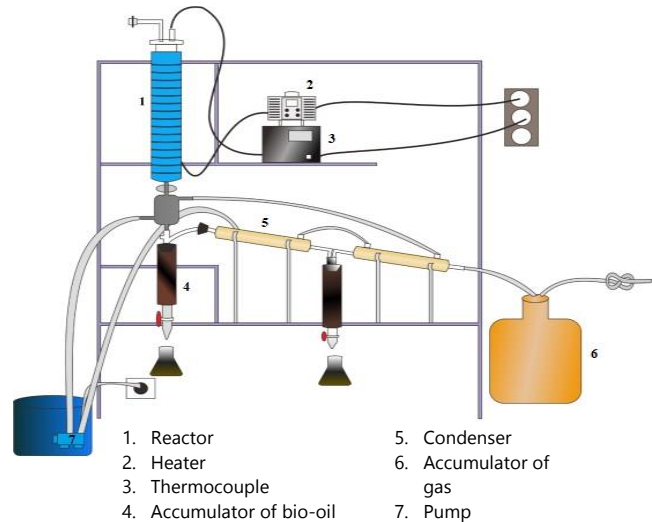
The research was conducted in several stages of the process: (1) preparation of materials, (2) preparation of pyrolysis equipment, and (3) pyrolysis process.

### 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.



**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 °C/minute. Pyrolysis was carried out with temperature variations of 300, 400, 500, 550, and 600 °C and monitored using a thermocouple. Condensable gas is condensed into the accumulator and the liquid was weighed. 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):

