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Spirulina Platensis Residue (SPR) Pyrolysis: Temperature's Effect on Yield and Biochar Characteristics

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ABSTRACT

Biochar has potential as alternative solution to overcoming the problem of renewable energy needs, improving land structure for agriculture, and supplying industrial needs as absorbent material with high absorption. Biochar has a high carbon content that it obtains from the biomass pyrolysis process. In this experiment, the main material was biomass obtained from the Spirulina platensis residual (SPR). The temperature effect on the yield and characteristic of biochar from SPR were studied. The research was conducted in the fixed-bed reactor with 40 mm of inside diameter, 44 mm of outside diameter, and 600 mm of height. The reactor was supported with an electrical heater from a nickelin coiled along the outside surface of reactor. The experiments were carried out with temperatures ranging from 300 to 700ºC. Biochar analysis was performed by the Brunauer-Emmett-Teller (BET) method. Results indicated that the yield of biochar decreased with increasing temperature. Conversely, the surface area, the total volume of pore, and the radius of pore increase with an increase in temperature. The best temperature conditions to produce the biochar are 600ºC, with the product yield of 27.9 wt.%, surface area of 13.5 m^2/gr, total pore volume of 0.041 cc/gr, and diameter of 2,688 nm.

1. Introduction

Biochar is stable charcoal with high content of carbon. Biochar is very promising for soil remediation applications to improve carbon sequestration, retain more water and nutrients, and raise crop yields and provide energy simultaneously [1-2]. There are several benefits of adding biochar for arid soils: it can enhance soil quality, increase the capacity to hold water due to the carbon in the biochar, increase the potential to retain nutrients and fertilizers with slow release properties, remove cations from the soil by carbon sequestration, remove organic matter from the soil by adsorption, and it can increase crop yields because it improves irrigation conditions and soil quality [3-4]. Biochar that meets the requirements of the Republic of Indonesia's Decree No. 261/KPTS/SR.310/M/4/2019, the Decree of the Minister of Agriculture, regarding the Minimum Technical Requirements for Soil Improvement, can be produced through biomass pyrolysis at temperatures between 300 and 700 degrees Celsius [5].

Biomass is an alternative energy source to produce environmentally friendly fuel. The potential of various types of biomass to produce biochar listed in Table 1. Table 1 shows that microalgae have good potential to produce biochar, namely in the range of 56.3-65.2%. Pyrolysis is one of the well-known thermochemical technologies, the method that has received the greatest attention to date, and has been demonstrated to be among of the most effective methods for creating biochar [6-8]. Biochar production via pyrolysis is affected by the biomass source, properties of the biomass, such as moisture content and particle size, and composition, such as cellulose, lignin, and ash, as well as process variables, such as heating rate, temperature, and residence time [9]. For high charcoal yields, low temperatures, and heating rates are recommended.

Table 1. Yield of biochar from pyrolysis of various kinds of biomass [7, 1]

Biomass Type	Temperature (°C)	Yield (wt.%)
Pine sawdust (<2.00mm)	300-450	26 - 58
Rice husk (0.25-1.00mm)	400-600	25.5 - 33
Corncob (0.50-4.00mm)	400-700	20.2 - 34.2
Corncob (0.50-2.20mm)	400-1000	5.7 - 30.6
Olive husk (0.50-2.20 mm)	400-1000	19.4 - 44.5
Sewage sludge	350-950	39 - 65.5
Microalgae (<1.00 mm)	300-700	56.3 - 65.2

The general biomass pyrolysis scheme is shown in Figure 1. Pyrolysis will produce three (3) main products, namely non-condensable gas/combustible gas, condensable gas (bio-oil and water phase), and biochar [2].

