Research Article

Comparative Analysis Between Pyrolysis Products of *Spirulina platensis* Biomass and Its Residues

Siti Jamilatun[a], Budhijanto[b], Rochmadi[b], Avido Yuliestyan[c], H. Hadiyanto[d] and Arief Budiman[b,e,*]

[a]*Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Ahmad Dahlan, Jalan Kapas 9, Yogyakarta 55166, Indonesia*

[b]*Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jalan Grafika 2, Yogyakarta 55284, Indonesia*

[c]*Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Pembangunan Nasional "Veteran" Yogyakarta, Jalan SWK 104, Yogyakarta 55283, Indonesia*

[d]*Center of Biomass and Renewable Energy, Chemical Engineering Department, Diponegoro University, Jl.Prof Soedarto,SH-Tembalang, Semarang Indonesia.*

[e]*Center for Energy Studies, Universitas Gadjah Mada, Sekip K1A, Yogyakarta 55284, Indonesia.*

ABSTRACT. Today's needs of energy are yet globally dominated by fossil energy sources, causing the depletion of non-renewable energy. Alternatively, a potential substitute is the energy of biomass. *Spirulina platensis* (SP) is a microalgae biomass which, if extracted, will produce solid waste called *Spirulina platensis* residue (SPR). This research explores the pyrolysis product, produced within the range of 300 – 600 ℃, from the pyrolysis of SP and SPR using fixed bed reactors. The influence of temperature on pyrolysis product's yield and characteristics are investigated by using mass balance method and gas chromatography – mass spectrometry (GC-MS) technique, respectively. The results from mass balance method present an optimum pyrolysis temperature of 550 ℃ to obtain the desired liquid product of bio-oil, presenting the percentage of 34.59 wt.% for SP and 33.44 wt.% for SPR case. Additionally, with the increasing temperature, the char yield decreases for about 30 wt.% and the yield of gas seems to sharp increase from 550 to 600 ℃. These tendencies are both applied for SP and SPR source pyrolysis product. Interestingly, the benefit use as fossil fuel substitute might be derived, thanks to high HHV at the bio-oil product (32.04 MJ/kg for SP and 25.70 MJ/kg for SPR) and also at the char product with of 18.85-26.12 MJ/kg for both cases. The additional benefit come from the high content of C in its char product (50.31 wt.% for SPR and 45.26 wt.% for SP) that might be able to be used as an adsorbent, soil softener or other uses in the pharmaceutical field.

1. Introduction

The decline in population growth from 2016 to 2018 does not necessarily in line with energy needs, as evidenced by the increasing need of crude oil by 1.6 % associated to a high demand in transportation and petrochemical industry (Roser and Ortiz-Ospina, 2017). In addition, gas and coal consumption rise up to 3 % and 1 %, respectively to cause an increase in carbon emissions of around 1.4 %, or equivalent to 32.5 Gtons (International Energy Agency, 2018). Although the contribution of renewable energy gains to 6.3 %, driven by the expansion of wind, solar and hydropower plants, the use of fossil energy is still around 81 % of the world's energy needs within the last 30 years (International Energy Agency, 2018).

Global reserves of fossil fuels, namely coal, natural gas and crude oil in 2018 are respectively 1,139 billion tons, 187 trillion m^3 and 1,707 billion barrels and are expected to be consecutively finished in 2169, 2068, 2066 (BP. Energy Outlook, 2018). Therefore, challenges in fulfilling energy demand and in the reductions of emission are to be answered immediately by providing sustainable energy sources, able to change market, political and social conditions (Pradana et al., 2018a).

Biomass is a sustainable energy source, where their availability in nature is abundant and it has renewable characteristic (Anggorowati et al., 2017; Pradana et al., 2018b). Other advantages of biomass may include: a) fairly fast CO_2 cycle; b) very low sulphur content; and c)

---

* Corresponding Author: Phone/fax: +62 274 902170, email: abudiman@ugm.ac.id

contribution by 10-15 % (or 45 ± 10 EJ) of current demand which is a half of the total energy demand in industrialized countries by 2050 (BP. Energy Outlook, 2018). Approximately 27 billion tons of CO_2 is emitted from burning fossil fuels annually and is expected to increase by around 60 % by 2030 (BP. Energy Outlook, 2018; Pradana et al., 2018a). Thus, using fuel from biomass is very important to reduce environmental damage.

Biomass raw materials can be obtained from a variety of organic materials such as wood, grass, algae, straw, corn, non-edible oil, wood waste, animal fat, agricultural residues, etc (Jamilatun et al., 2017). These raw materials can be processed to produce biofuel, which can be categorized as the first, second and third generations of biofuels. First generation biofuels are bioethanol and biodiesel synthesized from edible materials. Bioethanol is made by fermenting flour or sugar, while biodiesel is made from transesterification of oil from plants. Second-generation biofuels are derived from non-food flour and lignocellulosic biomass, e.g. grass, wood and straw. Meanwhile, the third generation biofuels are bioethanol, biodiesel, hydrogen and bio-oil from microalgae (Jamilatun et al., 2019a; Jamilatun et al., 2019b; Yuarrina et al., 2018).

The problem faced by the early stage biofuels are related to the competition with the raw materials used for food reserve resilience and the requirement of land for plantation, respectively for the first and second generation of biofuel (Giacomo et al., 2018; Pradana et al., 2017). Third generation biofuels raise to be the solution to those aforementioned problem where the use of microalgae as a source will not interfere the food reserve resilience, neither require large land for cultivation (Hadiyanto et al., 2012a).

