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Effect of pyrolysis conditions on the potential of rice straw derived biochar for carbon dioxide capture application

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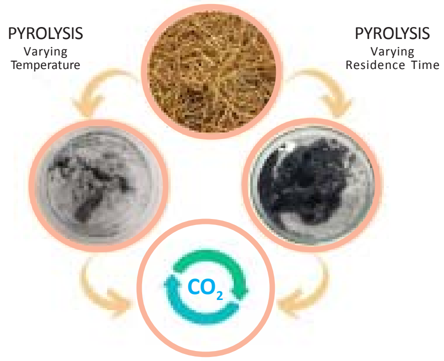
Graphical Abstract



Abstract

Global warming is being faced by humanity since the dawn of the third millennium. On the rise of emerging solutions to mitigate this phenomenon, adsorption is known for its effective carbon capture mechanism. This study determined the influence of pyrolysis conditions on the adsorption capacity of rice straw derived biochar adsorbents for potential application to carbon dioxide capture. Two pyrolysis conditions were varied: pyrolysis temperature and pyrolysis residence time. Under constant residence time of 2 h, the pyrolysis temperature was varied to 300°C, 400°C, 500°C, and 600°C. Meanwhile, under constant pyrolysis temperature of 600°C, the residence time was varied to 1 h, 2 h, 3 h, and 4 h. The adsorbents were characterized using scanning electron microscope (SEM) and thermogravimetric analyzer (TGA). The SEM images of the rice straw samples showed successful development of pore sites and flaky layers after pyrolysis. Results showed higher CO_2 adsorption capacity for samples pyrolyzed at higher temperature. However, increasing the residence time at the highest temperature during pyrolysis did not result to higher adsorption capacity. The highest adsorption capacity of 2.81 wt% was observed for the sample pyrolyzed at 600°C for 1 h. The pyrolysis temperature compared to the residence time is more influential on the adsorption capacity of the rice straw-derived biochar.

Keywords: adsorption, rice straw, carbon dioxide, pyrolysis conditions

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INTRODUCTION

Environmental problems are considered to be one of the major concerns of this generation. Industrialization, overpopulation and natural resources exploitation are believed to be its drivers [1]. Over the past decades, it was concluded that human interventions have changed the world's climate pattern which consequently affects the human life in each aspect. High concentration of carbon dioxide in the atmosphere enhanced the natural phenomenon called greenhouse effect. The enhancement of this phenomenon is directly linked to the increase in global temperature that causes striking changes in the climate [2].

Efforts are being considered by various countries to mitigate this climate change problem. Preventive strategies are being employed and highly demanded to minimize its effect. Different approaches and technologies are being adopted to lessen the carbon dioxide emission [3]. Among the different approaches, carbon capture by adsorption is superior for its sustainability and versatility [4]. Adsorption is the process when a molecule, or ion, called adsorbate present in the gaseous or liquid bulk sticks on the surface of a solid [5]. Candidate adsorbents must satisfy the following: (1) low-cost raw materials, (2) low heat capacity, (3) high surface area (4) fast kinetics, and (5) thermal, chemical, and mechanical stabilities under extensive cycling, in order to be an ideal and promising adsorbent for CO_2 capture [6].

Due to its high porosity and large surface area, the biochar has deemed to be an ideal adsorbent for both liquid and gaseous systems [7]. Biochar is defined as highly porous, carbon rich, thermally compose material produced from various kinds of biomass like bagasse, corn cobs, rice husk and rice straw processed in different pyrolysis conditions [8]. Knowing that Philippines is an agricultural country with rice as the highest contributor in terms of agricultural yield as compared to other products according to the Philippine Statistics Authority, it can be inferred that behind the high production of crops is the high production of waste in the form of rice straw [9]. Rice straws are lignocellulosic biomass, which can also be converted into biochar with medium to high surface areas [10]. Lignocellulosic biomass, such as rice straw, are converted into biochar by pyrolysis technology [11]. With the great abundancy, stagnancy and potential of rice straw, this low-cost material can be highly utilized as an adsorbent in the form of biochar and can be used to treat industrial effluents. Thus, this research investigated the potential of rice straw derived biochar as an adsorbent for carbon dioxide capture application. Furthermore, the effect of pyrolysis conditions such as temperature and residence time on the characteristics and adsorption capacity of the resulting biochar was evaluated.

