ORIGINAL ARTICLE

PORE CHARACTERISTICS & ADSORPTION CAPACITIES OF BIOCHARS DERIVED FROM RICE RESIDUES AS AFFECTED BY VARIETY AND PYROLYSIS TEMPERATURE

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ABSTRACT

Background: Characterisation of the pore structure of biochar is important to their application in soil. For most cases, the biochar's pore structure is strongly affected by the original biomass feedstock and pyrolysis temperature. **Objectives:** The aims of this study were to investigate whether the porous structure of biochars & their surface area affected by the different parts of rice plant (straw and husk), different rice varieties and different pyrolysis temperature. **Methods:** In this study, *Koshihikari* straw and husk obtained from Japan and *IR50404* straw and husk obtained from Vietnam were pyrolysed under the temperature range of 300ºC – 800ºC. The surface physical properties was assessed through N_2 adsorption and I_2 adsorption. **Results:** The comparative N_2 adsorption isotherms illustrated the pore filling of micropores (type I) and capillary condensation (type IV) of biochars. In general, the adsorption volumes of N_2 increased as the pyrolytic temperature increased, reached a maximum at 700ºC, then finally decreased at 800ºC. The majority of studied biochars were in the range of 1.2- 9.9 nm, and biochars showed a tendency to smaller pore sizes as pyrolysis temperature increased. Most of surface area were occupied by micropores in biochars; however, the volumes of meso- and macropores were larger than volumes of micropores in many cases. BET surface area and iodine number showed well correlation to each other, increased with pyrolysis temperature, but not similar numbers. Rice-straw-based-biochar conventionally host more micropores, total pore volume, BET surface area and higher iodine numbers than rice-husk-based-biochar. Biochars produced from Vietnamese rice-residue showed a better adsorption capacity (due to a higher surface area) than from Japan. SEM analysis slightly indicated surface area and porosity changes with changing temperature. **Conclusions:** Differences in porous properties and surface area were observed among rice-husk-biochars and among rice-straw-biochars. Additionally, different parts of rice plant will have different adsorption capacities, which may due to the differences in cell wall compositions of rice straw and rice husk, differences in functional groups on the biochars' surface, and also differences in the ash content of biochars.

Keywords: *rice straw, rice husk, adsorption isotherm, surface area, iodine number.*

1. INTRODUCTION

Rice (*Oryza sativa*) is one of the most important crop for a large part of the world's human population. As a result, rice straw and rice husk are abundant lignocellulosic waste materials in the world. According to World Rice Production data in 2015, there was about 469 million tonnes of rice produced in the world & 90% came from Asia, where more than 1.2 million km^2 of land is used to grow rice. Vietnam alone contributed approximately 28 Mt y^{-1} of rough rice, meaning that around the same volume of straw and an estimated 6.2Mt y^{-1} of husk was produced in that year. Japan also produce a significant amount of rice straw and rice husk, with roughly 7.9 Mt y^{-1} & 1.6 Mt y^{-1}, respectively. While these rice residue wastes may not be burned in many prefectures in Japan due to strict environmental regulation; burning them right on the rice field where they were grown is one of the major practices for most Vietnamese farmers. The widespread and old practice of burning seriously increases air pollution and consequently affects public health.

Over past several years, there has been increasing interest in the use of agricultural waste, including rice waste, for biochar production. Biochar is defined as the porous carbonaceous solid produced by the thermochemical conversion of biomass materials in an oxygen-depleted atmosphere (pyrolysis), which has been promoted as a potential soil amendment to enhance soil fertility and water management [1]. The effects of biochar on soil improvement is mainly come from its chemical composition, its surface area and the porous structure [2]. Steiner et al. (2016) concluded that the surface area and porous characteristics not only are responsible for nutrient, organic compounds and water retention, but also provide a preferred habitat for microbes from predators [3]. According to Verheijen et al. (2010), surface area and porous structure of biochars can vary significantly depending on feedstock and processing conditions, such as pyrolysis temperature or heating time [4]. Biochars were found to keep possession of their parent feedstock' characteristics, for example, wood-based biochars generally have large macropores (diameter >10μm) due to the large cells of parent material, while the pore size of cellulosic straws biochars, with thinner walls and channels, belong to the range of 1 -10μm [5]. Jeong et al. (2012) reported that softwood biochar had a smaller surface area than hardwood biochar at 159 m^2/g versus 242 m^2/g [6]. At the same pyrolysis temperature of 400°C, wheat-straw biochar also was found to be lower in specific surface area and porosity than poultry-litter biochar [7]. There are numerous studies have found that biochars' surface area increases with pyrolysis temperature [8-11]. It was believed that increasing pyrolysis temperature increased lignin and cellulose decomposition in feedstocks [12] & removed H and O containing functional groups [13], leading to an increase in biochar surface area. By increasing the heating rate from 10 to 50ºC/min, the BET surface area and the pore volume values for rice residue biochars increased [14], while it showed a decreasing trend in synthetic wood chars [15]. Besides pyrolysis conditions and the nature of feedstock materials, other factors such as composition and availability of nutrient, content of organic matter, soil mineralogy and texture, pH/Eh conditions, presence of toxins in soil, soil biota, plants type can also influence biochar characteristics [16].

Nitrogen adsorption is usually used for characterization of pore structure of biochars surface as well as for determination of total surface area. An adsorption curve, namely adsorption isotherm, is generated by starting at low pressure and measuring the volume of nitrogen adsorbed. The BET (Brunauer–Emmett–Teller) method is commonly applied to calculate the specific surface area on the basis of nitrogen adsorption isotherm measurements at 77K. By comparing observed adsorption isotherms, some essential information on the presence of micropores can be obtained from the low relative pressure portion ($P/Ps<0.1$) of the adsorption isotherms & the larger pores can be seen in the region $P/Ps >0.1$, where P is the absolute pressure & Ps is the saturation vapor pressure [17, 18]. Beside nitrogen adsorption method, iodine adsorption method can also be used to characterise the surface area of biochar. The determination of nitrogen surface area is based on adsorption of nitrogen gas at liquid nitrogen temperature, whereas iodine method is based on an adsorption experiment with iodine as adsorbate. The iodine number is expressed as the milligrams of iodine adsorbed per gram of biochar sample under specific conditions, and the BET surface area is expressed as square meters per gram of dry biochar sample. The measured surface area consists of both external and internal area where the micropore volume mainly determines the size of the internal surface area and the larger pores volume determines the external surface area [19]. A procedure for the determination of the total surface area using the BET method and iodine number are described as ASTM D6556-10 and ASTM D4607-94, respectively.

