POROUS ACTIVATED CARBON PARTICLES FROM RICE STRAW WASTE AND THEIR ADSORPTION PROPERTIES

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Abstract

The purpose of this research was to synthesize porous activated carbon particles from rice straw waste and investigate their adsorption properties. Production of porous carbon particles involved several steps: (i) burning rice straw waste; (ii) ball-mill process; and (iii) the activation treatment. To achieve the optimum process in the activation treatment, the concentration of activating agent (i.e. potassium hydroxide) was varied. Experimental results showed that this method is effective to create porous carbon particles. Control of the porosity is also possible by managing the amount of activation agent (i.e. potassium hydroxide). The higher concentration of activation agent has a direct correlation to produce more cavities in the material. The study also confirms that the change in porosity has a direct impact to the ability of the product for adsorbing molecules. Since the present method is converting rice straw waste into useful and valuable porous carbon particles, further development of this study would give a positive impact for the reduction of rice straw waste emission.

Keywords: Rice straw waste, Ball-milling process, Etching treatment, Carbon material, Silica nanoparticles.

1. Introduction

Rice straw in agricultural country raises environmental issues [1]. Since the rice straw is a byproduct of rice, the existence of rice straw relates to the production of rice, while the production of rice increases every year [2]. For example, Indonesian Statistic Bureau in 2015 recorded that the rice production is 75.36 million tons [3]. Indeed, this huge amount of rice makes the number of rice straw waste reaching 12-15 tons per year.

In the conventional method, rice straw waste is typically used for roofing and packing material, feed, fertilizer, and fuel [2]. These methods used; however, will soon end as advanced economics and technology make them unprofitable. Further, un-utilized rice straw waste is then disposed and burned in the rice field, contributing severe air pollution issues [4]. Many methods have been suggested to be against the use of this abundant material, such as isolation of the silica component from the rice straw [5-9]. Other strategies are reported by utilizing the carbon component from the rice straw waste [10,11]. Although the above methods are good for further uses, there are questionable, specifically for the scale up process and highly utilization of rice straw waste. In fact, the highly application of rice straw waste is important for degrading the amount of this abundant byproduct.

In this context, based on our previous works on utilizing rice straw waste [4, 9, 12-15], this study aims to produce porous carbon particles from rice straw waste and to investigate their adsorption properties. The adsorption properties are important to comprehend, specifically for further applications, specifically as the adsorbent. Different from other report that uses directly activation treatment only [10], this report used combination of ball-mill process and activation treatment for making the produced carbon particles to have smaller sizes with larger surface area. Experimental results showed that porous carbon particles were prepared, and the utilization of ball-mill process is effective to reduce the particle size, shown by the electron microscope analysis. Control of the porosity is also possible by managing the amount of activation agent (i.e. potassium hydroxide). The concentration of activation agent has a positive impact on the creation of cavities in the material. Indeed, this has a direct correlation to the ability of the product for adsorbing molecules.

2. Experimental Method

2.1. Chemicals

Porous carbon materials were produced using the following raw materials: rice straw waste (Subang, Indonesia) and potassium hydroxide (KOH; 98%, technical grade, PT. Bratachem, Indonesia). We also used Rhodamine B (RhB; Wako Chemical, Japan) for investigating the adsorption ability of the product.

2.2. Production of porous carbon materials

The experimental procedure of the production of porous carbon particles involved several steps: (i) burning rice straw waste (for converting organic component in the rice straw waste into carbon); (ii) ball-mill process (for grinding and forming smaller-sized carbon particles); and (iii) the activation treatment (for removing

inorganic components from the burned rice straw to result higher surface area). Detailed information is described in the following.

2.2.1. Burning rice straw

Rice straw was washed, cut into small size (sizes of about 2 cm), and dried naturally for three days. After that, the dried rice straw was burned at 250°C for about 4 hours. The burned rice straw is namely rice straw ash. The rice straw waste was then put into the next step, i.e. ball-mill process.

2.2.2. Ball-mill process

The ball-milling process of rice straw ash was carried out in our ball-milling apparatus. To support the ball-milling process, 8-mm stainless steel balls were used. The mass ratio of the milling ball and the rice straw waste was fixed at 50. The ball-mill process was conducted in the atmosphere condition at 80 rpm for 60 minutes. The sample was then taking and separated from milling balls using a 5-mesh stainless-steel filter.

