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Effects of Temperature and Catalysts on the Yield of Bio-oil During the Pyrolysis of *Spirulina platensis* Residue

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Abstract- *Spirulina platensis* (SP) is aquatic biomass potentially grown as an energy source in the future. Extracting algae oil from SP will leave solid residue called *Spirulina platensis* residue (SPR). In this study, SPR processed by the pyrolysis process, both catalytic and non-catalytic. This study focused on the effects of different catalysts on the yield of bio-oil obtained from the pyrolysis process. Pyrolysis experiments conducted at a temperature range of 300 – 600ºC using three different catalysts: Ni-oxide, Fe-oxide, and silica-alumina, and performed at 550ºC in various amounts of 5%-30 wt. % for each catalyst. The effect of temperature on SPR catalytic and non-catalytic pyrolysis was studied. The result shows that the optimum yield of non-catalytic pyrolysis was 27.34 wt.% at 550ºC. The yield of bio-oil within catalytic pyrolysis indicates that the maximum pyrolysis oil obtained using Fe-oxide as catalyst with 30.00 wt.% bio-oil, followed with 23.37 wt.% using Ni-oxide catalyst, and 18.41 wt.% using silica-alumina catalyst. The water phase yield for each catalyst was relatively different for every catalyst in various amounts ranging from 5 - 30%. Char and gas yields were almost the same for each type of catalyst in all amount variations. The highest gas yield produced was using the silica-alumina catalyst, followed by Fe-oxide and Ni-oxide catalyst. The SPR catalytic pyrolysis process improves the bio-oil yield with the increasing of the bio-oil yield 2.66 wt.% compared to the SPR non-catalytic pyrolysis.

Keywords: Spirulina platensis residue, Pyrolysis, Ni-oxide, Silica-alumina, Fe-oxide.

1. Introduction

Interest in the development of renewable energy is increasing along with the increasing world energy demand. The current energy source is still very dependent on fossil fuels, but it has limited resources and environmental problems such as global warming and air pollution. One of the abundant and quickly developed renewable energy sources is biomass, including wood, herbaceous plants, aquatic plants, and manure [1]–[8]. One of the biomass-derived from marine plants is microalgae. Biofuel from microalgae has several advantages, such as (i) high growth rates (up to 20 g of dried algae per m^2 per day), (ii) high yields per area, 15 times higher than oil palm [9], [10], (iii) high efficiency in absorbing CO_2 and solar energy conversion (8%) [6], (iv) no competition with agriculture and food [11]-[15]. Also, microalgae can grow in open waters (seas and ponds) and photo-bioreactors in non-agricultural land [16], [17].

Algae biomass contains three main components; they are carbohydrates, proteins, and natural oils (lipids). Nowadays, biodiesel from algae is produced by lipid extraction with organic solvents, such as hexane, followed by methanol trans-esterification using an essential catalyst [18]-[20]. Solid residues from this process contain minerals (up to 10%) that can be applied back to the algae growth cycle. However, the remaining 60% is a residue that not utilized, making it less economically attractive. Therefore, it is necessary to find a solution to the residual wastes, using the pyrolysis process to process this spirulina residue. The pyrolysis of microalgae [18], [19] and macro-algae [20], [21] produce hydrocarbons mixture, has shown to have the potential for large scale applications. Interestingly, Çoban et al (2015)[7] have demonstrated that pyrolysis of algae (*chlorella*) produces high bio-oil yields, above 40% at the temperature range of 300-500ºC.

Microalgae conversion technologies to produce renewable energy can classify into four ways, biochemical conversion, thermochemical conversion, chemical reactions, and direct combustion or pyrolysis [22]-[24]. Microalgae with high lipid content are more suitable to be converted to biodiesel by chemical reaction (transesterification). In contrast, microalgae with low lipid content can treat by biochemistry or thermochemistry processes [23]. Pyrolysis is a thermochemical decomposition of biomass at a temperature range of 400-600 °C, taking place without the presence of oxygen so that the wood components broke down and produced three product forms: solid, liquid, and gas [22]-[24]. Pyrolysis technology is the most beneficial because the process is simple, does not require additives/solvents, operates at 400-600 ºC and low pressure [25]. Pyrolysis produces fuel products and leaves no waste [25]-[28].

