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Cite as: AIP Conference Proceedings **2248**, 060003 (2020); <https://doi.org/10.1063/5.0013164>
Published Online: 17 July 2020

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Catalytic and Non-Catalytic Pyrolysis of *Spirulina Platensis* Residue (SPR): Effects of Temperature and Catalyst Content on Bio-oil Yields and Its Composition

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Abstract. Problems associated with the development of the first and second generations of biofuel, especially regarding its raw materials and complex processes, have led to the evolution of the third generation one, a microalgae-based bio-oil through pyrolysis. This research explored the effect of temperature ranging between 300–700 °C and the presence of Silica–alumina (Si-Al) catalyst at the variation of 5–20 wt.% on the pyrolysis process of *Spirulina platensis* microalgae solid residue, in search of optimum condition for collecting maximum bio-oil yield and its desired composition. The experiments without catalysts reached their optimum yield of 28 wt.% at 550 °C. While the involvement of 5 wt.% of Si-Al catalyst in the reactor resulted in a higher yield than that of without catalyst beyond 550 °C. Furthermore, a high amount of catalyst content at 20 wt.% seems to improve bio-oil yield collection up to 34.10 wt.%. Interestingly, referring to its C atoms number, SPR-based bio-oil by catalytic pyrolysis tended to produce such a considerable amount of gasoline leading to *Pertamax*, and the one without catalyst produced gasoline leading to *Pertalite*.

INTRODUCTION

Despite being widely tested, first and second generations, biofuel leaves some issues regarding its availability and competition against the primary use of their raw materials [1,2]. First-generation biofuels (i.e., biodiesel, corn ethanol, sugar alcohol) from vegetable oils and corn sugar sources are constrained by the limited feedstocks and competition with food products [3]. In addition, the second-generation biofuels (i.e., hydrotreating oil, bio-oil, lignocellulose ethanol, butanol, mixed alcohols) raise a problem for its extensive agricultural land requirement, although it comes from non-edible oil, non-food, cheap and abundant plant waste biomass sources [4,5]. Such situations stimulate the researcher to find an alternative to overcome the problems mentioned before. Development of third-generation

biofuels (biodiesel, bioethanol, biohydrogen, biomethane) based on microalgae biomass offers a simpler production process of pyrolysis and non-competing sources [6].

Moreover, microalgae may provides many advantages, such as: (i) environmentally friendly, (ii) not competing with food and agricultural land, (iii) very high oil products (iv) simple cellular structure, (v) lipid-rich (40–90% in percent dry weight), (vi) rapidly growing rate, (vii) able to grow in brine and poor conditions, (viii) evolved from CO₂ gas produced by power plants, and (ix) containing no sulfur, non toxic and highly biodegradable [7-9]. On these ground, microalgae seem very potential to be developed as a source of energy for the future.

Basically, microalgae-based biofuel can be produced via biochemistry conversion, thermochemical conversion, chemical reaction, and direct burning. Among them, thermochemical conversion through the pyrolysis process seems quite promising due to its fairly simple process and without the need for additional chemicals [10-13,14]. Pyrolysis is the thermochemical decomposition of organic matter through the process of heating without oxygen or with little oxygen or without other chemical reagent addition, where the raw material will undergo chemical structure breakdown into the gas phase [14].

The process at atmospheric pressure and a relatively low temperature between 350 and 600 °C can produce bio-oil, gas, and char for later being used as fuel and adsorbent, respectively [4]. Therefore, such research in the area of microalgae-based bio-oil through pyrolysis gain significant priority.

Pyrolysis itself can be performed with or without catalyst [6,15-18]. Study on pyrolysis without catalyst using various raw materials (i.e., *Chlorella Vulgaris*, *Spirulina plantensis* residue, and *Saccharina japonica*) reported optimum bio-oil yield ranging between 24.5 and 32.7 wt.% at a temperature between 500 – 550 °C. The use of catalysts does not necessarily improve bio-oil yield uptake, as demonstrated by Lim et al. [17], presenting a fairly similar yield on pyrolysis of Palm oil with Br₂O₃ catalyst. Neither changing the type of catalyst (i.e., ZnO and Al₂O₃) would result in a significant difference of bio-oil uptake from Eastern giant fennel (*Ferula Orientalis*) [18].