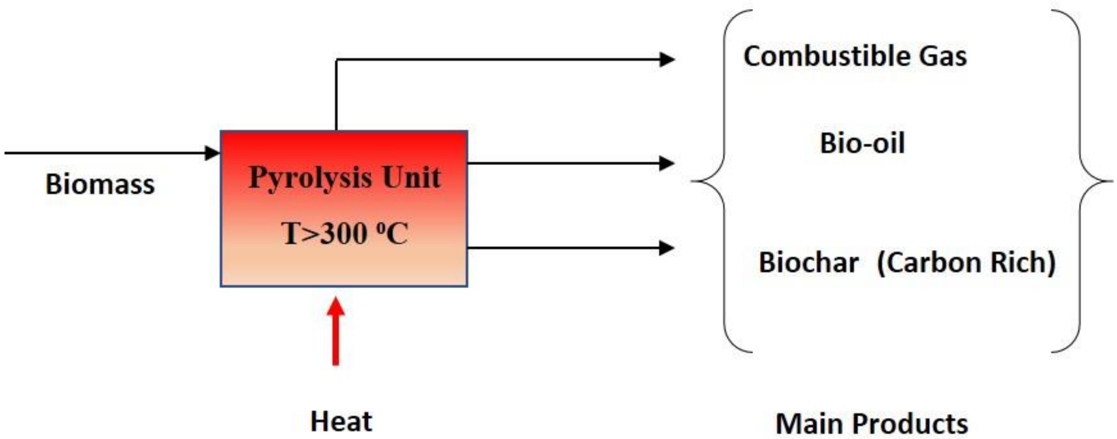

Fig. 1. Pyrolysis Process Scheme

In general, pyrolysis is divided into 6 types based on operating conditions. The division of pyrolysis types is shown in Table 2. The choice of pyrolysis type depends on the purpose of pyrolysis: to obtain the most product, whether liquid, solid, or gas. To get maximum biochar, slow pyrolysis is the right choice because it will produce biochar around 56-75% [2], [12], [17-18]

Table 2. Operating conditions of various types of pyrolysis [17]

Pyrolysis Type	Temperature (°C)	Heating Rate (°C /s)	Residence Time (s)	Particle Size (mm)	Product
Slow	300-800	0.1-1.0	300-550	5-50	Bio-oil, biochar, and syngas; Biochar dominant
Fast	500-650	10-200	0.5-10	<1	-
Flash	700-1100	>1000	<0.5	<0.5	Bio-oil, biochar, and syngas; syngas and bio-oil are dominant
Intermediate	500-650	1.0-10	0.5-20	1-5	Bio-oil, biochar, and syngas
Vacuum	300-600	0.1-1.0	0.001-1.0	-	Bio-oil, biochar, and syngas
Hydro	350-600	10-300	>15	-	CH_4, bio-oil, and biochar

The characterization of biochar resulting from pyrolysis can be identified from the amount of yield, pore radius, surface area, and total volume of pore. The BET method is used for flat surfaces (no curves), and no boundaries in each layer can be used to explain the surface area. This method is used based on the assumption that each surface has a homogeneous energy level (adsorption energy does not change with adsorption on the same layer), and there is no interaction while the molecules are being adsorbed. This method is applied to determine the surface area, the pore distribution of the material, and the adsorption isotherm of a gas on a material. In nanomaterials, BET can measure pore size and surface area. The surface area is the area occupied by one adsorbate/solute molecule, which is a direct function of the sample's surface area. It is therefore possible to define surface area as the number of pores in a sample's unit area and specific surface area as the surface area per gram of mass [10], [14]. The surface area of various types of microalgae shown in Table 3.

Table 3. Adsorption of contaminants uses various kinds of microalgae-derived biochar as Adsorbant [12]

Microalgae	Contaminants	Pyrolysis Conditions	Surface Area (m^2/g)
Chlorella sp.	p-Nitrophenols	600°C, 0.5 h	6.163
Coelastrum sp.	-	-	15.032
Chlamydomonas sp.	-	-	2.122
Scenedesmus dimorphus	Co (II)	500°C, −	–
Spirulina platensis	Congo red	450°C, 2 h	167
Blue-green microalgae	Tetracycline	Hydrothermal process	–
Spirulina sp.	Tetracycline	350°C, 2 h	0.310
		550°C, 2 h	1.550
		750°C, 2 h	2.630

This research uses the BET method to investigate the temperature's effects on product yield and biochar characteristic, namely pore radius, surface area, and total volume of pore. The research was performed with a fixed-bed reactor. By knowing the characteristic of biochar, data on its physical properties can be obtained, and its usefulness can be recommended. Then, biochar production can be carried out from microalgae pyrolysis to overcome environmental problems and solutions for industrial processes that require adsorbents with high adsorption capacity.

