# CHAPTER III
# EXPERIMENTAL

## 3.1 Materials and Equipments

### 3.1.1 Materials and Chemicals

#### 3.1.1.1 Adsorbents

The adsorbents used in this study were commercial activated carbon (bituminous coal-based activated carbons).

#### 3.1.1.2 Gases

Gases for methane adsorption experiment were high purity grade helium, high purity grade nitrogen, and ultra high purity grade methane.

Gas for ozone generator was high purity grade oxygen.

### 3.1.2 Equipment

The equipment for this research were the volumetric apparatus, BET Surface area analysis and FTIR spectroscopy.

## 3.2 Experimental Procedures

### 3.2.1 Characterization of Adsorbents

#### 3.2.1.1 Nature of Activated Carbon Surface

Approximately 2 grams of activated carbons was mixed with 50 ml distilled water, and then stirred for 1 min and settled for several minutes. UB-10 pH/mV Meter Denver Instrument were used to measure the pH of mixture.

#### 3.2.1.2 FTIR specetroscopy

#### 3.2.1.3 BET surface area analysis

BET surface area, micropore volume, total pore volume, and average pore diameter of the adsorbents were measured with the BET method on a Quantachrom/Autosorb1-MP instrument. Before analyzed, the humidity was removed the humidity on surface by out gassed under vacuum at 150 °C for approximately 20 hours. After that, the adsorbent was analyzed by nitrogen adsorption isotherms at -196°C. $S_{BET}$ (BET surface area) was obtained from multiple

point BET (Brunauer-Emmett-Teller) method which was derived from BET equation.

$$\frac{1}{W\left((P_0/P)-1\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \qquad (3.1)$$

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

$W_m$ = 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.

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

$$V = V_0\left[-\left(\frac{A}{\beta E_0}\right)^2\right] \qquad (3.2)$$

Where:  V  = Volume of gas adsorption

$V_0$  = Micropore volume

$E_0$  = Characteristic energy of adsorption

A  = Free adsorption energy

$\beta$  = 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.

- Average pore diameter

### 3.2.2 Methane Adsorption of Activated Carbons

#### 3.2.2.1 Samples Preparation: Activated Carbon

Activated carbons in this research were commercial activated carbons (bituminous coal-based activated carbons) The activated carbons were crushed and sieved to a size range of 20-40 mesh then, dried in the oven at 100°C for 24 hours. After degassing the activated carbons, put into the sample cell and weighed. Finally the sample cell was placed in the volumetric apparatus.

#### 3.2.2.2 Adsorption Experiment

- Volumetric Apparatus

The volumetric apparatus was used for study methane adsorption on activated carbons. This apparatus consists of a sample holder, a vacuum pump, and pressure transducer. Ultra high purity grade methane (99.999% purity) was used in the adsorption study. The schematic diagram of volumetric apparatus for this research is shown in Figure 3.1.
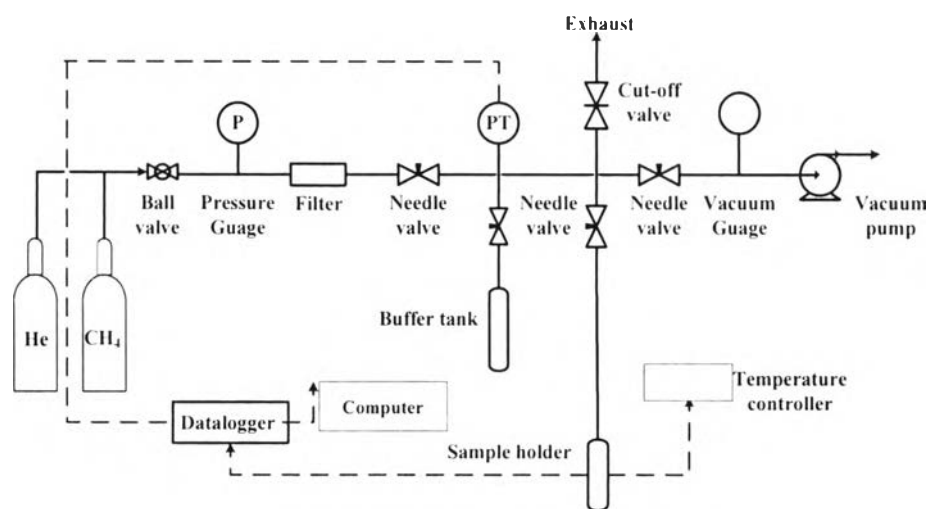


**Figure 3.1** Schematic of the volumetric apparatus.

A gas reservoir was a high pressure stainless steel reactor and the pressure regulator with 4,000 psig maximum limit was installed to control a gas flow rate into the system. A K-type thermocouple was used for measuring the

temperature of gas inside the reactor. The system pressure was measure by pressure transducer in the range of 0 to 3,000 psig with 0.13% error.

