IOP Conf. Series: Earth and Environmental Science **479** (2020) 012024 doi:10.1088/1755-1315/479/1/012024

Carbon Dioxide Adsorption Equilibrium Rates Comparative Temperature Study Using Palm Kernel Shell Sorbent.

Dzulkarnain Mohd Sahri[1], Nabilah Zaini*[1], Noor Shawal Nasri[2], Husna Mohd Zain[2], Norhana Mohamed Rashid[3], and Anis Shahirah Noor Shawal[4].

[1] SHIZEN Conversion and Separation Technology, Department of Chemical Process Engineering, Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia, 54100 Kuala Lumpur, Malaysia
[2] Sustainable Waste-To-Wealth Program, UTM-MPRC Institute for Oil and Gas, Resource Sustainability Research Alliance, Universiti Teknologi Malaysia, UTM Johor Bahru, Johor, Malaysia.
[3] Department of Energy Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, UTM Skudai, Johor, Malaysia.
[4] Faculty of Business & Management, Universiti Teknologi Mara (UiTM), 40450 Shah Alam, Selangor, Malaysia.

*Corresponding author e-mail: nabilah.zaini@utm.my

Abstract. Greenhouse effect is the serious environmental issue whereby the gaseous component involved is dangerous. One of the gases that contributed to atmosphere is carbon dioxide (CO_2), in which is more than 80%, followed by methane and nitrous oxide that resulted from human activities, industrial sector and transportation. Activated carbon (AC) is the best adsorption technology due to simple design and ability to capture carbon dioxide efficiently. This paper was aimed to produce activated carbon derived from waste material, to determine adsorption rate at different pressures and temperatures and to relate adsorption kinetics and isotherms equilibrium to describe adsorption processes. Palm Kernel Shell (PKS) was selected as raw material to produce AC. Char was produced via carbonization process at 700 °C ± 20 °C for 2 h with 10 °C/min heating rate under inert gas flow. The sample is then grinded and sieved to 0.65mm to 0.8mm, followed by chemical treatment by using potassium hydroxide with ratio of 1:1 and directly undergoing microwave treatment. Adsorption rate performances were investigated by different temperatures of 25 ^{0}C and 10 ^{0}C and pressures of 5, 15 and 25 bar. The sample were characterized by thermo-gravimetric analysis, surface area analysis, and ultimate analysis. AC-PKS shows the highest surface area. As a result, increase in pressure led to increase in CO_2 adsorption while decrease in temperature in CO_2 adsorption. In conclusion, the findings revealed that the potential of AC-PKS to capture CO_2 in order to enhance environmental sustainability and economically.

1.0 INTRODUCTION

Greenhouse effect is the serious environmental issue whereby gaseous component involved is dangerous. One of the gases that contributed to atmosphere is carbon dioxide (CO_2), which is more than 80%, followed by methane and nitrous oxide that resulted from human activities, industrial sector and transportation. Carbon dioxide is the gas that makes a harmful contribution to the environment, especially for greenhouse effect and global warming. Human activities are the main cause of the greenhouse effect. Statistics from National Research Council showed that 81.6% of carbon dioxide gas is contributed by human activities [1]. Also, human activities can be categorized into a few sectors including transportation, industry and commercial. Electricity and transportation have the largest contribution followed by industry and residential [2]. Many methods have been used for carbon dioxide capture such as absorption, membranes separation, distillation and adsorption [3]. Adsorption is the best method for capturing process due to simple design and ability to capture CO_2 efficiently [4]. Currently, activated carbon is one of the adsorption technologies due to large pore volume and which leads to better adsorption performance. However, the commercial activated carbon is highly expensive because of raw material used such as coal [5]. Therefore, many researchers are interested to produce activated carbon derived from agricultural waste material such as Palm Kernel Shell, Coconut Shell and Empty Fruit brunch in order to enhance sustainability and preserve environmental quality [6,7]. PKS is the shell that is separated from nut after crushing from palm oil mill. Kernel shells are a fibrous material that can be easily handled in bulk directly from the product line to the end use. Large and small shell fractions are mixed with dust-like fractions and small fibre [8]. Moisture content of PKS is the range of 11 to 13% and quite low compared to other biomass residuals. Furthermore, PKS is the best and higher quality biomass in terms of uniform size distribution, ease of handling and crushing, and limited biological activity due to low moisture content compared to other biomass in industry around Malaysia [9,10]. Adsorption equilibrium describes the interactions between adsorbent and adsorbate to applied gas with various conditions [11,12]. Hence, synthesis of PKS bio-char and activated carbon was carried out. The sorbent was characterized by using Thermal-gravimetric analysis, Surface area analysis, and Ultimate analysis.