2. Research Methodology

1. Materials

SPR was gathered from the solid residue of Spirulina platensis (SP) extraction, while SP was arrived from the Nogotirto Algae Park.

Tool

The SPR microalgae pyrolysis experiment was performed in a stainless steel fixed-bed reactor with the following dimensions: height = 600 mm, outside diameter = 44 mm, and inside diameter = 40 mm. A nickelin heater is encircling on the outer reactor cylinder [17-18]. The fixed-bed reactor setup is shown in Figure 2.

2. Procedures

SPR setup

SPR is produced from the extraction residue of SP in a wet state. Prior to usage, it is sun-dried for about three days and then washed to remove any dirt or lumpy SPR granules. After stirring to homogenize the size distribution, it is sealed and kept dry.

Procedure

Fifty g of SPR was added within the securely sealed reactor, which was heated outside by an electric heater. An external NiCr-Ni thermocouple was used to control the reactor's temperature. The SPR samples were heated from room temperature (27 ºC) to the target temperature (300–700 ºC) at a heating rate of 5-35 ºC/min. Following pyrolysis, the gas is condensed, the liquid product exiting the condenser is gathered in an accumulator, and the quantity of gas product is quantified. The bio-oil and the water phase were decanted and weighed. The amount of biochar (solid residue) left over from the experiment is measured and weighed. The yields of pyrolysis product are determined using equations (1)–(5). The experiment was performed in triplicate [17].

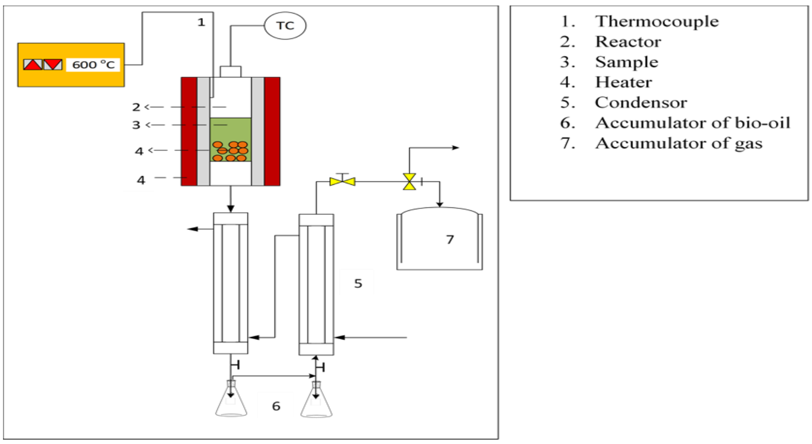

Fig. 2. Experimental equipment

Yield Calculation

The following equations are used to calculate the pyrolysis [17]:

$$Y_L = \left(\frac{W_L}{W_M}\right) x\ 100\ \% \quad (1)$$

$$Y_{Bo} = \left(\frac{W_{Bo}}{W_M}\right) x\ 100\ \% \quad (2)$$

$$Y_A = \left(\frac{W_A}{W_M}\right) x\ 100\ \% = Y_L - Y_{Bo} \quad (3)$$

$$Y_C = \left(\frac{W_C}{W_M}\right) x\ 100\ \% \quad (4)$$

$$Y_G = 1 - (Y_L + Y_C) \quad (5)$$

Where, YL, YA, YBo, YC, and YG are the liquid, bio-oil, water phase, char, and gas product. Meanwhile, WM, WL, WBo, WA, and WC are the weight of sample SPR, liquid, bio-oil, water phase, and char, respectively.

