Ex-Situ Catalytic Upgrading of *Spirulina platensis* Residue Oil Using Silica Alumina Catalyst

Siti Jamilatun *, Arief Budiman **‡, Heni Anggorowati ***, Avido Yuliestyan ***, Yano Surya Pradana**, Budhijanto**, Rochmadi**

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

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

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

(sitijamilatun@che.uad.ac.id, abudiman@ugm.ac.id, heni.anggorowati@upnyk.ac.id, avido.yuliestyan@upnyk.ac.id, yanopradana@ugm.ac.id, budhijanto@ugm.ac.id, rochmadi@ugm.ac.id)

‡ Corresponding Author; Arief Budiman, Jalan Grafika 2, Yogyakarta 55284, Indonesia, Tel: +62 274 902170,

Fax: +62 274 902170, abudiman@ugm.ac.id

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Abstract- This paper discusses the effect of rising temperatures pyrolysis and the use of silica-alumina catalysts located in a dedicated chamber to improve the quality of bio-oil in terms of O/C, H/C, HHV values, oxygenated, and aromatic compounds. Pyrolysis is carried out in a fixed-bed reactor consisting of two reactors in series with an inner diameter of 40 mm (2 mm of thickness) and a total length of 600 mm. The upper reactor (R1) is filled with the SPR sample and the lower reactor (R2) is for silica-alumina catalyst being in placed. Pyrolysis is conducted at a temperature range of 300−600 °C by using a heating rate of 5-35 °C/min produced by controlled electrical heating and in the presence of silica-alumina catalyst (10−40 wt.%). The gas produced from pyrolysis is condensed to obtain a liquid consisting of two layers, the top layer of bio-oil, and the bottom layer of the water phase. From GC-MS, the data on mass percentages of C, H, O, N, and S of each compound in bio-oil is obtained, besides its mass percentages of aromatic and oxygenate compounds. The results shows that the pyrolysis at fairly high temperature (300-600 ºC) without or with the catalyst, causes the increased values of H/C, HHV, and aromatic compound content, in contrast to the values of O/C and oxygenated compounds which is found decrease. Those respective increase are by 108.44, 34.20, and 54.32 %, conversely to the decrease value in O/C and compounds oxygenates of 54.98 and 65.86 %. The ex-situ catalytic by the use of silica-alumina catalysts (10-40 wt.%) seems to be an alternative method for obtaining the upgraded quality of bio-oil.

Keywords Catalytic upgrading, silica-alumina, oxygenate, compounds, aromatic.

1. Introduction

The solid residue from microalgae extraction of *Spirulina platensis* or called *Spirulina platensis* residue (SPR) still contains a lot of carbohydrates and proteins that will cause pollution if discharged into the environment. The utilization of SPR by fermentation will produce ethanol, while pyrolysis will produce char, biogas, and bio-oil [1-7].

The oxygenate content in the SPR bio-oil is still quite high, which can cause corrosion to the engine and instability in its use [8,9]. The high oxygenate and low HHV in bio-oil microalgae are due to the high protein content (around 45-60

%) in microalgae biomass, so it is necessary to proceed with the addition of solid catalysts [10-12]. Catalytic pyrolysis is one way of upgrading bio-oil by reducing the O content by adding solid catalysts in a gas phase heterogeneous reaction with a specific ratio [13-15]. Furthermore, bio-oil derived from upgrading can mix with hydrocarbons resulting from petroleum refining of around 5-20 % [16,17].

Several studies have conducted regarding the effect of solid catalysts on microalgae *Nannochloropsis* sp. [18]; *Chlorella* [16], lignocellulose biomass [19,20], and plant biomass. Pyrolysis with catalysts was carried out by Pan et al. (2010) [19] with residual raw materials as *Nannochloropsis* sp. Of catalyst used by HZSM-5 in a fluidized-bed reactor with nitrogen flow, the results of the bio-oil analysis showed a decrease in oxygen content from 30.09 to 19.5 wt.% and higher heating value (HHV) increased from 24.4 to 32.7 MJ/kg when compared without a catalyst.