Pyrolysis study was conducted with a solid catalyst with HZSM-5 (19), hybrid composites (hexagonal mesoporous silicate (HMS) and ZSM-5 with impregnation of Ni, Fe, or Ce (20), metal oxides supported by TiO₂ (21), silica-alumina [19], and silica-alumina reuse [22]. Silica - amorphous alumina is the most widely used solid acid catalyst in supporting the production of petrochemicals, chemicals, and renewable energy. High acidity (low Si/Al) can be used in the process of cracking petroleum to increase oxidation of CO [23]. Rather than that, the use of catalysts may be seen as a composition changer to the extends of the way hydrocarbon is chemically modified. Silica-alumina [Si-Al], which widely available on the market as a cheap commodity, may play such a role.

This paper discusses the effect of temperature and catalyst (Si-Al) content on the pyrolysis of *Spirulina platensis* residue (SPR) on bio-oil yield and its composition. Product yields were observed referred to its the mass-basis of each component. Whilst gas chromatography/mass spectrometry (GC-MS) technique was employed for characterizing bio-oil compositions.

METHODS

Materials

Spirulina platensis Residue (SPR)

SPR was obtained from solid residue extraction of *Spirulina platensis* with a size of 80–140 mesh (0.177–0.105 mm). The proximate analysis was performed to characterize the moisture content, ash, volatile matter, and fixed carbon. Whilst

C, H, O, and N content were quantified by ultimate analysis. The calorific value, conducted at the Research and Development Center for Mineral and Coal Technology (TEKMIRA), Bandung, Indonesia, was done using a calorimeter bomb where the results are in Table 1.

TABLE 1: Main characteristic of SPR [15]

Components	(SPR)
Proximate analysis (wt.%)	
Moisture	9.99
Ash	8.93
Volatiles	68.31
Fixed carbon	12.77
Ultimate analysis (wt.%)	
Carbon	41.36
Hydrogen	6.60
Nitrogen	7.17
Oxygen	35.33
Sulfur	0.55
Lipid	0.09
Carbohydrate	25.59
Protein	49.60
Higher heating value (MJ/kg)	18.21

Silica-alumina catalyst

The silica-alumina catalyst was kindly supplied by PT. Pertamina, Balongan, Indonesia. Silica-alumina properties, including the ratio, specific surface area, pore-volume, pore diameter, and SEM–EDX, were analyzed at LPPT–UGM [14,18]. The results are shown in Table 2.

TABLE 2: Silica–alumina catalyst specifications [19]

Si-Al specification	Value
SiO ₂ /Al ₂ O ₃	1.67
Pore surface area	240.553 m ² /g surface area
Pore diameter	3.3 nm
Average pore volume	0.199 cm ³ /g total pore volume
Compositions (wt.%)	
C	12.33
O	55.73
Al	15.42
Si	16.51

Experimental methods

SPR pyrolysis was performed in a 40 cm ID and 60 cm length of a fixed-bed reactor system, depicted in Fig. 1 [17].