2.0 EXPERIMENTAL METHODOLOGY

2.1 Char and Activated Carbon Preparation

Raw Palm Kernel Shell was loaded into stainless steel tabular reactor with the specifications of 5 cm internal diameter, 15 cm length and 500 g max capacity and placed in a well lagged vertical tube furnace. The grinded sample was heated starting from temperature room of approximately 25^0C until carbonization temperature of 700 ^{0}C at heating rate of 10 ^{0}C/min by using nitrogen flow at 1L/min to produce bio-char during carbonization process. The experiment was conducted in 2 hours period before cooled down to room temperature for 24 hours. Details of carbonization process was taken from previous work [13]. The bio-char was further grinded and sieved to 0.65mm to 0.8mm. 50 g of bio-char PKS was impregnated with 1.0 M of Potassium Hydroxide solution (KOH) using 1:1 weight ratio. The mixture was stirred for about 2 hours at temperature 85 ˚C with stirrer speed at 7-8 rotation per minute (rpm). Once the reaction is finished, the slurry was filtered and put in oven at temperature 105 ˚C for 24 h. Afterwards, the filtered sample underwent microwave treatment. The 50 g of prepared samples were charged at quartz reactor with high temperature. Then, the sample was pre-heated in microwave oven with 200 ml/min nitrogen gas flow rate. The gas flow was switched over to carbon dioxide gas with same flow rate. The power level used was 400W with 6 min of irradiation time [14,15].

2.2 Carbon dioxide performance test for adsorption process.

The carbon dioxide adsorption and desorption process are carried out in carbon dioxide adsorption system at ambient and low temperature. A purified carbon dioxide gas will flow into the loading cell before being transferred to the reactor containing the sample. The gas that flows into the reactor will be compressed at variety of pressures. The adsorption time will be taken as the gas is compressed to the sample in the reactor. After adsorption time is reached, the gas will be released from the reactor. The adsorption process will be conducted up to three cycle operations in order to stabilize the samples throughout this study. The amount of gas adsorbed [16] was calculated using the equation (1) below:

$$Q = 1/m\ (V_V/R\ (|P/ZT|_I - |P/ZT|_{eq})_a + V_I/R\ (|P/ZT|_I - |P/ZT|_{eq})_I) \quad (1)$$

where, P is pressure, T is temperature, V is volume, R is gas constant, a is adsorption cell, l is loading cell, I is initial state, eq is adsorption at final equilibrium state, m is adsorbent mass, q is amount of gas absorbed and Z is compressibility factor.

The carbon dioxide gas which adsorbed in adsorption cell was released to fume cupboard by opening the vent valve below the adsorption cell. The time taken and pressure of the cell was recorded until there is no gas left inside the adsorption cell [17].

2.3 Material Characterization

The material characterization consists of three parts which are Thermalgravimetric Analysis (TGA), Surface Area Analysis and Ultimate Analysis.

2.3.1 Thermalgravimetric Analysis.

The thermal property of the raw PKS was determined using thermogravimetric analysis. Approximately 10 mg of raw PKS was placed in crucible (aluminium type) and then placed in furnace. The moisture content and volatile matter were obtained from TGA by continuous heating by 10 °C/min from room temperature (approximately 25°C) to 600 °C rate of and nitrogen flow rate of 10 mL/min. The temperature was increased until 900°C in order to get fixed carbon content with the same rate of heating and nitrogen gas flowrate. The residue of the sample can be considered representing the ash content [18].