Recent studies have explored the physical and chemical characteristics of biochars derived from rice residue materials [8, 14, 20, 21]. However, to our knowledge, there are no systematic comparison or evaluation porous characteristics of the rice-residue-derived biochar obtained from different rice varieties or different regions/countries in any published paper. The main objectives of this study were: (1) to investigate the surface characteristics, including BET surface area, micropore and external surface area, total pore volume, micropore volumes, particle size distribution of biochars derived from *Koshihikari* straw and husk (obtained from Japan) and *IR50404* straw and husk (obtained from Vietnam), (2) to compare the differences in surface characteristics and adsorption properties between: (a) JRH (Japanese-rice-husk) & VRH (Vietnamese-rice-husk) biochar; (b) JRS (Japanese-rice-straw) and VRS (Vietnamese-rice-straw) biochar; and (c) rice-straw biochar and rice-husk biochar; (3) to determine the effect of rice variety and pyrolysis temperature on the surface properties of rice husks and straws obtained from Japan and Vietnam. As the nitrogen adsorption isotherm gives qualitative information about the specific surface area, the pore volume as well as particle size distribution, the focus of this paper will be on the interpretation of nitrogen adsorption data. This is followed by an evaluation on the total pore volume and particle size distribution. The next will be a comparison the results of biochars' surface area obtained from two adsorption methods: iodine adsorption and nitrogen adsorption (BET surface area). Finally, scanning electron microscopy (SEM) was carried out to visualize porosity distribution and pore sizes of the samples.

2. MATERIALS AND METHODS

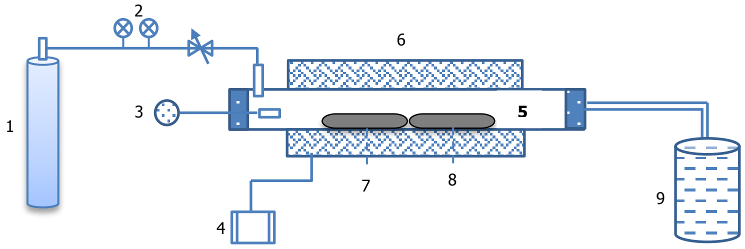
2.1 Materials

The rice residues, including rice straw and rice husk, from two different varieties were used in this study. Short grain rice husk and straw *Koshihikari* was grown in Nigata prefecture of Japan. Long grain rice husk and straw *IR 50404* was grown in the Mekong Delta of Vietnam. Rice residue samples were dried in an oven for at least 8 hours at 105°C to expel moisture before pyrolysis.

2.2 Preparation of biochar

Rice straw and rice husk were cut into small pieces of about 10mm using the RETSCH Cutting Mill SM100 and starch was added at 4%. The mixture was poured into a frame, then was heated at 120ºC in 15 mins to form granules of about 7mm diameter and 10mm length.

Pyrolysis was carried out in a tubular electric furnace at temperature range from 300 ºC to 800ºC. The experimental set up was shown schematically in Fig. 1. Briefly, it consisted of a quarts glass tube inserted into a cylindrical ceramic heater, a thermocouple for measuring and controlling the temperature of the inner surface of the furnace, a N_2 compressed gas tank connected to flow meters, two stainless steel containers for separating samples from Japan and Vietnam, and a cooling system.



1. Nitrogen cylinder 2. Flowmeter 3. Thermocouple 4. Temperature controller
5. Quartz class tube 6. Tubular furnace 7. Japanese samples 8. Vietnamese samples 9. Cooling system

Figure 1: The figure presents the schematic diagram of biochar production system.

Approximately 10 gram of raw material was placed on containers & then put into the middle of the glass tube. In order to remove all oxygen remaining in the reactor, nitrogen gas was pumped to the furnace at a flow rate of 200 mL/min at 20 ºC, 1 atm for 30 mins. The pyrolysis temperature was increased at the heating rate of 10 ºC/min in the nitrogen gas stream, then was maintained at the desired temperature for 120 mins. After cooling period (usually required more than 3 hours), the solid product biochars were removed from the pyrolysis reactor and weighed immediately. The biochars were stored in glass jars at room temperature under dry conditions until analysed.

In this study, rice-husk-derived biochars were denoted as JRHxxx, VRHxxx, JRSxxx, VRSxxx, where "xxx" describes pyrolysis temperature (ºC), JRH means Japanese Rice Husk, VRH means Vietnamese Rice Husk, JRS is Japanese Rice Straw, & VRS is Vietnamese Rice Straw.

2.3 Nitrogen adsorption isotherm, specific areas, pore volume and particle size distribution

The surface physical properties of all studied biochars were characterized by nitrogen adsorption using a Shimadzu Micromeritics TriStar 3000 system. Before the gas adsorption measurements, the samples were first degassed in a vacuum system (Shimadzu Micromeritics VacPrep 061), for at least 7 hours at 200ºC. The samples were then weighted and transferred to the measurement ports. Nitrogen adsorption isotherm was measured at liquid nitrogen temperature (77K) and nitrogen pressure ranging from 10^{-6} to 0.995 P/Ps (relative pressure of nitrogen). The isotherms were generated by starting at low pressure & measuring the volume V adsorbed (expressed in cm^3 STP g^{-1}). The BET surface area was calculated from the isotherms by using the BET model. The particle size distribution and average pore diameter were obtained through the Barrett-Joyner-Halenda (BJH) method using the adsorption branch. The micropore volume, micropore surface area, the external surface area of all studied biochars were obtained from the t-plot methods. The total pore volume was calculated from nitrogen adsorption data as volume of liquid nitrogen at a relative pressure of approximately 0.99 single point. The percentages of micropore surface area was presented by ratio between micropore area and total surface area multiplied by 100, and the percentages of micropore volume was the ratio of micropore volume to its total surface volume multiplied by 100. The sum of mesopore & macropore volume was estimated by the subtracting the micropore volume from the total volume. According to the International Union of Pure and Applied Chemistry (IUPAC), pore sizes of less than 2 nm, 2-50 nm, and greater than 50nm were termed micro-, meso-, and macropores, respectively.