EXPERIMENTAL

Materials. The rice straw utilized in this study was obtained from Castillejos, Zambales, Philippines. The Thomas Wiley Mill Model 4, Proctor and Schwartz Tray Dryer, W.S. Tyler Sieve Pan No. 40, W.S. Tyler Sieve Shaker Model RX-29-16 and Cole-Parmer Muffle Furnace Model EW-33858-70 used for the pre-treatment and pyrolysis of the rice straw were all provided by the Chemical Engineering Laboratory and the TM3000

Tabletop Scanning Electron Microscope (Hitachi) and Perkin-Elmer Thermogravimetric Analyzer used for the characterization and analysis of the biochar were provided by the Research Center for the Natural and Applied Sciences (RCNAS) of the University of Santo Tomas (UST) in Manila, Philippines.

Preparation of biochar. The collected rice straws were dried at 120°C using the tray dryer for 2.5 h to remove its moisture content. The size of the dried sample was reduced by milling using the Willey Mill, then sieved for 5 min using the sieve shaker with the sieve tray having a 40 mesh number with a nominal sieve opening of 420 μm. The sieved rice straw was placed in crucibles and prepared for pyrolysis. The crucibles were covered to minimize the presence of oxygen during the thermal decomposition of the biomass. For this study, two pyrolysis conditions were varied, the pyrolysis temperature and pyrolysis residence time. For varying pyrolysis temperature (VPT), the residence time was held constant for 2 h at the following pyrolysis temperature: 300°C, 400°C, 500°C, and 600°C. On the other hand, for the varying residence time, the pyrolysis temperature was set constant at 600°C at the following pyrolysis residence time: 1 h, 2 h, 3 h, and 4 h. The pyrolysis of the sample was done using the muffle furnace. After the pyrolysis, the crucibles were stored inside a desiccator to ensure that the biochar samples do not absorb moisture.

Characterization and evaluation of the CO_2 adsorption efficiency of biochar. To investigate the morphology of the biochar samples, these were subjected to qualitative inspection using the scanning electron microscope (SEM). After which, to determine the potential of the samples for CO_2 capture application, the samples undergone CO_2 adsorption test using the thermogravimetric analyzer (TGA). The samples for each run were first pre-treated to eliminate the moisture and impurities associated with it. Firstly, the sample was heated from 30–150°C at a rate of 10°C/min under nitrogen gas flowing at a rate of 50 mL/min. The temperature of 150°C was held constant for 30 min to purge moisture and other gases adhering to the surface of the biochar. Afterwards, it was cooled down to 30°C at a rate of 20°C/min. Once it reached 30°C, the gas was switched to carbon dioxide at a flow rate of 50 mL/min and the system was held isothermally for 30 min. The change in weight obtained during the isothermal part of this method was used to determine the amount of carbon dioxide that was adsorbed by the biochar.

The biochar pyrolyzed at 600°C for 1 h, which showed the highest CO_2 adsorption capacity, underwent further analyses such as nitrogen adsorption, repeatability and regenerability tests. For the nitrogen sorption test, the sample was first pre-treated following the same procedure prior to the CO_2 adsorption test. After pre-treatment, once it reached 30°C, the nitrogen gas was maintained at 50 mL/min and the system was held isothermally at 30°C for 30 min. The change in weight obtained during the isothermal part of this method was used to determine the amount of nitrogen that was adsorbed by the biochar. For the repeatability test, the CO_2 adsorption test was repeated two more times to obtain three CO_2 adsorption capacity measurements. Finally, for the regenerability test, CO_2 adsorption-desorption test was conducted to determine the reusability of the adsorbents over time. After pre-treatment of the samples, the cooled sample at 30°C was exposed to CO_2 gas flowing at 50 mL/min isothermally for 30 min. Afterwards, it was heated again from 30–150°C at a rate of 20°C/min. The temperature was held constant at 150°C for 15 min to desorb the CO_2 adsorb from the previous step. It was then cooled down to 30°C at a rate of 20°C/min, which was held isothermally for 30 min. The temperature swing adsorption-desorption process was repeated for five times.

RESULTS AND DISCUSSION

For the rice straw biochar produced at VPT for 2 h, the samples produced at 300°C, 400°C, 500°C, and 600°C were herein referred to as RB300, RB400, RB500 and RB600, respectively. Meanwhile, for the rice straw biochar produced at varying pyrolysis residence time (VRT) at 600°C, the samples produced at residence time of 1 h, 2 h, 3 h, and 4 h were referred to as RB1, RB2, RB3 and RB4, respectively.