Some microalgae types such as *Botryococcus braunii* (25-75 %), *Chlorella sorokiniana* (19-22 %), *Chlorella sp.* (10-48%), *Nannochloropsis sp.* (20-56 %), *Scenedesmus obliquus* (11-55 %) are available with a very high lipid content and are very suitable for biodiesel production (Suali et al., 2012; Yang et al., 2019). Whilst, low lipid microalgae such as *Spirulina platensis* (4-16.6 %), *Spirulina maxima* (4-9 %), *Chlorella pyrenoidosa* (2 %) and *Tetraselmis sp.* (12.6-14.7 %) with food grade quality are for food and health purposes, and feed grade quality are for animal feed or for producing chemicals (Chaiwong et al., 2013; Hadiyanto et al., 2012b).

Biodiesel can also be produced from microalgae by means of chemical reaction, namely transesterification (Pradana et al., 2017), but this method requires an expensive additional material and a high lipid content of microalgae (Suali et al., 2012). The use of microalgae and microalgae residues with very low lipid content for producing biofuels through pyrolysis technique is very beneficial due to its process simplicity and no additional ingredients required (Maity et al., 2014; Zighmi et al., 2016).

Pyrolysis of lignocellulosic raw material produces 25-30 % yield of bio-oil with higher heating value (HHV) of 21-25 MJ/kg (Wang et al., 2016). Meanwhile, it can produce up to 30-36 % yield of bio-oil with HHV 25-37 MJ/kg when microalgae is used as raw materials (Jamilatun et al., 2017). Another advantage of using microalgae is its lower sulfur content. Microalgae with high lipid content are more suitable when processed into biodiesel or bioethanol, while those with low lipid content are better hydrolyzed into biofuel (Maity et al., 2014; Wicakso et al., 2016).

From extraction of *Spirulina platensis* (SP) with chloroform/methanol (1: 2 v/v) solvents, the lipids can be obtained at around 8.9 wt.%. Then, the esterification process using sulfuric acid as a catalyst turns the lipids to *Fatty Acid Methyl Esters* (biodiesel) with the conversion of up to 79.5 %. However, based on its biomass weight, the biodiesel yield is only around 7.1 % (Sumprasit et al., 2017). Such quantity is evidently quite low and not sufficiently worthy the from the production perspective, considering the quantity and the price of chemicals needed for the process. In that sense, pyrolysis, as another processing method to obtain valuable product from *Spirulina platensis* and its solid residues (*Spirulina platensis* residue), might be considered as an interesting research topic, due to the potential benefit derived from their products. In addition, this process might probably be seen as solution to overcome residual waste (SPR) that cause pollution due to the dangerous chemicals released to environment.

The purpose of this study is to compare pyrolysis products of *Spirulina platensis* residue (SPR) from extraction process and *Spirulina platensis* (SP). SP and SPR with very low lipid content (0.09-0.25 wt.%) were first analyzed for ultimate and proximate and heat values. The effect of pyrolysis temperature on the yield and product characteristics, namely liquid products (bio-oil and water phase), char and gas was also studied.

2. Materials and Methods

2.1 Materials

The materials used for this study are *Spirulina platensis* (SP) and *Spirulina platensis* residue (SPR). SP was obtained from Algae Park of Gadjah Mada University, while SPR was obtained as solid residues from the extraction of SP with methanol and hexane. SP and SPR were dried at 60 °C and then screened to obtain dry and uniform size (0.105-0.177 mm) of raw materials. Ultimate SP and SPR were analyzed for ultimate (C, H, O, N and S), proximate (lipids, carbohydrates and proteins), and higher heating valves (HHV) at the Laboratory of Chemistry, Biochemistry of Food and Agricultural Products, Department of Agriculture Technology, Gadjah Mada University, Yogyakarta and at Center for Research and Development of Mineral and Coal Technology, Bandung. The results of the ultimate, proximate and HHV of SP and SPR analysis is presented in Table 1.

2.2 Pyrolysis methods

The pyrolysis device consists of three main parts, namely the fixed-bed reactor, condenser and flow meter as shown in Figure 1 (Jamilatun et al., 2017). The reactor is a cylindrical tube filled with sample where pyrolysis was taken place. After the reactor, the second part is a double tube condenser for condensing the condensable gas stream using counter current water scheme. The last one, the flow meter is used to measure the velocity of non-condensable pyrolysis gas that has passed from the condenser.

Table 1
Main characteristic of *Spirulina platensis* (SP) and *Spirulina platensis* residue (SPR)

Component	SP	SPR
Composition analysis (%)		
Lipid	0.25	0.09
Carbohydrate	46.13	38.51
Protein	44.72	49.60
Cellulose*	27.20	26.50
Hemicelullose*	33.47	32.07
Lignin*	9.96	7.67
Proximate analysis (%)		
Moisture	11.83	9.99
Ash	8.63	8.93
Volatiles	67.03	68.31
Fixed carbon	12.51	12.77
Ultimate analysis (%)		
Sulfur	0.49	0.55
Carbon	41.91	41.36
Hydrogen	6.82	6.60
Nitrogen	8.89	7.17
Oxygen	33.04	35.33
Higher heating value (MJ/kg)	20.09	18.21

(Jamilatun et al., 2017)
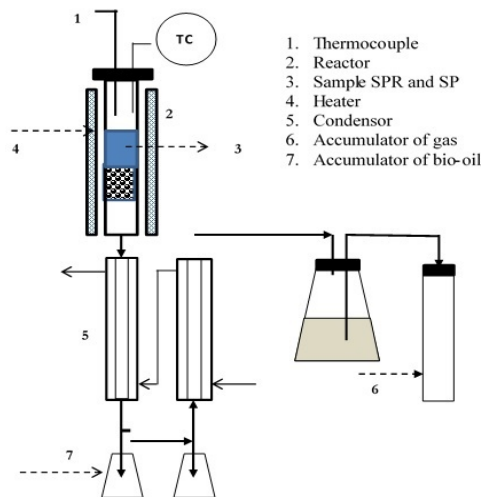
Fig. 1 The schematic diagram of the fixed bed tubular reactor (Jamilatun et al., 2017)

1. Thermocouple
2. Reactor
3. Sample SPR and SP
4. Heater
5. Condensor
6. Accumulator of gas
7. Accumulator of bio-oil

Samples of SPR and SP which had been dried and screened with a uniform size were put in a 50 gram reactor, then closed tightly. The water coolant was flowed and the electric heater was turned on. The heating was done with a heating coil connected to the outer cylinder of the reactor. After reaching the desired temperature, the temperature was hold for 1 hour. Condensate and the formed gas were collected and measured in volume, while char was weighed after the pyrolysis process was complete.