Researches on the use of various solid catalysts have been, such as metal oxides and acid solids in the catalytic cracking of bio-oil that can encourage the breaking of C-C and C-O bonds [21]. Aho et al. (2013) reported that Al_2O_3 might promote the formation of aromatic compounds, such as polycyclic aromatic hydrocarbons. And SiO_2 with low acidity might also reduce oxygenate compounds (phenol, ketone, aldehydes, acids, and alcohol) and inhibit the formation of coke on the catalyst because of its porosity medium. Thus, aluminosilicates, such as ZSM-5 and HZSM-5, are widely used in catalytic pyrolysis. These materials show the active and robust acidity of Brønsted in oxygenating cracking [22]. Sharp acidity will increase cracking activity and the ability to transfer hydrogen from the catalyst. As a result, many aromatics and hydrocarbons are formed [23]. Some pyrolysis studies with solid catalysts include HZSM-5 [14,17,24,25], hybrid composites (hexagonal mesoporous silicate (HMS) and ZSM-5 with impregnation of Ni, Fe, or Ce (10 % metal loading) [26], metal oxides supported by TiO_2 (an oxide form of Ce, Ni, and Co) [27], Magnetite (Fe_3O_4) [28], silica-alumina [25] and silica-alumina reuse [29].

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 use in the cracking process of petroleum, whose function is to increase the oxidation of CO [30]. With a melting point (1818 ºC) and a high surface area, various alumina phase silica catalysts in the reaction system (solid catalyst phase and gas phase reagents) are suitable for upgrading bio-oil and are relatively resistant and stable in processes run at temperatures high. In the form of pellets, besides, the catalyst is easily separated from the product [31].

Catalytic pyrolysis can be carried out by mixing biomass with a catalyst (in-situ catalytic pyrolysis) [13,24,27] or separating biomass and catalyst (ex-situ catalytic pyrolysis) [32,33]. In-situ catalytic pyrolysis is between biomass and catalyst mixed in one reactor, while ex-situ catalytic pyrolysis is biomass, and catalyst separated in reactors 1 (R1) and 2 (R2). The influence of in-situ and ex-situ pyrolysis on product yield and selectivity with the HZSM-5 catalyst is that the ratio of catalyst to biomass strongly influences the increase in-situ, and on ex-situ, the most influential is the temperature at reactor 2 (R2) [34,35].

This paper discusses the pyrolysis of *Spirulina platensis* residue (SPR) as well as upgrading bio-oil by using a solid catalyst of silica-alumina simultaneously in a single step process with a different reaction phase. The fixed-bed reactor consists of two series cylinders arranged vertically. The first reactor (R1) filled with SPR for pyrolysis, and the second reactor (R2) filled with silica-alumina for upgrading. Pyrolysis gases in Reactor 1 were as feed-in Reactor 2, and heterogeneous catalytic reactions occurred in Reactor 2 (ex-situ catalytic pyrolysis). SPR raw material analyzed for ultimate, proximate, and higher heating value (HHV). Silica alumina investigated by BET (Brunaur, Emmett, and Teller), SEM-EDX (Scanning Electron Microscope − Energy Dispersive X-ray), and X-ray fluorescence (XRF). GC-MS and HHV analyzed the liquid product.

2. Experiment

2.1. SPR and Alumina-silica Catalysts Preparation

Dry *Spirulina platensis* residue (SPR) derived from the by-product extraction of *Spirulina platensis* (SP) in the form of solid residue, while SP derived from Nogotirto Algae Park Yogyakarta Indonesia. *Spirulina platensis* residue (SPR) obtained from the extraction was in a wet state. Before used, it first dried in the sun for about three days, and then cleaned first from dirt and clumping SPR granules. The SPR stirred for homogeneous size distribution, and then stored in a dry and closed place [17,21].

Catalysts obtained from PT. Pertamina Balongan Indonesia was in the form of powder, and before being used for pyrolysis of silica-alumina, it printed in pellet form. Pellets were made by mixing silica-alumina 95 wt.% with kaolin 5 wt.% and adding distilled water to taste. After the mixture was homogeneous, it printed with a diameter of 4 mm pellet and a height of 6 mm. The catalyst pellets were dried by heating them to the furnace at 500 °C for 2 hours and then cooled in a desiccator [19].