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

$$Y_B = \frac{W_B}{W_M} \times 100 \% \quad (2)$$

$$Y_{WP} = \frac{W_{WP}}{W_M} \times 100 \% \quad (3)$$

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

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

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

$$X = \frac{(W_B + W_{WP} + W_G)}{W_M} \times 100 \% \quad (7)$$

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

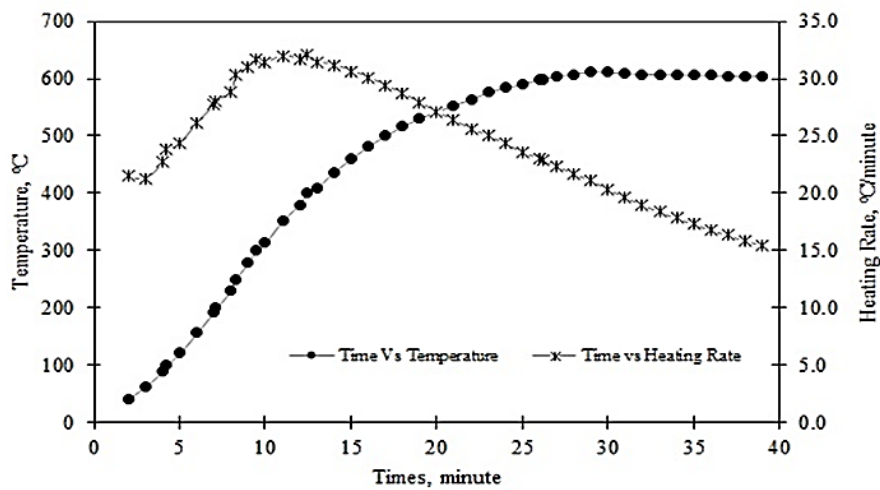


Figure 4. The relationship between time, temperature, and heating rate

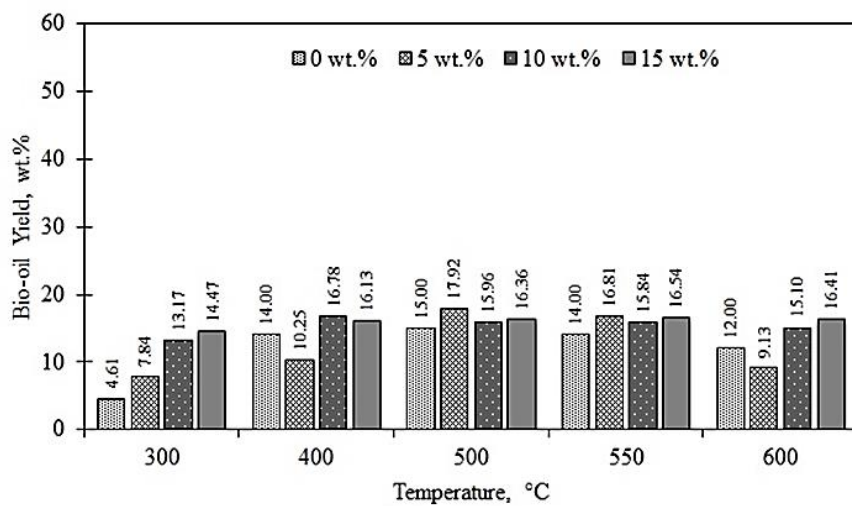


Figure 5. Effect of temperature and the amount of catalyst C12-4 on bio-oil yield

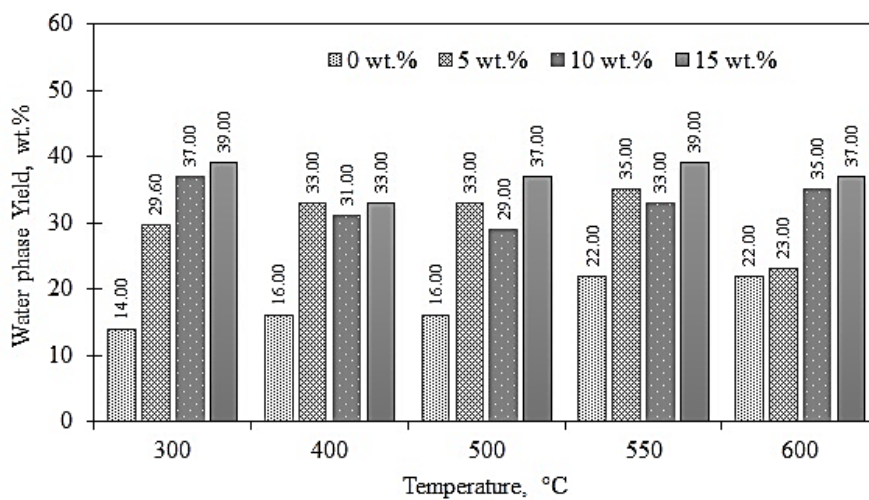


Figure 6. Effect of temperature and the amount of catalyst C12-4 on water phase yield

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 °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 °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 °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 °C; the more the catalysts, the lower the yield. However, at a 400-600 °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 °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 °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.