The process began by heating the reactor from the initial temperature of 30 ºC to the desired temperature (300-600 ºC) with a heating rate of 5-35 ºC/minute and by operating it at atmospheric pressure. Once the expected temperature reached, this operating condition was maintained constant for about 1 hour to ensure that the pyrolysis had finished completely. The heating characteristics of the fixed-bed reactor was explained by the evolution of temperature of pyrolysis with time, as presented in Figure 2. It can be seen that for acquiring the desired pyrolysis temperature, the reactor obviously requires different times, for instance having the temperatures of 300, 400, 500, 550, and 600 are consecutively achieved at minute 46, 61, 64, 68 and 72.
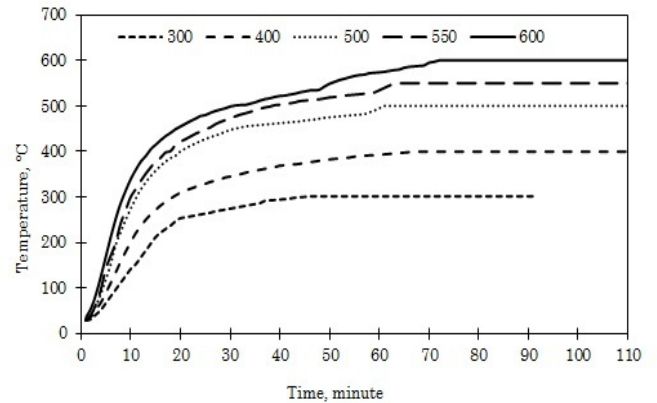

Fig 2. The relationship between time and heating rate at various pyrolysis temperature

2.3. Analysis method

The yield of bio-oil, water phase, char and product gas were calculated by mass balance method as represented in the following equation (Jamilatun et al., 2017; Jamilatun et al., 2019b):

$$Y_{Liq} = (W_{liq}/W_B) x \ 100 \ \% \qquad (1)$$

$$Y_{Char} = (W_{Char}/W_B) x \ 100 \ \% \qquad (2)$$

$$Y_{Gas} = 100 - (Y_{liq} + Y_{Char}) \qquad (3)$$

$$Y_{Bio} = (W_{Bio}/W_B) x \ 100 \ \% \qquad (4)$$

$$Y_{Wtr} = (Y_{Liq} - Y_{Bio}) \qquad (5)$$

SP and SPR pyrolysis conversion (X) can follow equation 6.

$$X = \frac{W_{Bio} + W_{Wtr} + W_{Gas}}{W_B} x \ 100 \ \% \qquad (6)$$

Y_{liq}, Y_{char}, Y_{gas}, Y_{Bio} and Y_{wtr} were yield liquid, char, gas, bio-oil and water phase, while W_{liq}, W_{char}, W_{bio} and W_B were weight, char, bio-oil and SP/SPR respectively.

The characteristics of liquid product were analyzed using gas chromatography–mass spectrometry (GC-MS) technique on Shimadzu GC-MS at Integrated Research Laboratory Faculty of Pharmaceuticals - Ahmad Dahlan University, Indonesia.

Initially, 1 g of liquid samples were dilute in methyl alcohol (2 ml), using 1.0 µl injector to the GC. The GC oven temperature was programmed to follow three steps i) holding at 100 ºC for 5 min, ii) ramping at 5 ºC min-1 up to 225 ºC and iii) holding for 5 min. The injector temperature and split ratio were at 200 ºC and 105.4 respectively. The MS was set at an ionizing voltage of 1.02 kV+0.00 kV and the interface temperature was maintained at 325 ºC. The GC-MS chromatogram could provide the area percentage of various compounds, which was considerably regarded as a good approach for semi-quantitative analyses of pyrolytic liquid product (Sumprasit et al., 2017).

3. Results and Discussion

3.1. Pyrolysis product

Pyrolysis product yield (bio-oil, water phase, char and gas) which has been obtained from SPR and SP samples for a pyrolysis process carried out at a temperature range of 300-600 ºC is presented in Figure 3.

As can be observed, pyrolysis products of bio-oil, water phase, char and gas, presents similar tendency with temperature despite having a slight difference in its percentage between the two yields of SP and SPR sourced pyrolysis products.
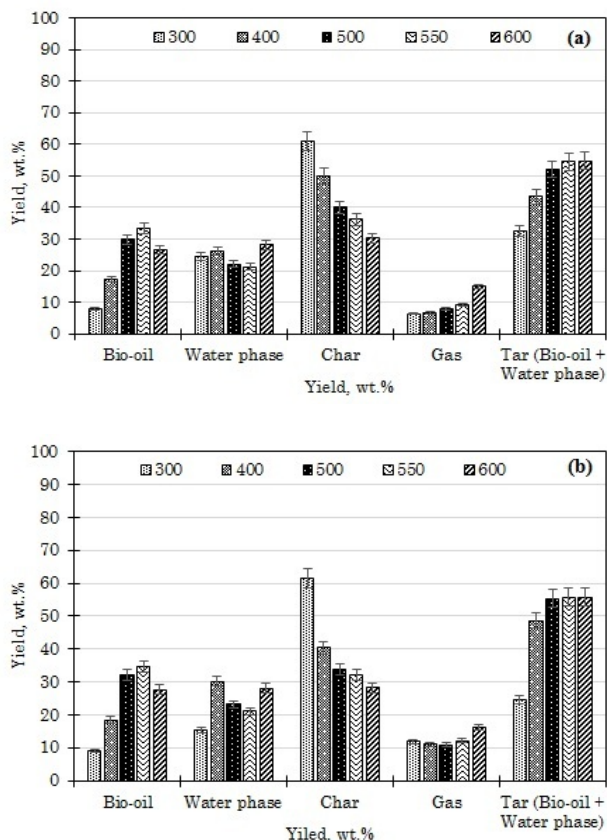