For each experiment, about 1.0-2.0 g of adsorbents was weighed and put into the sample holder. Next, the adsorbent was degassed by using a rotary vacuum pump prior to the methane adsorption. The temperature was controlled for each adsorption experiment. The pressures of gas were recorded before and after each gas expansion.

### 3.2.1.3 Measurement of methane adsorption and calculation

The pressure transducer was calibrated for every adsorption experiment. The vacuum pressure of -14.7 psi was used as the reference pressure. With this pressure, the relative was set to zero under vacuum condition.

- Determination of the Sample Holder Volume Using

Helium

The volume of the sample holder was determined by helium expansion at 30°C, 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.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \tag{3.4}$$

Where:

$P_1$ = Pressure of helium before helium expansion

$V_1$ = Volume of the system excluding volume of sample holder

$T_1$ = Temperature before helium expansion

$P_2$ = Pressure of helium after helium expansion

$V_2$ = Total system volume

= $V_1 + V_{sample\ holder}$

$T_2$ = Temperature after helium expansion

- Determination of the Methane Adsorption on Adsorbents

Determination of the methane adsorption was carried out at different constant temperatures; 35, 40, and 45°C; and pressure up to 1,000 psia. Temperature was heated up to the temperature at = 35, 40, and 45°C. At desired pressure, methane was introduced from a high pressure cylinder into a sample holder. During the experiment, the time to reach the equilibrium of methane adsorption was within approximately 20 min. The methane pressures were recorded before and after each methane expansion.

The ideal gas law and conservation of mass were also used for determining the amount of methane adsorbed on the adsorbents. The amounts of methane adsorbed by activated carbons can be obtained by the following equation.

$$n_{ad} = n_{ad-1} + \frac{P_i V_1}{zRT_i} - \frac{P_{f-1} V_2}{zRT_{f-1}} - \frac{P_f (V_1 + V_2)}{zRT_f} \qquad (3.5)$$

Where: $n_{ad}$ = Total amount methane adsorbed by activated carbons (mole)

$n_{ad-1}$ = Amount methane adsorbed at previous stage (mole)

$P_i$ = Initial pressure of methane before methane expansion into the sample holder (psia)

$P_{f-1}$ = Final pressure of methane after methane expansion into the sample holder in the previous stage (psia)

$P_f$ = Final pressure of methane after methane expansion into the sample holder (psia)

$V_1$ = Volume of manifold excluding volume of sample holder (cm³)

$V_2$ = Volume of the sample holder (cm³)

$Z$ = Compressibility factor of methane

$T_i$ = Initial temperature of methane before methane expansion into the sample holder (K)

$T_f$ = Final temperature of methane after methane expansion into the sample holder (K)

$T_{f-1}$ = Final temperature of methane after methane expansion into the sample holder in the previous stage (K)

R = Gas constant, 82.0578 atm cm$^3$/mol K

### 3.2.3 Ozone treatment process

The activated carbon was treated with ozone in a fixed bed reactor loaded with 5 g of carbon under a constant ozone flow of 165 ml of O$_3$/min, operating at room temperature and atmospheric pressure. Ozone was produced in a Revozone corona discharge ozone generator and fed to the horizontal reactor for different exposure times (5, 10, 15, 25, 30, 35, 40, 45, 60, 120 and 240 min) and rotate the reactor 180° every 30 second. After treatment, the carbon was withdrawn from the reactor and dried in the oven. Finally, ozonized activated carbons were brought to a methane adsorption experiment and characterized by BET Surface Area Analysis
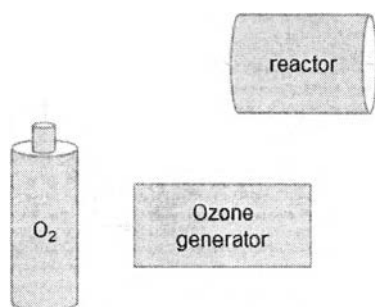


**Figure 3.2** Schematic diagram of ozone treatment process.