2.2.3. Activation treatment

The resultant of the ball-milling process was put into the extraction process using the alkaline solution (containing KOH) under a specific condition (temperature of 60°C; stirring rate of 600 rpm; 2 hours of reaction). The mixed solution was then filtered, and the carbon product was taken in the filter. To ensure the impact of alkaline solution on the activation treatment, a mole ratio of KOH and heated rice straw was varied from 0 to 3. The ratio of 0 defines that the burned rice straw was washed using the ion-exchanged water without KOH.

2.3. Characterizations

Morphology and size of the product were analyzed using a scanning electron microscope (SEM, JSM-6360LA; JEOL Ltd., Japan) and a Transmission Electron Microscopy (TEM, JEM-1400, JEOL Ltd., Japan). The elemental structure of the product was analyzed using an X-Ray Diffraction (XRD; PANalytical X'Pert PRO; Philips Corp., The Netherland), a Thermo Gravity Differential Thermal Analysis (TG-DTA, DTG 60A TA 60 WS, Shimadzu Corp., Japan), an Atomic Absorption Spectroscopy (AAS, Varian Spectra 240 FS, Varian Inc., US), a Fourier Transform Infra Red (FTIR, FTIR-8400, Shimadzu Corp., Japan), and gravimetry analysis. To observe the specific surface area of the prepared materials, Brunauer–Emmett–Teller measurements (BET; BELSORP28SA, Bel Japan, nitrogen adsorption isotherms at 77.15K) were performed.
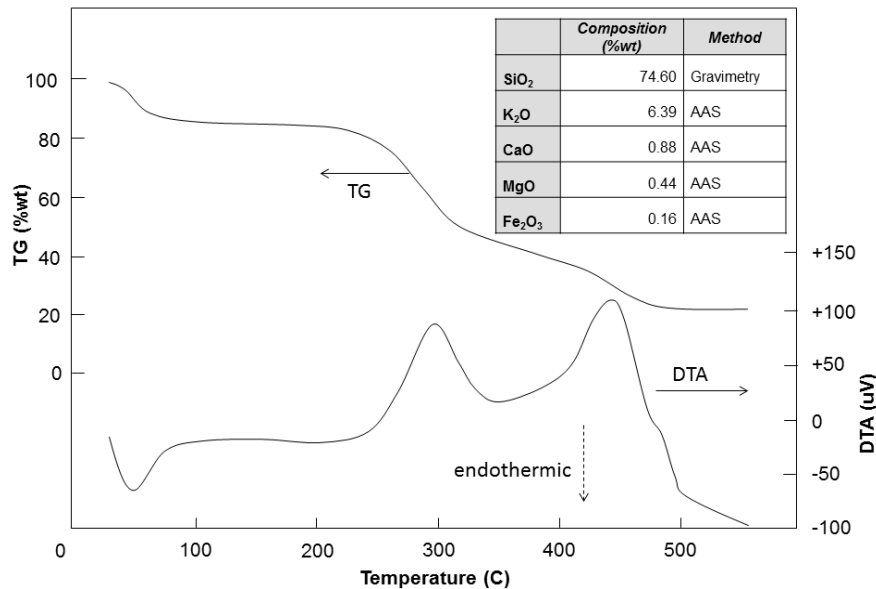
To examine the chemical adsorption ability, the prepared carbon particles were mixed with RhB. The sample was taken every several minutes, and the concentration of RhB was analyzed using UV-Vis spectrophotometer (UV-3150; Single beam; Shimadzu, Japan).

3. Results and discussion

Figure 1 represents the TG-DTA analysis of rice straw waste. The TG analysis showed the changes in the mass during the heating process, whereas the DTA analysis detected some exothermic and endothermic reactions. The chemical composition analysis confirmed that the burned rice straw waste has about 84 wt.% of silica. During the heating process, several incidents happened:

i.   20-100°C (5.20wt% of mass reduction due to the evaporation of water with an endothermic peak at 50.06°C);

ii. 250-320°C (47.80wt% of mass reduction due to the cellulose and hemicellulose degradation with an exothermic peak at 298.54°C) [7, 16].

iii. 330-470°C (24.73wt% of mass reduction due to the lignin degradation with an exothermic peak at 442.47°C) [7].

iv. Higher than 500°C (no mass reduction, indicating that organic components in the rice straw had been fully converted into ash with a final mass of 22.27 wt%).

Based on the results above, the minimum temperature for rice straw decomposition is 250°C. Although higher temperature is possible to start the decomposition, the amount of the carbon produced will be less than the decomposition process of the rice straw at 250°C. Thus, this is the fundamental reason for the selection of the temperature (250°C) for the burning process in the study.