2.2. Fixed-bed Reactor

SPR pyrolysis experiment was conducted with and without catalysis in fixed-bed reactors made of stainless steel with dimensions: inner diameter = 40 mm, outer width = 44 mm, and height = 600 mm [11,12,17,36,37]. The reactor equipped with an electrical heater, consisting of two reactors arranged in series, the first of which (R1) filled with SPR biomass, and the second of which (R2) filled with silica-alumina catalysts. Pyrolysis gas produced from R1 directly flowed to R2 through the catalyst pile. A diagram of the tool for ex-situ catalytic pyrolysis fixed-bed reactors presented in Figures 1 and 2.

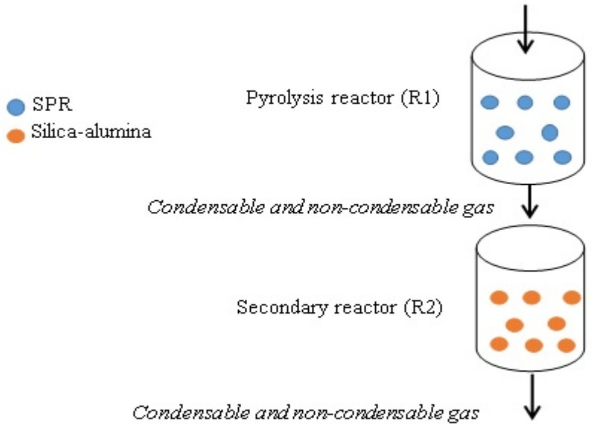


Fig.1. Reactor setup for the ex-situ upgrading

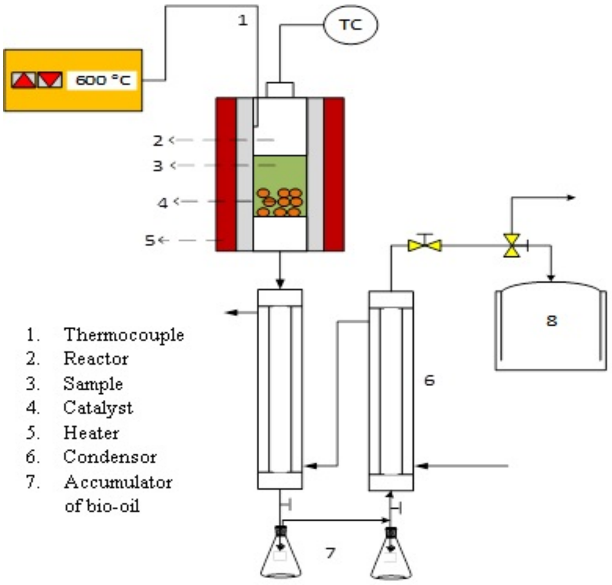


Fig. 2. Series of pyrolysis tool [11]

2.3. Research Method

Fifty (50) g of SPR was put into R1, while silica-alumina (10-40 wt.%) was put in R2, then tightly closed and heated. The reactor was heated externally by an electric furnace, and the temperature-controlled by a NiCr-Ni thermocouple placed outside the stove. The SPR samples tested were heated with a heating rate in the range of 5-35 ºC/min from room temperature (30 ºC) to the desired temperature (300-600 ºC), then the temperature was held constant for 1 hour. Temperature increases recorded every minute, and the heating rate was regulated. The pyrolysis gas was condensed, the liquid product coming out of the condenser was collected in an accumulator, and it tested by GC-MS [11]. The pyrolysis experiment procedure without catalyst done the same as pyrolysis with catalyst, but only R2 emptied without being filled by the catalyst.

2.4. Analysis

SPR Sample

SPR sample analyses conducted were proximate, ultimate, and higher heating value (HHV). Proximate analysis (protein with the Kedah method; carbohydrates with the Anthrone method; lipids with the Soxhlet method) and HHV (Bomb calorimeter) was carried out at the Food and Agricultural Product Laboratory, Department of Agricultural Technology and the Laboratory of Food and Nutrition of the Inter-University Center, UGM Indonesia. Meanwhile, the ultimate (C, H, O, N, and S with a standard D 2361) conducted at the Testing Laboratory, Research Center for Tekmira, Bandung Indonesia.

