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ORIGINAL ARTICLE

Porous Carbon Black Microsphere from Palm Oil Black Liquor

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ABSTRACT – The aim of this research is to synthesize porous carbon black microspheres from palm oil black liquor through an in-house spray pyrolysis system. The in-house spray pyrolysis (SP) system was developed using a horizontal furnace. To test the developed SP equipment, the temperature profiles within the developed spray pyrolysis chamber were examined at three different setting temperatures (800, 900, and 1000°C). These temperatures were also applied for synthesizing the carbon black microspheres, with and without nitrogen as carrier gas. The morphology of carbon black produced using SP equipment was tested by a 3D optical microscope and field emission scanning electron microscope (FE-SEM). The optimum temperature obtained in this study is 1000ºC according to the characterization of carbon black microspheres produced. The FE-SEM analysis indicated the presence of spherical carbon having microstructures. This indicates that the in-house spray pyrolysis machine has been successfully developed for synthesizing carbon black microspheres.

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INTRODUCTION

Indonesia is one of the world's largest producers of palm oil. The country has a large area of land suitable for cultivating oil palms and a long history of growing crops. The industry is a major source of income for many small-scale farmers, as well as for larger companies [1]. Palm oil is used in a wide range of food products, as well as in non-food products such as cosmetics [2], biogas [3], and biofuels [4]. In the process of bioethanol production, empty fruit brunch (EFB) is delignified and bleached, which also produced by-products. The brownish oily liquid by-product is called black liquor. It typically contains a small amount of lignin, carbohydrates, inorganic compounds, organic compounds, and water. This black liquor has a high heating value and usually being used as fuel to generate steam and electricity in a recovery boiler. Since black liquor contains lignin and organic compounds, it can be used for other purposes by extracting its carbon content [5]. Several techniques can be used to extract carbon from black liquor, such as spray pyrolysis, gasification, carbonization, and solvolysis. From all those techniques, spray pyrolysis is considered one of the cheapest techniques to extract carbon from black liquor. This process is also relatively simple and can be carried out at low temperatures [6].

Spray pyrolysis (SP) is a technique for material synthesis by atomizing a precursor solution into a fine mist and passing it through a hot zone, where the droplets are vaporized, and the precursor is decomposed and deposited onto a substrate. SP is a versatile technique that can be used for the synthesis of a wide range of materials, such as carbon black [7]–[9], carbon nanotubes [10], and graphene [11]. The properties of the synthesized materials can be tailored by selecting precursor and carefully controlling the process parameters such as precursor solution flow rate, hot zone temperature, and substrate temperature. One of the main advantages of SP is its versatility. It can be used to synthesize a wide range of materials with a high degree of crystallinity [12] and uniform size distribution [9]. Additionally, the process is relatively simple, which can lead to lower costs [13]. SP is also a technique that allows for precise control over the material properties, which can lead to more efficient use of energy and resources[12]. Hence, spray pyrolysis is the most suitable method for producing carbon black from black liquor.

The utilization of carbon black is already common in the industry. It can be used for many applications, such as a colorant [14] and reinforcing filler in tires [15] and other rubber products [16]–[18], pigment and wear protection additive in plastics [19], paint [16], and ink pigment [20]. Some countries also use it as a food colorant [21]. Due to its high conductivity, it could also serve as an additive to make conductive ink [22].

In this paper, we designed the spray pyrolysis system to process black liquor into a more beneficial product. The black liquor consists of lignin, carbohydrates, inorganic compounds, organic compounds, and water, which are difficult to

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nebulize using ultrasonic process homogeneously. The common steaming process of black liquor can only nebulize water. Thus, another steaming method is necessary to be developed for this spray pyrolysis process.

In order to test the developed SP equipment, the temperature profiles within the developed spray pyrolysis chamber were examined at three different setting temperatures (800, 900, and 1000ºC), while the characteristics of the obtained carbon black with and without nitrogen carrier gas in aforementioned temperature were observed using optical microscope (OM).

EXPERIMENTAL METHOD

Experimental Procedure

Empty palm fruit bunches are delignified using 10% NaOH at 150°C and 4 bar for 30 minutes. To obtain the black liquor, Lignin was separated using delignification and bleaching processes [23]. The by-product of this process is called black liquor.

Before the experiment, the spray pyrolysis (SP) machine was preheated for an hour to stabilize the furnace temperature. The black liquor was poured into the diffuser, and the feeding was set to 16,73 ml/min. The experiments were carried out for 10 minutes at 800, 900, and 1000°C, respectively. To study the effect of additional carrier gas, the spray pyrolysis system was infused with laboratory-grade nitrogen gas at a rate of 100 ml/min. The carbon formed will be collected on the wire mesh #1000 on a stainless pipe.

Tests and Measurements

In order to identify the thermal profile of the pyrolysis reactor, the temperature distribution of the inner side of the alumina tube was measured. The measurements were carried out by recording the temperature of the different positions (for each cm) on the inner wall of the alumina tube at setting temperatures of 800, 900, and 1000ºC, respectively. An hour of pre-heating was applied prior to the measurements.

The thermal characteristics of black liquor were investigated using a laboratory-made differential thermal analyzer (DTA).