The chemical reaction of pyrolysis is [29]:

$$(C_6H_{12}0_6)_m[a] \rightarrow (H_2+CO+CO_2+CH_4+...+C_5H_{12})[b]+$$

$$(H_2O+CH_3OH+CH_3COOH+...)[c]+C[d]$$

$$\text{Biomass}[a] \rightarrow \textit{non-condensable gas}[b]+\textit{Condensable-}$$

$$\textit{gas}[c]\ +\textit{Char}[d] \qquad (1)$$

From Equation (1), biomass pyrolysis products are non-condensable gas (H_2, CO, CO, short-chain hydrocarbons such as CH_4, C_2H_6, C_2H_4, C_3H_8, and other gases such as NH_3, NO_X, SO_2), condensable gas (H_2O, CH_3OH, CH_3COOH, etc.), and char. The condensed gas is a thick black liquid called bio-oil or pyrolysis oil, bio-crude oil, bio-fuel oil, wood liquid, wood oil, liquid smoke, wood distillates, or pyro-ligneous tar [28]-[30]. In bio-oil production, no waste produced because all of the raw materials converted into bio-oil and charcoal. At the same time, non-condensable gas returns to the process as an energy source [29], [30].

The effects of catalyst in pyrolysis process are (i) significantly decreases the biomass decomposition temperature, (ii) influences the reaction tissue, for example, deoxygenation which allows the increase of bio-oil yield by reducing oxygenate compounds, (iii) reduces polymerization to stabilize bio-oil, the reaction more effective, (iv) releasing more CO, CO_2, and H_2O, and (v) increases coke formation [29]-[31].

This paper discussed the effects of temperature, type, and concentration of catalyst on the yield of bio-oil, the conversion, and the product composition. There are two types of catalysts used. The first one is an acid catalyst, silica-alumina, and the second type is a metal catalyst, Ni-oxide, and Fe-Oxide. This paper also compared pyrolysis performances between non-catalytic and catalytic pyrolysis. The concentration of catalyst used in pyrolysis was ranging from 5 - 30% wt. Pyrolysis carried out on fixed bed reactors at temperatures ranging from 300 to 600ºC, the pressure of 1 atm, and the heating rate of 20 - 35ºC / min.

2. Material and Method

2.1. Spirulina Plantesis Residue (SPR)

Dry *Spirulina platensis* residue (SPR) was obtained from *Spirulina platensis* (SP) solid residue extraction, while SP received from Nogotirto Algae Park, Yogyakarta, Indonesia. SPR samples were analyzed to obtain proximate value, the ultimate value, and high heating value (HHV). Proximate analysis carried out to receive a percentage of moisture content, ash, volatile matter, and fixed carbon. Ultimate study (C, H, O, N, and S with standard D-2361) conducted at Laboratorium Pengujian, Puslitbang Tekmira, Bandung (Testing Laboratory, Research Center Tekmira, Bandung). High Heating Value (HHV) was analyzed by bomb calorimeter at the Food and Agricultural Product Laboratory, Department of Agricultural Technology, and the Laboratory of Food and Nutrition of the Inter-University Center, UGM. The analyzed SPR composition was protein, carbohydrates, and proteins. Protein analysis used was the Kjeldahl method; the carbohydrates analysis used was the Anthrone method; lipids analysis used was the Soxhlet method.

2.2. Catalysts

There were three catalysts used in this experiment, Ni-oxide, and Fe-oxide, which were metal catalysts and silica-alumina, which is an acid catalyst. The alumina-silica catalyst was obtained from PT Pertamina Balongan in powder form, while Ni and Fe-oxide catalyst was from PT Pupuk Kujang, Cikampek, Indonesia. Each of the catalysts was analyzed by SEM and SEM-EDX (Scanning Electron Microscope – Energy Dispersive X-Ray) at Laboratorium Penelitian dan Pengujian Terpadu (LPPT) UGM (UGM Integrated Research and Testing Laboratory). SEM analysis performed to learn more about the shape and size of the catalyst particles. SEM-EDX analysis performed to identify the elemental composition of catalysts' materials.

