Comparative Study of Methane Adsorption on Activated Carbon and Metal Organic Frameworks

Atsadawuth Siangsai[a], Narumon Kumpoomee[a], Pramoch Rangsunvigit[a], Boonyarach Kitiyanan*[a], Santi Kulprathipanja[b]

[a]The Petroleum and Petrochemical College, Chulalongkorn University, Patumwan, 10330 Bangkok, Thailand
[b]UOP, A Honeywell Company, Des Plaines, IL 60017, USA
boonyarach.k@chula.ac.th

This study compared the methane adsorption on activated carbon with and without the treatment with sulphuric acid (H_2SO_4) and potassium hydroxide (KOH) and metal organic frameworks (MOFs)–Basolite C300 and Basolite Z1200. In the experiment, methane gas was pressurized up to 500 psia and the temperature was set at 303 K. The results showed that, gravimetrically, Basolite C300 had the highest methane adsorption capacity of 8.95 mmol/g. The chemical treatments of activated carbon, both H_2SO_4 and KOH, resulted in the increase in the surface area and pore structure of the activated carbon. Moreover, based on a 70 L storage tank, the addition of H_2SO_4 treated-activated carbon increased the amount of methane gas in the tank up to 51.7%.

1. Introduction

The consumption of natural gas as a vehicular fuel has continuously increased due to cheaper cost than other fossil fuels, and the compatibility in the existing internal combustion engine. It can be combusted efficiently and produces less air pollutants than petroleum-based fuel (Yulong et al., 2008). However, it is difficult to store natural gas in a high density since methane is a small molecule. Currently, natural gas can be stored in three different techniques, which are liquefied natural gas (LNG), compressed natural gas (CNG), and adsorbed natural gas (ANG). LNG requires a special insulated vessel and high cost of liquefaction, while CNG requires high-pressure (around 3000 psi) to compress natural gas into a storage container (Inomata et al., 2002). ANG offers a promising and efficient technique to store natural gas by using porous materials as an adsorbent. The advantage of this technique is low operating condition, at a relative low pressure and ambient temperature. However, the major problem of ANG process is the development and the material that is suitable for storing methane (Lozano-Castelló et al., 2002a and 2002b).

Many studies focused on the improvement of materials to be used for ANG, particularly carbon-based materials, which provide high adsorption capacity. Microporous activated carbon is the most attractive adsorbent for gas storageand others application. For examples, Natale et al. (2007) used activated carbon to remove Cd(II) from aqueous solution. Erto et al. (2013) used activated carbon for trichloroethylene adsorption. Rashidi et al. (2013) investigated the kinetics of carbon dioxide capture on activated carbon. Therefore, it is suitable to utilize the activated carbon as an ANG adsorbent due its high specific surface area and pore volume(Prauchner and Rodríguez-Reinoso 2008). In order to increase the adsorption capacity, the preparation of activated carbon is important due to the effectiveness of the porosity and surface area on methane adsorption (Bagheri and Abedi 2011). It has been suggested that the amount of methane uptake strongly depends on the physical characteristic of activated carbon such as surface area, micropore volume, and pore size distribution (Salehi et al., 2007).

This work focused on the improvement of activated carbon for methane adsorption by using sulfuric acid (H_2SO_4) and potassium hydroxide (KOH) for the treatment process. Moreover, The amount of methane
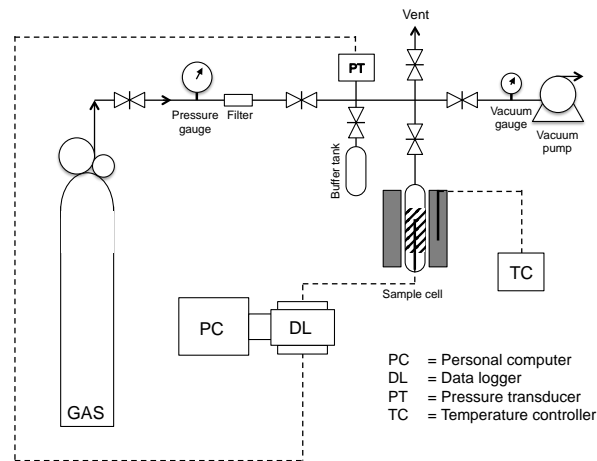
Figure 1: Schematic diagram of volumetric apparatus.