The macrostructure of carbon was observed using VHX-5000 optical microscope (Keyence), while the microstructure of carbon black was examined using FE-SEM JIB-4610F.

RESULTS AND DISCUSSION

Spray Pyrolysis Equipment

Figure 1 shows the schematic of the developed spray pyrolysis (SP) equipment. The SP equipment consists of three main components, namely the precursor feeder, which serves the conversion of source material into droplets that will be brought by carrier gas to the pyrolysis reactor, a vertical or horizontal reactor tube which is enveloped by electric heaters as a heat source, and powder collector to collect the resulting carbon black powder [8]. SP equipment uses a nano steam sprayer gun (Erade technology) as a precursor feeder. This feeder pumps the precursor into the heated reactor tube in the form of mist. The feeding flow is adjusted using a pumping speed adjuster. In order to increase the flow, one experimental variation where the sprayed precursor was mixed with N_2 carrier gas was also carried out. Herein, the final flow was manually measured using the analog flow meter.

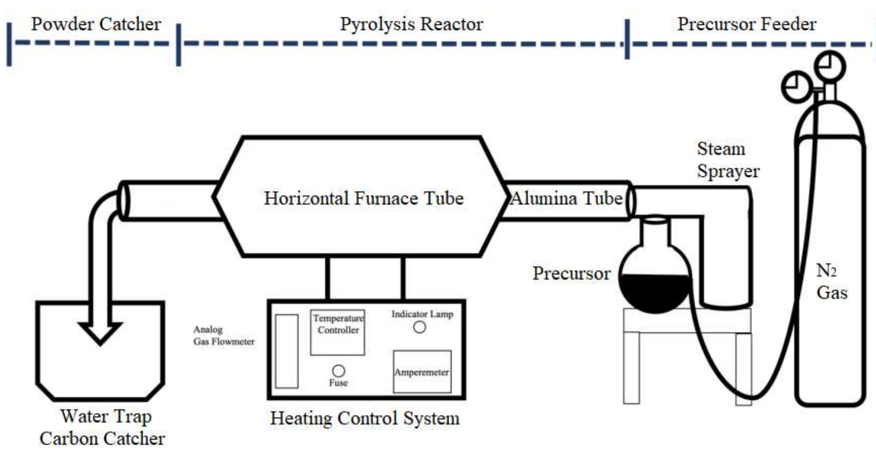


Figure 1. Schematic of spray pyrolysis (SP) equipment

The pyrolysis reactor was designed to have high-temperature stability with evenly distributed heating zone (wide plateau). Herein, the pyrolysis reactor consists of an alumina tube with an inner diameter of 38 mm and a length of 1000 mm, enveloped by a heating element in its middle section. One end is connected to the precursor feeder, while the other end is connected to the powder collector. The heating system is supported by automatically controlled specific circuitry, as seen in Figure 2. The red line is an AC power that supplies the power to all electrical instruments in a tubular reactor. A miniature circuit breaker (MCB) and fuse are used to protect electrical circuits from damage caused by overcurrent or short-circuit conditions. PXF4 temperature controller is used to control the heater by sending a DC signal to the DC power supply (Autonics) in order to control the input power to the heater. The actual temperature of the reactor is measured using a K-type thermocouple, which is connected to the PXF4 input. The heating stability was then maintained by optimizing the proportional, integral, and differential (PID) parameters of the PXF4 temperature controller. In order to monitor the electric current consumed by the heater, an analog ampere meter (Fort) is added to the system.

In general, the obtained carbon powder is very fine that it cannot be captured by the #1000 sieving mesh. In addition, direct contact with the ambient atmosphere could initiate the oxidation reaction of carbon, leading to the burned carbon powder. In this research, the powder is collected by passing the pyrolytic gaseous product through water, which is intended to trap the carbon power before it can interact with oxygen in the ambient. Separately, a double-sided tape is placed on the inner side of the alumina tube before entering the water trap to sample the carbon product for morphological observation.