2.3.2 Surface Area Analysis.

The standard method for determining surface areas known as BET analysis was used to analyse the surface area of three samples which are raw, biochar and activated carbon. All samples were sent for BET analysis. In BET laboratory, liquid nitrogen at -196 ˚C was absorbed in the sample that was used for surface area estimation. This was achieved using the volumetric techniques (Micrometrics ASAP 2020). The surface area was evaluated by taking an average microspore of the activated carbon. The adsorption data at relative pressure (P/P_o) range of 0.04 to 0.2 was considered in order to calculate the surface area by using the BET method. [19].

2.3.3 Ultimate Analysis (CHNS).

Ultimate analysis was carried out using elemental analyser. The samples that need to be studied are raw, bio char 500^0C and 700^0C. Carbon (C), Hydrogen (H), Nitrogen (N), and sulphur (S) is the elements that need to be covered and analysed. The composition of oxygen is calculated by using the percentage of differential elements [20].

3. RESULTS AND DISCUSSIONS

3.1 Material Characterization

There are three characterizations involved in adsorption process which are Thermalgravimetric (TGA) analysis, Surface area analysis and Ultimate analysis.

3.1.1 Thermalgravimetric Analysis.

Figure 1 shows TG curve and derivative TG curve profiles with temperature range of 0-1000 ˚C on Activated Carbon Palm Kernel Shell.

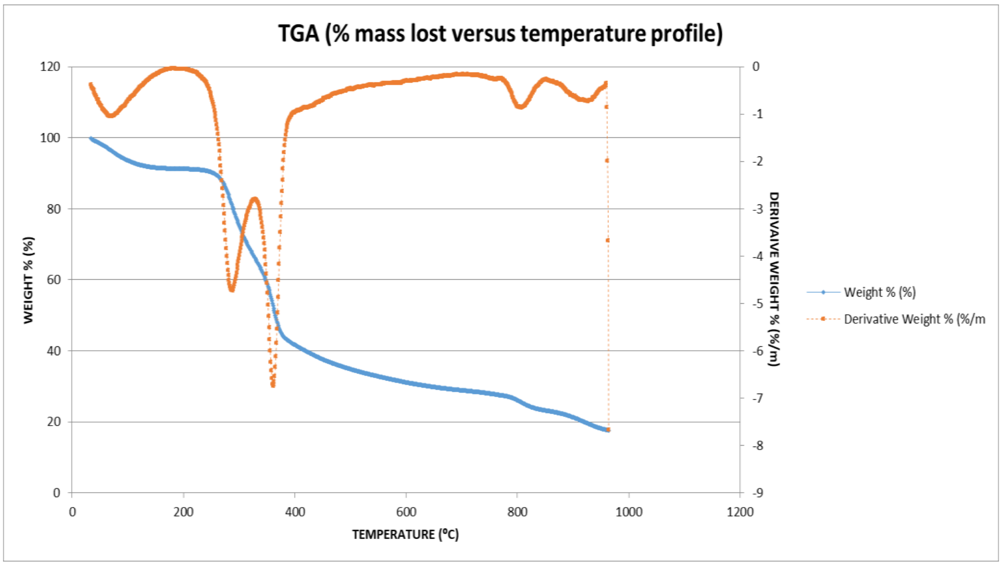

Figure 1. TGA Analysis of Palm Kernel Shell Activated Carbon Produced.

From that figure, it can be analysed that the highest of derivative temperature is about 600 ˚C. Basically, there are two peaks that appear at range of 280-300 ˚C and 350-370 ˚C. The first peak represents hemicellulose decomposition and the second peak is cellulose decomposition. After 400 ˚C, some amount of lignin decomposed as well [21]. The mass loss of AC-PKS is around 70%. The mass loss is mainly occurred at the point where the TG curve was beginning to flat and some lignin structure is not decomposed. The curve flatten represents that no decomposition occurs in AC-PKS and beyond around 650 ˚C or higher, it is a good condition to do carbonization process [22].