2.3. Sample Preparations

The *Spirulina platensis* residue (SPR) obtained in wet conditions. The SPR was dried under the sun for three days to reduce water content, then cleaned of dirt and lumps of SPR beads. SPR stirred to homogenize the size distribution; then, it stored in a dry and closed place.

The silica-alumina catalyst made into the pellet-shaped catalyst. Pellets were prepared by mixing silica-alumina 95 wt.% with kaolin five wt.% and then adding distilled water. After the mixture was homogeneous, it molded into a pellet-shape with 4 mm in diameter and 6 mm in height. The pellet-shaped catalyst was dried in a furnace at 500°C for 2 hours and then cooled in a desiccator. In contrast, Ni and Fe-oxide catalysts were pellet-shaped catalysts that had the same size as silica-alumina.

2.4. Pyrolysis Experiment

2.4.1. Instrument

SPR microalgae pyrolysis experiment, both catalytic and non-catalytic reactions, were performed in a fixed-bed reactor with an inner diameter of 40 mm, the outer diameter of 44 mm, and a height of 600 mm. The reactor made of stainless steel. The reactor equipped with a heater, with two cylinders, the first cylinder was for biomass SPR (R1), and the second cylinder was for silica-alumina (R2) catalyst. The pyrolysis gas produced from R1 directly flowed to the catalyst stack in R2. The reactor arrangement sees in Figure 1, and the diagram for the fixed-bed reactor system see in Figure 2.

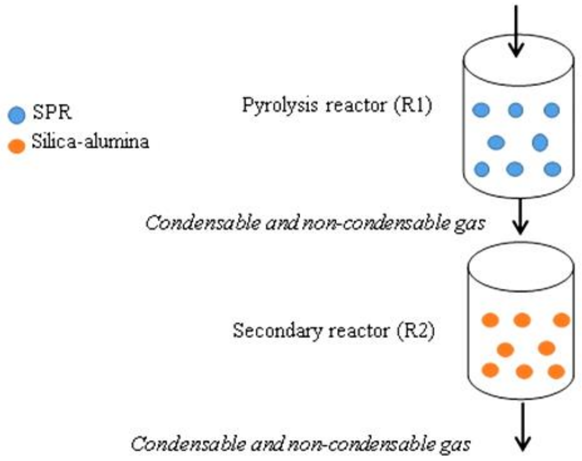


Fig. 1. Fixed-bed reactors arrangement [32]

2.4.2. *Product Yield and Conversion Calculations*

The total liquid or tar product (bio-oil and water phase), and gas were calculated by the equation [10], [23], [26], [32]:

$$Y_L = (W_L / W_M) \times 100\% \tag{2}$$

$$Y_{BO} = (W_{BO} / W_M) \times 100\% \tag{3}$$

$$Y_A = (W_A / W_M) \times 100\% = Y_L - Y_{BO} \tag{4}$$

$$Y_C = (W_C / W_M) \times 100\% \tag{5}$$

$$Y_G = 1 - (Y_L + Y_C) \tag{6}$$

The following equation calculated SPR pyrolysis conversion:

$$X = \frac{W_{BO} + W_A + W_G}{W_M} \times 100\% \tag{7}$$

In this case, Y_L, Y_A, Y_{Bo}, Y_C, and Y_G notations are respectively, liquid product yields, water phase, bio-oil, char, and gas. In contrast, W_M, W_L, WA, W_{Bo}, and W_C are respectively the weight of the initial SPR, the yield of the liquid product, the water phase, bio-oil, and char.

2.4.3. *Non-Catalytic Pyrolysis*

Fifty grams of SPR was fed into reactor R1, tightly closed and heated. The R1 reactor was heated externally by an electric furnace, and the temperature-controlled by NiCr-Ni thermocouple placed outside of the reactor. The SPR samples heated with a heating rate in the range of 20 - 35ºC/min from 30ºC to the desired temperature (300 - 600ºC). Then, the temperature was held constant for 1 hour. The temperature was recorded every minute, and the heating rate and installed at the specified range. The pyrolysis gas was condensed, the liquid product came out, the condenser collected in the accumulator, and the produced gas was measured. The bio-oil and the water phase separated by decantation. After the experiment finished, the remaining char was taken and weighed. The yield of bio-oil, water phase, char, and gas was calculated by equation (2) - (6), while conversion calculated by equation (7). The experiment was repeated three times for each variable tested.