2.4 Iodine adsorption

The iodine number of biochars was determined according to the Japanese Industrial Standard (JIS) test method (K1474:2014). To obtain homogeneous samples, at least 80% of studied samples was passed through a 325-mesh screen (45µm) using an electromagnetic sifter MS-200, ITOH. The samples then was added to a 0.1 N solution of iodine, whereupon they were shaken at the speed of 120 rpm for 15 mins in a dark room under the temperature of 20ºC, after that the samples were centrifuged by using Hitachi himacCT6E (10 mins, 3000rpm) to separate the solid. The resulting solution was titrated with standardised 0.1 N sodium thiosulfate $Na_2S_2O_3$, using starch as the indicator, to an endpoint (the solution turned a pale yellow in color). The titration process was repeated 3 times in each sample. The amount of iodine that adsorbed to the biochar was calculated using the equation (1) below:

$$A_I = \frac{(10*\mathrm{f}' - K*f)*12.69*5}{\mathrm{S}} \qquad (1)$$

Where A_I = adsorption quantity of iodine (mg/g)
S= quantity of dried biochar (g)
f'= factor of 0.05N iodine solution
f= factor of 0.1N sodium thiosulfate
K=average quantity of 0.1N sodium thiosulfate solution (mL)

2.5 Scanning Electron Microscopy (SEM) analysis

Scanning Electron Microscopy (SEM) is a microscopy technique that employs electrons reflected from the surface of a scanned material to form an image. The microstructure of the studied samples was examined by SEM (JEOL Ltd., JCM-5700 CarryScope). The SEM micrographs were recorded at different magnifications using an electron beam at 20 kV.

3. RESULTS

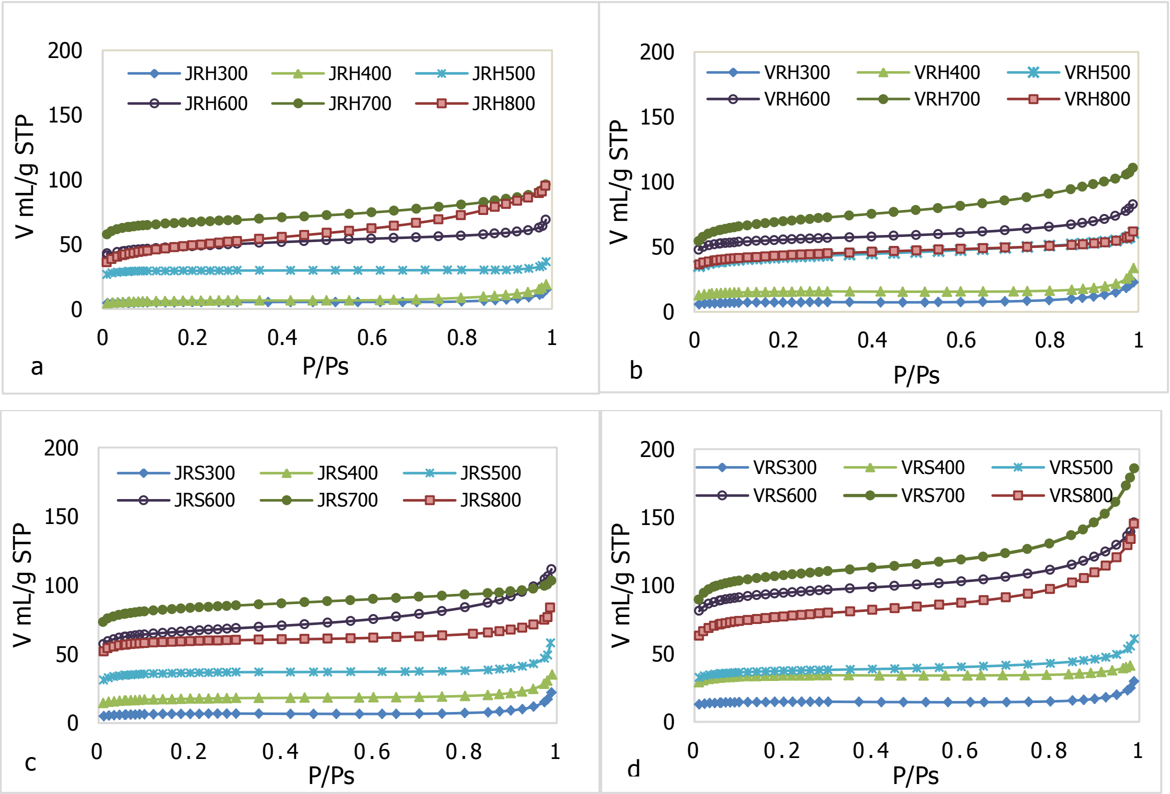


Figure 2: The figure presents the volume of N2 adsorption isotherm versus relative pressure for all studied biochars.

