

CHAPTER III EXPERIMENTAL

3.1 Materials

- C Gigantic Carbon Co., Ltd. coconut shell
- C Gigantic Carbon Co., Ltd. eucalyptus
- Untreated activated carbon Calgon
- Untreated activated carbon Norit
- Ultra High Purity Grade methane (99.999% purity)
- High Purity Grade helium
- Potassium hydroxide KOH
- Hydrochloric acid HCl
- Nitric acid HNO₃
- Sulfuric acid H₂SO₄

3.2 Equipment

- Thermo-volumetric apparatus
- Surface area analyzer (SAA)
- Scanning electron microscope (SEM)

3.3 Methodology

3.3.1 Experimental Set Up

The thermo-volumetric apparatus is used to study the gas-solid interaction. The schematic diagram of the experimental set-up is shown in Figures 3.1.

- a) The set-up consists of a high pressure stainless reactor which holds the sample and part of stainless steel tube as a gas reservoir.

- b) The pressure transducer is used to measure pressure of the system for measuring in the range of 0 – 3,000 psig with 0.13% global error.
- c) The pressure regulator with 4,000 psig maximum is installed to control gas flow rate into the whole system.
- d) Inside the reactor, the K-type thermocouple is placed to measure temperature.

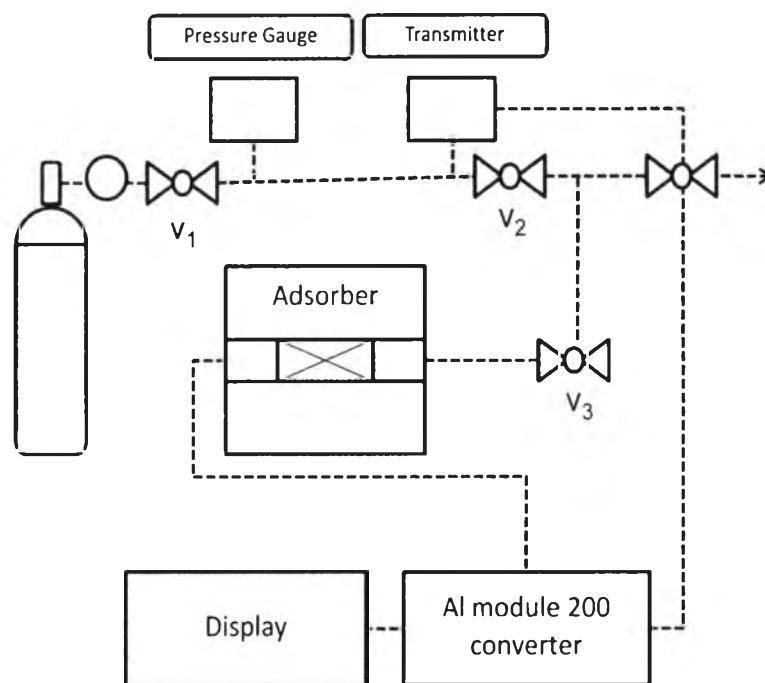


Figure 3.1 Schematic diagram of the experimental set-up.

3.3.2 Activated Carbon Modification

3.3.2.1 *Chemical Treatment*

- a) Soak 2 g of activated carbon into solution for 2 hours
 - ❖ 1g of KOH
 - ❖ 40 ml of 1M HCl
 - ❖ 40 ml of 1M HNO₃
 - ❖ 40 ml of 1M H₂SO₄.
- b) Filtrate the solution with whatman filter paper

- c) Neutralize treated activated carbon with distilled water until sample become neutral measured by universal indicator.
- d) Dry sample at 120°C over night

3.3.2.2 Hydrocarbon Treatment

- Mix 0.5 g of activated carbon with 0.025 g of n-decane before filling it into reactor

3.4 Measurement of Methane Adsorption and Calculation

The pressure transducers must be calibrated for each adsorption experiment. Atmospheric pressure was used as the reference pressure

3.4.1 Helium Expansion

The volume of the sample cylinder was determined by helium expansion at room temperature basis on the assumption that no helium adsorbed on activated carbon as shown in following steps.

- The reactor was placed into reactor holder.
- V_2 valve was closed when 500 psi of helium applied into the instrument.
- Open V_2 to allow helium to expand into the reactor.
- Measure helium pressure after expansion.

To calculate volume of instrument after helium expansion, V_2 , mole balance basis was used.

$$n_1 = n_2 - n_3$$

where n_1 = Mole of helium before open V_2 valve
 n_2 = Mole of helium after open V_2 valve
 n_3 = Mole of air in instrument

$$P_1V_1 = P_2V_2 - P_A V_2'$$

$$V_2' = V_2 - V_1$$

$$P_1V_1 = P_2V_2 - P_A V_2 + P_A V_1$$

$$V_2 = \frac{P_1V_1 - P_A V_1}{P_2 - P_A}$$

where P_1 = Pressure of helium before open V_2 valve
 V_1 = Volume of instrument between V_1 to V_2 valve
 P_2 = Pressure of helium after open V_2 valve
 V_2 = Total volume of instrument
 P_A = Atmospheric pressure

3.4.2 Methane Adsorption

3.4.2.1 Time Required to Reach Methane Adsorption Equilibrium

Methane adsorption experiment was done under 40°C temperature. About 0.5 g of a solid sample was placed into the reactor, which was placed into the testing unit afterwards. 700 psi pressure of methane was applied into reactor. Then the system was allowed to reach equilibrium for 3 hours. The pressure were recorded every minute.