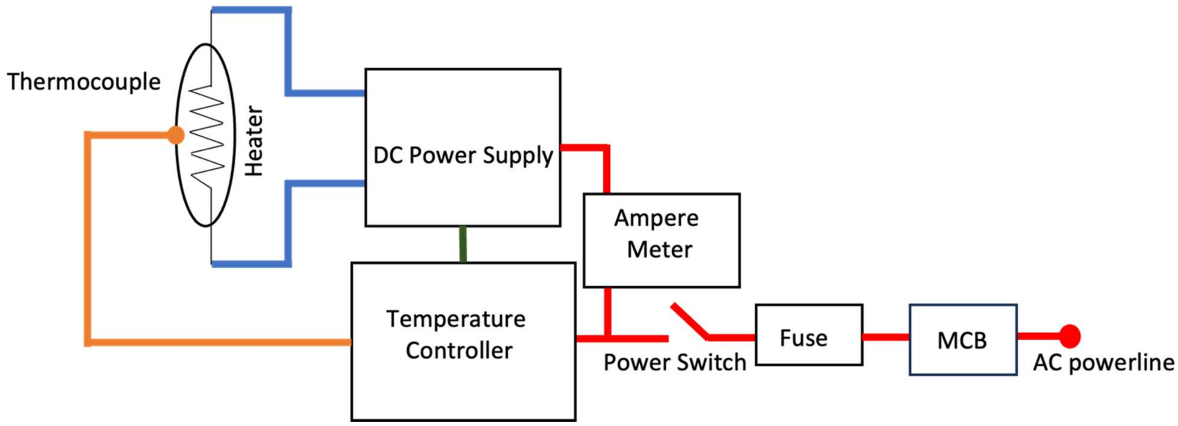


Figure 2. Electrical wiring from tubular furnace to pyrolysis reactor

Thermal Distribution on Spray Pyrolysis Equipment

The temperature was varied to 800, 900, and 1000^{o}C to investigate thermal distribution inside the horizontal furnace. Temperature distribution from the SP machine is shown in Figure 3. X-axes in Figure 3 are the position of the measured temperature, which means the temperature measured at the center of the alumina tube. The negative notation means temperature measurement at the left side of the center, and the positive notation means the right side of the center. The data in Figure 3 (a) presents the temperature distribution inside the alumina tube during the operation of a reactor. The temperature is observed to be highest at the center. The temperature started to rise exponentially at a distance of 30–40 cm away from the center of the pipe. After reaching the highest point, the temperature decreases and eventually drops below 100^{o}C at the same distance from the center as previously mentioned. This behavior is similar for all set temperatures, as the heater is located in the center of the tube. This means that the further away from the center of the tube, the lower the temperature, and the closer to the center, the higher the temperature. When we compare the measured temperatures on the right (gas inlet) and left (gas outlet) sides of the tube, it can be seen that there are differences when the gas flows. This is reinforced in Figure 3 (b), which shows the measurement results in the middle of the tube without gas flow, showing no temperature difference between the left and right sides. When the carrier gas is turned on, the temperature difference is seen again, as shown in Figure 3 (c).