	Composition (%wt)	Method
SiO_2	74.60	Gravimetry
K_2O	6.39	AAS
CaO	0.88	AAS
MgO	0.44	AAS
Fe_2O_3	0.16	AAS

Fig. 1. TG-DTA analysis results of rice straw waste.
The insert table is the chemical composition in rice straw.

Figure 2 shows the electron microscope images and the nitrogen sorption analysis results of burning rice husk samples before and after the activation treatment. After the burning process, the high magnification of electron microscope images in Figs. 2(a)-(b) depicted the solid and dense material. Then, after the activation treatment (Figs. 2(c)-(d)), porous structures in the material was detected. The sizes of the pores were less than 10 nm.
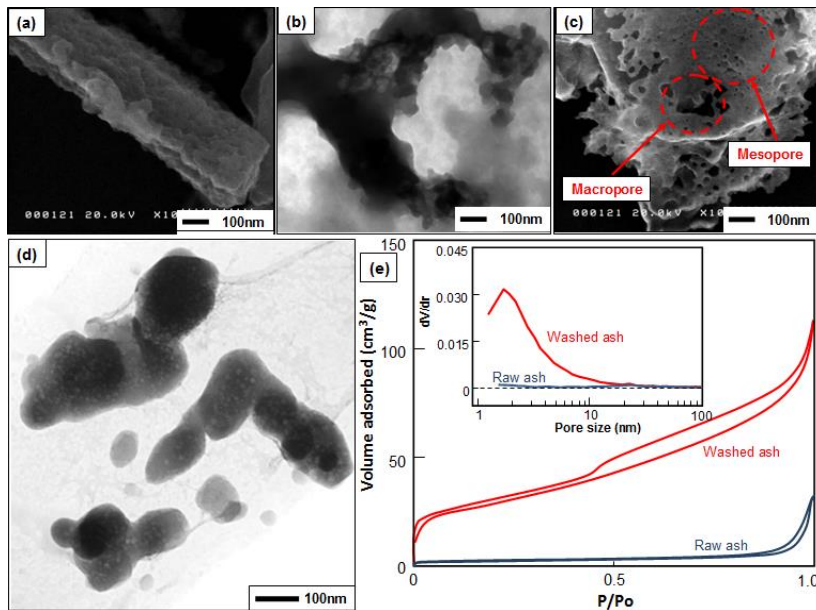
Fig. 2. SEM (a and c), TEM (c and d), and nitrogen sorption (e) analysis results of rice straw ash. Figures (a) and (b) are for rice straw ash sample before the activation treatment, whereas Figures (c) and (d) are for sample after the activation treatment. The insert image in Figure (e) is the BJH result for pore analysis result. The activation process was conducted with the KOH-and-ash ratio of 1.00.

Figure 2 shows the nitrogen analysis results of samples before and after the activation treatment. The nitrogen sorption analysis showed that the sample after the activation treatment exhibited a characteristic type-II isotherm, whereas the isotherm of the sample before the activation treatment was relatively constant. The maximum volume adsorption for the sample before the activation treatment was negligible compared with that for the sample after the activation treatment ($112 \text{ cm}^3/\text{g}$).

The Barrett–Joyner–Halenda (BJH) results show differences between the curve distributions of the samples (see insert image in Fig. 2(e)). The curve distribution for the sample before the activation treatment was relatively constant, showing no mesopore detection in the sample. In the case of sample after the activation treatment, pore sizes were in the range of mesopore with the maximum peak of 2 nm, which is in a good agreement with the TEM result in Fig. 2(d). The specific surface areas (using Brunauer–Emmett–Teller (BET) theory) of samples before and after activation treatment were 7.45 and $100.77 \text{ m}^2/\text{g}$. The increases in the surface areas (more than 100 times) were due to the existence of porous structure in the final material. The activation treatment was used to remove the impurities relating to silica component (by dissolving this material becoming aqueous ions) [10]. Silica was the main target for the removal process because this material is the most occupied inorganic components in the rice straw [9, 12, 13, 17]. The removal silica promotes the obtainment of high purity carbon product with large surface area.