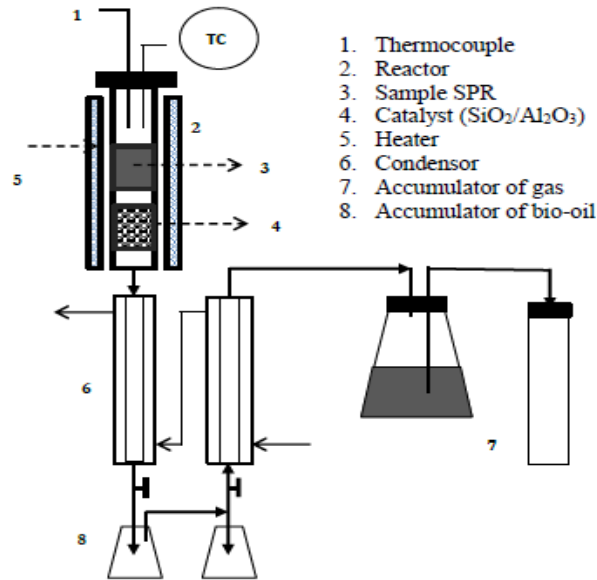


FIGURE. 1: The schematic diagram of the fixed bed tubular reactor [15]

The reactor consists of an upper and bottom part for placing SPR and Si-Al catalysts, respectively. A nickel wire heater, coiled outside the reactor tube, is provided for maintaining an operating temperature between 300 and 700 °C. In addition, the condenser was used for bio-oil and gas products for cooling. Fifty (50) g of SPR was inserted into the reactor chamber. The heat was then introduced at a constant rate of 10-20 °C/min from ambient to the processing temperature. Then, the pyrolysis process was always maintained for 1 hour. After the reaction finished, bio-oil and gas could be collected in their corresponding accumulator, following their path through the condenser for temperature cooling. It is noted that bio-oil would first require to be separated by decantation from its water in the liquid phase. Lastly, the amount of solid (biochar) left behind in the reactor chamber was picked up and weighed. Si-Al catalyst was used for pyrolysis of 5, 10, 15 and 20 wt.% (2.5; 5; 7.5 and 10 grams). Product data collection was carried out at a temperature of 30 to the desired temperature, and it was then held for 1 hour to ensure that pyrolysis was running perfectly.

Tests and measurements

The weight percentage of yield product analysis

Weight of liquid products (refer to bio-oil and water), gas, and bio-char were calculated by the following equation [15]:

$$Y_{bo} = (W_{bo}/W_M) \times 100 \% \quad (1)$$

$$Y_{wtr} = (W_{wtr}/W_M) \times 100 \% \quad (2)$$

$$Y_{Char} = (W_{Char}/W_M) \times 100 \% \quad (3)$$

$$Y_{Gas} = 100 - (Y_{liq} + Y_{Char}) \quad (4)$$

Y and W represent yield percentage and weight, respectively. Its corresponding subscripts, of M, bo, wtr, gas, and char, are for initial SPR, bio-oil, water, gas, and bio-char.

Characterization of Bio-oil Compositions

Bio-oil obtained from pyrolysis liquid product (light phase) was tested for its composition using Gas chromatography-mass spectrometry (GC-MS) with the Shimadzu brand. GC-MS was run at an injection temperature of 150 °C, pressure 41.4 kPa with a total flow of 88.8 mL/min, column flow 0.85 mL/min, linear velocity 33.4 cm/sec, and purge flow 3.0 mL/min. The temperature in the oven column was initially 50 °C (hold time 5 minutes), increasing to 290 °C at a speed of 20 °C/min. (hold time 8 minutes), and the maximum temperature reached 320 °C with a speed of 15 °C/min. (hold time 3 minutes). Then, based on the number of C constituent atoms, bio-oil compositions were grouped into fractions of LPG ($C \leq 4$), gasoline (C5-C11), diesel (C12-C18) and heavy naphtha ($C \geq 19$).

To compare the bio-oil fraction of pyrolysis results with and without catalyst with the fraction, fuel from fossils in the form of pertalite, Pertamina and diesel was tested with the GC-MS, and the results were divided into fractions $C \leq 4$, C5-C11, C12-C18 and $C \geq 19$. Results of GC-MS of pertalite, pertamax, and diesel at the Integrated Research Laboratory of the Faculty of Pharmacy, Ahmad Dahlan University, Yogyakarta, are presented in Table 3.

TABLE 3. GC-MS results on *pertalite*, *pertamax* and diesel.