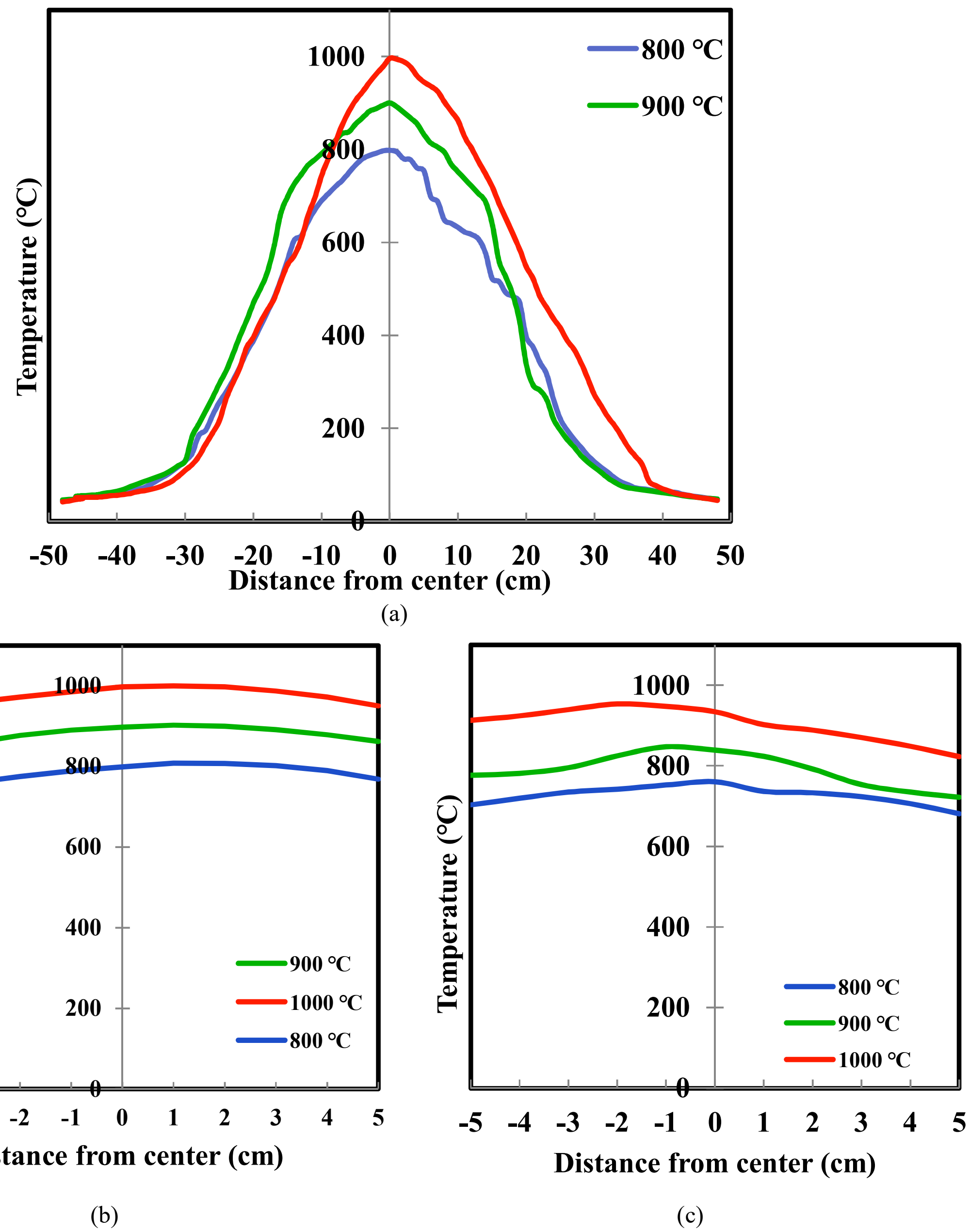


Figure 3. (a) Overall temperature distribution within the alumina tube of the SP machine, (b) temperature distribution in the (heating zone) center of glass pipe without carrier gas, and (c) temperature distribution in the (heating zone) center of glass pipe with carrier gas where the right side was inlet gas and the left side was outlet gas

Retention Time from Pyrolysis Process

The black liquor was introduced from the precursor feeder into the horizontal reactor with a flow rate of 16.73 ml/min for 10 minutes. The retention time of the steam entering the reactor can be calculated using the assumption as follows: first, the black liquor (with a real water content of 95–96%) consists of 100% water. Second, the heat is homogeneously distributed within the center of the heating zone of 10 cm length and 38 mm diameter, as seen in Figure 3 (b) and Figure 3 (c), at setting temperatures of 800, 900, and 1000°C, respectively. Herein, all black liquor precursor is assumed to be completely converted into a gaseous phase with the same temperature as the setting temperature and completely pass through the heating zone. If the transformation from the liquid into the gaseous phase is calculated using the ideal gas equation, the retention time of the gas when passing through the heating zone at a certain temperature can be obtained, as in Table 1. It can be seen that the retention time to pass through the 10 cm heating zone is in the range of 64–78 ms. However, the precursor steam has already experienced pre-heating at a lower temperature of 20–30 cm distance before entering the heating zone and 20–25 cm distance after leaving the heating zone, as can be observed from the reactor thermal distribution in Figure 3 (a).

Table 1. Retention Time

Temperature (°C)	Retention Time (ms)	
	With Carrier Gas	Without Carrier Gas
800	70.19	70.50
900	64.21	64.49
1000	59.17	59.43

Synthesis and Characterization of Carbon Black from Black Liquor

Thermal activities of black liquor precursor are characterized using differential thermal analysis (DTA). DTA graphic shows that black liquor has exothermic reaction starting from room temperature. The reaction proceeds until completed at 210°C, with the highest reaction rate at 149,9°C. This demonstrates that the reaction releases heat, which could compensate the thermal drop within the reactor, even though 95% of black liquor content is water. The DTA results (Figure 4) show that the thermal activity area is 30–210°C. It shows that the pyrolysis process must be carried out at high temperatures. Therefore, so that the temperature does not drop, the pyrolysis temperature in this study was set at a minimum of 800°C to ensure a complete pyrolysis. Retention time data shows that the pyrolysis process occurs very quickly, only 64–77 ms. Therefore, the temperature was increased to 1000°C, expecting that there would be a lot of production within a short time.

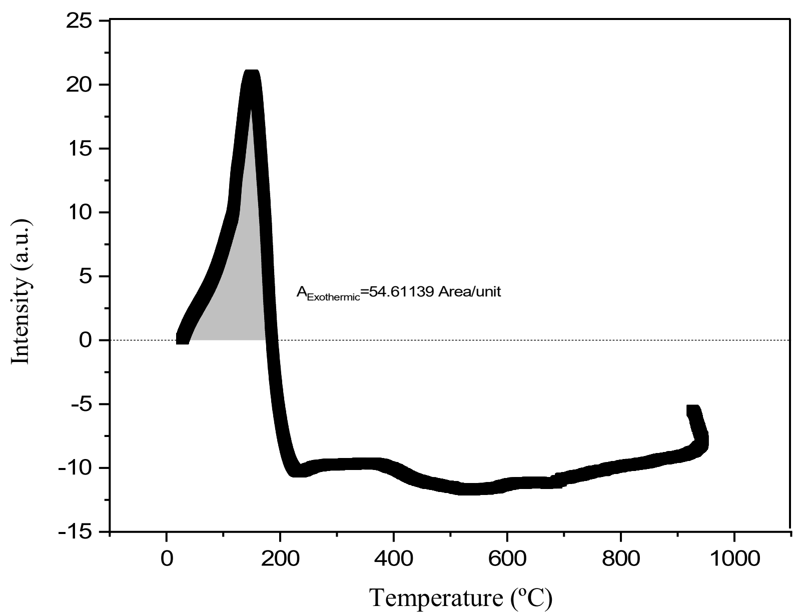


Figure 4. DTA and exothermic area of black liquor generated by spray pyrolysis

Black liquor was pyrolyzed with and without nitrogen gas carrier to form a carbon black material. The carbon black produced was then tested using a VHX-5000 digital microscope to investigate the morphology. The morphology of carbon black can be seen in Figure 5 (a), Figure 5 (b), Figure 5 (c), and Figure 5 (d), where carbon black produced was agglomerated. Agglomeration is a common issue that occurs during the SP process when using black liquor as a carbon source. The phenomenon can be observed in the carbon produced without using a carrier gas. As seen in Figure 5 (a), at a temperature of 800°C, the size of the agglomerates is quite large. However, as the temperature increases to 900°C, as seen in Figure 5 (b), the amount of agglomeration decreases. The least size of agglomeration is observed at a temperature of 1000°C, as seen in Figure 5 (c). One of the main causes of agglomeration during SP is low temperatures.