Morphological characterization. The SEM images shows qualitative information regarding the morphology of the samples using focused beam of high-energy electrons. The SEM images at ×1500 magnification in Fig. 1 show the surface condition before the pyrolysis and the developments occurred in the surface of the rice straw derived biochar adsorbents after the pyrolysis process at varied conditions are shown in Fig. 2 and Fig. 3.

The rice straw before pyrolysis in Fig. 1 shows no evident adsorption pore sites. It only shows flat smooth surface without pores and crevices due to its lignocellulosic properties. However, after pyrolysis at varying temperature as shown in Fig. 2, appearance of adsorption sites is already visible in the form of pores and flaky layers. The surface morphology of the samples changes evidently following pyrolysis. The biochar becomes rougher at some parts due to the presence of the pore sites that develop as the pyrolysis temperature increases. This is expected since the process of pyrolysis degrades the cellulose, hemicellulose and lignin of the rice straw paving the way for the opening of the pore sites [12].

Varying the residence time also affects the surface morphology of the samples. The development in the surface morphology of the rice straw derived biochar adsorbent after the pyrolysis process at varying residence time are shown in Fig. 3. The SEM images of the rice straw pyrolyzed at VRT shows minimal difference unlike the evident changes that was observed for samples that undergone pyrolysis at VPT. Adsorption pore sites are still visible together with the appearance of crevices and flaky layers.

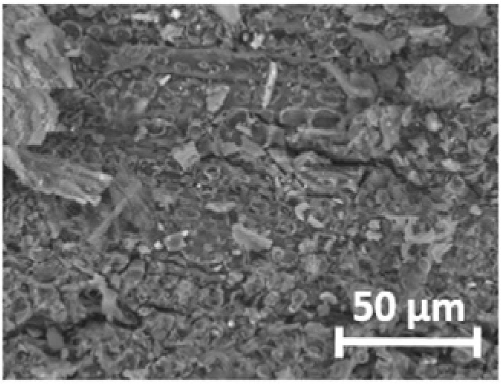

Figure 1. SEM image of rice straw before pyrolysis

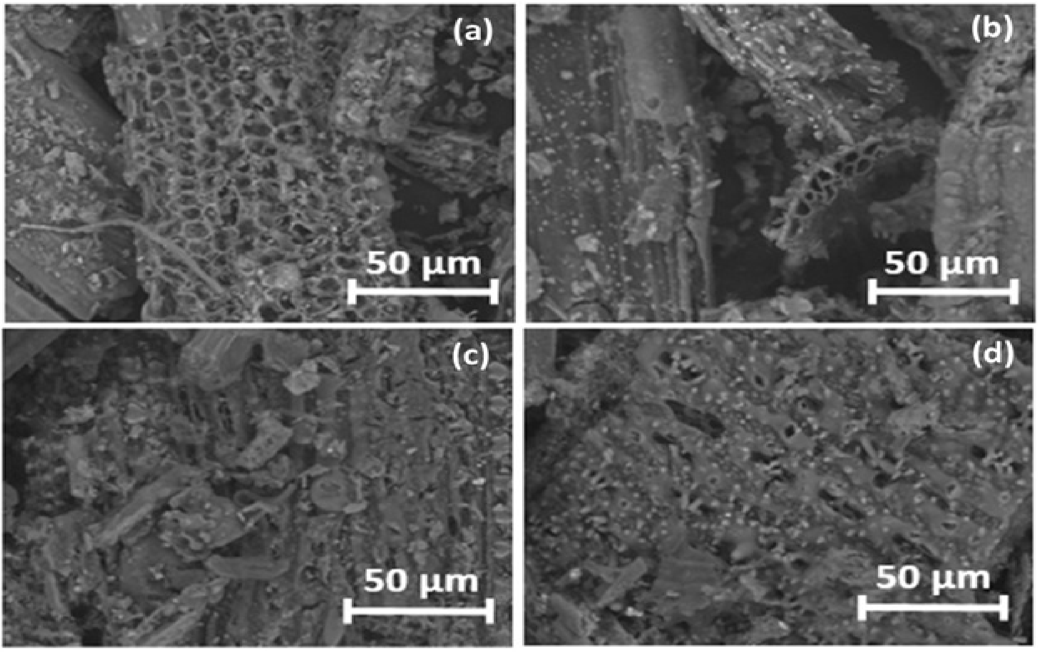

Figure 2. SEM images of pyrolyzed rice straw at varying pyrolysis temperature: (a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C