Type of fuel oil	Amount of C, wt. %			
	$C \leq 4$	C5-C11	C12-C18	$C \geq 19$
<i>Pertalite</i>	7.81	1.48	47.81	42.9
<i>Pertamax</i>	0	84.81	14.39	0.76
Diesel	0	3.35	73.68	22.96

RESULTS AND DISCUSSION

Effects of Temperature and Catalyst Content on Pyrolysis Yield Product

Figure 2a showed the yield products of bio-oil, gas, char, and water phase obtained from the pyrolysis process without using a catalyst for various temperatures between 300 and 700 °C. It might be expected that the more heat introduced into the system resulted in more hydrocarbon decomposition. Such a phenomenon was perhaps seen by the reduction of solid product (and bio-char) yield from 61.55 to 17.3 wt.% with increasing temperature, prior to stabilizing at 600 °C and above. Along with that, solid texture analysis exhibiting gradual changes from soft to hard texture was reported. This would mean decomposition initially occurred by releasing some hydrocarbon compounds, followed by gradual compositional changes, and finally reached bio-char stable composition [16-18]. From another perspective, this would mean that the remaining hydrocarbon was converted to gas and liquid products.

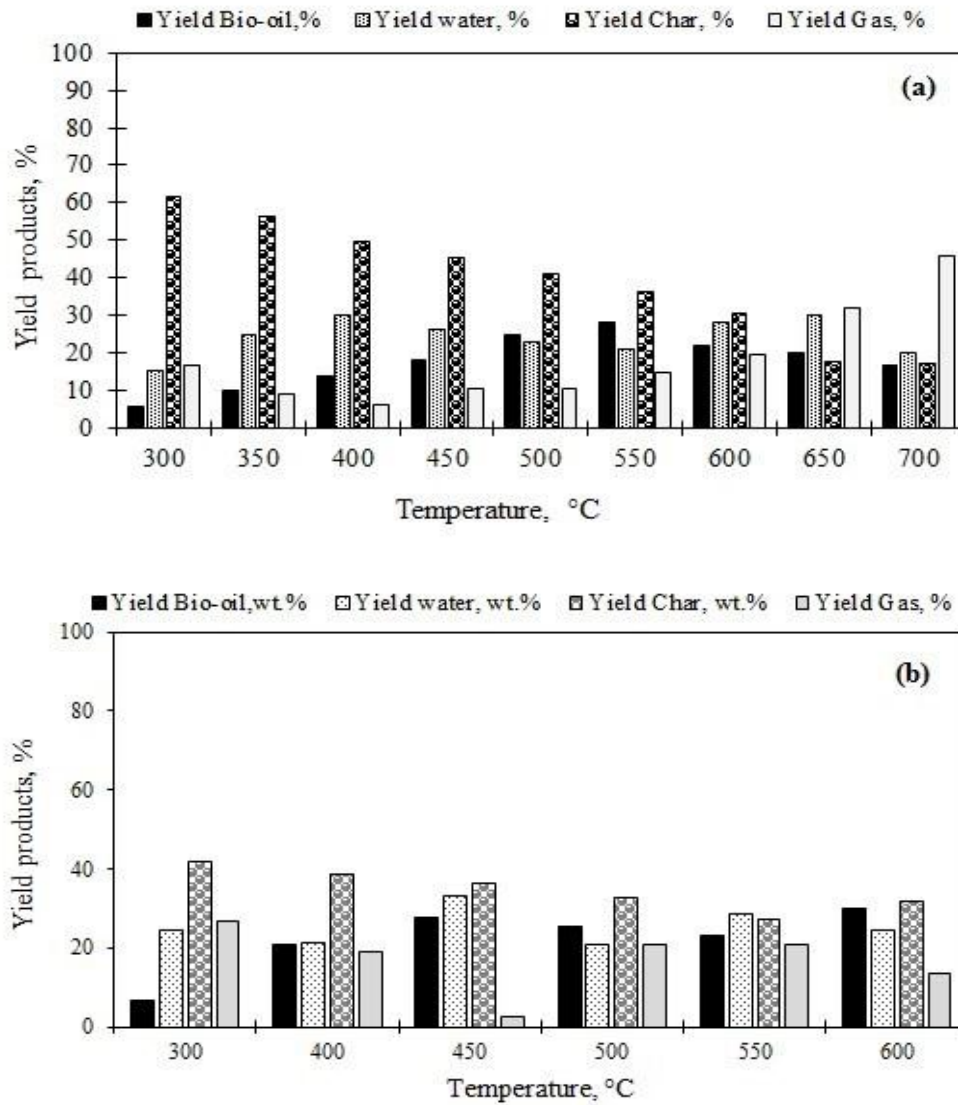


FIGURE. 2: Effect of temperature on yield products, obtained from SPR pyrolysis process a) without and b) with the presence of 5 wt.% Si-Al catalyst

The liquid products consisted of water, and bio-oil was initially collected at 300 °C. At this point, bio-oil presented the lowest yield of 6 wt.%. The trend of increasing bio-oil uptake was then observed, following their 50 °C incremental increase in processing temperature up to 550 °C. Interestingly, discontinuation on that trend, seen by sudden yield decrease, resulted in considering 550 °C as peak maximum temperature for SPR pyrolysis without a catalyst. Such a phenomenon was quite typical, as similarly reported