When the droplets of black liquor are atomized and introduced into the reactor, they need to be heated to high temperatures for the pyrolysis process to occur. If the temperatures are too low, the droplets may solidify before they can fully vaporize and decompose. This can lead to particles that are not fully formed and have a tendency to clump together or agglomerate. To investigate the effect of the carrier gas on agglomeration, an experiment was conducted at a temperature of 1000°C with the addition of a carrier gas of nitrogen. The test results showed an increase in agglomeration on the carbon. This is likely due to the fact that the addition of the carrier gas results in a decrease in temperature during the SP process, as shown in Figure 5 (c). The drop in temperature causes the aforementioned phenomenon of droplets solidifying before they have a chance to fully vaporize and decompose, leading to increased agglomeration. Figure 5 (d) shows carbon black produced at 1000°C without gas carrier, and it is concluded to carefully control the temperature during the SP process and consider the use of a carrier gas to minimize the occurrence of agglomeration.

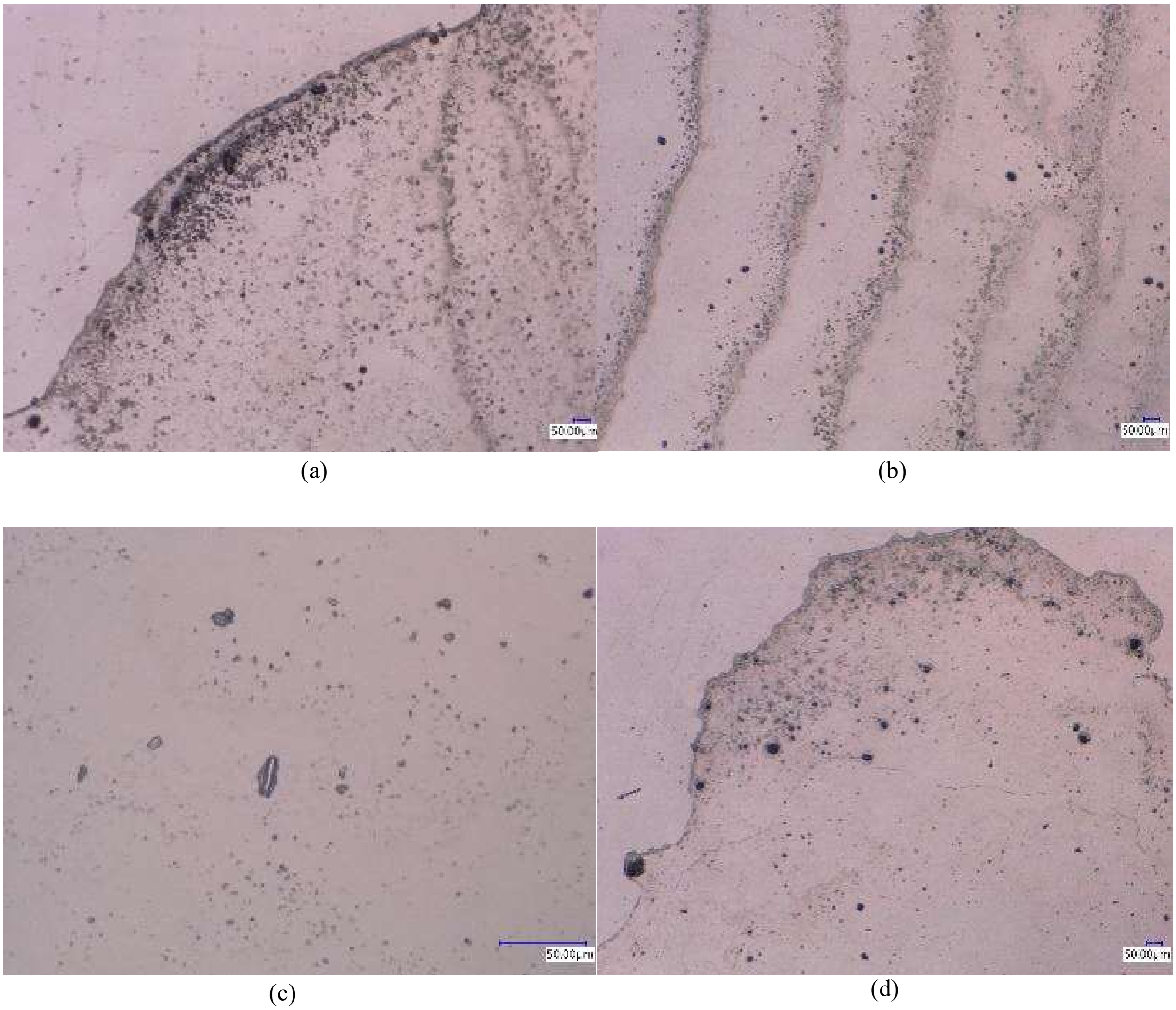


Figure 5. Macrostructure morphology observation of carbon black using optical microscope at (a) 800]°C using nitrogen gas, (b) 900°C using nitrogen gas, (c) 1000°C using nitrogen gas, and (d) 1000 °C without using nitrogen gas