Figure 3 is the TEM images of the resulting carbon materials after the activation treatment with various mole ratios of KOH and rice straw ash. Figures 3(a), (b), (c), (d), and (e) are the samples prepared with the ratios of 0.00; 0.32; 0.65; 1.00; and 3.00, respectively. In the initial condition (without additional KOH; see Fig. 3(a), the dense particles are revealed. The increases in the KOH amount resulted in the formation of porous structure. The pores were detected when using the ratio of higher than 0.32 (See Fig. 3(b)). Further increases in the KOH concentration result the porous-structured particles (See Figs. 3(c-e)). Based on the above TEM results, porous carbon was successfully synthesized when using the ratio of higher than 1.00 with an average pore size of 8.50 ± 1.41 nm (See Fig. 3(d)). Aggregation of carbon particles decreased with increasing mass of KOH.

To confirm the effect of KOH amount on the formation of porous structure, gravimetric analysis of samples after the activation treatment with various amounts of KOH was conducted, as shown in Fig. 3(f). The result showed that the more additional KOH has a consequence to the less remained silica in the sample. The more KOH has ability to remove silica. Thus, this result was in a good agreement with the TEM result in Fig. 3(d). However, excess KOH amount seemed to have no impact on the porous structuration in the particle.
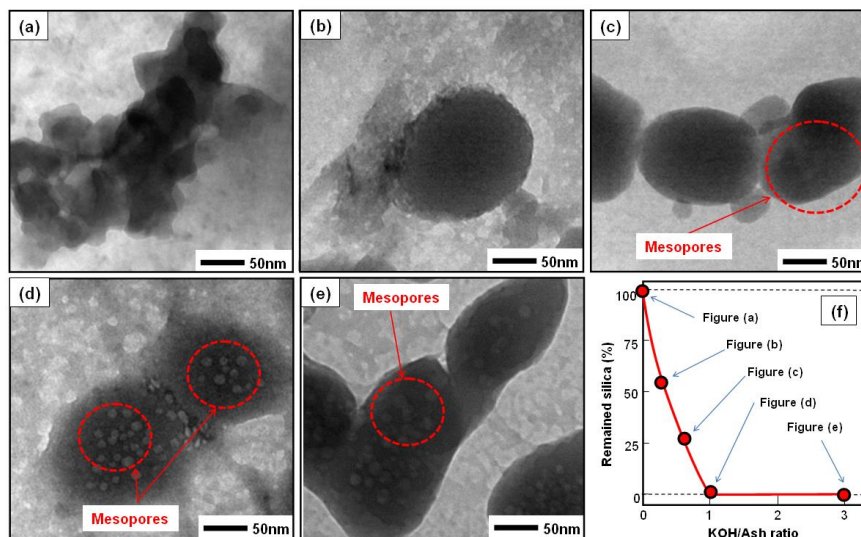

Fig. 3. TEM images of samples treated using various KOH amounts.
(a), (b), (c), (d), and (e) are the samples prepared with the mole ratios of 0.00;
0.32; 0.65; 1.00; and 3.00, respectively; (f) is the remained silica component
in the sample using conventional gravimetry.

Figure 4(a) is the XRD results of rice straw after the burning and activation treatment with various mole ratios of KOH and rice straw ash. In general, the majority of XRD pattern for all samples are amorphous. In the case of rice straw ash, the broadening curve in the range of 17 and 35° indicates the existence of amorphous silica. Then, several peaks were detected, which were identical to $CaMgSi_2O_5$, $CaMg(CO_3)_2$, and graphite. After the activation process, the peaks shifted. When sample was activated with water only (the ratio of 0.00), the peaks

of $CaMgSi_2O_5$, $CaMg(CO_3)_2$, and graphite were revealed clearer. Then, when sample was activated with alkaline solution, no peak of $CaMgSi_2O_5$ was identified, and the major peaks of graphite appeared at 27°. However, when sample was activated with excess amount of alkaline, peaks relating to K_2CO_3 and K_2O dominated in the sample.