elsewhere [24]. Above 600 °C, bio-oil yields tended to decrease due to the secondary cracking reaction that resulted in further decomposition into gas and char (24). Response to bio-oil secondary cracking might be confirmed by the inverted gas yield plot presenting a peak minimum at a temperature between 300 and 400 °C, followed by sharp yield increase to 45.7 wt.% at 700 °C.

For a comparative analysis, the yield result of pyrolysis at various temperatures in the presence of 5 wt.% Si-Al catalyst is presented in Fig. 2b. As observed, the trend of biochar and water yield remain fairly similar. However, no such peak maximum saw on bio-oil yield since it would rather show an increase of bio-oil with increasing temperature. Conversely, gas yield fluctuated, followed by a tendency to decrease at the later stage around 550 °C and above, in the presence of a catalyst.

Hence to further understand the influence of 5 % Si-Al catalyst, each yield in Fig. 2b was then compared against results shown in Fig. 2a for their corresponding temperature. It was evident that the catalyst was able to boost bio-oil uptake at a temperature between 300 and 450 °C, considered to be primary phase decomposition. Moreover, the more significant bio-oil yield was perceived for the pyrolysis process conducted at a temperature higher than 550 °C, taking into account that the relative data on the curve "without catalyst" lean toward decreasing trend as opposed to increasing trend on the one with catalyst.

As the focus was paid on maximizing bio-oil uptake, there might be a possibility that the amount of bio-oil would further increase with temperature. For that reason, the SPR pyrolysis with Si-Al catalyst was further experimented to study the effect of the amount % catalyst between 5 and 20 % at the highest temperature previously tested of 700 °C, where the results are shown in Fig. 3.