Carbon black achieved is characterized using FE-SEM JEOL – JIB 4610F with 750, 5.000, and 25.000× magnification. In Figure 6, it is seen as a highly graphitized carbon black particle. The shape resembles an eggshell since graphitic layers bend continuously around the core of carbon particle, which as a whole exhibit a polyhedron shape [8].

Figure 7 (a), Figure 7 (b), and Figure 7 (c) show the morphology of carbon black produced under 800, 900, and 1000ºC, using nitrogen gas, respectively. Figure 7 (d) shows the morphology of carbon black produced under 1000ºC without nitrogen gas. The morphology shown in Figure 7 can be seen as an eggshell. The shell of carbon black produced under 800ºC using nitrogen gas has cracked. It stays surrounding the microsphere carbon black core but has not fallen off, as seen in Figure 7 (a). Figure 7 (b) shows the morphology of carbon black produced under 900ºC using nitrogen gas. The shell layer is leaving the microsphere core, and the microsphere core is showing. The microsphere carbon black in Figure 7 (c) is shown as a porous carbon produced under 1000ºC using nitrogen gas. The shell layer completely leaves the microsphere core, and the porous microsphere core is showing. These results indicate that as the temperature increases, the shell layers of the microsphere are leaving layer by layer, generating a porous microsphere carbon black. However, the morphology of carbon black produced under 1000ºC without nitrogen gas in Figure 7 (d) shows that the shell layer is not detached even though it is synthesized at very high temperatures. This indicates the impact of nitrogen gas presence is significant. Carbon black, which is synthesized under 800 and 900ºC using nitrogen gas, shows the shell layer has cracked and fallen off the living carbon black core. However, without the addition of nitrogen gas, even with higher temperatures, carbon black microsphere cannot be obtained. These results support previous studies indicating that the shell is formed from continuous layers surrounding the carbon black core, which, as the temperature increases, the shell cracks and the layers surrounding the carbon black core leave the core [7], [9], [24], [25].

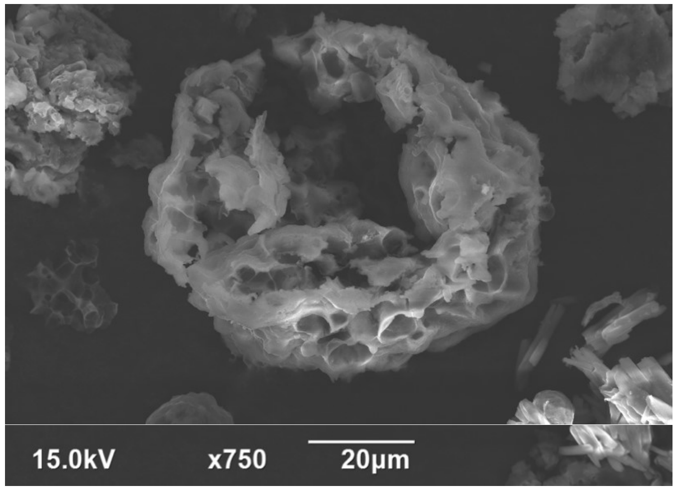


Figure 6. Morphology of carbon black synthesized under 1000°C without nitrogen gas on 750× magnification