Silica alumina catalyst

Analyses of BET and SEM-EDX were carried out at UGM's Integrated Research and Testing Laboratory, and X-ray fluorescence (XRF) analysis was carried out at the International Frontier Division, Dept. Transdisciplinary Science and Technology School of Environmental and Society, Tokyo Institute of Technology, Japan. Tested in catalyst were (a) BET: (i) silica-alumina ratio, SiO_2/Al_2O_3, (ii) pore surface area, (iii) average pore volume / total pore volume; (b) SEM-EDX: content of C, O, Al and Si; and (c) XRF: composition of SiO2 and Al_2O_3 [11]. The catalyst test results presented in Figure 3 and Table 1.

Liquid product

Liquid product in the form of bio-oil is the derivation of condensation of pyrolysis gases, coming out at the bottom of the condenser. Liquid products analyzed for composition (oxygenate and aromatic) with GC-MS, Shimadzu GCMS type [GCMS-QP2010 SE] Rastek Rxi-5MS column length 30 m, ID 0.25 mm with Helium carrier gas, 200 ºC injector temperature, 50 pressure, 4 kPa, total flow 128 mL/min, column flow 0.85 mL/min conducted at the Research Laboratory, Faculty of Pharmacy, Ahmad Dahlan University.

3. Result and Discussion

3.1. Characteristics of Spirulina platensis Residue (SPR)

SPR sample analysis results, the ultimate analysis for components C, H, N, and O were 41.36, 6.60, 7.17, and 35.33 wt.%. In contrast, for the SPR proximate analysis, it was found that lipids, proteins, and carbohydrates were 0.09, 49.60, and 38.51 wt.% [11,12,17], respectively.

3.2. Silica-alumina Catalysist Characteristics

The results of the SEM-EDX analysis in the form of a catalyst weight percentage can see in Figures 3 and 4 and Table 1.

Figure 3 shows the magnitude of the voltage (keV) used and the total number of counts of each catalyst constituent (C, O, Al, and Si). Si, it is obtained at 1.739 keV with a total count of 2400, while Al achieved at 1,486 keV with 6800 counts. Figure 4 presents the microstructure test with SEM at a magnification of 100, 1000, 5000, and 10,000 times. Figures 4 (a) and (b) silica-alumina show a magnification of 100 and 1000 times, SiO_2 and Al_2O_3 appear to be white, still difficult to distinguish between the two.

In Figures 4 (c) and (d) with a magnification of 5000 and 10,000, it is clear that SiO_2 mixed with Al_2O_3 in one grain, which is transparent white granules such as glass and visible cavities in the catalyst.

The results of the investigation with XRF, BET, and SEM-EDX showed in Table 1.