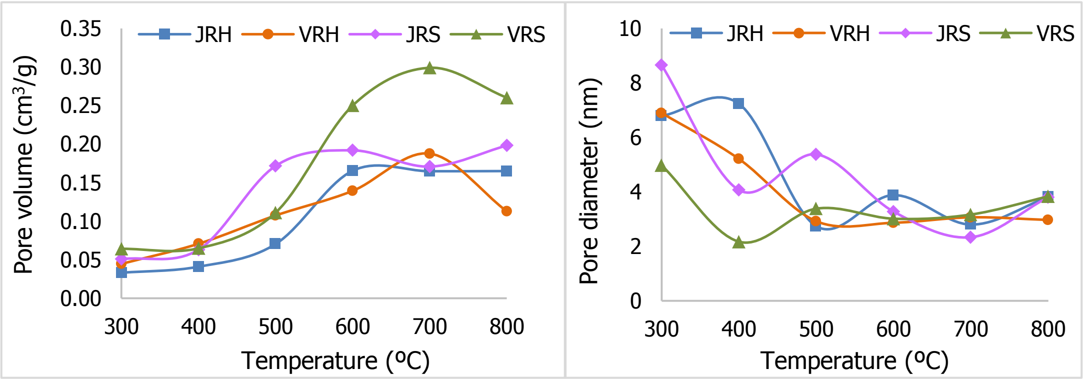


Figure 3: The figure presents the changes in total pore volume and average pore diameter.

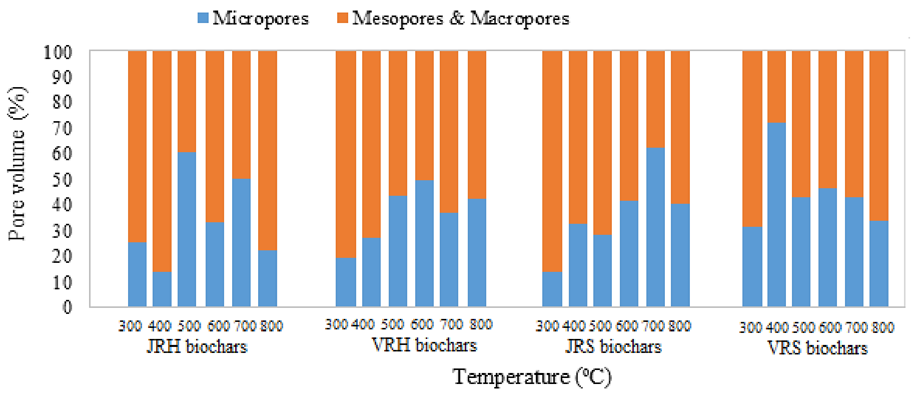


Figure 4: The figure presents the ontribution of micro-, meso- and macropore volume in the total pore volume

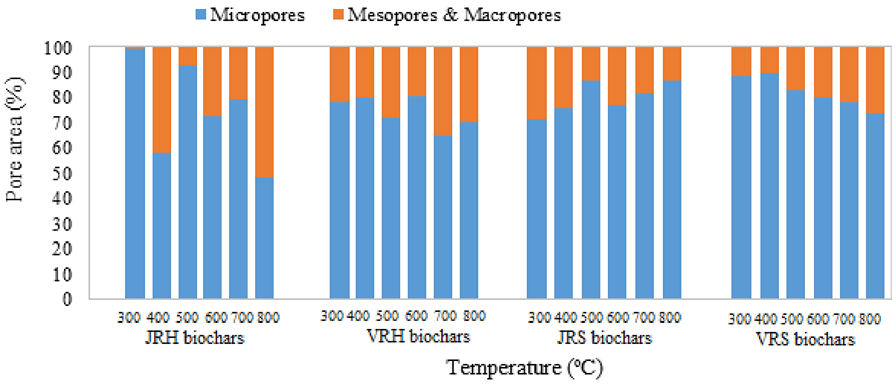


Figure 5: The figure presents the contribution of micro-, meso- and macropore area in the total surface area

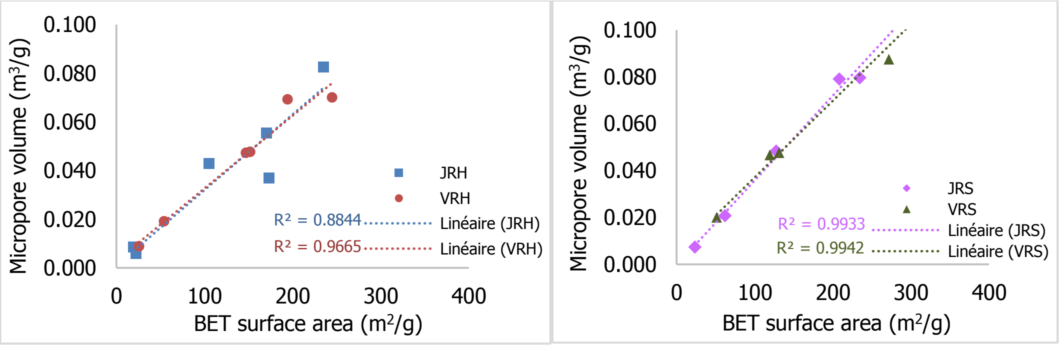
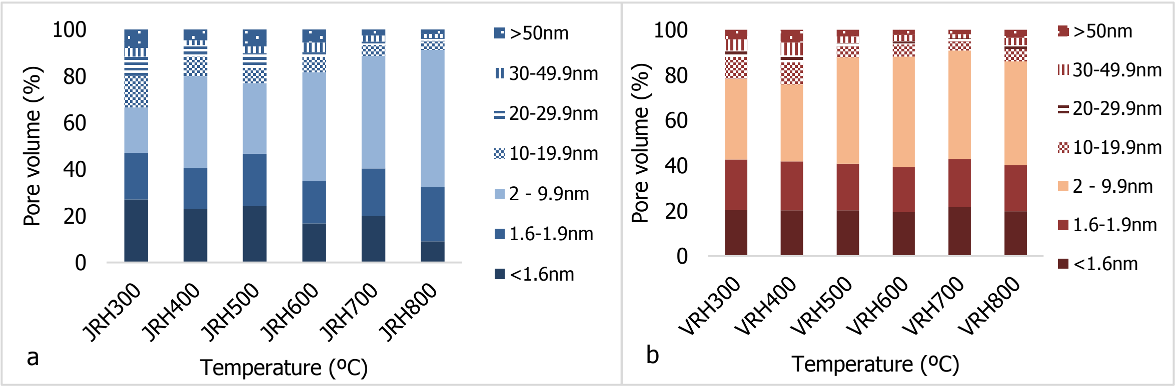


Figure 6: the figure presents the correlation between micropore area and BET surface area.