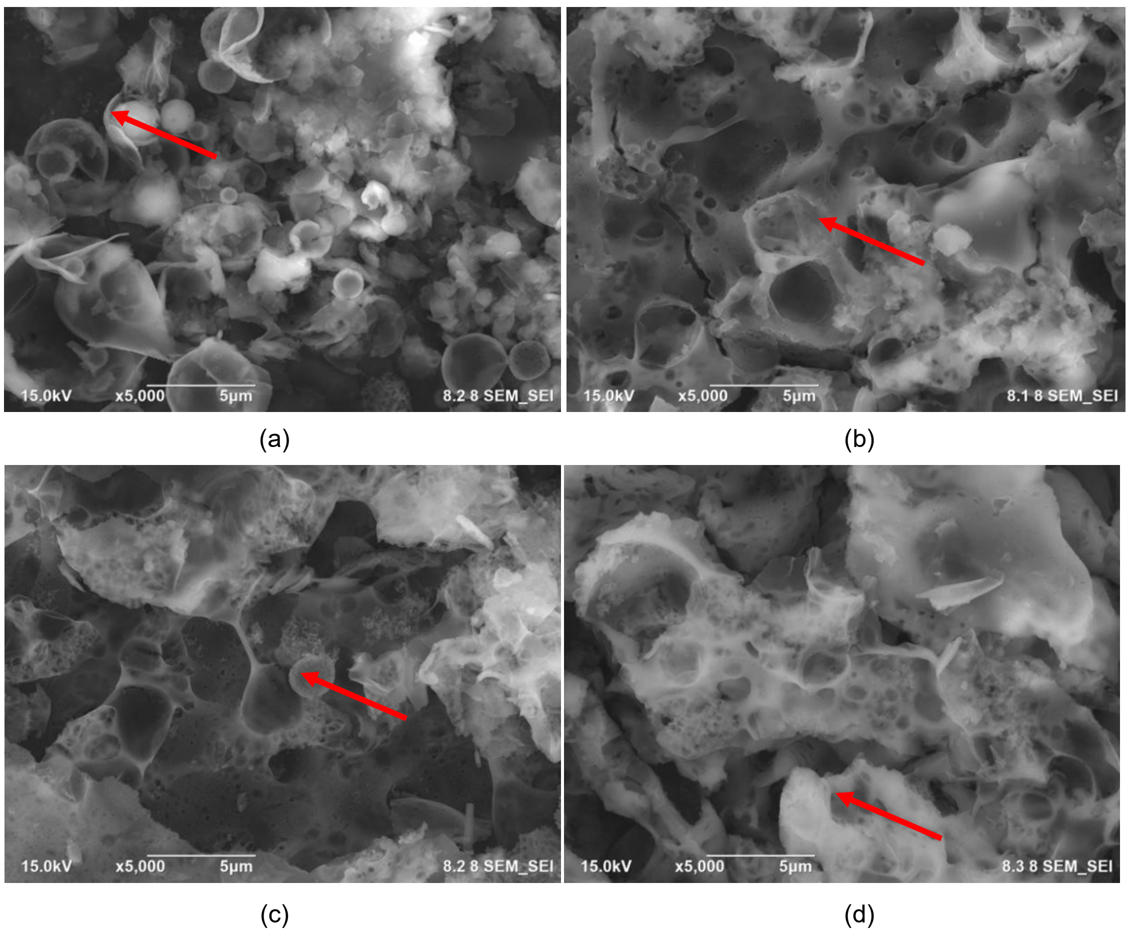
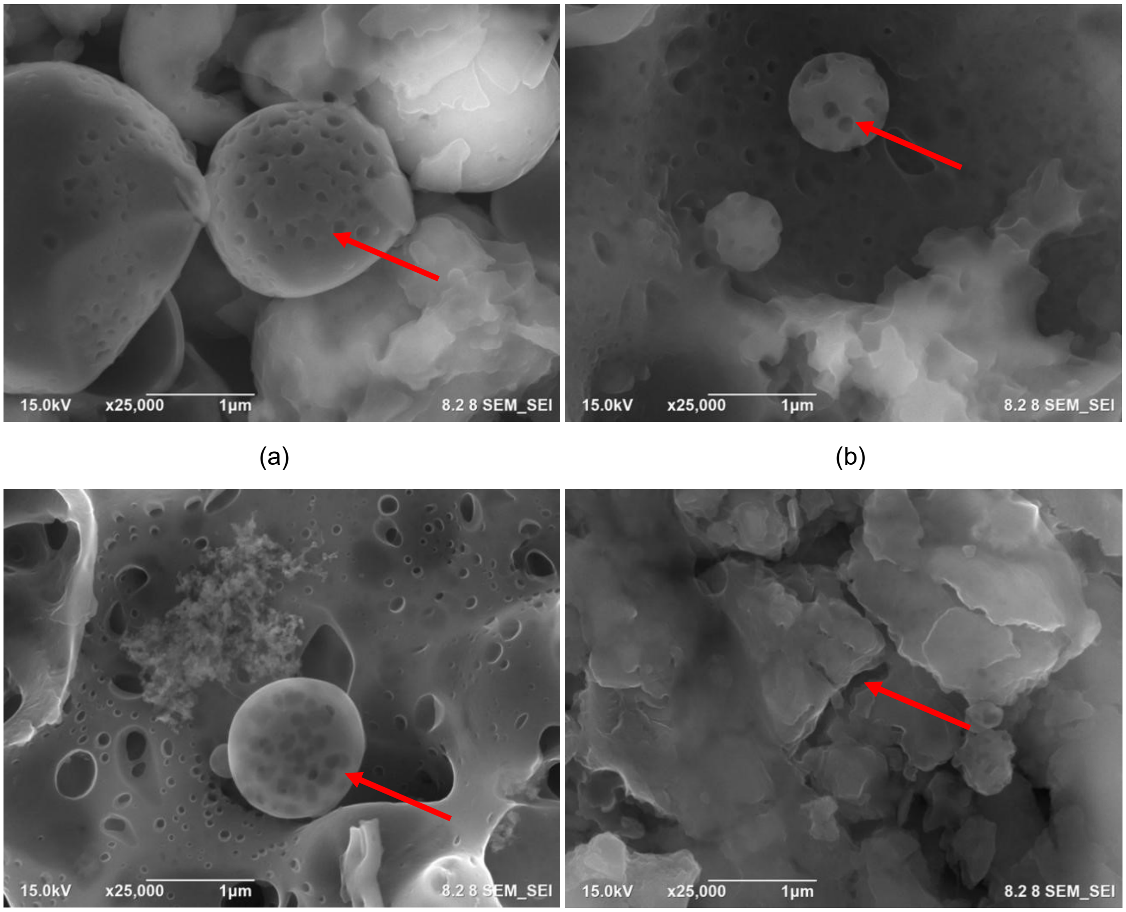