Figure 4(b) is the FTIR results of rice straw before and after the activation treatment with various ratios of KOH and rice straw ash. The spectra of rice straw ash showed the absorption peaks for the functional groups of carbon and silica. In all samples, peaks at 1385 and 1660 cm^{-1} were detected, reflecting C – H bending [18] and C = O stretching [19], respectively. In the case of rice straw ash, peak at about 1100 cm^{-1} was detected, which was identical to Si-O-Si asymmetric stretching [20]. This silica peak decreased with the additional activation treatment, and the peak disappeared after activated with ratio of more than 0.65, confirming the removal of silica component. In addition, when activated with excess amount of alkaline (see sample with ratio of 3.00), unique peaks that are different from other samples were detected. These peaks were possibly due to the existence of potassium-related compound in the product.
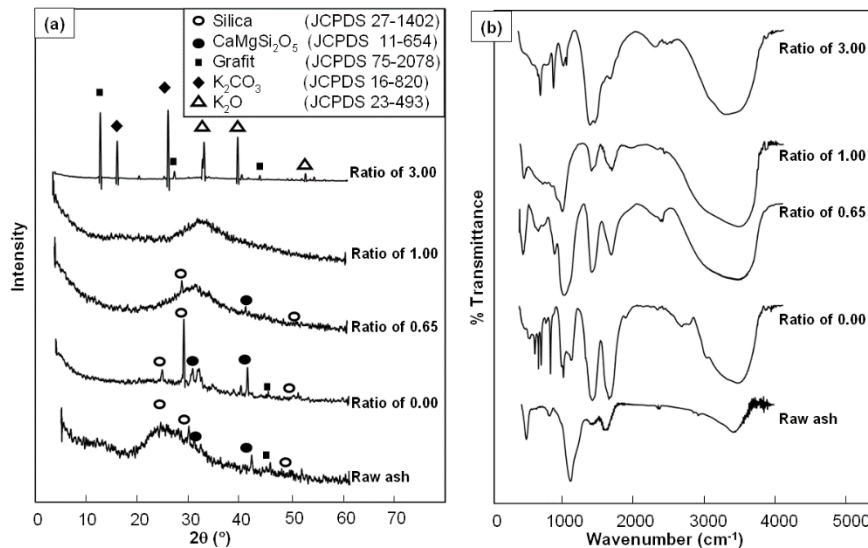
**Fig. 4. The XRD (a) and FTIR (b) analysis results
of samples prepared with various ratios of KOH and raw ash.**

Based on the above XRD and FTIR results, the major loss of silica-related components demonstrates the successful extraction of silica from the rice straw ash. The more additional KOH amount in the activation treatment allows to the less fraction of silica remained in the material. This hypothesis is in a good agreement with the above TEM images in Fig. 3. However, the amount of potassium used for activation treatment must be considered. Too much concentration of potassium leads to the domination of potassium itself (forming the impurities of K_2CO_3 and K_2O). Further, excess amount of KOH proceeds intercalation of potassium ion into the carbon structure, which in turn catalyzing the oxidation of carbon material, forming composite, and changing the porous

structure. Further, this intercalation promotes to the formation of anomaly result such as some crystalline graphite structure. However, to ensure this phenomenon, further analysis must be done and will be conducted in our future work.

To ensure the detailed adsorption properties of the sample, the Beer's law at 550 nm in the UV Vis spectra result is shown in Fig. 5. The RhB concentration decreased along with the increase in adsorption time. This was due to the adsorption of the RhB by the particles. Different rates of adsorption were found, depending on the use of samples. When there is no additional samples (see sample "RhB only" in the dashed-and-dot line), there is no change in the RhB concentration. However, when the rice straw ash was added, the concentration of RhB starts to decrease (see sample "RhB + raw ash" in the dashed line). Additional sample etched without alkaline solution (See "RhB + sample (ratio of 0.00) results in the small change in the adsorption rate. The small change is due to the change of particle size (impact of the ball mill process) and release of some inorganic ions (effect of activation treatment with water on the leaching some salts, e.g. NaCl, KCl, etc.). Then, adding samples etched with alkaline solution leads to the faster decreasing rate of RhB concentration. The higher concentration of KOH in the activation treatment is proportional to the faster decreasing rate of RhB concentration. After 15 minutes of the adsorption process, the remained concentration of RhB after adsorbing by samples with raw ash was about 70 wt.%. The use of sample with different ratios showed changes in the adsorption process of RhB. Furthermore, the samples were proven to have better adsorption performance than those using raw ash. The remained concentrations of RhB after 15 minutes of adsorption process using sample with ratios of 0.00; 0.32; 0.65; 1.00; and 3.00 were about 64, 59, 53, 49, and 43 wt.%, respectively.