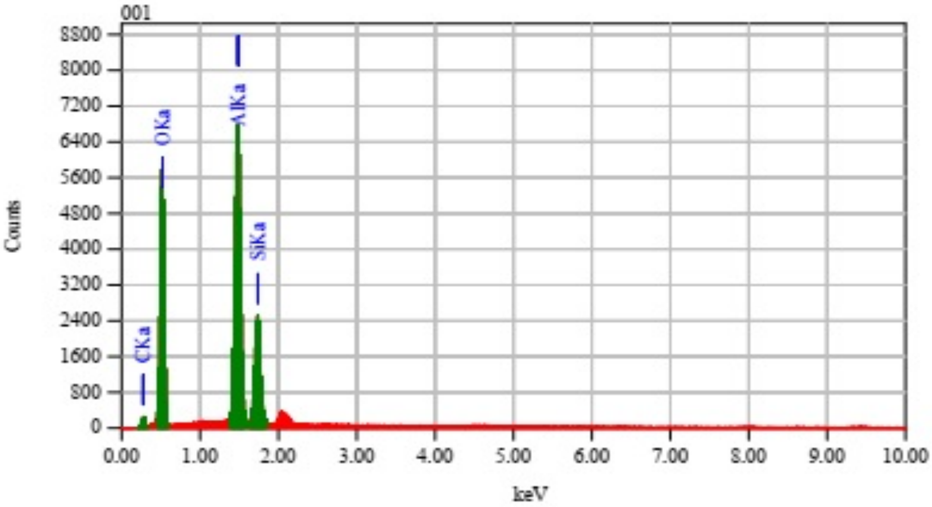
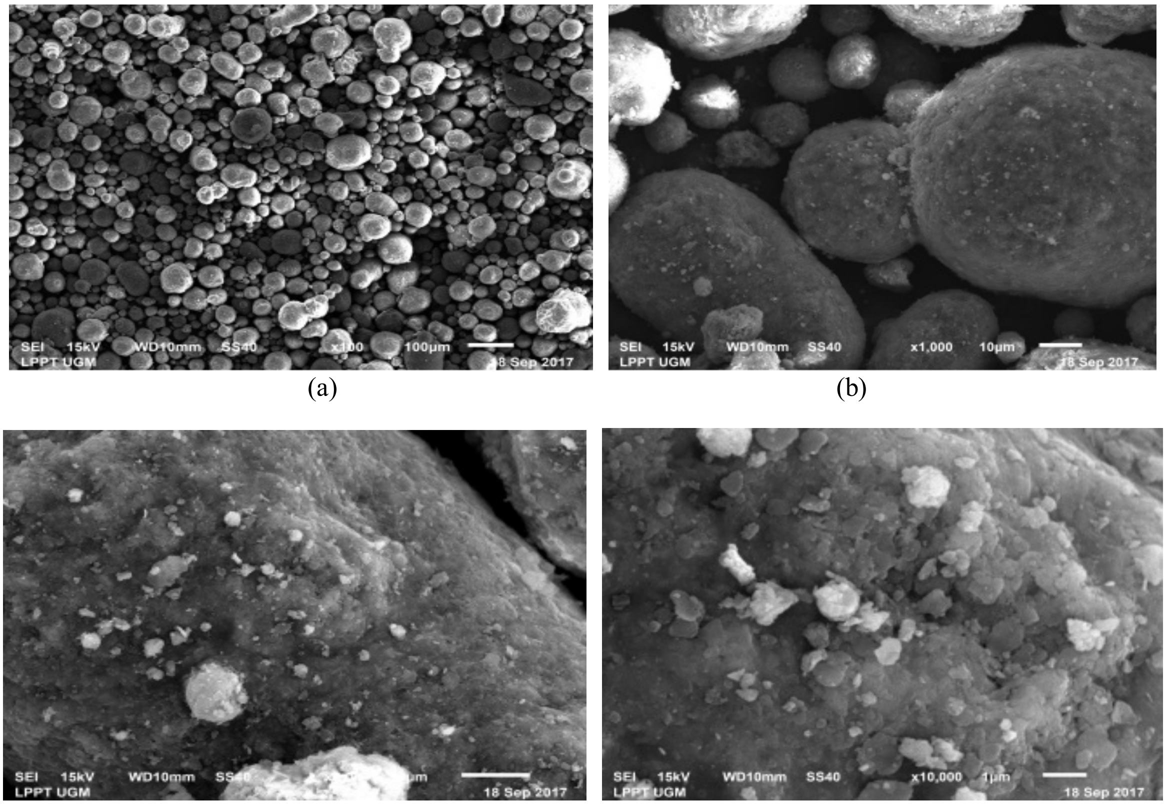


Fig. 3. Results of SEM-EDX analysis of Silica alumina



(a) (b)

(c) (d)

Fig. 4. SEM silica-alumina analysis at magnification, (a) 100 times, (b) 1000 times, (c) 5000 times and (d) 10,000 times

Table 1. Silica alumina catalyst specifications

Si-Al *specification*	**Value**
XRF	
SiO_2	60.28 *wt.*%
Al_2O_3	35.25 *wt.*%
SiO_2/Al_2O_3	1.71
BET	
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*
SEM-EDX	
	Weight, *wt.*%
C	8.41
O	55.78
Al	24.64
Si	11.17

3.3. Temperature and Silica-alumina Catalyst Effect on O/C, H/C, HHV Bio-oil

The quality of bio-oil from pyrolysis can see from the composition of its constituents, namely the content of C, H, and O. Therefore, the evaluation of bio-oil upgrading can be calculated on the value of O/C, H/C, and HHV. The C, H, and O contents obtained from GC-MS and HHV results calculated by eq. 1. The amount of C, H_2, O_2 H_2, and S are in weight percent [12].

$$HHV= 33.95(C) + 144.2(H_2) - O_2/8) + 9400(S)...MJ/kg \quad (1)$$

Bio-oil upgrading by adding catalysts to pyrolysis is intended to reduce the content oxygenate compounds or reduce the O/C ratio. The influence of temperature (300-600 ºC) and catalyst usage (10-40 wt.%) on O/C, H/C, and HHV values presented in Figures 5, 6, and 7. O/C, H/C, and HHV values are the average values of catalyst usage of 10-40 wt.%.