adsorption on the treated- and untreated-activated carbon was compared with the commercial metal organic frameworks (MOFs), including Basolite C300 and Basolite Z1200. The experiments were conducted at 303 K and pressure up to 500 psia by volumetric apparatus. In addition, the calculation of the amount of methane adsorption in a 70 L of CNG storage tank fully contained with the adsorbents was reported.

2. Experimental procedure

2.1 Materials preparation
Granular activated carbon (charcoal) purchased from Norit Americas Inc. was milled and sieved to 400-841 µm (20-40 mesh). For the activated carbon treatment, sulfuric acid (H_2SO_4, 98 %, Lab-Scan, Thailand) and potassium hydroxide (KOH, Lab-Scan, Thailand) were used. Approximately, 6.5 g of activated carbon were sonicated in 65 mL of 1 molar of acid or alkali solution for 45 min at 303 K. Then, the samples were washed adequately with deionized water until pH of filtered water was 7, and then dried at 393 K overnight in an oven. For MOFs, the samples were used as-received in the experiment.

2.2 Methane adsorption
The measurement of methane adsorption on the adsorbentswas performed by a volumetric apparatus as shown in Figure 1. This apparatus consists of a sample holder, a vacuum pump, and pressure transducer. High purity methane (99.999 %, Labgaz Thailand Co., Ltd.) was used in the adsorption study. In each experiment, approximately, 1 g of activated carbon was loaded intothesample cell. Before the methane adsorption, the activated carbon in the apparatus was degassed by a rotary vacuum pump. The temperature was controlled at 303 K along the experiment.

For the methane adsorption study, methane at the desired pressure was introduced from a high-pressure cylinder into the sample holder. The system was left for at least 20 min to allow the system to reach equilibrium. The system pressure was recorded via a pressure transducer. The amount of adsorbed methane by activated carbon samples was obtained from Eq(1):

$$n_{ad} = n_{ad-1} + \frac{P_i V_1}{ZRT_i} + \frac{P_{f-1}V_2}{ZRT_{f-1}} - \frac{P_f(V_1 + V_2)}{ZRT_f} \tag{1}$$

where;

n_{ad-1} = Amount of methane adsorption in previous stage (mol)
P_i = Initial pressure of methane before discharged to sample holder (psia)
P_f = Final pressure of methane gas after discharged to sample holder (psia)
P_{f-1} = Final pressure of methane gas after discharged to sample holder in the previous stage (psia)
T_i = Initial temperature of methane gas before discharged to sample holder (K)
T_f = Final temperature of methane gas after discharged to sample holder (K)
T_{f-1} = Final temperature of methane gas after discharged to sample holder in the previous stage (K)

V_1 = Volume of manifold without the sample holder (cm^3)
V_2 = Volume of sample holder (cm^3)
Z   = Compressibility factor of methane gas
R   = Gas constant, 82.0578 atm cm^3/mol K

2.3 Characterization of adsorbent

The surface morphology of activated carbonwas examined by field emission scanning electron microscope (FE-SEM, S-4800 Hitachi Corporation). The nitrogen (N_2) adsorption analysis of activated carbon was carried out by using Autosorp-1 MP gas sorption system (Quantachrome Corporation) to examine the surface area, total pore volume, and pore size distribution.

3. Results and discussion

3.1 Adsorbent characterizations

The physical specifications of the adsorbents were listed in Table 1. As shown in Table 1, it can be clearly seen that Basolite C300 shows the highest BET surface area and pore volumefollowed by Basolite Z1200, activated carbon, H_2SO_4 treated-AC, and KOH treated-AC, respectively. In the case of activated carbon treatment, there is a small increase in the surface area after the chemical treatment.In the H_2SO_4treatment, the acid solution possibly removes or eliminates inorganic matters and other impurities from the activated carbon leading to better accessibility of gas and increase the surface area and pore volume. The same effects with the H_2SO_4 treatment can also be observed with the KOH treatment.The results indicate that the physical characteristics of activated carbon, in particular, surface area and pore structure, were improved by the chemical treatment.