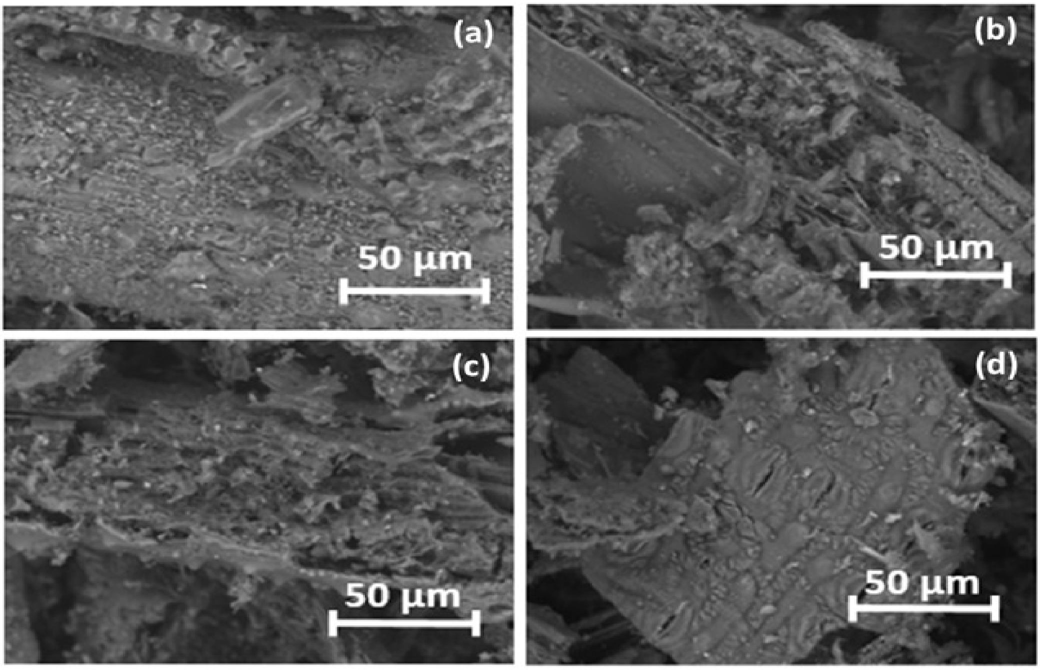

Figure 3. SEM images of pyrolyzed rice straw at varying residence time: (a) 1 h, (b) 2 h, (c) 3 h, and (d) 4 h

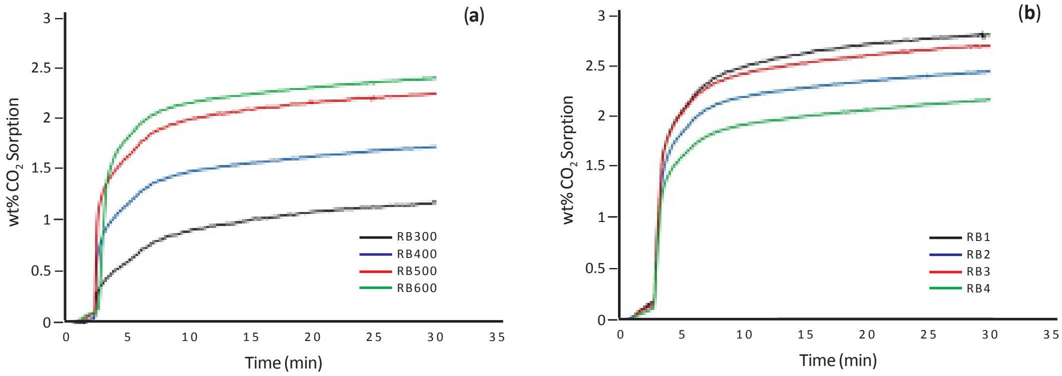

Figure 4. CO_2 adsorption capacity of biochar produced at (a) varying pyrolysis temperature and (b) varying residence time