Fig. 3 Effect of pyrolysis temperature on products yield percentage of, (a) *Spirulina platensis* residue (SPR), and (b) *Spirulina platensis* (SP) source

Figures 3(a) and (b) shows the effect of temperature on the yield of SPR and SP products, respectively. Figure 3a shows that, the lowest SPR bio-oil yield is obtained at a temperature of 300 ºC, which is 8.07 wt.%. At the same temperature, the lowest SP bio-oil is 9.23 wt.%, shown in Figure 3b. Bio-oil yield of SP source shows the value of 34.59 wt.% that is higher than that of SPR one of 33.44 wt.% at its considerably optimum temperature (550 ºC). At the temperature higher than that of the 550 °C, bio-oil yield will decrease, likely due to the secondary cracking reactions (cracking, polymerization, condensation), which means that the bio-oil product initially obtained from the primary cracking decomposes to gas.

Meanwhile the water phase obtained from different pyrolysis temperature of 300 - 600 ºC presents fluctuation in its amount, ranging between 21.13 - 28.12 wt.% for SPR and 15.50 - 30.2 wt.% for SP. The yield of the water phase is influenced by the water content of the biomass (SPR and SP) and water formation reactions during pyrolysis

(dehydration). According to Basu (2010), the water phase content in pyrolysis products averages about 20 wt.%.

Liquid product called tar is the sum between the bio-oil and water phase yield. The maximum SPR-sourced liquid product is obtained at temperatures around 550 and 600 ºC, with the yield in the range of 54.57- 54.64 wt.%. At the same temperature, the tar from SP-source is about 55.72- 55.79 wt.%.

The yield of char for both SPR and SP exsiccate sharply with the increasing temperature. It presents the decrease from 61.01 wt.% to 30.37 wt.% for SPR, and from 61.54 wt.% to 28.16 wt.% for SP. The gas seems to increase from 300 to 600 ºC, despite the presence of slight fluctuation in between for both SPR and SP. Noticeable amount of the gas increase is shown at 600 ºC, which is a consequence of a secondary cracking reaction (cracking, polymerization, condensation) producing gas, so called secondary gas (Jamilatun et al., 2019a). The total amount of non-condensable gas is the sum of produced from primary and secondary reactions, namely primary and secondary gases (Basu, 2010; Ojolo et al., 2013).

Pyrolysis conversion of SPR and SP is calculated by summing the weight of bio-oil, water phase and gas each of which is divided by the initial weight of SPR and SP (Equation 6). The information of the increase in pyrolysis conversion at a temperature of 300-600 ºC can be seen in Figure 4.
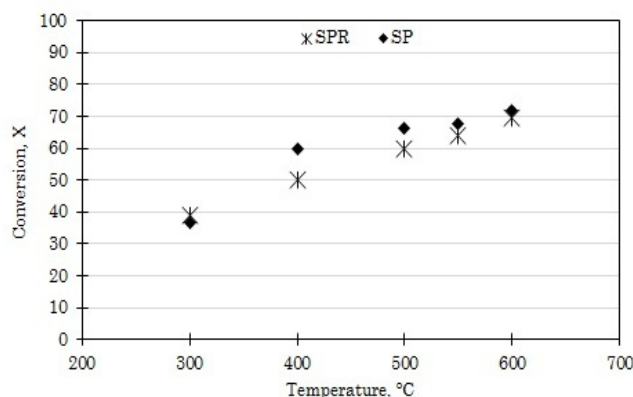

Fig.4. Effect of temperature (ºC) on conversion (%) of pyrolysis

Along with the increase in the temperature, the thermal decomposition becomes more effective so that the weight of the SPR and SP decreases and results in more product being converted. SP conversion at temperature of 400-600 ºC is slightly higher than SPR conversion, likely due to the higher lipid content on SP than SPR one. The increase in liquid and gas products indicates that the speed of the decomposition reaction increases as long as the temperature increases (Fogler, 2006).

3.2. Effect of pyrolysis temperature on product characteristics

3.2.1. Bio-oil

The results of ultimate analysis and heating value of bio-oil from SPR and SP are presented in Table 2, including two other sources of crude oil and wood for benchmarking purpose.

Table 2
Comparison of the composition of bio-oil from pyrolysis of SP, SPR, wood and crude oil

Composition, wt.%	Crude oil	Wood	SPR*	SP*
C	85	54-58	59.05	68.30
H	12	5.50-7	8.77	8.30
O	3.60	35-40	22.63	15.40
N	1.30	0-0.20	9.47	6.90
Ash	0.10	0-0.20	0.08	0.07
HHV (MJ/kg)	42.90	16-19	25.70	32.04
Viscosity at 50°C	180	40-100	40−68	40−68
Moisture (wt.%)	0.10	15-30	34.68	34.84
pH	-	2.50	9.00	9.00

*Experiment
(Chaiwong et al., 2013; Jamil;atun et al., 2017)

