CHEMICAL ENGINEERING TRANSACTIONS
VOL. 61, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors:Petar SVarbanov, Rongxin Su, Hon Loong Lam, Xia Liu, Jiří J Klemeš

ISBN978-88-95608-51-8; **ISSN** 2283-9216
DOI: 10.3303/CET1761206

Methane Adsorption on KOH Microwave Treated Porous Carbon from Sustainable Coconut Solid Waste Material

Umar S. Hayatu[a,c], Noor S. Nasri[a,*], Husna M. Zain[a,b], Abdulrasheed Abdulrahman[a,d], Norhana M. Rashid[a]

[a]Sustainable Waste-To-Wealth Program, UTM-MPRC Institute for Oil and Gas, Resource Sustainability Research Alliance , Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Department of Energy Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia
[c]Department of Chemical Engineering Technology, School of Engineering Technology, Federal Polytechnic P.M.B 35 Mubi Adamawa State, Nigeria.
[d]Chemical Engineering Department, Abubakar Tafawa Balewa University, Tafawa Balewa Way, P.M.B 0248 Bauchi, Bauchi state, Nigeria.
noorshaw@utm.my

The shorter driving range is the challenge of compressed natural gas (CNG) as a vehicular fuel. In this study, adsorbent is prepared from coconut shells using KOH microwave activation to overcome the challenge of CNG storage system. The CNG storage system has some disadvantages which include high-pressure operation with less safety guard, and heavy storage cylinders. The adsorbent is used as a potential Sorbent for methane (CH_4) storage at different pressures. The coconut shell was carbonized from ambient temperature to 700 ± 20 ^oC at 10^oC min^{-1} heating rate with 1 L min^{-1} N_2 flow rate. The carbonization temperature of the precursor was determined using thermo-gravimetric and derivative thermogravimetric (TG/DTG) analysis. The activation was achieved with well modified microwave equipment operated at 500W and 5 minutes. The CH_4 adsorption characteristics were conducted using volumetric adsorption equipment at an ambient temperature and pressures of 4, 5 and 7 bar. The CH_4 uptake achieved at 4, 5 and 7 bar are 2.9707, 3.0559 and 3.6685 mmol g^{-1}. The experimental data simulated using two common adsorption models: Langmuir and Freundlich. The experimental data was also evaluated using the common adsorption kinetic namely pseudo-first order, pseudo-second, order kinetics and Elovich. For the three initial pressures of 4, 5 and 7 bar, CH_4 adsorption show more fits to pseudo-second order with $R^2 > 0.967$, $R^2 > 0.967$ and $R^2 > 0.960$. The results reveal that coconut shell is a viable and sustainable material for synthesizing of the adsorbents for methane adsorption.

1. Introduction

Instability of selling prices of diesel and gasoline at global market coupled with its greenhouse gases (GHGs) emissions has influenced people's interest towards sourcing alternative fuel (Beckner and Dailly, 2015). Natural gas (NG) is a fossil fuel, predominantly constituted with methane (Nsaful *et al.,* 2015). NG predicted as a future promising fuel and a strong candidate for replacement of coal and oil in many energy services due to its cleanest burning characteristics (Chong *et al.,* 2016). However, application of methane as a mobile fuel is minimal, because at normal temperature and pressure (NTP) the gas has low energy density that contributed difficulties to its storage, in order to achieve a longer driving range (Blanco *et al.,* 2016). Compression and liquefaction are conventional methods used to improve the fuel energy density for several applications. But they have been engulfed with some disadvantages such as requiring high pressure and cryogenic conditions respectively. Adsorbed natural gas (ANG) technology is a proposed alternative for CNG and LNG storage system, in which the gas is stored on the surface of carbonaceous materials through adsorption at relatively lower pressure than CNG and ambient temperature (Liu *et al.,* 2014).
Various methods reported for the de-pollution of environments such as neutralization, precipitation, adsorption and filtration (Bilal *et al.,* 2014). Adsorption is reported as the most reliable at the current situation, due to its