The ideal gas law and mole balance are used for determining the amount methane adsorbed on activated carbon, n .

For the initial stage;

$$n_1 = n_2 - n_3$$

where n_1 = Mole of helium before open V_2 valve
 n_2 = Mole of helium after open V_2 valve
 n_3 = Mole of air in instrument

$$n_2 = \frac{P_1V_1}{zRT} + \frac{P_A V_2'}{zRT}$$

$$V_2' = V_2 - V_1$$

where n_2 = Mol of methane in the system after open V_2 valve
 P_1 = Pressure of methane before open V_2 valve
 V_1 = Volume of instrument between V_1 to V_2 valve
 P_A = Atmospheric pressure

For the methane adsorption at each point;

$$n_{ads} = n_{in} - n_{fi}$$

$$n_{ads} = n_2 - n_{fi}$$

where n_{ads} = Mol of methane adsorbed methane in gas phase
 n_2 = Mol of methane in the system after open V_2 valve
 n_{fi} = Mol of methane in gas phase at each point

$$n_{fi} = \frac{PV_2}{zRT}$$

where n_{fi} = Mol of methane in the system (mol)
 P = Pressure of methane in system (atm)
 V_2 = Total volume of instrument (cm^3)
 z = Compressibility factor
 R = Gas constant ($82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$)
 T = Temperature (K)

3.4.2.2 Methane Adsorption Isotherm

Methane adsorption isotherm was done at 40°C temperature and up to 700 psi (4.5 MPa) pressure. About 0.5 g of a solid sample was placed into the reactor, which was placed into the testing unit afterwards. Then the system was allowed to reach equilibrium for 2 hours. The pressure was recorded every minute.

The ideal gas law and mole balance are also used for determining the amount methane adsorbed on activated carbon, n .

For the first point;

$$n_{ads} = \frac{P_1 V_1}{zRT} + \frac{P_A V_2'}{zRT} - \frac{P_2 V_2}{zRT}$$

$$V_2' = V_2 - V_1$$

where n_{ads} = Mol of methane adsorbed methane in gas phase (mol)

P_1 = Pressure of methane before open V_2 valve (atm)

V_1 = Volume of instrument between V_1 to V_2 valve (cm^3)

P_2 = Pressure of methane after open V_2 valve (atm)

V_2 = Total volume of instrument (cm^3)

P_A = Atmospheric pressure (atm)

For other point;

$$n_{ads} = \frac{P_1 V_1}{zRT} + \frac{P_{n-1} V_2'}{zRT} - \frac{P_2 V_2}{zRT} + n_{ads-1}$$

$$V_2' = V_2 - V_1$$

where n_{ads} = Mol of methane adsorbed methane in gas phase (mol)

n_{ads-1} = Mol of methane adsorbed methane in gas phase from previous stage (mol)

P_1 = Pressure of methane before open V_2 valve (atm)

V_1 = Volume of instrument between V_1 to V_2 valve (cm^3)

P_{n-1} = Pressure of methane in system from previous stage (atm)

P_2 = Pressure of methane after open V_2 valve (atm)

V_2 = Total volume of instrument (cm^3)

3.5 Adsorbent Characterizations

3.5.1 Scanning Electron Microscope (SEM)

FE-SEM or field emission scanning electron microscope (S-4800 Hitachi Corporation) is used for examining the activated carbon at high magnification to see surface topography. SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern.

3.5.2 Surface Area Analysis (SAA)

Autosorb-1 MP Gas Sorption System (Quantachrome Corporation) is used to measure the surface area, total pore volume, and mean pore diameter of the catalysts. The equipment measurement is based on Brunauer-Emmet-Teller (BET) equation. This technique is done by calculating the physical multi-layer adsorption of nitrogen. Volatile adsorbents on the surface will be eliminated by heating under vacuum at 150°C for at least 12 h prior to the analysis. Nitrogen gas with the cross-sectional area of 1.62×10^{-19} m²/molecule will be adsorbed on the catalyst surface at liquid nitrogen temperature (-196°C). The surface area will be calculated from the 41 points nitrogen adsorption. The mean pore diameter and pore volume will be obtained at P/P₀ ratios close to unity. The result will be analyzed by Autosorb-1 MP Any gas Software version 2.1 using the BET equation, as shown in following equation.

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

- where P = Pressure of gas
 P_0 = Saturated vapor pressure of the liquid at the operating temperature
 W = Weight of gas adsorbed at a relative pressure, P/P₀
 W_m = Weight of adsorbate constituting a monolayer of surface coverage

C = Constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of the adsorbent/adsorbate interaction

The surface area will be calculated by following equation.

$$S = \frac{W_m \cdot A_n \cdot (6.02 \times 10^{23})}{M_{W,N_2}}$$

where S = Specific surface area (m^2/g)

A_{N_2} = Cross-sectional area of one molecule of N_2 (1.62×10^{-19} $\text{m}^2/\text{molecule}$ at -196°C)

M_{W,N_2} = Molecule weight of nitrogen (28 g/g-mol)