Figure 5 shows that without the use of a catalyst at a temperature variation of 300-600 ºC O/C ratio is in the range of 0.47 to 0.74, and with the use of a catalyst it is 10-40 wt.%, the average O/C falls in the range of 0.15-0.37. In the use of catalysts, the higher the temperature, the lower the average of O/C. The averages of O/C reduction before and after the use of catalysts at temperatures of 300, 400, 500, and 600 ºC are 50.45, 34.16, 46.91, and 79.71 %, so the average is 54.98 %. The optimum conditions achieved at 600 °C, in which the use of catalysts can reduce O/C by an average of 79.71 %. The quality of liquid products usually evaluated with O/C, H/C, and HHV ratios. High quality characterized by low O/C, H/C, and high HHV [15,38]. Tan et al., (2018) reported catalytic fast pyrolysis on durian skin with silica-alumina catalyst (surface area = 877.07 m^2/g; average pore diameter = 24.03 Å; pore size = 1.7-170 nm; total pore volume = 0.53 cm^3 / g; SiO_2/Al_2O_3 = 5) can reduce O/C from 0.21 to 0.05, ie a decrease of about 76.19 % [25].

From Figure 6, it can see that using catalysts will increase the average H/C; the higher the pyrolysis temperature, the higher the average of H/C. The optimum conditions for catalyst use achieved at 500 °C, with an average H/C of 2.44. The average H/C value without a catalyst is 0.97 (300-600 ºC), while the average catalyst usage is 2.02 (catalyst 10-40 wt.%), so an increase of 108.44 % occurs. From the results of Tan's et al. research (2018) pyrolysis with durian skin samples, the value of H/C without a catalyst is 1.67, whereas, with silica-alumina catalysts, it is 1.1. The H content of the sample influences the amount of H/C value. The H content in durian peels is 4.4 wt.%, while in SPR, it is 6.6 wt.% [25,29].

Figure 7 explains the effect of temperature rise and catalyst use on HHV bio-oil. In pyrolysis without catalyst, the higher the temperature, the higher the HHV due to the reduced O component in bio-oil. The use of a catalyst will cut the C-O bond in the bio-oil compound and release it as CO_2 resulting in a reduction in O in the bio-oil so that the HHV will rise sharply [11-12]. The average increase in HHV before and after the use of a catalyst (10-40 wt.%) at a temperature of 300-600 ºC is 16.66 to 22.36 MJ/kg, an increase of 34.19 %.