Please cite this article as: Hayatu U.S., Nasri N.S., Zain H.M., Abdulrahman A., Rashid N.M., 2017, Methane adsorption on koh microwave treated porous carbon from sustainable coconut solid waste material, Chemical Engineering Transactions, 61, 1249-1254
DOI:10.3303/CET1761206

enormous advantages such as easy handling, low cost and high efficiency (Manzoor *et al.,* 2013). In a general perspective, conversion of non-living wastes into activated carbon for mitigation of waste or environmental pollution is a very good option (Gupta and Balomajumder, 2015). The readily available agro-wastes in Malaysia for the production of activated carbon includes coconut shells (Mohammed et al., 2015), palm kernel shells (Hamza et al., 2015), rice husk, Kenaf, nut shells, tobacco stems and sugarcane bagasse (Mohd Din et al., 2009).

The coconut was selected for this research work due to its availability and impact on environmental pollution in this region. It is estimated that in Malaysia about 142,000 hectares of land for coconut plantation (Mohd Din et al., 2009). A lot of solid waste (shells) generated annually (Rout et al., 2016). Therefore, channeling the wastes for adsorption application is compulsory due to the current environmental problem (Igbal et al., 2016). Zeolites and commercial activated carbon are very popular in adsorption applications, but the process is expensive. However, activated carbons can be derived from readily available agricultural solid waste with an easier tailoring it textural and surface properties (Labus et al., 2014). Thus, there is an increase in demand for readily available adsorbent, less expensive for methane adsorption, particularly if the substrate is derived from waste materials. Conversion of coconut shells into activated carbon (waste - to - wealth) which can be used as an adsorbent for CH_4 could add value to this agricultural waste, help to reduce the cost of its disposal, and provide sustainable, reliable and cheap activated carbon that can serve the same purpose as the expensive commercial porous carbons.

Adsorption kinetic and isotherm models describe the behavior of absorbent and adsorbent towards their interaction and understanding of their adsorption process (Monemtabaryet al., 2013). Langmuir and Freundlich isotherm models have been used to study the interaction behaviors between adsorbent and adsorbent in this study. This study was conducted to investigate the adsorption potentials of methane on microwave treated coconut shell porous carbon under different conditions of initial pressures.

In this research work a suitable and an inexpensive porous carbon has been synthesized from a readily available agro-waste material (coconut shell). The aim focused on improving the volumetric energy density of the ANG storage system, in order to reduce the dependency on solid and liquid form of fuel. In addition to produce adsorbent from renewable waste material with reduced cost to the end users and mitigate the environmental negative impact. The novelty of this research work established on the adsorbent synthesis method and the precursor used. Most research conducted on coconut shells are on waste water purification and gas separation. To the best of our knowledge adsorption of CH_4 on coconut shells based adsorbent prepared using two-step activation has not been fully exploited.

2. Experimental

2.1 Activated Carbon Synthesis and CH4 Adsorption Application

Coconut shells were purchased from Johor, Johor State, Malaysia. The obtained coconut shells were washed with tap water for several times to remove the adhered particles and dirt attached to its surface, then dry under the sun. Further, using an electric furnace at 105^{o}C until constant weight was maintained. Prior to the above process, the precursor was tested for its thermal degradation using thermo-gravimetric (TGA) and derivatives thermo-gravimetric (DTGA). This was to determine its carbonization temperature, decomposition temperature of its components. The resulting materials were carbonized from ambient to 720±20^{o}C at a heating rate of10^{o}C min^{-1} under a flow of N_2 at 1 L min^{-1} for 2 h. The resulting char was ground and sieved to a particle size of 0.425mm - 0.841 mm, then chemically treated with KOH at 1.5:1 (KOH: char) weight ratio. For the activation, 30g of char was charged into a modified microwave (samsung ME0113M model) operated at 500 W for 5 min. The activated carbon was cooled and washed with 0.1 M then with deionized water to obtain neutrality state. The adsorption of CH_4 initiated using the adopted procedure elsewhere (Nasri et al., 2014).

