CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Materials

a) Fittings and valves

b) Mass flow controller

c) Thermometer

d) Coconut shell activated carbon (CSAC) (supported by Carbokarn Co., Ltd., Thailand)

e) Methane gas (99.99% purity purchased from Labgas Thailand Co., Ltd.)

f) Carbon dioxide gas (99.99% purity purchased from Labgas Thailand Co., Ltd.)

g) Helium gas (99.99% purity purchased from Praxair Inc.)

3.1.2 Chemicals

a) Ammonia ($NH_3.H_2O$), 25% GR

b) Potassium hydroxide (KOH), 85%AR

c) Acetic acid (CH_3COOH), 98%AR

d) Methyltriethoxy Silane (MTES), 98% AR

3.1.3 Equipments

a) Thermo-volumetric apparatus

b) Gas chromatograph, Hewlett Packard 5890 series II

c) Scanning electron microscope (SEM), Hitachi S-4800

d) Surface area analyzer (SAA), Quantachrom/Autosorb1-MP

e) CHN Analyzer, CHN2000

3.2 Experimental Procedures

3.2.1 Adsorbent Preparation

a) 20-40 mesh of CSAC was dried in oven at 120°C for 24 hr to remove moisture.

b) Keep in a desiccator.

3.2.2 Alkali Treatment

a) 20 g of CSAC was treated in 100 cm^3 of 4.2 M KOH and 90 cm^3 of 25% NH_4OH at 85 °C for 2 hr.

b) Treated CSACs were washed and adjusted pH with distilled water until pH 7 and dried in oven at 120°C for 24 hr.

c) Keep in a desiccator.

3.2.3 Silane Coupling Agent Solution Preparation

a) 0.051, 0.102, 0.204, and 0.306 cm^3 of 98% CH_3COOH was dropped into distilled water before adjusting the volume to 100 cm^3 for preparing the 0.005, 0.010, 0.020, and 0.030 wt% MTES concentration, respectively and heated at 65°C for 30 min.

b) 0.051, 0.102, 0.204, and 0.306 cm^3 of 98% MTES was dropped into CH_3COOH solution for preparing the 0.005, 0.010, 0.020, and 0.030 wt% of MTES concentration, respectively and stirred at 65°C for 1 hr to make a completely hydrolysis reaction.

c) MTES solutions were filtered by 0.5 micron of paper filter to remove the incomplete molecule in hydrolysis reaction.

3.2.4 Silane Coupling Agent Modification

a) 10 g of CSAC was grafted in 100 cm^3 of MTES solution with various concentrations at 40 °C for 2 hr.

b) Modified CSACs were filtered and dried at 120 °C for 24 hr to remove moisture.

c) Keep in a desiccator.

3.2.5 Adsorbent Characterization

a) The surface area, total pore volume, and pore size distribution of the adsorbent were measured by a Quantachrom/Autosorb1-MP instrument. The adsorbent was first out gassed to remove the humidity on its surface under vacuum at 300 °C for 16 hours prior to the analysis. After that, nitrogen was purged to adsorb on its surface. The volume-pressure data was used to calculate the BET surface area, total pore volume, and pore size distribution.

b) The morphology of the adsorbent was investigated by using the SEM, Hitachi S-4800, with an accelerating voltage of 2 kV and varying magnifications of 250, 1,000, 1,500, and 10,000. The adsorbent will be coated with platinum under vacuum condition before observation.

c) Quantities of carbon (C), hydrogen (H), and nitrogen (N) were measured by CHN2000/CHN analyzer. In the combustion process, C is converted to carbon dioxide; H to water; N to nitrogen oxide at 950°C. The combustion products are swept out of the combustion chamber by helium and passed over heated high purity copper at 850 °C. Detection of the gases is carried out by GC-TCD followed by quantification using thermal conductivity detection. The adsorbent was dried first at 120 °C for 24 hr to remove humidity. After that, the adsorbent was enwrapped with tin foil no. 502-186-200. The quantities of C, H, and N were calculated from under curve area, which was compared from the standard curve of EDTA. The quantity of oxygen (O) was derived from the total quantity of other components.