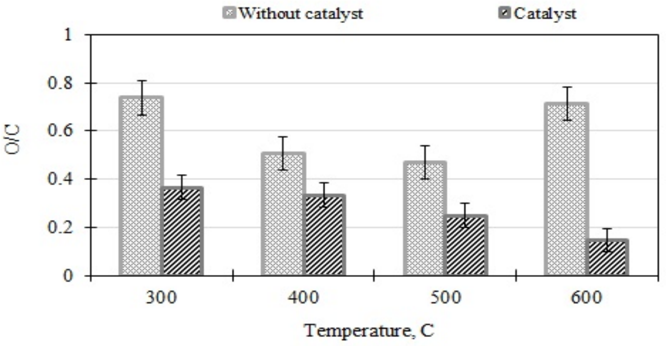


Fig. 5. Effect of temperature and use of catalyst on O/C bio-oil SPR

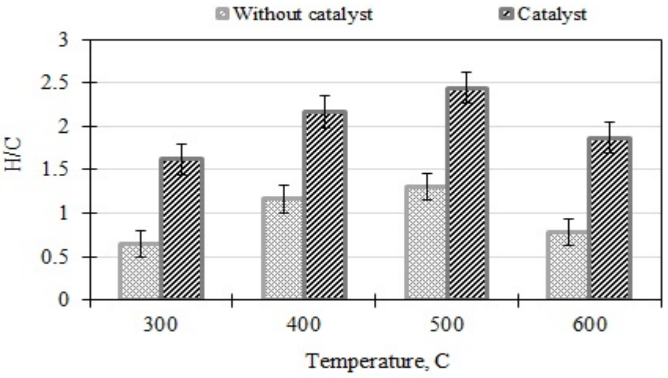


Fig. 6. Effect of temperature and use of catalyst on H/C bio-oil

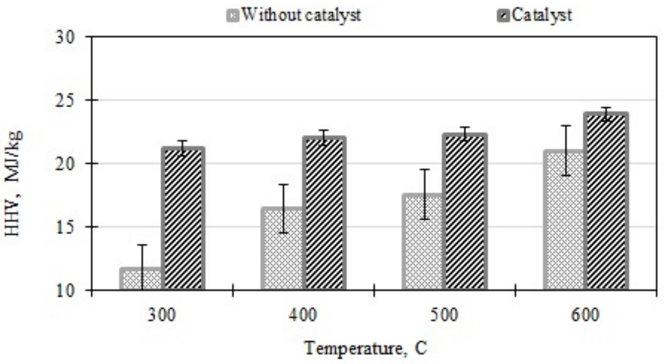


Fig. 7. Effect of temperature and use of catalyst on HHV bio-oil

Another consideration to assess the success of improving the quality of bio-oil with silica-alumina catalyst is to compare it with petroleum oil, bio-oil from wood, C. *Protothecoides* (CP) microalgae and SPR bio-oil without catalyst based on the results of GC-MS analysis [18,39]. The results are summarized in Table 2.

From Table 2, it can be seen that bio-oil from wood, microalgae of C. *Protothecoides* (CP), and SPR without catalyst have high oxygen content, which is 35-40, 20.19 and 35.63 wt.%. Meanwhile, the amount in petroleum oil is 0.05-1.5 wt.%. The use of silica-alumina catalyst in pyrolysis can reduce the O content to 7.82 wt. % and O decreases by 78.05%. In addition, using catalyst beneficially increases H by 500 %, which means that there is a very intensive C-H bond breaking by releasing H_2 gas, leading to an increase in HHV bio-oil.

Table 2. Comparison of the composition of petroleum oil, wood bio-oil, bio-oil microalgae of C, *Protothecoides* (CP) and bio-oil SPR [18,39,40]

Compo-sition, *wt.*%	***Petroleum oil***	**Wood**	**C.P.**	**SPR$^{(a)}$**	**SPR$^{(b)}$**
C	83.0-87.0	54-58	61.52	46.05	28.94
H	10.0-14.0	5.50-7.00	8.50	8.77	59.24
O	0.05-1.50	35-40	20.19	35.63	7.82
N	0.01-0.70	0-0.20	9.79	9.47	4.00
O/C	0.01	0.66	0.33	0.61	0.27
H/C	0.14	0.11	0.14	0.97	2.02
HHV (MJ/kg)	42	16-19	30	16.66	22.36

a: This experiment, non- catalytic pyrolysis

b: This experiment, catalytic pyrolysis

3.4. Effect of Pyrolysis Temperature and Silica-alumina Catalyst Use on Aromatic Compounds and Oxygenates

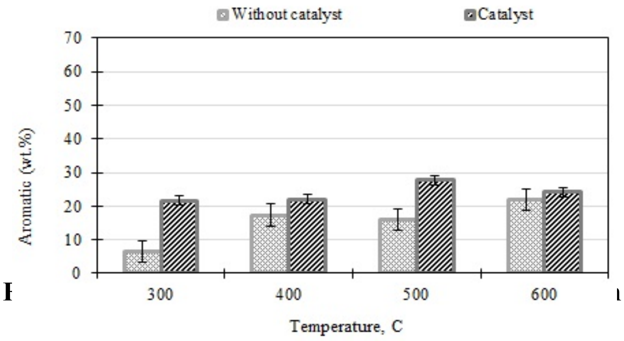
The quality of bio-oil can be assessed based on functional groups in bio-oil, changes in the content of oxygenating, and aromatic compounds that were selected before and after pyrolysis. The lower the oxygenate compound and the higher the aromatic compound, the better the quality of bio-oil as fuel. Figures 8 and 9 presented the effect of temperature and the use of catalysts on the content of oxygenated compounds and aromatic compounds in bio-oil.