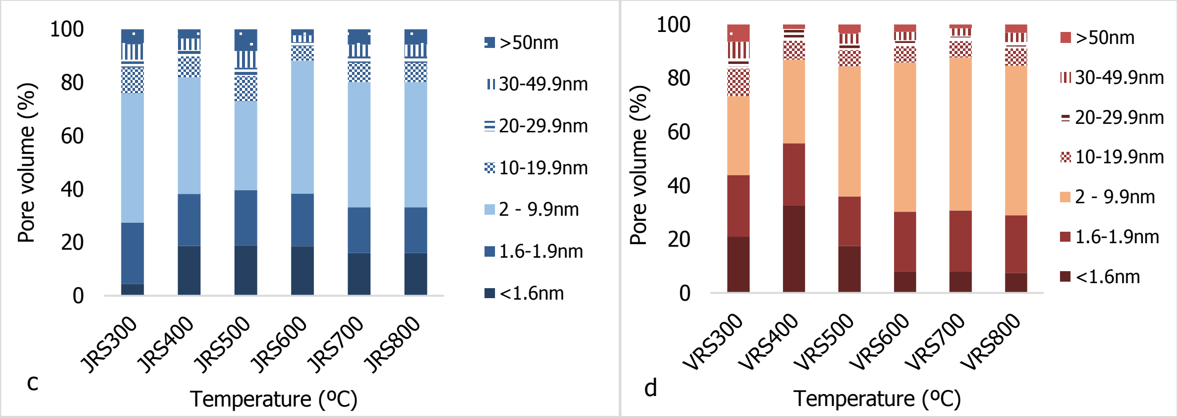


Figure 7: The figure presnts the particle size distribution of studied biochars.
(a) Japanese Rice-husk-derived biochars; (b) Vietnamese rice-husk-derived biochars;
(c) Japanese rrice-straw-derived biochars; (d) Vietnamese rice-straw-derived biochars.

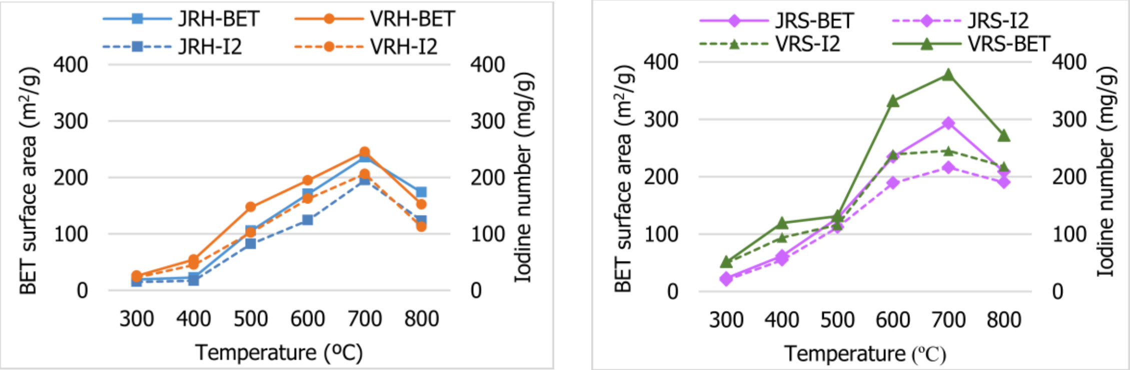


Figure 8: the figure presents the BET surface area and iodine number of biochars across the temperature range of 300-800ºC

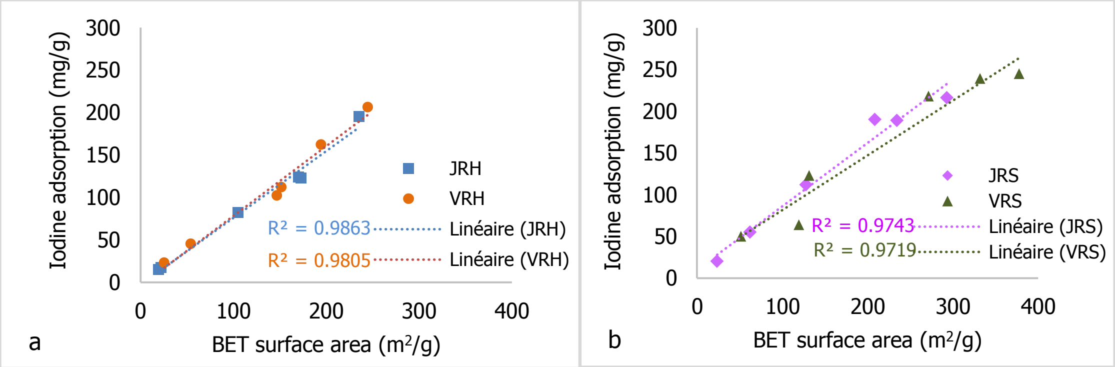
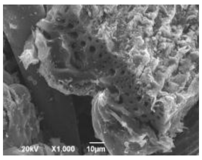
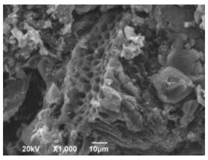
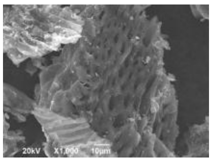
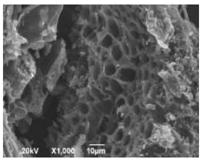


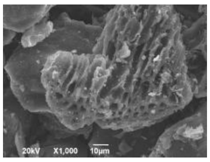
Figure 9: **c**correlation between iodine adsorption and BET surface area