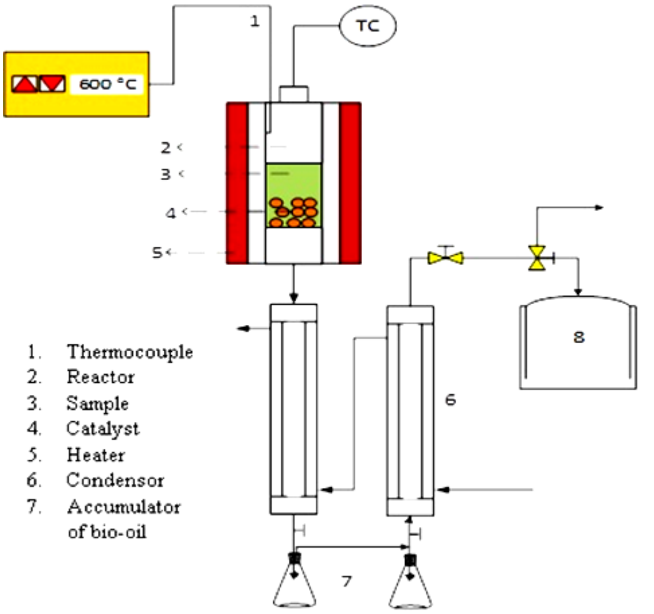


Fig. 2. The SPR pyrolysis system [32]

2.4.4. *Catalytic Pyrolysis*

Fifty grams of SPR fed into the reactor R1, and silica-alumina catalyst (5 - 30 wt.%) supplied in R2, then closed tightly and heated. The reactor heated externally by an electric furnace, and the temperature-controlled by a NiCr-Ni thermocouple placed outside of the reactor. The SPR sample heated with a heating rate in the range of 20-35ºC/min from 30ºC to 550ºC; then, the temperature was held constant for 1 hour. The same method and equation as the non-catalytic pyrolysis used to calculate the yield of bio-oil, water phase, char, gas, and conversion to catalytic pyrolysis [32], [33]. The experiments repeated using the same method for each Ni-oxide and Fe-oxide catalysts.

3. Result and Discussion

3.1. *Compositions of Spirulina Plantesis Residue (SPR)*

Table 1 shows the results of the proximate analysis of the SPR. The proximate analysis performed to determine the weight percentage of moisture content, ash, volatile matter, and fixed carbon. The proximate analysis shows the highest rate of SPR is the volatile matter (68.31%) and leaves relatively low content of ash (8.93%).

Table 1 also shows the results of the ultimate analyses of the SPR feedstock. The ultimate analysis carried out to determine the weight percentage of elemental component, carbon, nitrogen, hydrogen, and oxygen. The highest percentage was carbon (41.36%), followed by oxygen (35.33%), nitrogen (7.17%), and hydrogen (6.6%).

The high heating value of SPR found to be almost 18.21 MJ/kg. This result indicated that SP would be a better candidate if bio-energy production from renewable resources. The composition analysis shows that nearly half of the SPR composition is a protein (49.56%), followed by carbohydrates (38.51%), and a small amount of lipid (0.09%). This low lipid content in SPR is because the Spirulina Plantesis has been extracted and leaves this residue, which used in this experiment.

3.2. Characterization of Catalysts

Characterizations of catalysts were carried out by SEM and SEM-EDX analysis. The results presented in Table 2 and Figure 3. From Table 2, it can be seen that Ni-oxide consists of 4 components, they are O (46.01%), Al (34.39%), Ca (7.03%), and Ni (12.56%). Fe-oxide consists of 5 components, namely C (8.04%), O (28.75%), Cr (4.93%), Fe (56.64%) and Cu (1.64%). The silica-alumina consists of 4 components, namely C (8.41%), O (55.78%), Ca (24.64%) and Si (11.17%). Among the three types of catalysts, the most metal component is Fe at 56.64% in Fe-oxide catalysts with the addition of Cr 4.93% promoter.