Table 1. Summary of the CO_2 adsorption capacity of biochar samples

Sample Name	**Pyrolysis Conditions**		**CO_2 Adsorption**	
	Temperature (°C)	*Time (h)*	*wt% (g CO_2/g ads*100)*	*Mmol CO_2/ g ads*
RB300	300	2	1.21	0.27
RB400	400	2	1.76	0.40
RB500	500	2	2.29	0.52
RB600	600	2	2.44	0.56
RB1	600	1	2.81	0.64
RB2	600	2	2.44	0.56
RB3	600	3	2.70	0.61
RB4	600	4	2.16	0.49

Evaluation of the CO_2 adsorption efficiency of biochar. Thermogravimetric analysis was done to investigate the CO_2 adsorption capacity of the biochar produced at varying pyrolysis conditions. The change in the weight of the biochar upon isothermal exposure to CO_2 for 30 min at 30°C corresponds to the CO_2 adsorption capacity of the biochar. The amounts of CO_2 adsorbed with respect to time for biochar produced at VPT and at varying residence time are illustrated in Fig. 4. The wt% CO_2 adsorption of the biochar produced at varying pyrolysis condition is summarized in Table 1.

Generally, as shown in Fig. 4, the biochar shows increasing CO_2 adsorption with time with a steep slope within the first 5–10 min of the adsorption process. Comparing the adsorption capacity of biochar produced at VPT in Fig. 4a, it is evident that the adsorption capacity is higher for samples produced at higher pyrolysis temperature. Among the four samples produced at VPT, RB600 which was produced at the highest pyrolysis temperature of 600°C showed the highest CO_2 adsorption of 2.44 wt% (0.56 mmol CO_2/g ads). This can be attributed to the more evident pore sites observed in the SEM of RB600.

For the samples produced at VRT, the effect of the pyrolysis residence time on the CO_2 adsorption capacity of the resulting biochar cannot be strongly established. Among the four samples produced at VRT, RB1 which was produced at the shortest pyrolysis residence time of 1 h showed the highest CO_2 adsorption of 2.81 wt% (0.64 mmol CO_2/g ads). The adsorption capacity of RB2 (2.44 wt%) is lower than RB1. However, the adsorption capacity of RB3 (2.70 wt%) is higher than RB2.

These results can be supported by the study of Ronsse *et al.*, wherein it was established that at lower pyrolysis temperature, the biochar surface area was generally low, but gradually increases in biochar produced with longer residence times. Since higher surface area is more favorable for adsorption process, higher pyrolysis temperature produces the more efficient biochar. However, longer residence time at high pyrolysis temperature may produce more ash than the actual biochar. Thus, resulting to lower efficiency of CO_2 adsorption capacity [13].

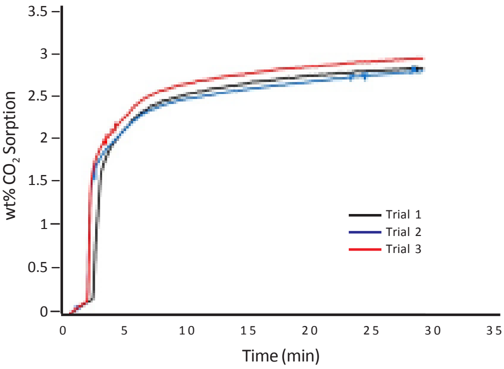

Figure 5. CO_2 adsorption test trials for RB1

With the data from the CO_2 sorption of all the biochar produced at various pyrolysis conditions, it is evident that higher temperature and shorter residence time will produce a more efficient biochar. This is observed for RB1, which was produced was produced at pyrolysis temperature of 600°C for 1 h, since it has the highest amount of CO_2 as compared to other samples.

Repeatability test. Repeatability verifies the accuracy in the measured results, particularly the CO_2 adsorption capacity, if the measurement is performed multiple times under same conditions. RB1, which exhibited the highest adsorption capacity, undergone two additional analysis of CO_2 sorption capacity to validate the measurement. The CO_2 adsorption capacity measurements for RB1 is shown in Fig. 5. The rate of adsorption in the three trials are relatively similar. Considering the wt% adsorption in the three trials, the value of the standard deviation for this sample is 0.01795. This indicates that the CO_2 sorption measurement of the biochar sample is repeatable.