3.3 Thermo-volumetric Apparatus

Thermo-volumetric apparatus was constructed to study the gas-solid interaction between methane/carbon dioxide and potential solid adsorbents. The schematic of the experimental set-up is shown in Figure 3.1.
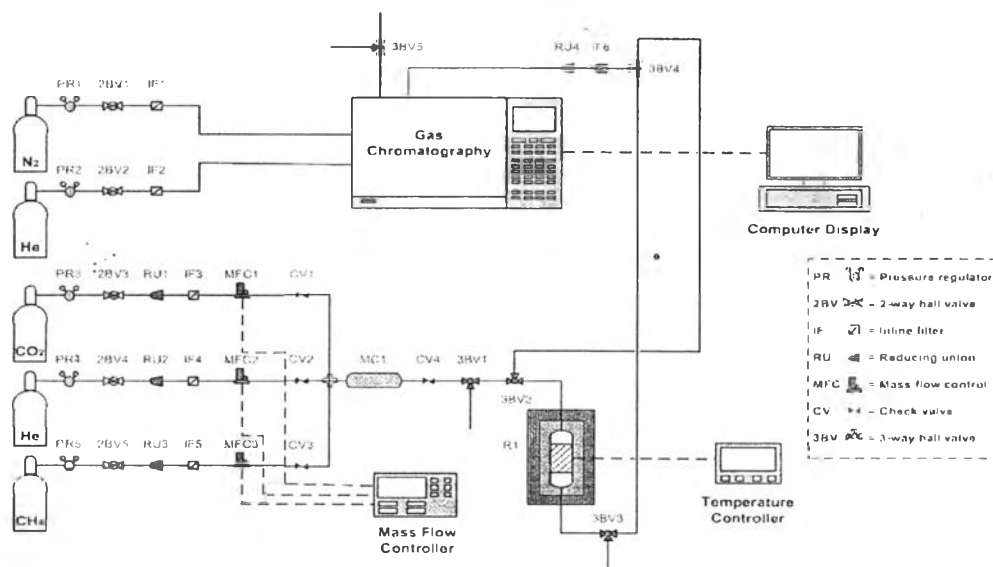
Figure 3.1 Schematic diagram of the experimental set-up.

a. The set-up consisted of a high pressure stainless reactor, which held the sample and part of stainless steel tube as a gas reservoir.

b. A pressure transducer was used to measure pressure of the system in the range of 0 - 3,000 psig with a 0.13% global error.

c. A pressure regulator with 4,000 psig maximum limit was installed to control a gas flow rate into the whole system.

3.4 Measurement of Gas Adsorption and Calculation

3.4.1 Methane and Carbon Dioxide Adsorption Isotherms

A methane and carbon dioxide adsorption experiment was carried out at atmospheric pressure and room temperature. Fill about 5 g of an activated carbon sample at the middle of packed colume. The feed stream consisted of 2.5 ml/min CO_2, 2.5 ml/min CH_4, and 20 ml/min He, which were controlled and monitored by a mass flow controller. The outlet gases (CH_4 and CO_2) from the column were analyzed by a Hewlett Packard 5890 series II gas chromatograph. The sampling loop was at every 2.5 min. The oven and detector temperature of the gas chromatograph

were 100 and 150 °C, respectively. Helium was used as a carrier gas and a diluting agent for the system. Pressure of the carrier gas, helium, was 70 psi.

3.4.2 Methane and Carbon Dioxide Adsorption Capacity

Methane and carbon dioxide adsorption capacity will be calculated by integration of the kinetic adsorption curves. Using Eq. (3.1) to calculate the adsorption capacity on activated carbon.

$$Q_{ads} = \frac{FC_0}{W} \int_0^\infty \left(1 - \frac{C}{C_0}\right) dt \qquad (3.1)$$

where
Q_{ads} = Adsorption capacity (Mole/g)
F = Gas flow rate (Mole/minute)
C_0 = Initial concentration of gas (Mole)
C = Concentration at any time (Mole)
t_g = Integrating time (Minute)
W = Weight of adsorbent (g)