From Table 2, it can be seen that the content of C and HHV for both SP and SPR bio-oil is in between crude oil and wood for each corresponding value. Those values are lower than crude oil and higher than wood to signify that the better quality of fuel can be anticipated for bio-oil use than that of wood (lignocellulose). Despite, it is likely to perform worse than crude oil as fuel.
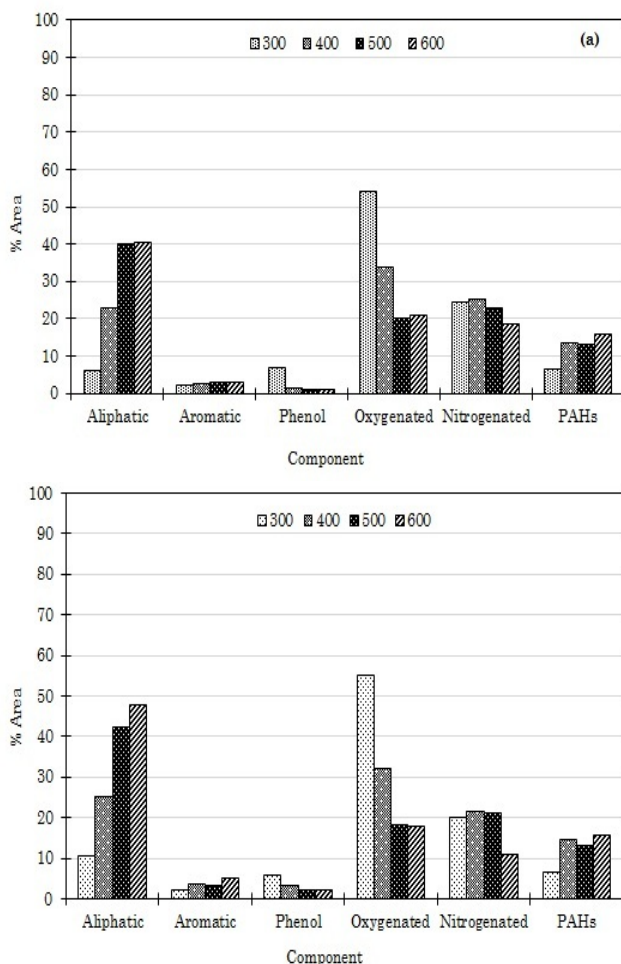

Fig. 5 Effect of pyrolysis temperature on the composition of bio-oil, (a) *Spirulina platensis* residue (SPR), (b) *Spirulina platensis* (SP)

Based on GC-MS analysis results, the chemical compounds in bio-oil is grouped into aliphatic, aromatic, phenol, nitrogenate, oxygenate and poly aromatic hydrocarbon (PAHs). Figure 5 presents the GC-MS results, represented as % area under curve vs associated compounds for each groups at four temperature of 300, 400, 500 and 600 ºC. As it can be seen in Figure 5(a), the aliphatic compound of SPR bio-oil increases from 6.23 to 45.82 % with the increase of pyrolysis temperature from 300 to 600 ºC. An opposite trend is presented for oxygenate compounds where it decreases from 56.16 to 9.56 %. The aromatics and phenol are produced in small quantity. Instead, nitrogenate is at quite high percentage showing maximum peak at 400 ºC. The increase of aliphatic and decreasing amount of oxygenate compounds in bio-oil by the increase of temperature indicate that pyrolysis is better conducted at a higher temperature despite of the requirement for further treatment to reduce oxygenated compounds (Huanga et al., 2017; Li et al., 2013). In addition, a slight difference in the weight percentage of functional group between SPR and SP pyrolysis products is observed. Its values such as aliphatic, aromatic and phenols in SP are slightly higher than those in SPR, while oxygenates and SP nitrogenates are lower than those of SPR. It may be due to lipid content of SP is higher than that of SPR. Moreover, the amount of lipid seems also to affect the number of functional groups produced.

Further analysis on bio-oil characteristics can be performed by observing the amount of C in each constituent of bio-oil (Sunarno et al., 2018; Huanga et al., 2017). Grouping into fractions of LPG (C≤4), gasoline (C5-C11), diesel (C12-C18) and heavy naphtha (C≥19), according to the amount of C can then be performed for each SPR and SP sourced bio-oil to analyze the most dominant group at those four different temperatures tested. The results of the observations are presented in Table 3.

Table 3 presents the fractions of LPG, gasoline, diesel and heavy naphtha, based on their number of C atoms, in bio-oil produced at all pyrolysis temperatures tested. It can be observed that the difference in percentage fractions between bio-oil sourced from SP and SPR is narrow. Hence, aiming to target gasoline fraction being dominant group in the fuel, pyrolysis process is better performed at temperature of 300-400 ºC for both SP and SPR sourced bio-oil, whilst for diesel fractions, pyrolysis conducted between 500 and 600 ºC seems more prominent. It is noted that this grouping is only based on the number of atoms C which does not consider the existence of other compounds such as alcohol, acid, aldehyde, ketone, nitrogenate, phenols and PAHs.

3.2.2. Water phase

The water phase is the liquid product obtained as the denser phase of the condensation product. The area percentage under the curve of GC-MS results is presented in Figure 6. As can be observed, the water phase contains several compounds such as aliphatic, aromatic, phenol, oxygenate (alcohol, aldehyde, ketone and acid), nitrogenate and polyaromatic hydrocarbons (PAHs) (Ledesma et al., 2016). Both SPR (Figure 6(a)) and SP (Figure 6(b)) pyrolysis products shows high contents of acid, alcohol, ketone, nitrogenate, and PAHs, in contrast to aldehyde, phenol, aliphatic and aromatic, that are quite low.