2.2 Adsorption Isotherm Models

Adsorption isotherms models help in describing the interaction between adsorbent and adsorbate to give a comprehensive understanding of their nature of the interaction (Monemtabary*et al*., 2013). For the analysis of this experimental data, two common adsorption isotherm models were used. The models are: Langmuir equation Eq (1), and Freundlich equation Eq (2).

$$\frac{p}{q} = \frac{p}{q_m} + \frac{1}{bq_m} \tag{1}$$

$$\ln q_e = \ln k_f + (1/n) \ln p \tag{2}$$

Where p is the bulk pressure of CH_4 at the gas phase, b and q_m are Freudlich adsorption constant, q (mmol/g) is the adsorption capacity with respect to time, q_e (mmol g^{-1}) is the adsorption capacity at equilibrium position, k_f and n are Langmuir constant.

2.3 Adsorption Kinetics Models

The three common kinetic models used for this research work are as shown in Eq (3), Eq (4) and Eq (5). This kinetics model evaluates the mechanism and effectiveness of the adsorption process as stated by (Delavar et al., 2012).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} - \frac{t}{q_e} \tag{4}$$

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \tag{5}$$

Where q_t (mmol g^{-1}) is the adsorption capacity with respect to time, t is time taken for the methane adsorption (mins.), q_e (mmol g^{-1}) is the adsorption capacity at equilibrium position,k_1 is the pseudo-1st order rate constant (min^{-1}), k_2 is the pseudo-2nd order rate constant (g mg^{-1} min^{-1}), a is the initial adsorption rate (mg g^{-1} min^{-1}), b is the energy for chemisorption and surface coverage (g mg^{-1}).

2.4 Model Validity and Fitting

The models fitting to the experimental data measured using Eq (6) known as root-mean-square deviation (RMSD) and Eq (7) known as coefficient of determination (R^2).

$$RMSD = \left[\frac{1}{n}\sum\left(q_{\exp} - q_p\right)^2\right]^{1/2} \tag{6}$$

$$R^2 = 1 - \frac{\sum_{n=1}^{1}\left(q_{\exp} - q_p\right)^2}{\sum_{n=1}^{1}\left(q_{\exp} - \bar{q}_p\right)^2} \tag{7}$$

Where RMSD is root-mean-square deviation, R^2 is the coefficient of determination, q_{exp} (mmol g^{-1}) is the experimental adsorption capacity, q_p (mmol g^{-1}) is the predicted adsorption capacity, $\bar{q}_p$ (mmol g^{-1}) is an average predicted adsorption capacity.

3. Results and Discussion

3.1 Thermal Degradation of Coconut shells

Figure1 shows thermo-gravimetric (TGA) and derivatives thermo-gravimetric (DTGA) depicted the correlation between weight loss and temperature. The first decomposition of 6 % was observed between ambient to 160 ^oC which occurs due to moisture evaporation. Decomposition of cellulose, hemicelluloses and lignin occur between 250 ^oC to 700 ^oC (Slopiecka et al., 2012) which leads to weight loss of around 72 %.Further, a negligible decomposition occurs, indicating the presence of fixed carbon (Hamza et al., 2015. From the curve, it was found that the suitable temperature of pyrolysis of coconut shell is between 550 to 700 ^oC.

3.2 Methane Adsorption Performance

Comparison of methane adsorption over three different initial pressures of 4, 5 and 7 bar were investigated. As shown in Figure 2, the impact of pressure on the adsorption is stronger in the higher-pressure region. The equilibrium methane adsorption capacity value is expressed in millimoles (mmol) of methane to the weight of adsorbent. In this work, the high uptake is in strong agreement and dependent on the higher initial pressure. The adsorption uptake over an adsorbent operated at 7 bar is significantly higher (3.6685 mmol g^{-1}) than that operated at 4bar and 5 bar (2.9707 and 3.0559 mmol g^{-1}).

