

CHAPTER III METHODOLOGY

3.1 Materials

3.1.1 Adsorbents

- Coconut Shell Granular Activated Carbon
- Coconut Shell Powder Activated Carbon
- Eucalyptus Powder Activated Carbon
- Calgon
- Copper Benzene-1,3,3-Tricarboxylate (Basolite C300)
- 2-Methylimidazole Zinc (Basolite Z1200)

3.1.2 Gases for Adsorption Experiment

- Ultra High Purity Grade Methane (99.993% purity)
- High Purity Grade Helium

3.2 Adsorbents Preparation Procedures

3.2.1 Granular Activated Carbons

The granular activated carbon in this study consists of Coconut Shell Activated Carbon and Calgon. The Coconut Shell Granular Activated Carbon was obtained from C. Gigantic Co., Ltd. and Calgon was purchased from S.M. Chemical Supplies Co., Ltd. The Granular Activated Carbons were ground and sieved with the 20 and 40 mesh sieves. Then they were degassed at the temperature of 373 K in the oven for 24 hours. After degassing, they were put into the sample cell and weighed. The sample cell was then placed into the volumetric apparatus as shown in Figure 3.2.

3.2.2 Powder Activated Carbons

The Coconut Shell and Eucalyptus Powder Activated Carbons were obtained from C. Gigantic Co., Ltd.. They were degassed at the temperature of 373 K in the oven for 24 hours. After degassing, they were put into the sample cell and weighed. The sample cell was then placed into the volumetric apparatus as shown in Figure 3.2.

3.2.3 Metal Organic Frameworks

Basolite C300 and Z1200 were purchased from S.M. chemical Supplies Co., LTD.. They were degassed at the temperature of 373 K in the oven for 24 hours. After degassing, they were put into the sample cell and weighed. The sample cell was then placed into the volumetric apparatus as shown in Figure 3.2.

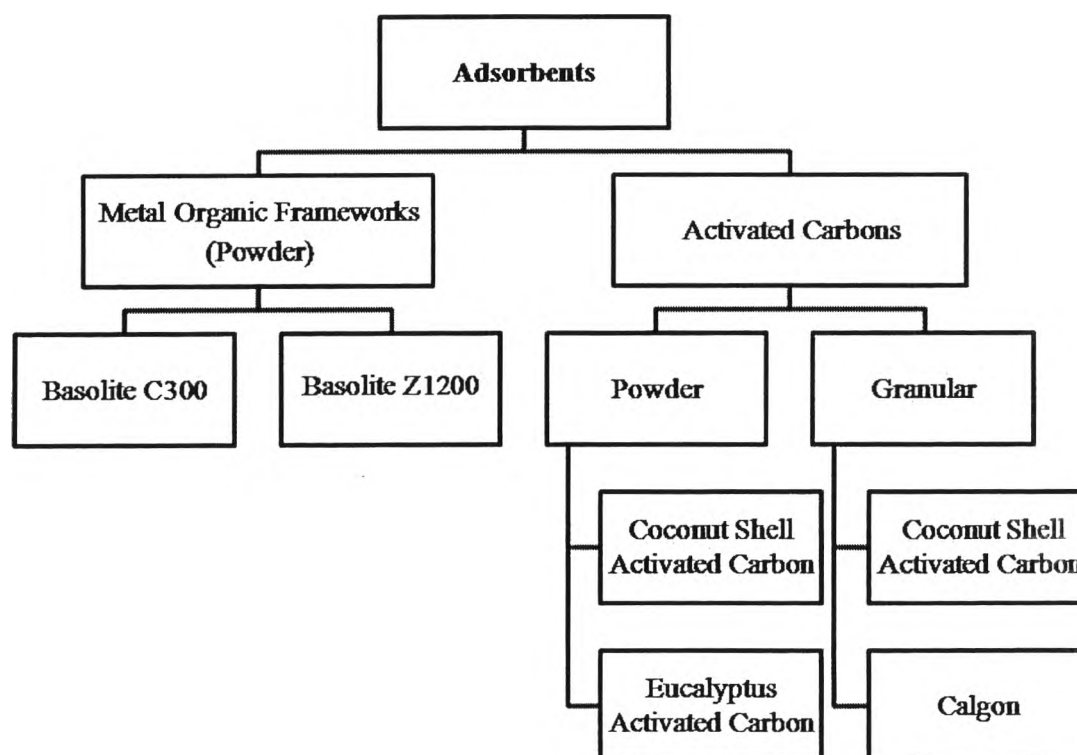


Figure 3.1 The adsorbents were used in this experiment.