Table 3
Effect of pyrolysis temperature on the SPR and SP bio-oil fraction based on the amount of C in various fuel fractions

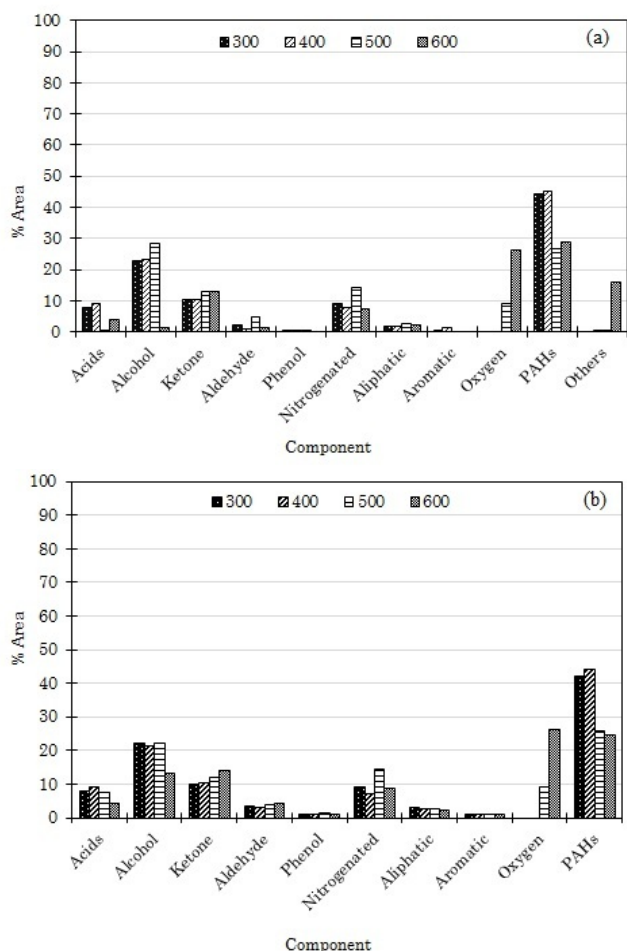| No	Temperature (ºC)	Amount of C							
		C≤4 (LPG)		C5−C11 (Gasoline)		C12−C18 (Diesel)		C≥19 (Heavy naphtha)	
		SPR	SP	SPR	SP	SPR	SP	SPR	SP
1	300	16.60	16.60	64.50	66.98	9.73	9.21	9.09	7.65
2	400	0.66	0.55	52.14	53.22	25.97	25.34	21.26	20.89
3	500	-	-	15.32	17.10	49.53	48.56	35.12	34.56
4	600	-	-	15.66	15.63	49.92	47.65	36.94	36.73

Fig. 6 Effect of pyrolysis temperature on the composition of water phase, (a) *Spirulina platensis* residue (SPR), (b) *Spirulina platensis* (SP)

The number of each component between SPR and SP products is almost the same, which is influenced by the content of lipids, proteins and carbohydrates from raw materials (Table 1). As a matter of information, its high acid, alcohol and ketone content has the potential to be further processed and utilized in the field of pharmaceuticals, food preservation and flavoring agents (Lingbeck et al., 2014). Meanwhile the high nitrogenate content might be useful for protein intake in preserved foods. Based on Figure 6, PAHs that have the potential to damage health can be reduced by increasing the pyrolysis temperature and later can be absorbed by using activated char (Samanya et al., 2011). The high alcohol content in bio-oil (22.30-23.30 %) at a temperature of 300-500 ºC may possibly be rooted from the extraction of SP using

methanol to obtain the raw material (Chaiwong et al., 2013). In addition, phenols, aldehydes, ketones and acids are highly beneficial components in the food field for preservatives and flavouring agents when added in a certain amount (Soares et al., 2016).

Taking into consideration water phase individual component observed by GC-MS, both SPR and SP water phase contains many useful chemical components such as 8'-Apo.beta.-caroten-8'-al (2.82-4.77 %) as precursor of vitamin A, prevention of the risk of stroke, cancer, body pain, *trans-Caryophyllene* (10.76-39.2 %) as anti-inflammatory, local anaesthesia and antifungal. While *Inosine* (CAS) (1.02-5.11 %) is to treat stroke patients to restore nerve function , *Benzo [g] pteridine* -2.4 (3H,10H) - *dione, 8-hydroxy-*7,10-*dimethyl-*(CAS) *8-Hydroxy-7,10-Dimethyl-Isoalloxazine* (1,02-9,5 %) for anti-cancer. And 2-*Isononenal* (CAS) Branched Chain *2-Nonenal* (0.79-15.95 %) are useful in the field of food and pharmacy (Enzing et al., 2014; Lingbeck et al., 2014; Ledesma et al., 2016).

3.2.3. Char

Char is the final product of pyrolysis in the form of solids. Comparison of char composition results from the ultimate analysis of SPR and SP is presented in Table 4, with a selected benchmark of Oak. From this Table it can be concluded that biomass char (microalgae and lignocellulose) has a high content of C (50.31−67.70 %) which can be used for materials fuel, adsorbent, softener soil and other purposes in the pharmaceutical field (Lingbeck et al., 2014).

Table 4
The ultimate analysis results of SPR, SP and Oak biochar

Composition, wt.%	Crude oil	Wood	SPR*	SP*
C	50.31	51.60	64.39	50.24
H	8.81	2.55	2.40	4.83
N	5.74	4.23	6.57	10.96
O	35.14	50.93	11.74	5.45
Ash	11.80	17.80	14,90	18.61
Heat Value (MJ/kg)	19.22	20.01	18.85	26.12

*Experiment
(Chaiwong et al., 2013; Jamilatun et al., 2017; Maity et al., 2014; Yang et al., 2019)