Figure 7. Morphology of carbon black generated under (a) 800 ºC, (b) 900 ºC, and (c) 1000 ºC using nitrogen gas; and (d) 1000ºC without using nitrogen gas on 5000× magnification



(a) (b)

(c) (d)

Figure 8. Morphology of carbon black generated under (a) 800ºC, (b) 900ºC, (c) 1000ºC using nitrogen gas, and (d) 1000ºC without using nitrogen gas on 25.000× magnification

Carbon black produced using nitrogen gas was identified as porous microsphere carbon, as seen in Figure 8 (a), Figure 8 (b), and Figure 8 (c). However, carbon black produced without nitrogen gas, the shell layer is piled up, generating an irregular carbon shape, as shown in Figure 8 (d). These results ensure that to obtain porous carbon black, the presence of nitrogen gas is necessary. The optimum temperature can be determined by the morphology. It is known that under nitrogen gas influence, the optimum temperature to synthesize carbon black is 1000ºC. Therefore, by running the spray pyrolysis system at 1000ºC, it successfully shows the best quality morphology, which is the porous microsphere core. These results indicate that as the temperature increases, the shell layers of the microsphere are leaving layer by layer and finally generating a porous microsphere carbon black. Thus, it can be concluded that by using spray pyrolysis equipment under 1000ºC using nitrogen gas, a porous microsphere carbon black can be obtained.

Nevertheless, the size and pore size of carbon black produced are uneven. It might be influenced by the atomization equipment, which is a gun diffuser. In order to obtain a homogenous shape, particle, and pore size, atomization equipment has to be changed. One of the most used methods is ultrasonic-assisted spray pyrolysis. This method can be installed in the spray pyrolysis system and produce a homogenous shape, particle size, and pore size of carbon black [7]. Ultrasonic-assisted spray pyrolysis is also well known for its economically efficient precursors, versatile and powerful tool, and has great potential to synthesize nanoscale powders [7], [24], [26].

Synthesis Mechanism of Carbon Black

The mechanism of spray pyrolysis from black liquor, as shown in Figure 9, was investigated to describe the morphological properties of the carbon black particles. Black liquor solution diffused and flowed the droplets to the horizontal furnace, droplets in the furnace from the outer and inner parts of the droplets. When the heat was transferred through from the outer part to the inner part, the solvent diffused and evaporated. After the precipitate formed, it was dried, and the solute decomposed. Carbon black was produced with a variation in morphology depending on its pyrolysis temperature and the gas used during the synthesis.

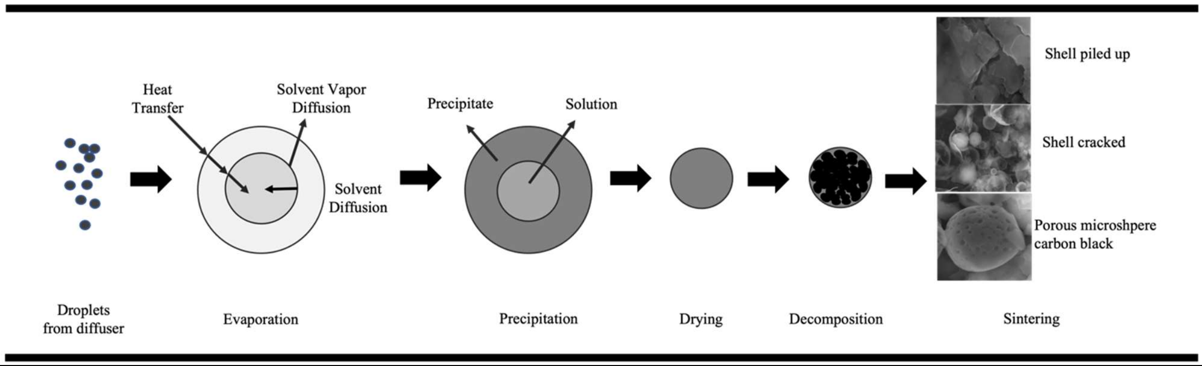


Figure 9. Synthesis of microsphere carbon black mechanism

CONCLUSION

The in-house spray pyrolysis (SP) machine is successfully developed by using electrical wiring that connected the temperature controller, heater, DC power supply (Autonic), type K thermocouple, and analog amperemeter (Fort). The furnace used as heat source is the horizontal furnace. This machine was applied to processed palm oil black liquor to produce carbon black. The thermal distribution of the SP system shows that the furnace center has the most precise temperature of all parts. The optimum temperature obtained in this study is 1000ºC according to the characterization of carbon black microspheres produced. It shows a spherical carbon on microstructure FE-SEM test results, which means the in-house spray pyrolysis machine has been successfully developed for synthesizing carbon black microspheres.

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