3.1.2 Surface area analysis

Table 1 shows surface area analysis for three different conditions of the sample.

Table 1. Porosity parameters of activated carbon obtained from nitrogen adsorption

Samples	BET (m^2/g)	V_{Total} (cm3/g)	V_{micro} (cm3/g)
Raw PKS	0.8	0.001	0.009
Char PKS	24.5	0.01	0.01
AC-PKS	322.5	0.2	0.105

The objective of the analysis is to compare the surface area of three samples, which are raw, bio-char and activated carbon of Palm Kernel Shell. Table 1 shows that the activated carbon is the highest surface area compared to raw and char. This is because activated carbon has ability to adsorb gases and basically nitrogen gas is used as adsorption test due to the highest purity and the most interaction bonding to all solids. The pores can be divided into three parts namely macropores (>50 nanometer), mesopores (2-50 nanometer) and micropores (<2 nanometer) [23]. It can be concluded that the higher BET surface area, the higher the gas adsorption rate because of ability to capture carbon dioxide gas at different conditions [24].

3.1.3 Ultimate analysis

Table 2 shows that the composition on elemental at three different samples which are raw PKS, PKS Char at 500^{0}C and 700^{0}C.

Table 2. Composition of element gases in three samples.

Samples Description	N (%)	C (%)	H (%)	S (%)	O (%)
Raw Palm Kernel Shell	0.34	47.97	6.06	0.05	45.59
Palm Kernel Shell Char at 500 ^{0}C	0.48	74.70	3.22	0.05	21.55
Palm Kernel Shell Char at 700 ^{0}C	0.59	86.84	1.96	0.03	10.58

The carbon number is increased due to carbonization process in which cellulose components were burnt and decomposed into bio-char [26]. The optimum temperature of PKS Char samples is about 700^{0}C due to moisture removal and lignition decomposition. The H content is decreased because at high temperature, some molecular chains break due to low stability [27].

3.2 Carbon Dioxide performance test for adsorption process.

Figure 2 shows the comparison of rate constant adsorbent at different temperatures conditions with three pressures applied in this study which are 5, 15 and 25 bars.

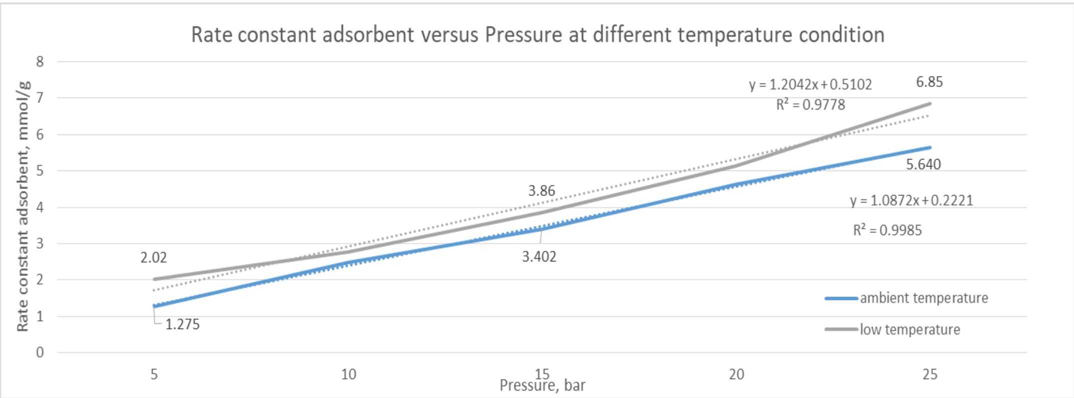

Figure 2. Rate constant adsorbent at both temperature conditions.

It can be described that increase in pressure led to increase in CO_2 adsorption while decrease in temperature led to decrease in CO_2 adsorption. This is because temperature plays role to adsorb the molecule energy sample to create Van Der Waal's attraction until reaching equilibrium [28,29].