The use of samples with higher ratios leads to the better adsorption performance. This informs that the ratio relates to the formation of pores in the carbon particles. The more number of kalium added (which leads to the removal of silica), the more cavities can be created.
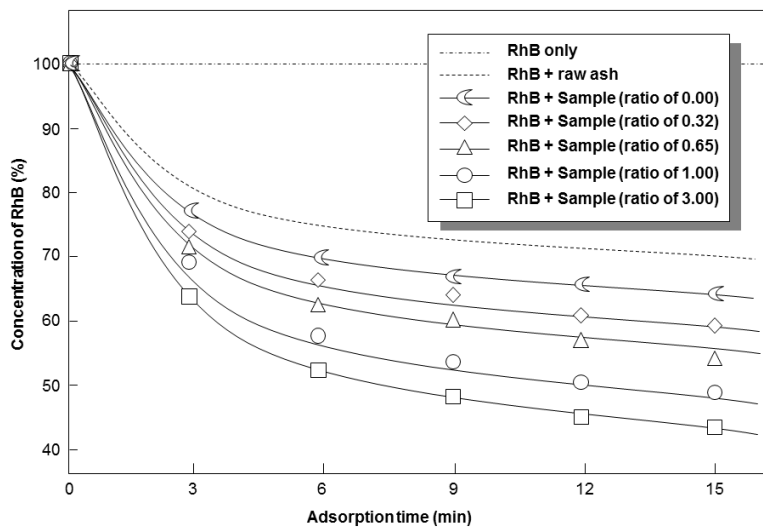

Fig. 5. Detailed adsorption of RhB as a function of time using various samples.

In addition, the use of sample with the ratio of 3.00 showed better adsorption process than that with the ratio of 1.00. However, the ratio of 3.00 creates problems, regarding the employment of too much amount of potassium in the process. Indeed, this allows the existence of potassium-related impurities in the final product. Although the impact of the existence of potassium-related impurities on the adsorption performance was not clarified yet in this study, the possibility of change in the other material performance can be created. This follow-up study will be done in our future work.

Figure 6 shows illustration mechanism for the production of carbon particles from rice straw waste based on the above results. The process requires at least three steps, including the burning process, the ball-mill process, and the activation treatment. The first step is a burning process. Since most of the rice straw components are organic-related compounds [5], burning the rice straw is effective to convert organic components into carbon material [2, 11]. Next, the second step is the ball mill process, which is effective for breaking the rice straw ash into smaller-sized particles. Finally, the last step is the activation treatment that is used for converting silica component (embedded in the ash) into silicic acid ($Si(OH)_4$) [17, 21]. Silicic acid is a water-dissolved chemical; thus, the removal of this silica component creates porous structure in the final particle. Based on the above result, the additional KOH has impacts on the creation of porous structure in the particle (verified in TEM images in Fig. 3). Indeed, the more pores in the particle would make the more possibility particle to adsorb RhB (confirmed in BET analysis results in Figs. 2(f)).
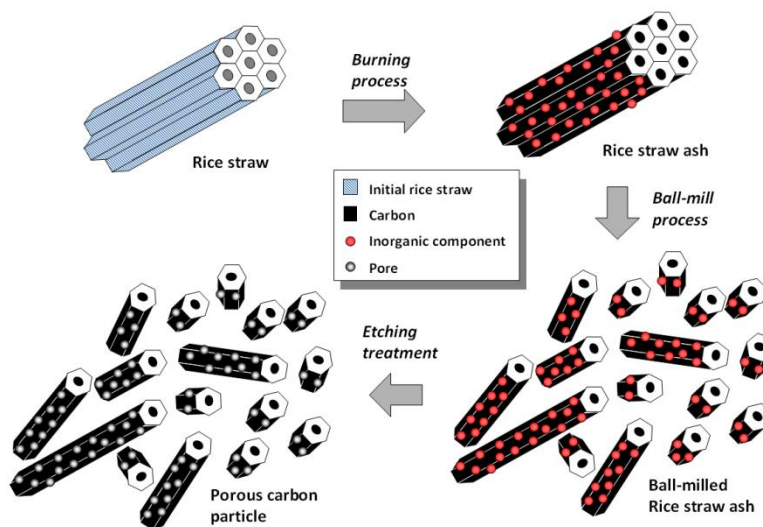
**Fig. 6. Schematic illustration of the formation
of carbon porous particles from rice straw waste.**

4. Conclusion

A method for the production of porous carbon particles from rice straw waste has been demonstrated. Experimental results showed that the present method is effective to create porous carbon particles. Control of the porosity is also possible

by managing the amount of activation agent (i.e. potassium hydroxide). The change in porosity has a direct impact to the ability of the product for adsorbing molecule. Since the present method is converting rice straw waste into useful and valuable porous carbon particles, further development of this study would give a positive impact for the reduction of rice straw waste emission.

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