3.3 Adsorbent Characterization Technique

The physical characteristic of adsorbents was carried out by using the surface area analyzer (Autosorb-1 MP).

- S_{BET} (BET surface area) was obtained from multiple point BET (Brunauer-Emmett-Teller) method which was derived from BET equation.

$$\frac{1}{W \left(\left(P_0 / P \right) - 1 \right)} = \frac{1}{W_m C} + \frac{C - 1}{W_m C} \left(\frac{P}{P_0} \right)$$

- Where :
- W = Weight of gas adsorbed at a relative pressure (P/P₀)
 - W_m = Weight of adsorbate forming a monolayer of surface coverage
 - C = A BET constant related to the energy of adsorption in the first adsorbed layer; its value is an indication of the magnitude of the adsorbent/adsorbate interactions.

- Micropores volume (V_{DR}) was obtained from DUBININ-RADUSHKEVICH (DR) method, which was calculated from the DR equation as followed.

$$V = V_0 \exp \left[- \left(\frac{A}{\beta E_0} \right)^2 \right]$$

- Where :
- V = Volume of gas adsorption
 - V₀ = Micropore volume
 - E₀ = Characteristic energy of adsorption
 - A = Free adsorption energy
 - β = Affinity coefficient

- Total pore volume was calculated from the amount of vapor adsorbed at a relative pressure close to unity, with the assumption that the pores were filled with liquid adsorbate.
- DA pore diameter was obtained DUBININ-ASTAKHOV (DA) method, which was calculated from the DA equation as followed.

$$W = W_0 \exp \left[- \left(\frac{-RT \ln P / P_0}{E} \right)^n \right]$$

Where : W = Weight of gas adsorbed at a relative pressure (P/P_0)

W_0 = Total weight of gas adsorbed

E = Characteristic energy

n = Non-integer value

In general, DA equation can fit adsorption data for heterogeneous micropore materials.

3.4 Adsorption Experiments

3.4.1 Volumetric Apparatus

The measurement of pure methane gas adsorption can be carried out by gravimetric method (Dreisbach *et al.*, 1998) or volumetric method (Salehi *et al.*, 2007). The volumetric apparatus was selected for this study. The schematic diagram of the volumetric apparatus is shown in Fig. 3.2. A high pressure and constant volume sample cell was made from stainless steel. Inside the reactor, a K-type thermocouple was placed to measure the temperature of gas. The pressure transducer was used to measure the pressure of the system ranging from 0 to 3,000 psig. A known amount of adsorbents was filled into sample cell. Then, the sample cell was connected to the volumetric apparatus. The pressures of gas were recorded before and after each gas expansion.

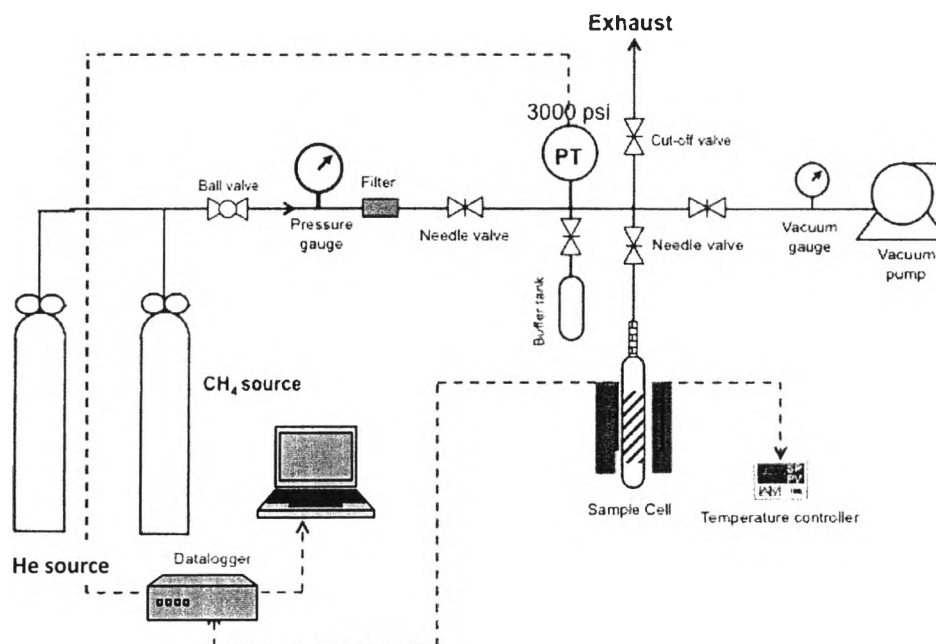


Figure 3.2 Schematic diagram of the volumetric apparatus.