Table 1: Physical characteristic of adsorbents

Adsorbent	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)	Average pore diameter (Å)
Untreated-AC	899	0.48	0.50	22.1
KOH treated-AC	935	0.50	0.52	22.2
H_2SO_4 treated-AC	975	0.52	0.55	22.5
Basolite C300	2434	1.27	1.33	21.9
Basolite Z1200	1449	0.78	0.88	24.3

Figure 2 shows the surface morphology of all adsorbents. It can be seen from the figure that the activated carbonsamples(Figures 2b and 2c) after the chemical treatment are cleaner than that of the untreated-AC (Figure 2a). This result complies with the physical characteristics of the activated carbon in Table 1 that the chemical treatment can develop pores and surface of the activated carbon (Xiao et al., 2008).This effects is confirmed by Sricharoenchaikul et al. 2008, thatthe chemical treatment enlarges the surface area and porous structure of activated carbon. Figures 2d and 2e show the micrographs of Basolite C300 and Basolite Z1200, respectively. The shapes of both MOFs have geometric appearance due to the specific synthesis of MOFs (Park et al., 2006). The surface of Basolite Z1200 (Figure 2e) is rougher than that of Basolite C300 (Figure 2d), which could be covered by the incomplete synthetic materials.In addition, all sides of MOFs consist of the small pores that may result in the high surface area of MOFs as shown in Table 1.
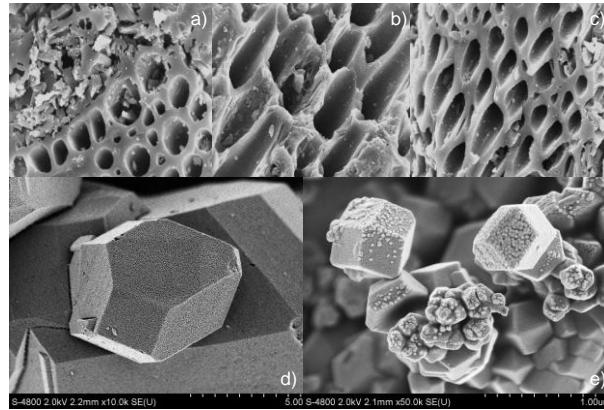
Figure 2: Micrographs of activated carbon: a) activated carbon, b) H₂SO₄ treated-AC, and c) KOH treated-AC at 2,000 magnifications, and MOFs: d) Basolite C300 and e) Basolite Z1200 at 10,000 and 50,000 magnifications.
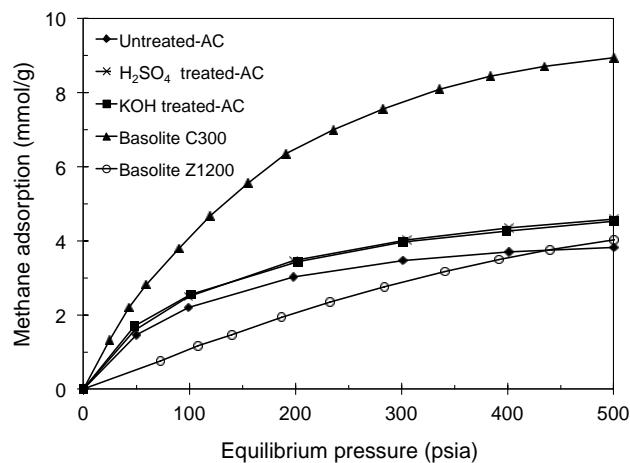
3.2 Methane adsorption

Figure 3: Methane adsorption isotherms of untreated-AC, H₂SO₄ treated-AC, KOH treated-AC, Basolite C300, and Basolite Z1200