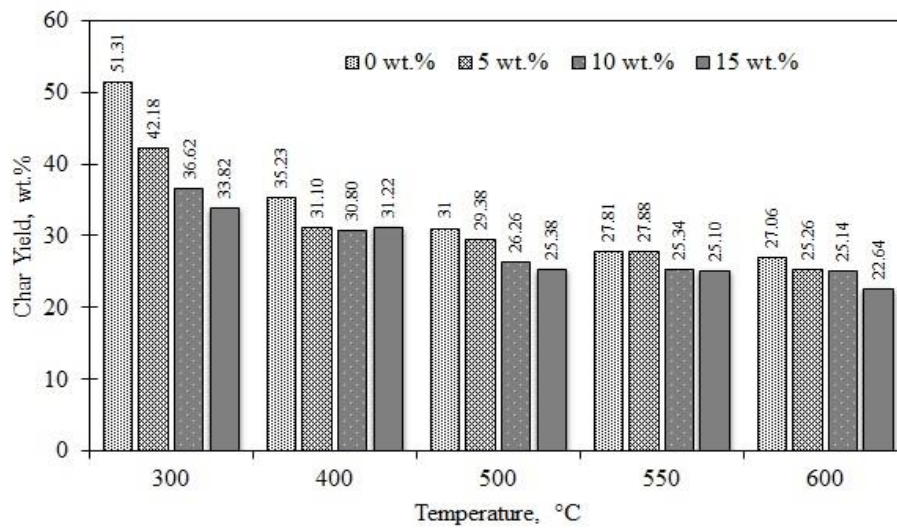


Figure 7. Effect of temperature and the amount of catalyst C12-4 on char yield

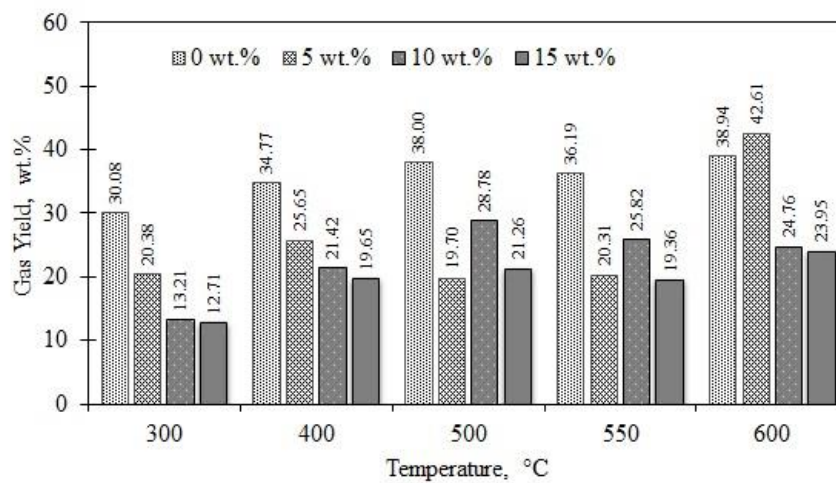


Figure 8. Effect of temperature and the amount of catalyst C12-4 on gas yield

### 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 °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 °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 °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 °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.

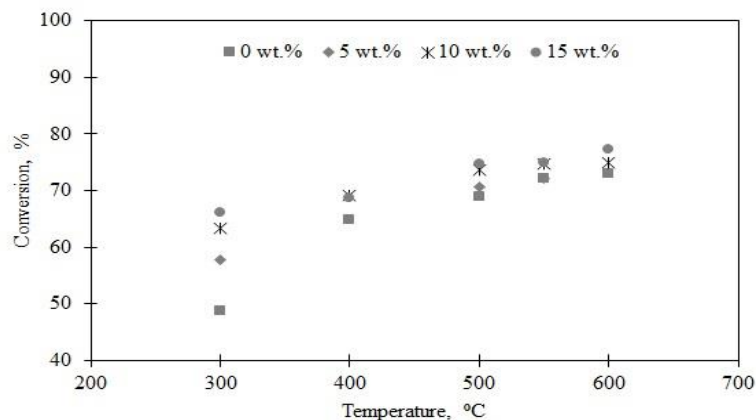


Figure 9. Effect of temperature on various amounts of catalyst on conversion

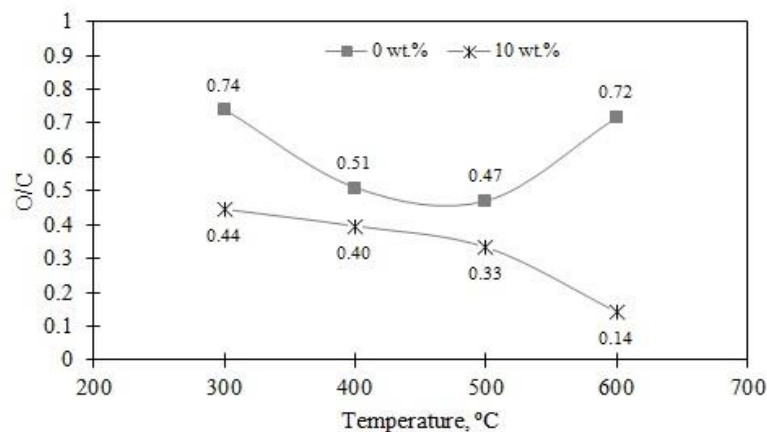


Figure 10. Effect of temperature on various amounts of catalyst on O/C ratio



Figure 10 shows the O/C for with and without catalyst at a temperature variation of 300-600 °C. 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 °C. The C12-4 catalysts ( $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{C} + \text{CuO} + \text{promoter}$ ) were used at 5, 10, and 15 wt.% with an average heating rate of 24.33 °C/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 °C with bio-oil yields 15.00, 17.92, 16.78, and 16.54 %, respectively. The temperature range of 300-600 °C 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 °C, i.e., the more catalyst, the less yield of char. However, at 400-600 °C, 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 °C. The average O/C ratio drop from 300 to 600 °C 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.

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