Evaluation of CO_2 selectivity. Main criteria for sorbent selection are large specific surface area, high selectivity and high regeneration ability. According to Gibson *et al.*, high-selectivity adsorbents are required to achieve relatively high CO_2 uptake at low partial pressures, which means that the separation process should be based on either very strong physisorption or chemisorption with thermal regeneration [14]. To evaluate if the biochar is selective to CO_2, RB1 which exhibited the highest adsorption capacity undergone N_2 sorption test. This test intends to investigate if the biochar will adsorb N_2 since most flue gases contain high N_2 concentration. The change in weight of the sample with respect to time upon exposure to N_2 and CO_2 gas to measure the adsorption capacity of RB1 for the two gases is presented in Fig. 6. The N_2 adsorbed (0.64 wt%) by RB1 is significantly lower than the CO_2 adsorbed (2.81 wt%). This indicates that RB1 has good selectivity to CO_2.

Evaluation of regenerability. The regeneration performance of a CO_2 adsorbent is an important parameter, as the adsorbent should retain stable CO_2 adsorption performance for a long period of cyclic operation. According to Yu *et al.*, there is need

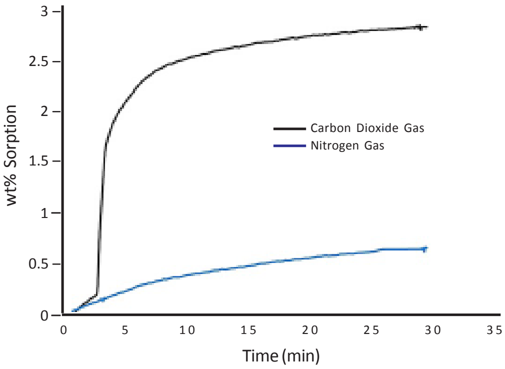

Figure 6. Comparison of N_2 and CO_2 adsorption tests for RB1

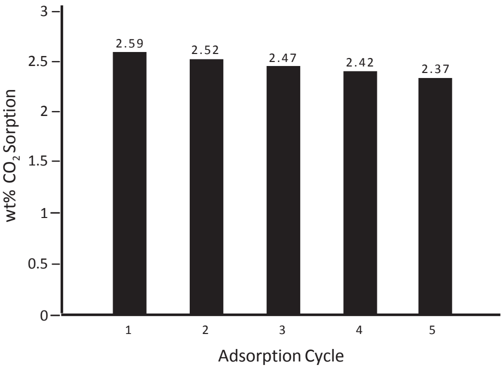

Figure 7. Adsorption-desorption test for RB1

to develop an effective and less energy-consumed regeneration of the CO_2 captured adsorbents to account for industrial applications [15]. In the regeneration test, the sample undergone temperature swing adsorption (TSA) process wherein it was exposed to CO_2 alternately at 30°C and 150°C to allow adsorption of CO_2 at low temperature then desorption at high temperature. The result of the regeneration test for RB1 is shown in Fig. 7. There is a slight decrease in the adsorption capacity as the adsorption-desorption cycle proceeds. The 87.97% regeneration performance of the biochar indicates that the biochar is thermally stable and can be repeatedly reuse. According to Ifthikar *et al.* and Wang *et al.*, a competitive adsorbent should express a good reusable and recycling ability for industrial applications and could reduce the cost of the biochar sorbents. Thermal regeneration is one of the most effective methods to achieve desorption [16, 17].

CONCLUSION

The research focuses on the conversion of rice straw waste to biochar by pyrolysis and to evaluate its potential as adsorbent for carbon dioxide. Specifically, the effect of pyrolysis conditions such as pyrolysis temperature and residence time on the adsorption efficiency of biochar were investigated. The biochar produced at various pyrolysis conditions were subjected to several quantitative and qualitative characterization.

From a smooth surface to the appearance of active pore sites and flaky layers, the SEM images of the raw rice straw and the rice straw biochar showed significant differences. The pyrolysis temperature has a more significant effect on the surface morphology of the biochar as compared to the residence time. Meanwhile, TGA of the biochar samples showed that biochar produced at higher temperature has higher adsorption capacity. However, the relationship between the pyrolysis residence time and CO_2 adsorption cannot be established.

From the results of the study, it is evident that higher temperature and shorter residence time will produce a more efficient biochar. This is observed for RB1 with 2.81 wt%

(0.64 mmol CO_2/g absorbent) capacity, which was produced at pyrolysis temperature of 600°C for 1hr, since it has the highest amount of CO_2 adsorption as compared to other samples. The RB1 sample was also proven repeatable, has a high selectivity and has a good regeneration performance of 87.97%. Generally, the waste rice straw was effectively utilized in producing rice straw-derived biochar, which can be an economic adsorbent for CO_2 capture application.

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