JRH300


JRH40


JRH500


JRH600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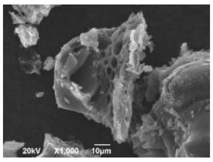
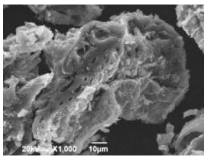
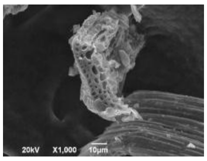
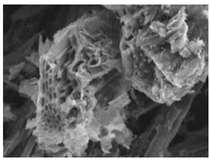
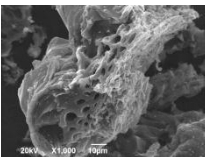
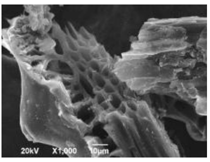

JRH800

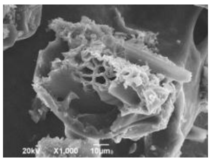

VRH300

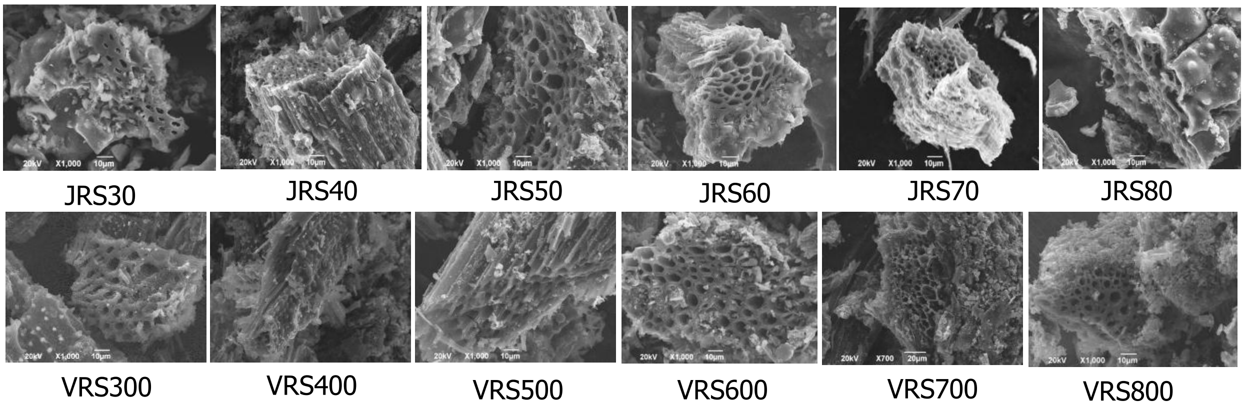

VRH400


VRH500


VRH600


VRH700


VRH800


JRS30 JRS40 JRS50 JRS60 JRS70 JRS80

VRS300 VRS400 VRS500 VRS600 VRS700 VRS800

Figure 10: The figure presents the SEM image of all studied biochars with a magnification of 1000

4. DISCUSSION

Nitrogen adsorption isotherms

The adsorption isotherms of all studied biochars were shown in Figure 2. As can be seen for the JRH biochars produced at high temperature (JRH600, JRH700, JRH800), displaced in Figure 2a, the volume absorbed increased gradually at low relative pressure P/Ps<0.1, and based on IUPAC classification, it resembled a type I isotherm, characteristics of microporous materials. Interestingly, there was a continued increase in the adsorption volume beyond a P/Ps of 0.1, which is found to be of type IV, indicates the presence of well-developed mesopores. However, the increasing of nitrogen adsorption of JRH300, JRH400 & JRH500 was very small at low relative pressure P/Ps <0.1, which was not easy to observe their general shape of their isotherms. It can be inferred that the fraction of micropores of JRH biochar produced at high temperature would be greater due to wider slopes compared to low temperature.

The isotherms for biochar samples from VRH in Figure 2b showed a similar trend to JRH isotherms, but the adsorption was somewhat enhanced at low P/Ps. In general, the amount of volume nitrogen adsorbed for VRH biochars was slightly higher than JRH biochars. That would indicate that biochars from VRH samples would have larger pore volume and little more surface area than those from Japan. The exception was for rice husk biochars at 800ºC, where the slope of JRH800 was significantly greater than that of VRH800 at relative pressure higher than 0.2, and it would be expected that the fractions of wider mesopores volume of JRH800 would be higher.

The adsorption isotherms of rice-straw-based biochars (Figure 2c & 2d) were similar to rice-husk-based biochars. Therefore, they could be considered as type I within P/Ps <0.1, type IV when P/Ps >0.1, contained both micropores as well as mesopores. Within the temperature range 300ºC-500ºC, the isotherms for JRS biochars (Figure 2c) and VRS biochars (Figure 2d) were very similar. In addition, the amount of adsorbed N_2 of these biochars was significantly lower than the higher temperature isotherms, indicating a lower in specific surface area and pore volume. A general comparison between Japanese straw biochars and Vietnamese straw biochars showed that the adsorbed volume of VRS biochars were notably higher compared to JRS biochars. That would indicate that biochars from VRS would have larger pore volume and more surface area than JRS, especially the pore volume and specific surface area for VRS600, VRS700 and VRS800 would be markedly higher than JRS at the same temperatures.

In conclusion, the observed adsorption isotherms of most of studied biochars were very similar and had a combination of a type I isotherm & type IV isotherms, contained both micropores as well as mesopores. According to Barton et al. (1999), adsorption by micropores is dominated by a strong interaction between nitrogen & the pore walls, whereas that in mesopores is mainly dominated by capillary condensation [22]. Therefore, the two isotherm types suggested that biochar samples followed two different adsorption mechanism: micropores filling (type I) and capillary condensation (type IV).