Figure 3 explains the 10,000 times magnification of each catalyst. In Figure 3(a), macroscopically, the Ni-oxide catalyst is a fine gray powder. As for microscopically, each particle in Ni-oxide powder looks like a three-dimensional net with irregular size and shape of pores. It is structurally and thermally stable and has a large BET surface area (100 m^2/g catalysts). Figure 3(b) is silica-alumina, it appears that SiO_2 mixed with Al_2O_3 in one grain, which is shown by transparent white granules such as glass and visible cavities in the catalyst with a pore surface area of 240.553 m^2/g catalysts [32], [33]. As for Fe-oxide in Figure 3(c), from the results of 10,000 times magnification, they are not homogeneous. The presence of cluster groups suspected because of the magnetic nature of Fe_2O_3, so it tends to cluster. The color of Fe_2O_3 tends to be black; Cu is orange, while the intensity of Cr determined by the ligands attached to the center of Cr with a pore surface area of 1.963 m^2/g catalysts.

Table 1. The proximate analysis of SPR

The proximate analysis of SPR		The ultimate analysis of SPR		The composition analysis of SPR	
Properties	**wt. %**	**Properties**	**wt. %**	**Properties**	**wt. %**
Moisture	9.99	C	41.36	Lipids	0.09
Ash	8.93	H	6.60	Carbohydrates	38.51
Volatile matter	68.31	N	7.17	Proteins	49.56
Fixed carbon	12.77	O[a]	35.33	HHV	18.21 MJ/kg

[a] Oxygen calculated by the difference

Table 2. Specifications of catalysts with SEM-EDX

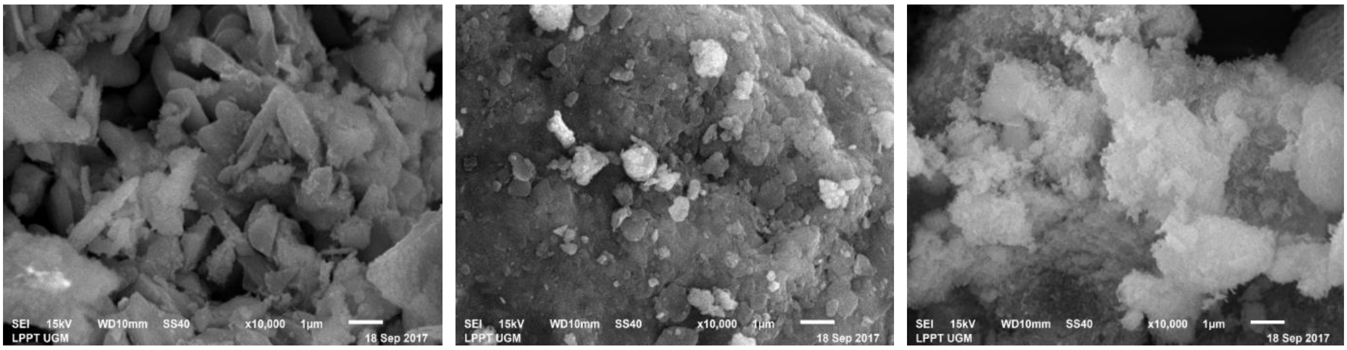
Nickel oxide	Mass, %	Ferro oxide	Mass, %	Silica-alumina	Mass, %
O	46.01	C	8.04	C	8.41
Al	34.39	O	28.75	O	55.78
Ca	7.03	Cr	4.93	Al	24.64
Ni	12.56	Fe	56.64	Si	11.17
		Cu	1.64		

3.3. Non-catalytic Pyrolysis Result

The effects of temperature on non-catalytic pyrolysis see in Figure 4. The pyrolysis process was performed at a temperature from 300 to 660°C. The maximum pyrolysis oil obtained at a temperature of 550°C. The result shows that the maximum pyrolysis oil was 27.34 wt.%, then the pyrolysis oil drops of 27.02 wt.% slightly at a temperature of 600°C (27.02 wt.%). The water yield obtained ranging from 22.17 wt.% to 28.82 wt.%. Tar is a liquid product from the addition of the bio-oil and water phase. The maximum tar yield obtained 56.16 wt.%. The char yield decreased significantly from 44.41 wt.% to 27.81 wt.% at temperatures of 300-600 °C. The gas yield was ranging from 14.57 wt.% to 24.88 wt.% at temperatures of 300 - 600°C.