4.0 CONCLUSION

In can be concluded that sustainable Palm Kernel Shell is a valid precursor for synthesized from waste material to activated carbon production for CO_2 adsorption via carbonization, chemical treatment with KOH and microwave treatment. The characterizations carried out in this study are TGA, BET and CHNS. The minimum temperature for PKS carbonization is 650^0C based on TGA result. BET results show that AC-PKS is the highest porosity with 322.5 m^2/g which is appropriate for gas phase application. The ultimate analysis revealed that PKS char at 700^0C contained 86.84% of carbon number. Carbon dioxide adsorption, there is an increased in time to reach equilibrium with increased in pressure and increase in adsorption rates but decrease in temperature. The amount of CO2 adsorbed at 5, 15 and 25 bars for ambient temperatures are 1.275. 3.402 and 5.640 mmol/g respectively while for low temperature are 2.02, 3.86 and 6,85 respectively. As findings of this paper, the potential of PKS as precursor has capability to improve its ability to capture CO_2 gas so that the environment is sustained more economically.

Reference

[1] NRC (2010). *Advancing the Science of Climate Change*. EXIT National Research Council. The National Academies Press, Washington, DC, USA.
[2] EPA, *Greenhouse gases threaten public health and the Environment Science overwhelmingly shows greenhouse gas concentration* at unprecedented levels due to human activity. Environment Protection Agency, 07 Dec. 2009.
[3] Abdullah, N., and Sulaiman, F. (2013). Chapter 3: *The oil palm wastes in Malaysia. Biomass Now-Sustainable Growth and Use*, Intech, 75-93.
[4] Su, F., Lu C., Cnen, W., Bai, Hsunling. and Hwang J.F. (2009). Capture of CO_2 from Flue Gas via Multiwalled Carbon Nanotubes. *Science of the Total Environment*, 407, 3017-3023.
[5] Abunowara, M., et al. (2016). *"Description of Carbon Dioxide Adsorption and Desorption onto Malaysian Coals under Subcritical Condition*." Procedia Engineering **148**: 600-608.
[6] Abechi, S. E., Gimba, C. E., Uzairu, A., and Dallatu, Y. A. (2013). *Preparation and characterization of activated carbon from palm kernel shell by chemical activation. Research Journal of Chemical Sciences,* **3(7),** 54-55.
[7] Tan.L., Islam, M.A., Asif, F. and Hameed, B.H. (2014). *Adsorption of Carbon Dioxide by Sodium Hydroxide-Modified Granular Coconut Shell Activated Carbon in a Fixed Bed. Energy,* **77**, 926 - 931
[8] Edmund, C. O., et al. (2014). "*Characterization of palm kernel shell for materials reinforcement and water treatment*." Journal of Chemical Engineering and Materials Science **5**(1): 1-6.
[9] Rashidi, N., & Yusup, S., "*Potential of palm kernel shell as activated carbon precursors through single stage activation technique for carbon dioxide adsorption*", *Journal of Cleaner Production*, 2017. **168**: 474-486.
[10] Al-Hajjaj, A., Zamora, B., Shah, A.A., Reguera, E., Bavykin, D.V. and Walsh F.C. (2011). *On the Application of Standard Isotherms to Hydrogen Adsorption in Microporous Materials.* Inter. Journal of hydrogen energy, **36,** 14464-14476.