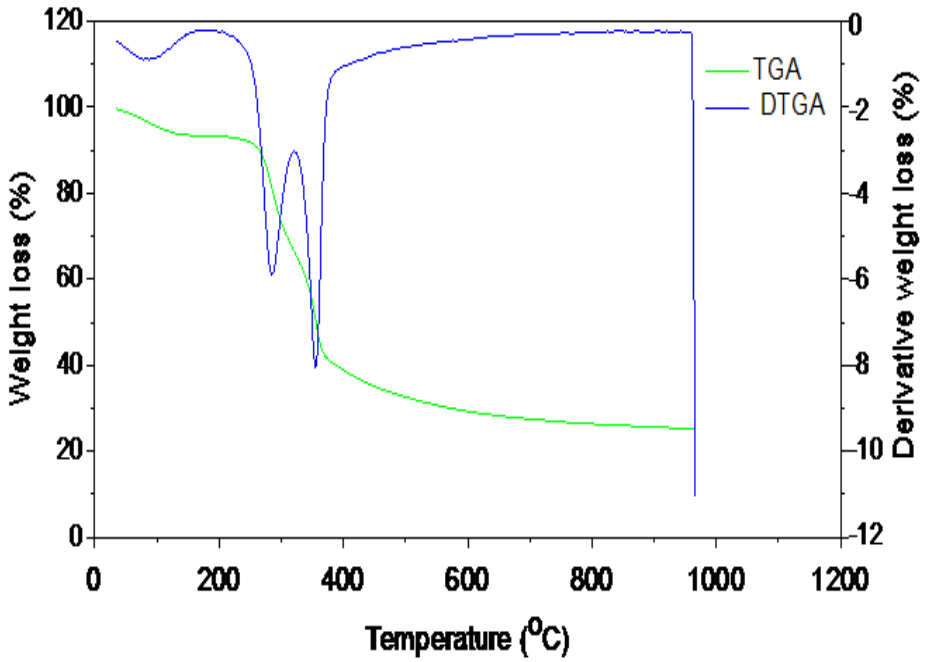

Figure1:Thermo-gravimetric (TGA) and derivatives thermo-gravimetric (DTGA) curves

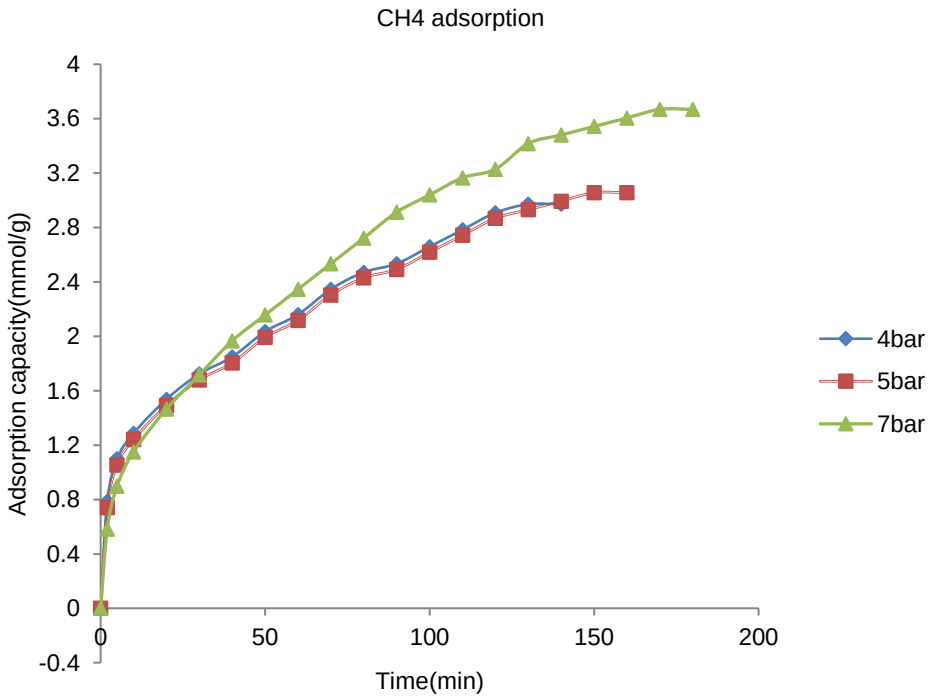

Figure2: Methane adsorption curve at different pressures

3.3 Adsorption Isotherms

The data obtained from this experiment using the models of adsorption equilibrium equations were displayed in Table 1. These equations were used to determine the affinity, properties and mechanism of the sorbent used towards the gas molecules. The data achieved in this experiment have been built-in into the equations to