3.2.4. Gas

Figure 7 presents gas volume percentage for pyrolysis product from a) SPR and b) SP sources. Four gases, of H_2, CO, CO_2, and CH_4, has been identified to indicate its potential for being used as fuel. From Figure 7(a) it can be seen that at the pyrolysis temperature of 400 ºC, H_2 and CO has started being produced and continue rising up to 600 ºC. This trend may still be continued at temperatures

above 600 °C, such that gasification to produce syngas (CO and H_2) has usually been carried out at that operating condition. On the other hand, CO_2 and CH_4 decrease with the rise of temperature. The tendency of the number of gas products from SPR and SP pyrolysis is almost the same, but only the amount of gas is slightly different. The amount of H_2 and CO from the results of SP pyrolysis is more than SPR, CH_4, CO_2 of SP and SPR are almost the same. The difference in the number of gas components is due to the slightly different lipid, protein and carbohydrate content of SPR and SP.
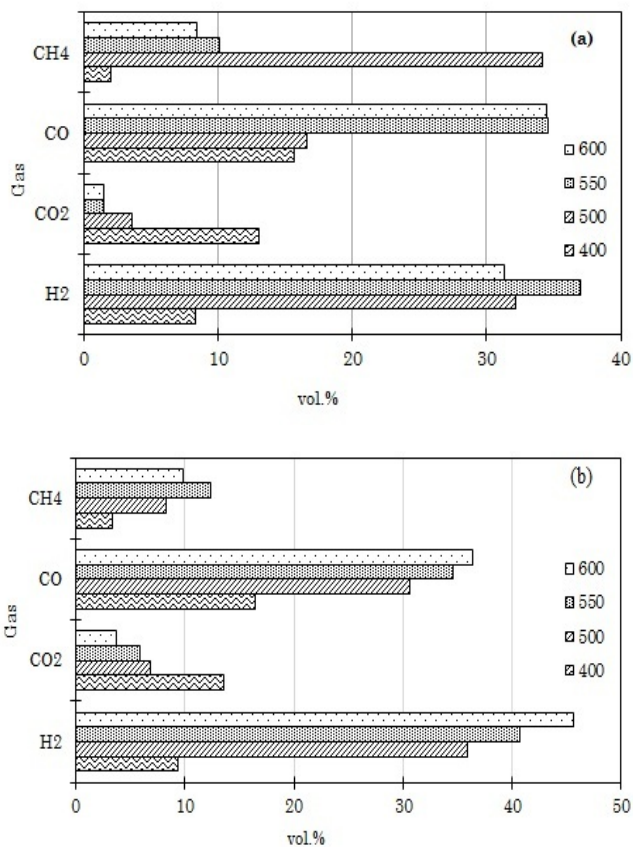

Fig.7 Effect of pyrolysis temperature on gas content: H_2, CO, CO_2 and CH_4, (a) *Spirulina platensis* residue (SPR), (b) *Spirulina platensis* (SP)

4. Conclusion

Some concluding remarks able to be derived from this research work are as follow: Microalgae with low lipid content, which in this study refers to SPR with 0.09 wt.%. and SP with 0.25 wt.% , can be processed by pyrolysis to produce bio-oil, water phase, char and gas containing some valuable chemicals for energy and food.

At optimum temperature of 550 °C, bio-oil yield from the pyrolysis of SP is 34.59 wt.%, that is slightly higher than those from SPR one with 33.44 wt.%. Whilst, the SP gas yield at 12.12 wt.% is 9.18 % lower than SPR one. Pyrolysis of SP produce char at 32.16 wt.%, that is fairly lower than SPR (36.25 wt.%). In addition, the water phase amount is quite similar at 21.13 wt.% for both cases. Interestingly, the aliphatic content and HHV value in bio-oil of both SPR and SP are quite high, i.e. consecutively in the range of 45.70-47.87 wt.% and 25.70-32.04 MJ/kg, hence it is potential to be further processed as fuel. Based on the amount of C grouping in bio-oil of SP and SPR

sourced, some fractions that corresponds to the gasoline or diesel oil fraction are identified.

Water phase of SPR and SP contains valuable chemicals predecessor that if processed further into active compounds might be useful for application in food and pharmaceutical sector.

The high content of C in char of SPR (64.39 wt.%) and SP (50.24 wt.%) might be used as an adsorbent, soil softener or other uses in the pharmaceutical field.

References

Anggorowati, H., Jamilatun, S., Rochim, B., Cahyono and Budiman, A. (2017) Effect of hydrochloric acid concentration on the conversion of sugarcane bagasse to levulinic acid, *IOP Conf. Ser.: Material Science and Engineering*, 299: 012092.

Basu, P. (2010) Biomassa gasification and pyrolysis practical design and theory, Elsevier, The Boulevard, Langford Lane Kidlington, Oxford, UK, pp. 77-82.

BP. Energy Outlook, https://www.bp.com/en/global/corporate/energy/Economics/energy-outlook.html, (25 January 2018).

Chaiwong, K., Kiatsiriroat, T., Vorayos, N. and Thararax, C. (2013) Study of bio-oil and bio-char production from algae by slow pyrolysis, *Biomass Bioenergy*, 56: 600-606.

Enzing, C., Ploeg, M. and Barbosa, M. (2014) Microalgae-based products for the food and feed sector: an outlook for Europe, Lolke Sijtsma, doi:10.2791/3339, Luxembourg: Publications Office of the European Union.

Fogler, H.S. (2006) Element of Chemical Reaction Engineering, 3nd Edition, Prentice-Hall International, Inc.

Giacomo, G.D. and Taglieri, L. (2018) Development and Evaluation of a New Advanced Solid Bio-Fuel and Related Production Process, *International Journal of Renewable Energy Research*, 3(2), 255-260.

Hadiyanto, Widayat and Kumoro, AC. (2012a), Potency of Microalgae as Biodiesel Source in Indonesia, *International Journal of Renewable Energy Development*, 1, 23-27.

Hadiyanto, Azimatun Nur, M.M. and Hartanto, G.D. (2012b) Cultivation of Chlorella sp. as Biofuel Sources in Palm Oil Mill Effluent (POME), *International Journal of Renewable Energy Development*, 1 (2), 45-49.

Huanga, F., Tahmasebia, A., Maliutinaa, K. and Yua, J. (2017) Formation of nitrogen-containing compounds during microwave pyrolysis of microalgae: Product distribution and reaction pathways, *Bioresource Technology*, 245: 1067–1074.