Total pore volume, micro-, meso-, and macro-pore volume and average pore diameter

The changes of total pore volume (measured in cm^3/g) and average pore diameter (measured in nm) were presented in Figure 3. As seen, the variation trends of average pore diameter and total pore volume were in the opposite. High pyrolysis temperature generally led to a larger pore volume, while the average pore diameter shifted toward lower values. In particular, for low temperature rice-residue-biochars at 300ºC & 400ºC, the total pore volume was small (<0.07 cm^3/g) and the values increased gradually at higher temperatures, slightly more than doubled. However, the data for JRS700, VRH800 & VRS800 was opposite to what might have expected, because their total pore volume were smaller than those at the lower temperature. This could occurs if, for example, the extremely small size particles formed by high temperature were pushed into the pores, resulting a decrease in total pore volume. The average pore size in studied biochars was in the range of 2 – 8 nm that fall into the small mesoporous regime. Abdullah & Wu (2009) also reported that particle size generally decrease with increase in the temperature in the range of 450-700ºC [23].

The percentages of the volume represented by the different pore sizes (micro-, meso-, and macro-) obtained in the samples were presented in Figure 4. The diagram revealed that macropores and mesopores were well-developed in most of biochars surface, accounting for over 60% of the total pore volume. However, the data from Figure 5, which shown the percentages of pore area, reported that the micropores contributed considerably to the total surface area, typically more than 70%. In other words, the mesopore and macropore surface area was small compared to the micropore surface area of biochars, except for JRH800 where the external surface area was slightly higher than the micropore surface area. As expected, there is good positive correlation between measured BET area and the micropore volume of biochars (Figure 6), with the regression coefficients (R^2) were 0.88, 0.96, 0.99, & 0.99 for JRH, VRH, JRS & VRS biochars, respectively. This result was similar to many studies, where the micropore range contributes the greatest proportion to the overall surface area of biochars [5, 9, 15].

In conclusion, while micropores in biochars were responsible for significantly larger surface areas than meso- & macropores, the meso- & macropore volume was larger than micropore volume in many cases. This findings were keeping with the results of literature [24]. It was also interesting to note that the micropore area of VRS biochars was higher than the rest, along with a higher micropore volume, and thus higher expected BET surface area.

Particle size distribution

The results of the particle size distribution (percentage by volume) of studied biochars were presented in Figure 7. It was obviously that the majority of particles of rice-husk-based samples (Figure 7a & 7b) were in the micropore and small mesopore range (<10 nm). In particular, 66.5 – 91.2% of JRH biochars and 75.9-90.8% of VRH biochars were in this range. In the range of 2 - 9.9 nm, the particle size distribution for the JRH biochars showed an increasing trend with the raising of pyrolysis temperature. VRH biochars also shared the same trend within the temperature of 300-700ºC, however there was a slightly decrease when the temperature reached 800 ºC. As can be seen, the macropores (diameter >50nm) make a small contribution to the total pore volume, typically less than 7,9% for JRH biochars and 5.6% for VRH biochars. In general, the micropores volume (diameter < 2nm) of VRH biochars in the higher temperature changed lightly; the figures for micropores of JRH biochars, however, fluctuated across the temperature range. It was predicted that at high temperatures, the notably increase in the pore area and volume of rice-husk-based biochar accounted basically for the mesopores of 2-9.9nm size.

Figure 7c & 7d showed that rice-straw-based biochars followed a very similar pattern to rice-husk-based biochar. This similarity suggested that small pores (<10nm) represented the majority (~80%), while pores with the size greater than 10nm accounted only for about 20% of the total specific pore volume. However, there were a significant differences in the proportion of micropores with size on the order of less than 1.6nm between JRS300 & VRS300, between JRS400 & VRS400. In particular, small micropores (<1.6nm) in JRS300 was only 4 percent—about one-fourth of VRS300, and JRS400 was slightly more than half of VRS400. Another differences were seen in pores in the size range 2-9nm between JRS500 & VRS500, where VRS500 was 48% compared to 33% of JRS500. In general, the percentage of micropore particles for the biochars produced from rice straw showed a decreasing trend at the high temperatures, while it showed an increase trend in mesopore particles. In this case, mesopores were created by widening micropores, in other words by sacrificing the existed micropores.

Bringing them all together, rice-husk-based biochars had a lower fraction of small particles (<10nm) than rice-straw-based biochars across the temperature range. This indicated that different parts of rice plant had different particle size distributions in the resulting biochars. This may be the results of differences in the chemical compositions (e.g. lignin, cellulose, hemicellulose, and the ash content) of rice husk and straw. Ioannidou & Zabaniotou (2007) found that lignin is favours the formation of macropores while cellulose is favours the formation of micropores [25]. Choosing biochars need to have a good particle size distribution because each of pore size has its importance and plays different roles. Particularly, micropores may provide a refuge site or micro-habitat for microbes to colonize, grow and reproduce when biochar applied to soil, or allows micro-molecules such as gases or solvents to be absorbed by the biochars [2, 26]. Meso- and macropores, on the other hand, are responsible for many important soil functions such as aeration and hydrology, movement of root hairs and microbial activity [27, 28].

BET surface area and iodine number

The values of BET surface area and iodine number of biochar samples were plotted in Figure 8. The BET surface area data (measured in m^2/g) was on the right axis, while the iodine number (measured in mg/g) was shown on the left axis. The dotted lines represented the changes in iodine number as a function of pyrolysis temperature, & the results of BET surface area across the temperature range can be observed in solid lines.

Generally, there was a gradual increase in specific surface area with final temperature increasing from 300ºC to 700ºC. The largest specific surface area obtained at VRS700 was 378 m^2/g, which was larger than that at 300ºC by 7.3 times. It was explained that at low temperature, tars block micropores which result in a lower surface area [29]; while at higher temperature, the evolution of volatile matters occurred & thus leading to an increase in the surface porosity [10].