determine their activities. Linearized graphs were plotted using the isotherm equations to determine the constant parameters including K_F, n, q_e, q_m and R^2 which obtained and shown in Table 1. The adsorption isotherms used in this study was applied to correlate the interaction between the adsorbate and adsorbent. Both the freudlich and Langmuir models indicated good fits to all the experimental data by displaying low root mean square deviation (RSMD) and higher value of n of greater than one. The models displayed favorable values of R^2 at all the three initial pressures of 4, 5 and 7 bar. The value of n>1 for all the adsorption models, this indicates the favorability condition of the adsorption processes. Both of the adsorption models generate low values of RSMD (0.0285 and 0.034) respectively. This shows how fitness to the adsorption data. Freudlich shows more fitness due to the possession of lower RSMD (Hamza et al., 2015).

3.4 Adsorption Kinetics

Kinetic equations namely pseudo-first order, pseudo- second order and Elovich were used for investigation of the mechanism and adsorption rate for the process. The kinetic equations, parameters and their values obtained at the three initial ranges of the pressures were shown in Table1. Table1 summarized the constant values for each adsorption kinetic and models and also shows the fitness of each towards the adsorption process. Pseudo-second order kinetic demonstrates more suitability on the adsorption process followed by pseudo-first order then Elovich demonstrates non-suitability. The amount of moles of methane adsorbed depends on the charged volume of initial pressure, while practically independent of its flowrate. The predicted or calculated methane uptake using the adsorption kinetics; pseudo-first order, pseudo-second order and Elovich for all the initial pressures were shown in Table1. The calculated values for all the initial pressures are higher than the experimental values.

Table 1: Pseudo-first, Pseudo-second Kinetics, freundlich and langmuir isotherm and fitting parameters for the adsorption of CH_4on porous carbons

Kinetics/Isotherms	Parameters	4bar	5bar	7bar
Pseudo-First-Order	R^2	0.911	0.841	0.944
	q_e(calc)		3.2479	3.8806
	K_1	2.6406	0.027	0.021
Pseudo-second		0.023		
Order	R^2		0.967	0.960
	q_e(calc)	0.967	3.2895	4.1332
	K_1	3.1547	0.0149	0.0078
Elovich		0.01882		
	R^2		0.932	0.931
	a	0.933	1.7762	0.3988
	b	0.68184	0.3111	1.3106
	q_e(exp)	1.86572	3.0559	3.6685
Freudlich		2.9707		
	n			2.5641
	K_f			1.6905
	R^2			0.921
	RSMD			0.0285
Langmuir				
	q_m			5.2083
	K_L			0.3168
	R^2			0.883
	RSMD			0.034

4. Conclusions

The study investigates both the experimental and modeling of CH_4 adsorption study on KOH microwave treated porous carbon. The CH_4 adsorption study was investigated using static volumetric equipment and method. The fitness and interaction between the adsorbent and adsorbate were evaluated using the three common kinetics and the common adsorption isotherm models. The amount of CH_4 adsorption uptake increases with increase in pressure. In all the initial pressures, the uptake is faster at initial time, then decrease with increase in contact time.

Acknowledgments

The authors appreciate and thank the financial support and contribution provided by the Ministry of Higher Education Malaysia and Universiti Teknologi Malaysia through the Research University Grant Q.J130000.2546.13H94 and Q.J130000.2509.10H89. Special an appreciation to the Sustainable Waste-To-Wealth Program of UTM-MPRC Institute for Oil and Gas, Universiti Teknologi Malaysia to provide technical supports and its technical service grant Q.J090401.23C9.01D08.