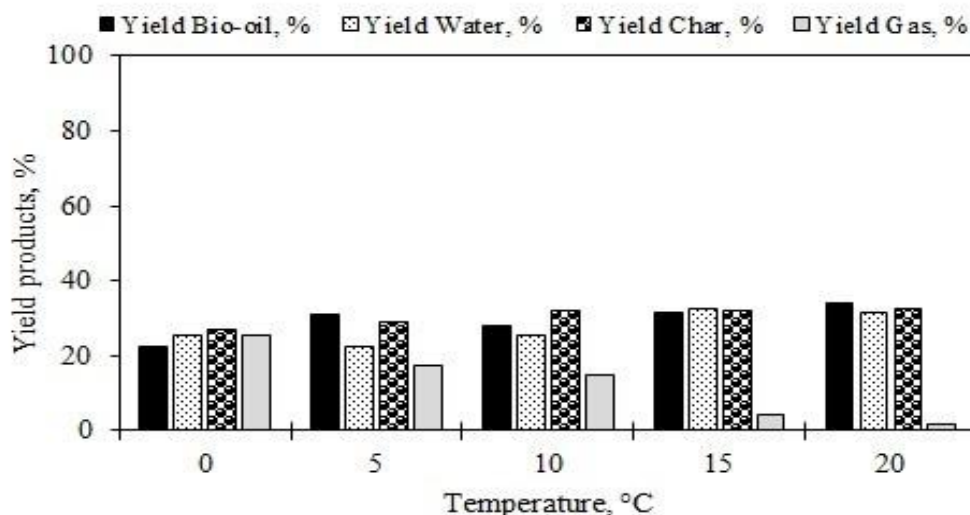


FIGURE. 3: The evolution of yield product percentage as a function of Si-Al catalyst percentage between 0 and 20 wt.% on SPR pyrolysis products at 700 °C

As seen, the result presented that yield gas decrease quite significantly from 17.47 to 1.70 wt.% with the increase of catalyst involved from 0 to 20 wt.%. Consequently, liquid products and bio-char seemed to increase. Liquid products, a total amount of Bio-oil and water, were increased by ±17.00 wt.% from 48.04 to 65.10 wt.% in which 12 wt.% increase was contributed from the raise of bio-oil uptake. In fact, the involvement of catalysts by only 5 wt.% has led to an increase of about 8%. A higher Si-Al catalyst percentage tested between 5 and 20 wt.% did not cause a significant rise despite its increasing trend. Regardless, its concurrent decrease in gas and bio-oil increase might suggest the occurrence of vapor condensation.

Fractional Composition (Based on C-Number Category Range) Of Bio-Oil Products as A Function of Temperature and Catalyst Content

Table 4 presented the fractional composition, referring to their number of C atoms (LPG, gasoline, diesel, and heavy naphtha) of bio-oil obtained by pyrolysis without catalyst at a temperature of 300, 400, 500 and 600 °C.

TABLE 4. Bio-oil composition referring to its C-atom category, obtained at various pyrolysis temperature between 300 and 600 °C, without catalyst

Pyrolysis temperature, °C	Amount of C, wt.%			
	C≤4	C5–C11	C12–C18	C≥19
	(LPG)	(Gasoline)	(Diesel)	(Heavy Naptha)
300	16.60	64.50	9.73	0.09
400	0.66	52.14	25.97	21.26
500	–	15.32	49.53	35.12
600	–	15.66	49.92	36.94

At 300 °C, bio-oil consisted of LPG (C≤4), gasoline (C5–C11), diesel (C12–C18), and heavy naphtha (C≥19) in which their corresponding content was 16.60, 64.50, 9.73, and 0.09 wt.%, respectively. At 400 °C, LPG fraction started to disappear, showing only 0.66 wt.% collected. As expected, this fraction was not found at temperature 500–600 °C. In addition, gasoline fraction also exhibited a sharp decrease in weight percentage from 64.50 to 15.66 with the raise of tested temperature. Consequently, other fractions would rise, given the fact that diesel increased from 9.73 at 300 °C to 49.92 wt.% at 600 °C, besides the presence of 36.94 wt.% of heavy naphtha at 600 °C from almost none at 300 °C. By combining information summarized in Fig.F 2a and Table 4, bio-oil uptake could be obtained maximum at 550 °C, where its composition likely consisted of about 15, 50, and 35, respectively, for LPG, gasoline, and diesel. Interestingly, such composition seemed to present its potential for being used as future fuel due to its similarity on hydrocarbon content as compared to fuel derived from crude oil [17]. Table 3 shows that the GC-MS test results for pertalite petroleum fuels consist of C≤4, C5-C11, C12-C18, and C≥19, respectively, with the values of 7.81, 1.48, 47.81 and 42.90 wt.%. It can be concluded that the bio-oil produced by pyrolysis of the SPR at a temperature of 500-600 °C is equivalent to pertalite.