Biochar analysis: BET (Brunauer-Emmett-Teller) and Ultimate analysis

Biochar was degraded for 10 h at 150 °C prior to adsorption-desorption isotherm analysis. BET methods are used to determine the specific surface area BET (SBET). Single point adsorption total pore volume analysis was used to determine the total volume of pore (Vtotal). The mean pore diameter (D) was estimated using 4V/SBET in accordance with the BET method. BET analysis was conducted at the Chemical Engineering Instrumental Analysis Laboratory (ANINS), UGM. Meanwhile, the biochar ultimate analysis was performed at the Center for Food and Nutrition Studies, PAU, UGM.

2. Results and Discussion

1. Temperature's Effect on Product Yield

The yields of pyrolysis products are strongly influenced by temperature, the relationship between pyrolysis temperature and the yield of each product is given in Figure 3.

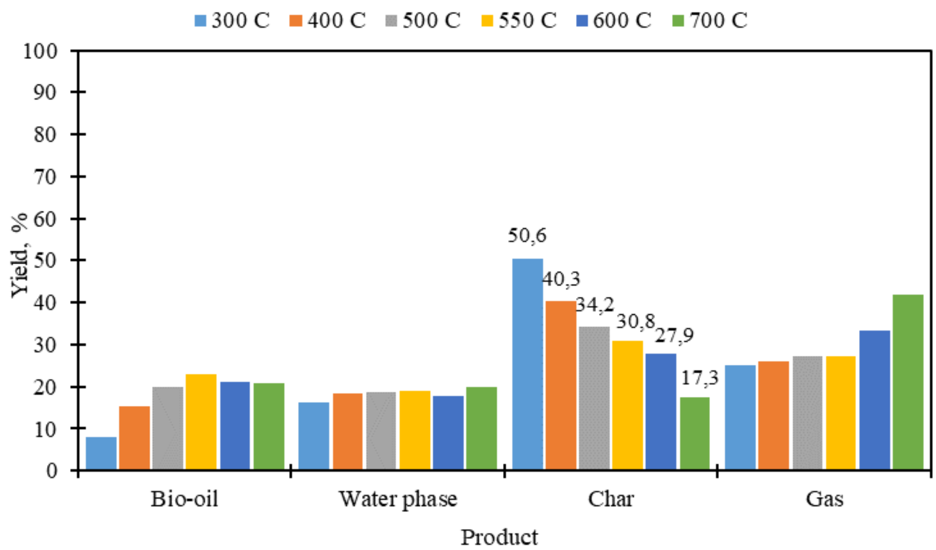

Fig. 3. Temperature's effect on yield of pyrolysis product

From this, it can be seen that the yield of bio-oil and gas increases with increasing pyrolysis temperature (300–700ºC). The optimal temperature for bio-oil is 550 C, yielding 23.06%, while the optimal temperature for gas is 700ºC, yielding 41.95%. Meanwhile, the water phase is relatively stable at 16.33-20% (300-700ºC). The yield of biochar decreases with an increase in temperature of pyrolysis, ranging from 50.6 to 17.3%. The optimum yield of 50.6% was achieved at 300 C.

2. Temperature's Effect on The Characteristic of Biochar

The temperature's effect on the characteristics of biochar, namely surface area, total volume of pore, and pore radius are shown in Figure 4, 5 and 6.