Figure 3 shows the methane adsorption isotherms of untreated-AC, H_2SO_4 treated-AC, KOH treated-AC, Basolite C300, and Basolite Z1200.It can be seen that increasing the pressure, the amount of adsorbed methane also increases, but the increase is not significant at the high pressure because of the saturation of adsorbent, especially for the treated- and untreated-activated carbon (Salehi et al., 2007). Furthermore, Basolite C300 exhibits the highest methane adsorption capacity followed by H_2SO_4 treated-AC, KOH treated-AC, Basolite Z1200, and untreated-AC at 313 K and 500 psia. The methane adsorption capacity and adsorption isotherms of the adsorbents are significantly affected by the physical characteristics of each adsorbent as shown in Table 1. In other words, Basolite C300 has the highest surface area and pore volume, resulting in the highest methane adsorption capacity at the same condition. Though Basolite Z1200 has a higher surface area and pore volume than that of treated-ACs, the amount of methane adosprion is lower because the pore width of Basolite Z1200 is larger than the optimum pore size for methane storage (11.4 Å) as shown in Figure 4 (Matranga et al., 1992). Moreover, in Figure 3, the kinetics of methane adsorption on Basolite Z1200 is slower than of the other adsorbents due to its large pore width. This results can imply that the methane adsorption isotherm of Basolite Z1200 may not reach the equilibrium at the experimental pressure (500 psia).
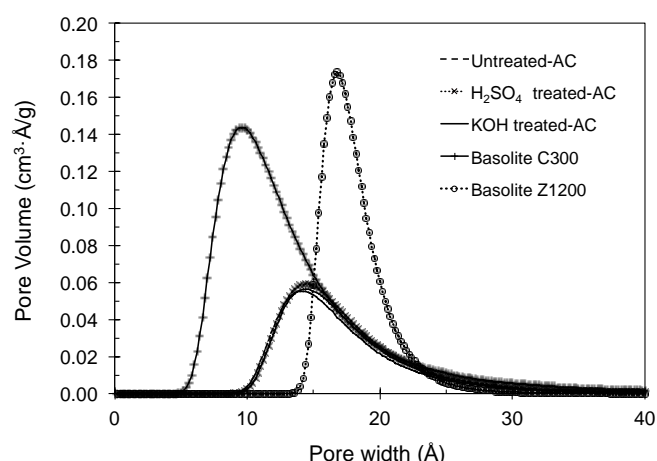
Figure 4: Pore size distribution of untreated-AC, H_2SO_4 treated-AC, KOH treated-AC, Basolite C300, and Basolite Z1200.

Table 2: Methane uptake on the adsorbents at 303 K and 500 psia in a 70 L storage tank

Adsorbent	Apparent density (g/cm³)	Gravimetric amount of methane adsorption (mmol/g)	Volumetric amount of methane adsorption (V/V)	Methane uptake (kg)	Percentage (%)
Empty	-	-	-	1.63	-
Untreatd-AC	0.48	3.82	44.1	2.06	+26.3
KOH treated-AC	0.48	4.51	52.1	2.43	+49.1
H_2SO_4 treated-AC	0.48	4.59	53.0	2.47	+51.7
Basolite C300	0.23	8.95	49.5	2.31	+41.8
Basolite Z1200	0.29	4.02	28.0	1.31	-19.7

Table 2 presents the methane uptake on the adsorbents at 303 K and 500 psia in a 70 L storage tank.The results were theoretically calculated for storing methane gas in a 70 L tank with fully packed based on the apparent density.As seen from Table 2, a 70 L storage tank can accommodate only 1.63 kg of methane gas at 303 K and 500 psia. Moreover, H_2SO_4 treated-AC can store methane gas higher than the empty tank up to 51.7 % followed by KOH treated-AC, Basolite C300, and untreated-AC, respectively. Meanwhile, the amount of methane gas that can be stored in the tank filled with Basolite Z1200 is lower than the empty tank. From these results, it should be noted that at the same volume of the adsorbents, the apparent density of the adsorbents is one key factor for storing methane aside from the surface area, pore volume, and pore width of the adsorbents.