We can observe from figure 8that pyrolysis without catalyst and with the use of a catalyst (10-40 wt.%) at a temperature of 300-600 ºC will reduce oxygenate compounds on average from 37.47 to 12.26 %, a decrease of 65.80 %. The increase in temperature, cracking mixtures of phenol, ketone, aldehydes, acids, and alcohols is faster, so that oxygenate compounds cut into aliphatic and aromatic by releasing CO, CO_2 gas, etc. Decomposition will also produce lighter hydrocarbon compounds, methane, hydrogen, CO_2, and CO, resulting in decreased O content in bio-oil. At high temperatures, the acid group instability occurs, so that oxygenate groups decompose to form CO and CO_2 [35]. The decrease in oxygenating compounds indicates that the quality of bio-oil is getting better with an increase in pyrolysis temperature, which is optimum at 600 °C (22.49 wt.%).

It can be explained from Figure 9 that the increase in temperature (300-600 ºC) and the use of a catalyst (10-40 wt. %) may increase the content of aromatic compounds from 15.48 to 23.89 wt.%, i.e., an increase of 54.32 %. This sharp increase indicates that the cyclization of olefins works very effectively, explained by an explanation of catalytic pyrolysis of lipids, proteins, and carbohydrates [40-41].

Lipids in the form of triglycerides are broken down by cutting the acyl chains from glycerol to produce long-chain fatty acids. Fatty acids undergo decarboxylation, decarbonization, deoxygenation, and cracking to form ketones, aldehydes, acids, alcohols, and short-chain hydrocarbons (such as olefins). Olefins can convert to aromatic hydrocarbons through cyclization and aromatization reactions [41]. The amino acid side chains in proteins during pyrolysis produce most of the aromatic hydrocarbons (such as toluene, xylene, and phenol) and N-heterocyclic compounds as indoles [42]. Olefin can also create several intermediates through cracking, deoxygenation, and deamination reactions.

Furthermore, proteins can combine with carbohydrates through the Maillard reaction to form Amadori compounds, which in turn react to form various aromatic compounds such as phenols, pyridine, pyrroles, and indoles [41,42]. Carbohydrates in microalgae cells are in the form of polysaccharides and oligosaccharides. The main products of carbohydrate pyrolysis are anhydrosugars and furfurals produced through hydrolysis, cracking, and dehydration. Reactions such as decarboxylation and deoxygenation can produce ketones, aldehydes, acids, and alcohol, then continue cracking to form olefins. The cyclization reaction converts olefins to aromatics [41,42].



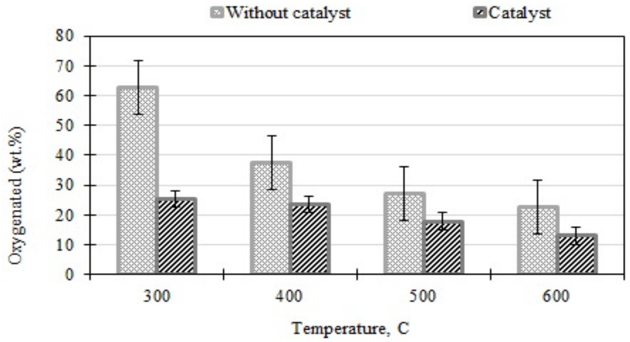


Fig. 9. Effect of pyrolysis temperature and catalyst use on aromatic compounds

4. Conclusion

This work aims to investigate the use of a dedicated reactor for the Silica Alumina catalyst, apart from the reactor where SPR biomass material is placed, on the quality of bio-oil produced through SPR biomass pyrolysis. The experiment was performed by passing pyrolysis gas from Reactor 1 (R1) through a bed of silica-alumina catalyst in Reactor 2 (R2) prior to being condensed to obtain bio-oil. It has been reported that the ratio of H/C, HHV, and aromatic compounds has increased, respectively, from 0.97 to 2.02, from 16.66 to 22.36 MJ/kg and from 15.48 to 23.89 % by weight. In percentage, the increase of those three respective parameters is 108.44, 34.19 and 54.32 %. Conversely, O/C ratio has shown decreased from 2.43 to 0.27 (a decrease by 54.98 %), as well as its oxygenate compounds from 37.47 to 12.82 % by weight (a reduction of 65.80 %). Based on those resutls, the use of these two reactors arranged in series (with a dedicated catalyst chamber) can improve the quality of bio-oil.

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