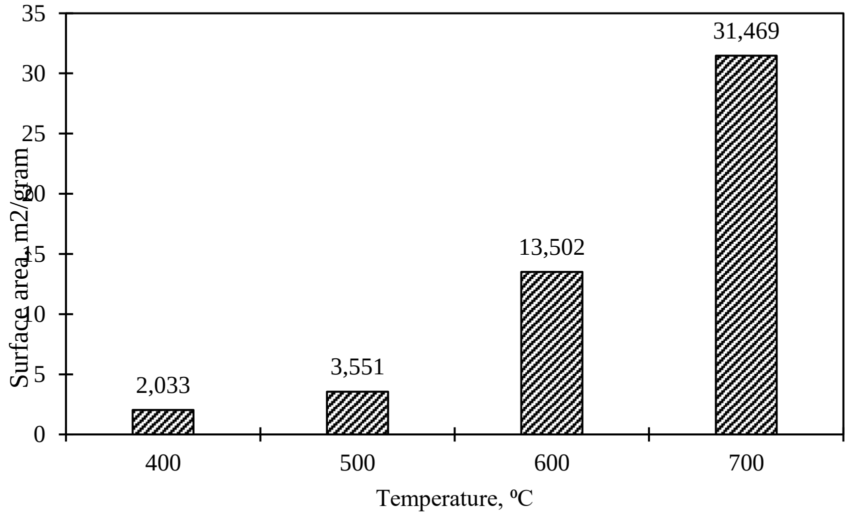

Fig. 4. The temperature's effect on the biochar surface area

From Figure 4, it can be noticed that the surface area of biochar increases with an increase in pyrolysis temperature. At a temperature of 400, the surface area is 2,033 m^2/gram; this value will increase sharply at a temperature of 600 to 700ºC from 13,502 to 31,469 m^2/gram; from a temperature of 400 to 700 ºC there is an increase of almost 16 times. This could mean that activated charcoal can be made from biochar derived from microalgae, whose surface area can be increased by physical or chemical activation. Its benefits will be much more significant for various fields.

The optimum conditions for biochar pyrolysis are achieved at a temperature of 700ºC with the largest surface, namely 31,469 m2/g; however, if you look at the yield of biochar from pyrolysis, the lowest result will be obtained, namely 17.3%. For this reason, to get an excellent characteristic of biochar, the temperature at which the pyrolysis is conducted must be taken into consideration. Zheng, 2017 has investigated the pyrolysis experiment at a temperature of 600 ºC on Chlorella sp. and produced biochar with a surface area of 6,163 m^2/g [19]. In comparison with this study, biochar derived from SPR pyrolysis at 600ºC has a significantly larger surface area namely 13,502 m2/gram. The surface area of biochar for different types of biomass was affected by the variations in the size, shape, and arrangement of the pores in the particles affect. [2].

The effect of temperature on the total pore volume is depicted in Figure 5. This figure demonstrates that the total pore volume increases with increasing pyrolysis temperature. An increase from 400 to 700 ºC, causes increasing from 0.008 to 0.064 cc/g, increases the total pore volume eight (8) times. This can be interpreted as the volume of space in 1 g of charcoal increasing by 0.008-0.064 cc. The relationship between pyrolysis temperature and pore radius is presented in Figure 6. The pore radius increases with an increase in pyrolysis temperature (400–700 C), although relatively small, from 2,684 to 2,689 nm. The size of the pore radius is one factor in the size of the surface area. The pore radius of biochar from SPR is quite large compared to that of silica alumina, namely 2.3 nm [18].