International Energy Agency, 2018, Key world energy statistics, http://data.iea.org//payment/products/118-world-energy statistics-2018-edition.aspx., 2017 (5 Januari 2018),

Jamilatun, S., Budhijanto, Rochmadi, and Budiman, A. (2017) Non−catalytic slow pyrolysis of Spirulina platensis residue for production of liquid biofuel, *International Journal of Renewable Energy Research*, 7(4): 101−1908.

Jamilatun, S., Budhijanto, Rochmadi, Yuliestyan, A., and Budiman, A. (2019a) Effect of grain size, temperature, and amount of catalyst on characteristics of pyrolysis products from spirulina platensis residue (SPR), *International Journal of Technology* 10(3): 541-550.

Jamilatun, S, Budhijanto, Rochmadi, Yuliestyan, A., and Budiman, A (2019b) Valuable Chemicals Derived from Pyrolysis Liquid Products of Spirulina platensis Residue, *Indones. J. Chem.*, 19 (3), 703 – 711.

Li, G., Zhou, Y., Ji, F., Liu, Y., Adhikari, B., Tian, L., Ma, Z. and Dong, R. (2013) Yield and Characteristics of Pyrolysis Products Obtained from Schizochytrium limacinum under Different Temperature Regimes, *Energies* 2013, 6, 3339-3352.

Lingbeck, J.M., Cordero, P., O'Bryan, C.A., Johnson, M.G., Ricke, S.C. and Crandall, P.G. (2014) Functionality of liquid smoke as an all-natural antimicrobial in food preservation, *Meat Science*, 97: 197–206.

Ledesma, E., Rendueles, M. and Díaz,M. (2016) Contamination of meat products during smoking by polycyclic aromatic hydrocarbons: Processes and prevention, *Food Control*, 60: 64-87.

Maity, J.P., Bundschuh, J., Chen, C-Y. and Bhattacharya, P. (2014) Microalgae for third generation biofuel production, mitigation of greenhouse gas emissions and wastewater treatment: Present and future perspectives, A mini review. *Energy*, 78: 1-10.

Ojolo, S.J, Oshekub, C.A., and Sobamowoa, M.G., (2013) Analytical investigations of kinetic and heat transfer in slow pyrolysis of a biomass particle, *Int. J. Renew. Energ. Dev.*, 2 (2), 105-115.

Pradana, Y.S., Hidayat, A., Prasetya, A. and Budiman, A. (2017) Biodiesel production in a reactive distillation column catalyzed by heterogeneous potassium catalyst, *Energy Procedia,* 143: 742-747.

Pradana, Y.S., Masruri, W., Azmi, . F.A., Suyono, E.A., Sudibyo, H. and Rochmadi, (2018a) Extractive-transesterification of Microalgae Arthrospira sp. Using Methanol-Hexane Mixture as Solvent, *International Journal of Renewable Energy Research*, 8 (3), 1499-1507.

Pradana, Y.S., Azmi, F.A., Masruri, W. and Hartono, M. (2018b) Biodiesel Production from Wet Spirulina sp. by One-Step Extraction-Transesterification, *MATEC Web of Conferences*, 156: 03009.

Roser, M. and Ortiz-Ospina, E. (2017) World Population Growth, https://ourworldindata.org/world-population-growth,   (10 Desember 2017).

Suali, E. and Sarbatly, R. (2012) Conversion of microalgae to biofuel, *Renewable and Sustainable Energy Reviews,* 16, 4316– 4342.

Sumprasit, N., Wagle, N., Glanpracha, N. And Annachhatre, A.P. (2017) Biodiesel and biogas recovery from *Spirulina platensis*, *International Biodeterioration and Biodegradation,* 119, 196-204.

Samanya, J., Hornung, A., Jones, M. and Vale, P. (2011) Thermal stability of Sewage Sludge Pyrolysis oil, *International Journal of Renewable Energy Research*, 1(3), 66-74.

Sunarno, Rochmadi, Mulyono, P., Aziz, M. and Budiman, A. (2018) Kinetic study of catalytic cracking of bio-oil over silica-alumina catalyst, *Bioresources,* 13(1), 1917-1929.

Soares, J.M., da Silva, P.F., Puton B.M.S., Brustolin A.P., Cansian R.L., Dallago R.M. and Valduga E. (2016) Antimicrobial and antioxidant activity of liquid smoke and its potential application to bacon, *Innovative Food Science and Emerging Technologies*, 38 (2016) 189–197.

Wang N, Tahmasebi A, Yu J, Xu J, Huang F. And Mamaeva A. (2016) A Comparative study of microwave-induced pyrolysis of lignocellulosic and algal biomass, *Bioresource Technol.*, 190 (2015) 89–96.

Wicakso, D.R., Sutijan, Rochmadi, and Budiman, A (2016) Catalytic decomposition of tar derived from wood waste pyrolysis low grade iron ore as catalyst, *AIP Conference Proceedings* 1737 (2016), 060009.

Yuarrina, W.P., Pradana, Y.S., Budiman, A., Majid, A.I., Indarto, and Suyono, E.A. (2018) Study of cultivation and growth rate kinetic for mixed cultures of local microalgae as third generation (G-3) bioethanol feedstock in thin layer photobioreactor, *Journal of Physics: Conference Series*, 1022: 012051.

Yang, C., Li, R., Zhang, B., Qiud, Q., Wang, B., Yang, H., Ding, Y., and Wang, C. (2019) Pyrolysis of microalgae: A critical review, *Fuel Processing Technology*, 186, 53–72.

Zighmi, S., Ladjel, S., Goudjil, M.B. and Bencheikh, S.E. (2016) Renewable Energy from the Seaweed Chlorella Pyrenoidosa Cultivated in Developed Systems, *International Journal of Renewable Energy Research*, 7(1), 50-57.