4. Conclusion

This work investigated the methane adsorption capacity of untreated-AC, H_2SO_4 treated-AC, and KOH treated-AC compared to Basolite C300 and Basolite Z1200 at 303 K and 500 psia. The results showed that Basolite C300 exhibited the highest methane adsorption capacity of 8.95 mmol/g due to its highest surface area, pore volume, and suitable pore width. The use of H_2SO_4 and KOH resulted in the increase in the surface area and pore volume of activated carbon by removing inorganic contents or dust, which covered the surface and blocked the pore and of activated carbon. In addition, the kinetics of methane adsorption on the adsorbents is strongly affected by the pore width. Basolite Z1200 showed a slow kinetics

rate of methane adsorption due to its high average pore width. Based on a 70 L storage tank, the addition of the H_2SO_4 treated-AC could increase the amount of methane gas in the tank up to 51.7`%. However, Basolite Z1200 has lower methane uptake than the empty tank.

Acknowledgement

References

Bagheri N., Abedi J., 2011, Adsorption of methane on corn corbs based activated carbon, Chemical Engineering Research and Design, 89, 2038-2043.

Inomata K., Kanazawa K., Urabe Y., Hosono H., Araki T., 2002, Natural gas storage in activated carbon pellets without a binder, Carbon, 40, 87-93.

Lozano-Castelló D., Cazorla-Amorós D., Linares-Solano A., Quinn D.F. 2002a, Carbon monoliths for methane storage: Influence of binder, Carbon, 40, 2817-2825.

Lozano-Castelló D., Alcañiz-Monge J., Casa-Lillo M.A., Cazorla-Amorós D., Linares-Solano A, 2002b, Advances in study of methane storage in porous carbonaceous materials, Fuel, 81, 1777-1803.

Natale F.Di., Erto A., Lancia A., 2007, Cd(II) removal from aqueous solutions by adsorption onto activated carbon, Chemical Engineering Transactions, 11, 689-694.

Erto A., Lancia A., Musmarra D., 2013, Fixed-bed adsorption of trichloroethylene onto activated carbon, Chemical Engineering Transactions, 32, 1969-1974, DOI: 10.3303/CET1332329.

Rashidi N.A., Yusup S., Loong L.H., 2013, Kinetic studies on carbon dioxide capture using activated carbon, Chemical Engineering Transactions, 35, 361-366, DOI: 10.3303/CET1335060.

Matranga K.R., Myers A.L., Glandt E.D., 1992, Storage of natural gas by adsorption on activated carbon, Chemical Engineering Science, 47, 1569-1579.

Park K.S., Ni Z., Côté A.P., Choi J.Y., Huang R., Uribe-Romo F.J., Chae H.K., OKeeffe M., Yaghi O.M., 2006, Exceptional chemical and thermal stability of zeoliticimidazolate frameworks, Proceeding of the National Academy of Science of the United States of America, 103, 10186-10191.

Prauchner M.J., Rodríguez-Reinoso F., 2008, Preparation of granular activated carbons for adsorption of natural gas, Microporous and Mesoporous Materials, 109, 581-584.

Salehi E., Taghikhani V., Ghotbi C., Lay E.N., Shojaei A., 2007, Theoretical and experimental study on the adsorption and desorption of methane by granular activated carbon at 25 °C, Journal of Natural Gas Chemistry, 16, 415-422.

Sricharoenchaikul V., Pechyen C., Aht-Ong D., Atong D., 2007, Preparation and characterization of activated carbon from the pyrolysis of physic nut (JatrophaCucas L.), Energy and Fuels, 22, 31-37.

Xiao D.D., Xin M.L., Guofeng Z., Ling Q., Ke Q., Zi F.Y., 2008, Treatment of activated carbon for methane storage, Asia-Pacific Journal of Chemical Engineer, 3, 292-297.

Yulong W., Fei W., Guohua L., Guoqing N., Mingde Y., 2008, Methane storage in multi-walled carbon nanotubes at the quanty of 80 g, Materials Research Bulletin, 43, 1431-1439.