The reduction of tar yield above the optimum temperature caused by secondary cracking (cracking, polymerization, condensation) reactions, the tar product in first cracking will partly decompose into gas so that the tar yield drops [34]-[36]. The amount of water in pyrolysis products comes from the SPR (9.99% free water) and the reaction of water formation during pyrolysis (dehydration). According to [33]-[37], the average water content in tar in biomass was above 20 wt.%.

From equation 7, we can calculate the SPR pyrolysis conversion, i.e., the total weight of bio-oil, water phase, and gas divided by the initial weight of the SPR. Conversion of SPR pyrolysis without catalyst at a temperature of 300-600°C can see in Figure 5. With the increase in pyrolysis temperature, the thermal decomposition of the SPR is more effective so that the weight of the SPR decreases, increasing conversion. Improvements in liquid and gas products indicated that the speed of the decomposition reaction rises as long as temperature increases.



(a) (b) (c)

Fig. 3. SEM analysis at magnification 10,000 times (a) Ni-oxide, (b) Silica-alumina, (c) Fe-oxide

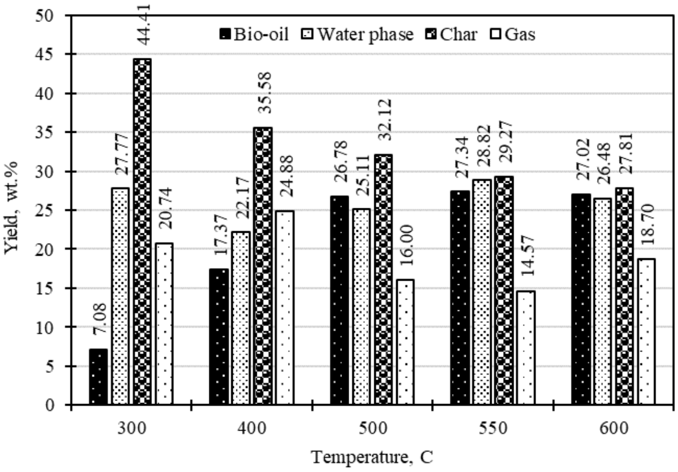


Fig. 4. The effects of temperature on the SPR non-catalytic pyrolysis yield

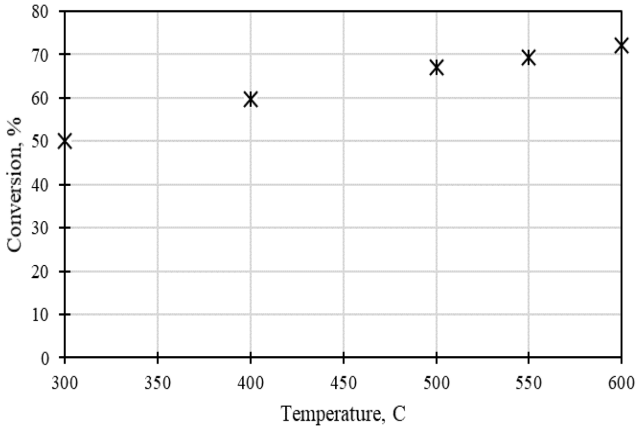
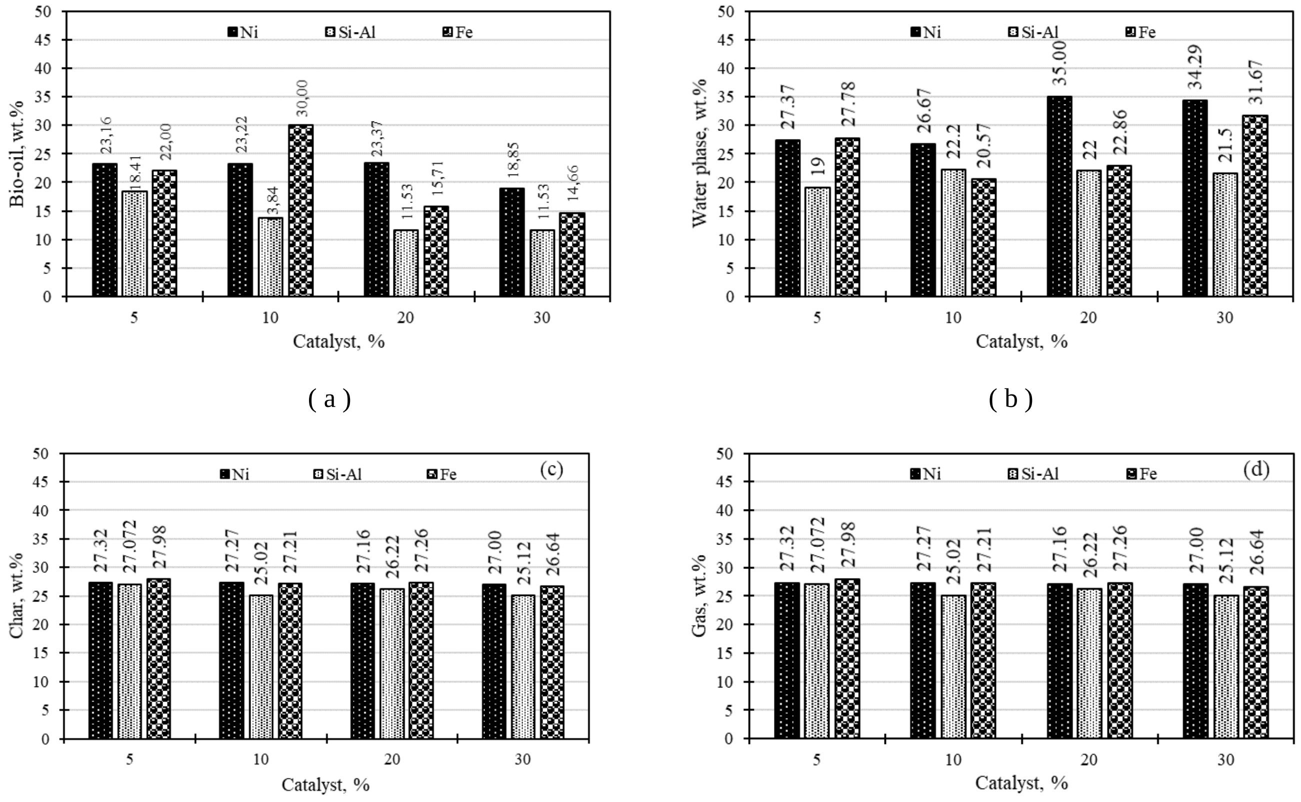


Fig. 5. The effects of temperature on conversion of the pyrolysis.

3.4. Catalytic Pyrolysis Result

The effects of catalyst on SPR pyrolysis using three types of catalyst: Ni-oxide, Fe-oxide, and silica-alumina with varying amounts of 5 - 30 wt.% at 550ºC presented in Figure 5. At 550ºC, the optimum temperature obtained in pyrolysis without a catalyst.

From Figure 6 (a), we can see the effects of the amount of catalyst on the yield of bio-oil products. Bio-oil mostly obtained from a 10% Fe-oxide catalyst. The amounts of bio-oil products at 550 ºC with a variation of the quantity of catalyst 5-30% for Ni-oxides, silica-alumina, and Fe-oxides are respectively in the range of 18.86 - 23.38; 11.53 - 18.41, and 14.67 - 27 wt.%. It can conclude that the highest yield of bio-oil obtained by the use of a Fe-oxide catalyst, followed by Ni-oxide and the least was by silica-alumina.