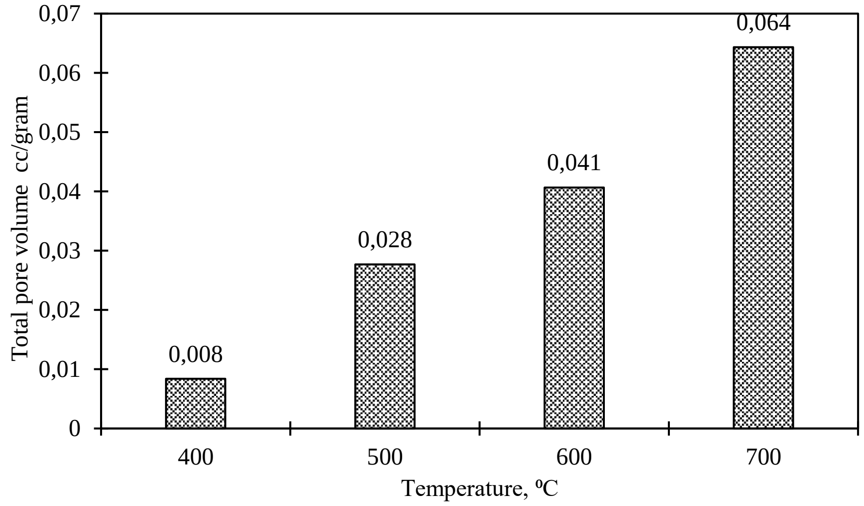

Fig. 5. Effect of pyrolysis temperature on total pore volume

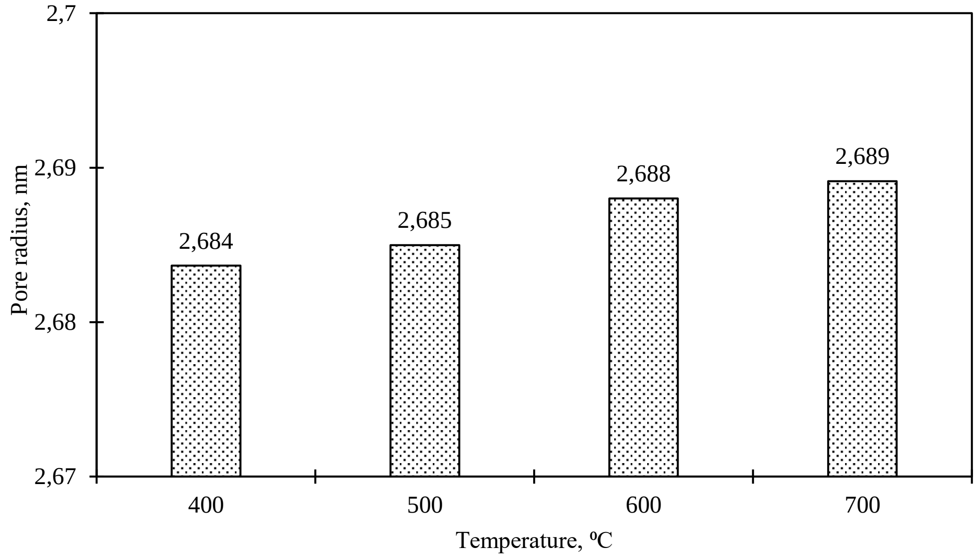

Fig.6.Effect of pyrolysis temperature on biochar pore radius

3. Comparison of the results of the ultimate SPR biochar analysis with other biomass

To assess the quality of the biochar produced, the biochar must be subjected to an ultimate analysis to determine the composition of C, H, O, and N. The composition comparison is shown in Table 4. The C content in SPR biochar is relatively high, almost 60%, so SPR biochar has the potential to be used as active carbon for adsorption, soil softening, and other purposes. From the standards of the Decree of the Indonesia's Minister of Agriculture, the minimum C content in biochar is at least 60%. Hardwood such as hardwood (oak) has a C content (88%) and a very high surface area (153.1 m^2/g). Surface areas for softwood such as softwood (pine), Spirulina platensis residue, and spirulina platensis are respectively as follows: 4.9, 31.47 and 19.16 m^2/g.

Table 4. Results of ultimate and characteristic analysis (BET) of biochar from various types of biomass

Component (wt.%)	Hardwood (Oak), % [4]	SPR, %*	Spirulina Platensis, % [9]	Softwood (Pine), % [4]
C	88.00	47.80-59.24	84.70	71.20
H	2.55	2.8-4.43	2.48	2.88
N	0.44	5.75-10.60	0.31	0.91
O	14.80	33.6	6.72	11.6
S	-	-	0.25	-
Ash	11.80	11.80	5.54	14.90
Calorific Value (MJ/kg)	-	19.22	-	-
SBET, m2/g	153.1	31.47	19,16	4.90
Vtotal, cc/g	-	0.064	0.07	-
D (nm)	-	5.38	15.58	-

*This research

4. Conclusion

Biochar SPR pyrolysis can overcome various problems in industry, including the agricultural sector, by improving soil structure and increasing crop yields. From SPR pyrolysis, biochar is produced with good characteristics. The study revealed that the pore radius, total pore volume, and surface area increased with the pyrolysis temperature. Optimum conditions were achieved at a temperature of 600 ºC, with the biochar yield, surface area, total pore volume, and pore diameter were 27.9 %, 13.502 m^2/g, 0.041 cc/g and 2.688 nm, respectively. The ultimate analysis found that the C content of SPR's biochar was still relatively high, namely 59.24%.

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