3.4.2 Measurement of Methane Adsorption and Calculation

The pressure transducers must be calibrated for every adsorption experiment. The vacuum pressure of -15 psi was used as the reference pressure. With this pressure, the relative was set to zero under vacuum condition.

3.4.2.1 *Determination of the Sample Cell Volume Using Helium*

The volume of the sample cell was determined by helium expansion at 303 K, based on the assumption that no helium was adsorbed on the adsorbents. The pressures before and after each helium expansion were recorded.

To calculate the volume of instrument after helium expansion, V_2 , Ideal Gas Law was used as followed.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Where :

- P_1 = Pressure of helium before helium expansion
- V_1 = Volume of the system excluding volume of sample cell
- T_1 = Temperature before helium expansion
- P_2 = Pressure of helium after helium expansion
- V_2 = Total system volume
= $V_1 + V_{\text{sample cell}}$
- T_2 = Temperature after helium expansion

3.4.2.2 Determination of the Methane Adsorption Isotherm on Adsorbents

Determination of the methane adsorption isotherm was carried out at various constant temperatures; $T = 303, 308, \text{ and } 313 \text{ K}$; and pressure ranging from 0 to 900 psi. The vacuum the system is required to do at the early stage. Dimmer-heating source to heat up and control the temperature is turned on to get the temperature constant at the target $T = 303, 308, \text{ and } 313 \text{ K}$. During the experiment, the time to reach each equilibrium of methane adsorption was within 10 minutes. The methane pressures were recorded before and after each methane expansion.

The Ideal Gas Law and mole balance were also used for determining the amount of methane adsorbed on the adsorbents.

For the first point;

$$\frac{P_i V_1}{z_i R T_i} - \frac{P_f (V_1 + V_{\text{sample cell}})}{z_f R T_f} = n_{\text{ad}}$$

where

- n_{ad} = Amount of methane adsorbed in each adsorbent (moles)
- P_i = Pressure of methane before methane expansion (psi)
- P_f = Pressure of methane after methane expansion (psi)
- V_1 = Volume of the system excluding volume of sample cell (cm^3)
- $V_{\text{sample cell}}$ = Volume of sample cell (cm^3)

Z_i	=	Compressibility factor for methane uptake before methane expansion
Z_f	=	Compressibility factor for methane uptake after methane expansion
T_i	=	Temperature before methane expansion (K)
T_f	=	Temperature after methane expansion (K)
R	=	Gas constant
	=	8.314 J/mol.K

For subsequent points;

$$\frac{P_{in}V_1}{Z_{in}RT_{in}} - \frac{P_{fn-1}V_{\text{sample cell}}}{Z_{fn-1}RT_{fn-1}} - \frac{P_{fn}(V_1 + V_{\text{sample cell}})}{Z_{fn}RT_{fn}} + n_{ad(n-1)} = n_{ad(tot)}$$

where	$n_{ad(tot)}$	=	Total amount methane adsorbed on each adsorbent (moles)
	$n_{ad(n-1)}$	=	Amount methane adsorbed on each adsorbent at previous stage (moles)
	P_{in}	=	Pressure of methane before methane expansion at that stage (psi)
	P_{fn-1}	=	Pressure of methane after methane expansion at previous stage (psi)
	P_{fn}	=	Pressure of methane after methane expansion at that stage (psi)
	V_1	=	Volume of the system excluding volume of sample cell (cm ³)
	$V_{\text{sample cell}}$	=	Volume of sample cell (cm ³)
	Z_{in}	=	Compressibility factor for methane uptake before methane expansion at that stage
	Z_{fn-1}	=	Compressibility factor for methane uptake after methane expansion at previous stage
	Z_{fn}	=	Compressibility factor for methane uptake after methane expansion at that stage

- T_{in} = Temperature before methane expansion at that stage (K)
 T_{fn-1} = Temperature after methane expansion at previous stage (K)
 T_{fn} = Temperature after methane expansion at that stage (K)
R = Gas constant
= 8.314 J/mol.K