References

Beckner M., Dailly A., 2015, Adsorbed methane storage for vehicular applications, Applied Energy, 149, 69–74.

Bilal N., Ali S., Iqbal M, 2014, Application of advanced oxidations processes for the treatments of textile effluents, Asian J. Chem. 26, 1882–1886.

Blanco A.A.G., Vallone A.F., Korili S.A., Gil A., Sapag K., 2016, A comparative study of several microporous materials to store methane by adsorption, Microporous and Mesoporous Materials, 224, 323-331.

Chong Z. R., Yang S. H. B., Babu P., Linga P., Li X., 2016, Review of natural gas hydrates as an energy resource: Prospects and challenges, Applied energy,162, 1633-1652.

Delavar M., Ghoreyshi A.A., Jahanshahi M., Khalili S., Nabian N., 2012,Equilibria and kinetics of natural gas adsorption on multi-walled carbon nanotube material, RSC Advances, 2, 4490–4497.

Gupta A., Balomajumder C., 2015, Simultaneous adsorption of Cr (VI) and phenol onto tea waste biomass from binary mixture: Multicomponent adsorption, thermodynamic and kinetic study, J. Environ. Chem. Eng. 3, 785–796.

Hamza U.D., Nasri N.S., Amin N.S., Mohammed J., HusnaM. Zain.,2015. Characteristics of oil palm shell biochar and activated carbon at different carbonization times, Desalination and Water Treatment, 1, 1-8.

Hamza U.D., Nasri N.S., Amin N.S., Mohammed J., Husna M. Zain.,2015,CO2 Adsorption Equilibria on a Hybrid Palm Shell-PEEK Porous Carbons,Chemical Engineering Transactions,45, 301-306.

Iqbal M., Iqbal N., Bhatti I.A., Ahmad N., Zahid M., 2016, Response surface methodology application in optimization of cadmium adsorption by shoe waste: A good option of waste mitigation by waste, Ecological Engineering, 88, 265–275.

Labus K., Gryglewicz S., Machnikowski J.,2014, Granular KOH-activated carbons from coal-based cokes and their CO_2 adsorption capacity, Fuel,118, 9–15.

Liu B., WangW., Wang N., Au C. T., 2014, Preparation of activated carbon with high surface area for high-capacity methane storage, Journal of Energy Chemistry,23, 662–668.

Manzoor Q., Nadeem R., Iqbal M., Saeed R., Ansari T.M., 2013, Organic acids pre-treatment effect on Rosa bourbonia phyto-biomass for removal of Pb (II) and Cu(II) from aqueous media, Bioresource Technology 132, 446–452.

Mohd Din A.T., Hameed B. H., Abdul L., Ahmad A. L., 2009, Batch adsorption of phenol onto physiochemical-activated coconut shell, Journal of Hazardous Materials161, 1522–1529.

Mohammed J., Nasri N.S., Zaini M. A. A., Hamza U. D., Ani F.N., 2015, Adsorption of benzene and toluene onto KOH activated coconut shell based carbon treated with NH_3,International Biodeterioration & Biodegradation, 102, 245-255.

Monemtabary S., Niasar S. M., Mohsen J. M., Ghoreyshi A.A., 2013,Equilibrium and Thermodynamic Studies of Methane Adsorption on Multi-Walled Carbon Nanotube,Iranica J. Energy & Environ., 4 (1), 17-23

Nasri N.S., Hamza D.U., Ismail S.N., Ahmed M.M., Moshen R., 2014, Assessment of porous carbons derived from sustainable palm solid waste for carbon dioxide capture. Journal of Cleaner Prodution, 71, 148-157.

Nsaful F., Collard F., Carrier M., Görgens J. F., Knoetze J. H., 2015,Lignocellulose pyrolysis with condensable volatiles quantification by thermogravimetric analysis. Thermal desorption/gas chromatography–mass spectrometry method, Journal of Analytical and Applied Pyrolysis, 116, 86–95.