Table 5 presented the result of LPG, Diesel, and Heavy naphtha fraction on bio-oil yield obtained from the pyrolysis process with Si-Al catalyst having content from 5 to 20 wt.%. In the presence of a catalyst, none of the heavy naphthas was produced regardless of the catalyst content to suggest the suppression of longer chain hydrocarbon production. In addition, diesel, having chain numbers between 12 and 18, exhibited a decrease as well. Thereof, gasoline was the major fraction produced, around 80 wt.%.

The influence of catalyst content on bio-oil fraction was rather inconclusive at this point. Statistically, gasoline and diesel fraction composition were around 80 and 20 wt.% Regardless of the catalyst content, except for the result when using 10 wt.% of Si-Al catalyst. This great amount of gasoline fraction agreed with the study reported by Sunarno [10] that the rise in pyrolysis temperature and the use of silica-alumina catalysts by impregnation of Ni metal will increase the gasoline, kerosene and phenol fractions, while, the oxygenate compound will decrease. In any case, the introduction of only 5 wt.% Si-Al catalyst was able to drive the pyrolysis process to lean toward the production of gasoline, which would be prospective to replace crude oil-based gasoline fuel. The existence of about 20 wt.% of the C12-C18 (diesel) fraction is still tolerated as a by-product in gasoline. Table 3 shows that the GC-MS test results for fuel from Pertamina petroleum consist of C≤4, C5-C11, C12-C18, and C≥19, respectively, with values of 0, 84.81, 14.39, and 0.76 %. It can be concluded that with the use of Si-Al catalysts: 5, 15, and 20 %, the bio-oil fraction consists of C5-C11 with an average of 82.84 % and C12-C18 with an average of 16.73 %, the resulting values lead to Pertamina.

TABLE 5. Component of bio-oil SPR based on the amount of C on various wt.% of the amount of Silica–alumina catalyst

Catalyst (%)	Amount of C, wt.%		
	C \leq 4	C5–C11	C12–C18
	(LPG)	(Gasoline)	(Diesel)
5	-	80.06	19.34
10	-	41.48	57.06
15	-	86.56	13.13
20	-	81.89	17.73

CONCLUSION

This research aimed to study the influence temperature and catalyst content on the pyrolysis process of *Spirulina Plantensis Residue* (SPR) with and without the Silica-Alumina (Si-Al) catalyst. Pyrolysis process of SPR, for both without and with the catalyst, produced liquid product (bio-oil and water phase), gas, and char. On the basis of weight percentage, the optimum bio-oil uptake of 28 wt.% was obtained from pyrolysis at temperature 550 °C, considered as a peak maximum within the range of tested temperature (300-700 °C). At this temperature, the resulting bio-oil compositions were likely to consist of gasoline (C5–C11), diesel (C12–C18) and heavy naphtha (C \geq 19), considering similarity on such fraction obtained at 500 and 600 °C

On the other hand, the pyrolysis of SPR with catalyst presented the absence of such peak maximum, since bio-oil yield seemed to keep increasing with temperature. At 700 °C, the use of 20 wt.% Si-Al catalyst was able to produce 34.10 wt.% of bio-oil, where its fraction was mainly composed of gasoline leading to pertamax, whereas without a catalyst, it led to pertalite by referring the number of C atoms in bio-oil.

ACKNOWLEDGMENTS

The author is very grateful for the funding support from Directorate General of Higher Education, Ministry of Research Technology and Higher Education, the Republic of Indonesia in the scheme of "International Research Collaboration and Scientific Publication" under the supervision of Direktorat Penelitian, Gadjah Mada University, Yogyakarta, Indonesia. We also gratefully acknowledge the funding from USAID through the SHERA program - Centre for Development of Sustainable Region (CDSR).

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