(a) (b)

(c) (d)

Fig. 6. The effects of catalyst (Ni oxides, silica-alumina, and Fe oxides) on product yields at 550ºC: (a) Bio-oil; (b) Water phase; (c) Char and (d) Gas

The yield of the water phase in various types and amounts of catalyst can be seen in Figure 6 (b), the yield of the water phase for multiple types of catalysts at the same amount is significantly different. The range of water phase yields with catalysts Ni-oxides, silica-alumina, and Fe-oxides for the amount of catalyst 5-30% is 26.67 - 35, respectively; 19 - 22.2 and 20.57 - 31.67 wt.%. This difference in yield can be due to the water content in the SPR sample and the reactions of water formation during pyrolysis. The use of catalysts can increase the dehydration reaction, which produces a certain amount of water [38]-[42]

From Figure 6(c) and (d), it can see that the char and gas yield in the use of various types and amounts of catalyst, the yield of char and gas is relatively the same. For the yield of char produced in the use of Ni-oxide catalysts, silica-alumina, and Fe-oxide, the amounts are 27 - 27.32%; 25.02 - 27.07% and 26.64 - 28 %, Meanwhile, for gases, the measures are respectively 14.47 - 22.84%; 35.52 - 41.85% and 22.24 - 34.17 wt.%. The most gas produced is in pyrolysis using a silica-alumina catalyst, the next is Fe-oxide, and the least one is with Ni-oxide catalyst. According to [33], the Ni-oxide has effected on the activation energy.

Pyrolysis conversion can achieve by using various types and amounts of catalysts is presented in Figure 7. From this figure, it can see that the more catalyst used, the higher the conversion. Pyrolysis use Ni-oxide, silica-alumina, and Fe-oxide catalysts in the amount of 5 - 30% obtained in the range of 45.36 - 46.11%; 45.86 - 49.76% and 44.04 - 46.72%. The highest conversion is achieved in the pyrolysis of silica-alumina catalysts, followed by Ni-oxides and Fe-oxides with almost the same range.

4. Conclusion

The maximum pyrolysis yield in the non-catalytic pyrolysis is 27.34 wt.% at a maximum temperature of 550ºC. Then yield dropped at 27.02 wt.% as the temperature increase in the temperature of 600ºC. In the temperature ranging from 300 to 600ºC, the yield of the water phase, char, and gas was 16.6 - 19.04 wt.%; 27.92 - 49.86 wt.% and 25.02 - 42.10 wt.%. The pyrolysis conversion will increase from 50.15 to 72.08 wt.% as the pyrolysis temperature increases.

Pyrolysis with the catalyst conducted at 550ºC using various catalysts (Ni-oxides, silica-alumina, and Fe-oxides), and the amount of catalyst was 5 - 30 wt. %. The highest yield of bio-oil was found from the use of Fe-oxide catalysts in the range of 14.67 - 27 wt.%, followed by Ni-oxide of 18.86 - 23.38 wt.% and the lowest by silica-alumina of 11.53 - 18.41 wt.%. The water phase yield was significantly different from each catalyst. The range of water phase yields with catalysts Ni-oxides, silica-alumina, and Fe-oxides for the amount of catalyst 5-30% are 26.67 - 35 wt.%; 19 - 22.2 wt.% and 20.57 - 31.67 wt.% respectively.

The char and gas yield was relatively similar. The yield of char produced in the use of Ni-oxide catalysts, silica-alumina, and Fe-oxide was 27 - 27.32 wt.%; 25.02 - 27.07 wt.% and 26.64 - 28 wt.% respectively. While gases yields were 14.47 - 22.84 wt.%; 35.52 - 41.85 wt.% and 22.24 - 34.17 wt.% respectively. Most of the gas produced was in the use of silica-alumina catalyst, then Fe-oxide, and Ni-oxide catalyst.

The more amount of catalyst used, the higher the conversion. Conversions with Ni-oxide, silica-alumina, and Fe-oxide catalysts are in the range of 45.3 - 46.11 wt.%.; 45.86 - 49.76 wt.%. and 44.04 - 46.72 wt.%. The highest conversion obtained using silica-alumina catalysts, followed by Ni-oxides and Fe-oxides with almost the same range.

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