However, there was a reduction in surface area at temperature 800ºC, properly due to the loss of microporous structure [2]. The surface areas for the JRH800, VRH800, JRS800, and VRS800 were determined to be 173, 151, 208 & 271 m^2/g, respectively, which was less than those made at 700ºC by approximately 7%. Consistent with this finding, Brown et al. (2006) found that the surface area of pine biochars increased with processing temperature, then decreased dramatically as the temperature increased to 800ºC [30]. In general, the final results showed that specific surface area of biochars from VRH higher than about 1.5 times compared to JRH biochars, except for JRH800 where it was slightly higher than VRH800 by 1.2 times. Biochars from VRS also showed higher results than JRS by approximately 1.5 times. These differences may be due to variations in climatic conditions, soil type, methods of cultivation and type of fertilizer used. Compared them together, rice-straw-based biochars had higher surface area, micropore area and external surface area than rice-husk-based biochar by 1.5 times, which suggested that different parts of rice plant (straw and husk), with different lignin, cellulose & hemicellulose components, would affect the surface properties of the studied biochars. The results of Wang et al. (2013) also consistent with this finding [21]. However, the present results were contrary with a previous study [8], where the rice husk biochar had higher surface area than the rice straw biochar. These results, again, demonstrated the possible influence of rice varieties on the final biochars' characteristics.

The data for iodine adsorption revealed the similar trend with specific surface area, & increasing with the pyrolysis temperature. It was believed that the iodine number has the same values as the BET surface area [31]. However, the received data for biochar samples were not consistent with the theory, where the iodine number was generally lower than the BET surface area (Figure 9). The area per molecule of adsorbed iodine in these experiments was consistent to what reported by Jindo et al. (2014) [8]. Hess & Herd (1993) also confirmed that the adsorption of iodine is not a true specific surface area [32]. As can be seen from Figure 8, the higher temperature of pyrolysis, the larger gap between iodine number and true surface area. The gap between them for rice-straw-based biochars (Figure 8a) showed significantly higher than for rice-husk-based biochars (Figure 8b). These differences properly because of two main reasons. Firstly, the iodine molecules are comparatively larger than nitrogen molecules. The diameter of the iodine molecule is around 10 angstrom (1 nm), while the diameter of nitrogen molecules is 3.5 angstrom. This indicated that iodine number could reveal the presence of pores in the same dimension or greater only, while the small size of nitrogen molecule enables it to reach into pores that are inaccessible to the iodine molecule [33]. Thus, results from N_2 adsorption based on BET method were sometime obtained in excess with iodine value [34]. Secondly, iodine value is sensitive to surface chemistry, i.e., it is affected by any entities or impurities on the surface that may react chemically with iodine. For example, the presence of tar or poly-aromatic hydrocarbons is known to interfere with iodine adsorption resulting in lower iodine numbers [35, 36]. Hess & Herd (1993) pointed that the presence of high levels of oxygen complexes on the surface, such as carboxyl group, can react with the potassium iodine in the test solution, which may cause a reduction in the iodine number [32]. As a result, it was predicted that the lower value of iodine in this study would be due to the differences in the functional groups & the ash content between rice-straw-biochar and rice-husk-biochar, or the probability of rice feedstocks contained soil pollutants, which cause the final biochars to be contaminated. It can be concluded that the iodine number could not be considered to be an accurate absolute predictor of specific surface area of studied biochars.

Although iodine number was lower than the true surface area, a strong linear correlation between iodine number and BET surface area was obtained (Figure 9). The regression coefficients (R^2) were 0.98 for rice-husk-based biochars, and above 0.97 for rice-straw-based biochars.

SEM analysis

To visualise the aggregate microstructure, SEM images of the biochars has been taken and presented in Figure 10. The morphology of these biochars was not very pronounced. It was observed that biochars have tube-like structures and complicated pore structure, consisting of interconnection networks of micropores, mesopores and macropores. At highest temperatures, surface samples displayed many cracks and there was an apparent reduction in the number of micropores on the samples' surface. It is believed that the cracks were a result of high temperature, where the mesopores or macropores were produced by destroying the walls of adjacent micropores [37].

5. CONCLUSION

The results presented in this work showed that the pyrolysis temperature and the variety of rice dramatically affect the porous characteristics and surface area of the final biochars. The study found that the surface area of rice-residue-biochars was related to the pore size and the total pore volume, that is, the smaller the pore size of biochars, the higher the surface area, and the larger the pore volume, the larger the surface area. Furthermore, while micropores make the greatest contribution to the overall surface area of biochars, their volume was smaller than the larger pores in many cases. As expected, the specific surface area showed a high correlation with both micropore and iodine number; however, the values for iodine number of biochars was smaller than their surface area. In general, the surface area & pore volume of biochars increased with increasing process temperature, reaching a maximum at 700ºC, then decreased with further increasing temperature. Biochar from Vietnam-rice-straw were higher in iodine number & specific surface area than from Japan, & the data for Vietnam-rice-husk-biochar also showed higher compared to Japanese-rice-husk-biochar. These differences demonstrated the influence of variety coming from different countries, which may due to the fact that different rice varieties collected from different countries may have many variations in weather conditions, soil types, soil contamination status, cultivation methods, fertilizer used, growing duration, planting time and harvesting time. The study also found a significant dissimilarity in total pore volume and surface area value between rice-straw-biochars and rice-husk-biochars, which may come from the differences in chemical compositions of rice straw and rice husk, differences in functional groups on the biochars' surface, and also differences in the ash content of biochars.

There is increasing concern about toxic and possibly carcinogenic polycyclic aromatic hydrocarbons (PAHs) in biochars, which can be produced from feedstocks under high pyrolysis temperature (>700ºC). This raise the question whether it is beneficial to produce a biochar with very high specific surface area because high surface area biochars obtained from high temperature may have the high risk of PAHs formation. It is therefore recommended that choosing biochars for soil application should have a high surface area with low intrinsic content PAHs. This requires careful selection of the feedstock as well as good control of pyrolysis conditions to minimize PAHs formed in biochars. It is predicted that PAHs levels in biochars will also be different between rice straw and rice husk, between Japanese and Vietnamese rice material. Therefore, further studies should be carried out to analyse the above-mentioned factors which can result in the differences in surface properties & possibly variances in the concentration of PAHs in these biochars prior to application.

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