[11] Ayawei, N., Ebelegi, A. N., & Wankasi, D. (2017). *Modelling and Interpretation of Adsorption Isotherms Modelling and Interpretation of Adsorption Isotherms, (September).* https://doi.org/10.1155/2017/3039817
[12] Qiu, H., Lu, L.V., Pan, B., Zhang, Q., Zhang, W., and Zhang, Q. (2009). *Critical Review in Adsorption Kinetic Models*. *J Zhejiang Univ Sci A*, 10(5),716-724.
[13] Li, W., Yang, K., Peng, J., Zhang, L., Guo, S., Xia, H., (2008). *Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and acti-vated carbons derived from carbonized coconut shell chars.* Ind. Crops Prod. **28**, 190-198.
[14] Yang K., Peng J., Srinivasakannan C., Zhang L., Xia H., Duan X., 2010, *Preparation of high surface area activated carbon from coconut shells using microwave heating, Bioresource Technology* 101 (**15**), 6163 – 6169.
[15] Yang, K., Peng, J., Srinivasakannan C., Zhang L., Xia H. and Duan X. (2010). *Preparation of High Surface Area Activated Carbon from Coconut Shells Using Microwave Heating.* Bioresource Technology, **101**, 6163 – 6169.
[16] Fatemi S., Vesali-Naseh M., Cyrus M., Hashemi J., 2011, *Improving CO2/CH4 Adsorptive Selectivity of Carbon Nanotubes by Functionalization with Nitrogen-Containing Groups*, Chemical Engineering Research and Design **89**, 1669 - 1675.
[17] Usman, D., Siti , N., Murtala, M., Rahmat Mohsin, & Noor S., N. (2014). *Assessment of Porous carbons Derived From Sustainable Palm Solid Waste For Carbon Dioxide Capture.* Journal of Cleaner Production **71**, 148-157.
[18] Omar, R., Idris, A., Yunus R., Khalid K. and Isma M.I. (2011). *Characterization of Empty Fruit Bunch for Microwave-Assisted Pyrolysis.* Fuel, **90**, 1536-1544.
[19] Rodriguez-Reinoso F. and Sabio M. M. (2011). *Textural and Chemical Characterization Of Microporous Carbons.* Advances in Colloid and Interface Science. 76-77, 271-294.
[20] Hu, Z., Srinivasan, M.P., and Ni, Y. (2011). *Novel Activation Process for Preparing Highly Micropurous and Mesoporous Activated Carbons*. Carbons, **39**, 877-866.
[21] Rodriguez-Reinoso F. and Sabio M. M. (2011). *Textural and Chemical Characterization of Microporous Carbons*. Advances in Colloid and Interface Science. 76-77, 271-294.
[22] Hidayu, A. R. and N. Muda (2016). *"Preparation and Characterization of Impregnated Activated Carbon from Palm Kernel Shell and Coconut Shell for CO2 Capture*." Procedia Engineering **148**: 106-113.
[23] Tan, I. A., Abdullah, M. O., Lim, L. L. P., & Yeo, T. H. C. (2017). *Surface Modification and Characterization of Coconut Shell-Based Activated Carbon Subjected to Acidic and Alkaline Treatments.* Journal of Applied Science & Process Engineering. 4(2).
[24] Aleksandra h., a., esentia, M. and Stewart, J S. (eds) 2010. Benchmarking worldwide CO2 saline aquifer injections. Working paper 2010/3. www.sccs.org.uk/ publications.html.
[25] Edmund, C. O., et al. (2014). *"Characterization of palm kernel shell for materials reinforcement and water treatment."* Journal of Chemical Engineering and Materials *Science* **5**(1): 1-6.
[26] Yang, H. Y., Yan, R., Chen, H., Lee, D. H., & Zheng, C. (2007*). Characteristics of hemicellulose, cellulose and lignin pyrolysis.* Fuel. **86**(12-13), 1781-1788.
[27] Yueping, Q., Yaru, W., Xiaobin, Y.,Wei, L. and Wei, L. (2012). *Experimental Study on Dynamic Gas Adsorption.* International Journal of Mining Science and Technology, **22**, 763–767.
[28] Hidayu, A. R. and N. Muda (2017). "*Impregnated Palm Kernel Shell Activated Carbon for CO2 Adsorption by Pressure Swing Adsorption*." Indian Journal of Science and Technology **10**(2).
[29] Hossain M.A., Ngo H.H. and Guo W. (2013). *Introductory of Microsoft Excel. SOLVER Function Spreadsheet Method for Isotherm and Kinetics Modelling of Metals Biosorption in Water and Wastewater.* Journal of Water Sustainability, **3(4),** 223–237.

ACKNOWLEDGEMENT

The authors would like to thank to the Sustainable Waste to Wealth Program of UTM-MPRC Institute for Oil and Gas (IFOG), Universiti Teknologi Malaysia for technical support provided as well as technical staff involved