

CHAPTER III

EXPERIMENTAL SECTION

Natural clinoptilolite was used as an adsorbent for water vapor removal from natural gas at 1 atm and 30°C. The experimental section consists of materials, adsorbent modification, adsorbent characterization, and adsorption experiment.

3.1 Materials

Natural clinoptilolite from Turkey was used as an adsorbent in this work. The modification of the zeolite was achieved by using 99.9% sodium chloride, 99% magnesium chloride, both of which were from Ajax Chemicals, Australia, 99.5% potassium chloride supplied by Merck, Germany, 99% calcium chloride dihydrate, obtained from Fluka, Switzerland, and 65% nitric acid supplied by Riedel-do Haen AG., Germany. All chemicals were used without further purification.

3.2 Adsorbent Modification

Clinoptilolite was crushed and sieved to select the 0.1–0.3 mm fraction, which was then washed with distilled water at 30°C for 14 hours in a rotary evaporator for the removal of water-soluble impurities, then dried at 110°C. The resulting sample, called pretreated clinoptilolite, was further treated by one of the four modification techniques.

3.2.1 Thermal Treatment

The pretreated clinoptilolite was calcined at different temperatures, 300, 400, and 500°C, for 2 hours in a CARBOLITE CSF 1200

automatic furnace by setting parameters at SP=110°C, $r_1=10^\circ\text{C}/\text{min}$, $L_1=300$, 400, and 500°C, respectively, $d_1=20$ sec, $r_2=10^\circ\text{C}/\text{min}$, and $d_2=1000$ sec. After the treatment, the modified clinoptilolite was stored in a vacuum desiccator.

3.2.2 Acid Treatment

The treatment started with mixing one gram of the pretreated clinoptilolite with 50 ml of HNO_3 at 80°C for 5 hours in a rotary evaporator. Three HNO_3 concentrations, 0.1, 1, and 3 molar, were used here. After 5 hours, the acid solution was drained, and the zeolite was washed thoroughly with distilled water at 30°C for 14 hours to remove excess acid solution before drying at 110°C.

3.2.3 Ion Exchange

One gram of the pretreated clinoptilolite was immersed in 50 ml of either 1 molar NaCl, KCl, MgCl_2 , or CaCl_2 at 80°C for 5 hours in a rotary evaporator. This was followed by rinsing with distilled water at 30°C for 14 hours to eliminate excess chloride salt and drying at 110°C.

3.2.4 Acid Treatment prior to Ion Exchange

One gram of the pretreated clinoptilolite was brought into contact with 1 molar HNO_3 at 80°C for 7 hours in a rotary evaporator. The sample was then rinsed with distilled water to eliminate excess acid solution. This was followed by the ion-exchange step with 50 ml of either 1 molar NaCl, KCl, MgCl_2 , or CaCl_2 at the same conditions in a rotary evaporator. Then, the zeolite was washed with distilled water at 30°C for 14 hours, dried at 110°C, and stored in a vacuum desiccator.



3.3 Adsorbent Characterization

3.3.1 BET Surface Area Measurement

Surface areas, total pore volumes, and average pore diameters of all adsorbents were determined with an Autosorb-1 Gas Sorption system (Quantachrome Corporation), with the Brunauer-Emmer-Teller (BET) method. The characterization started after 0.2 g of a sample was dried and outgassed in the sample cell at 200°C for at least 2 hours to eliminate adsorbed volatiles. The sample was then saturated with nitrogen. The quantity of nitrogen adsorbed was measured. The surface area of adsorbent was evaluated at 0.1 P/P₀, the total pore volume and average pore diameter were evaluated at 0.995 P/P₀.

3.3.2 X-Ray Diffraction (XRD) Analysis

X-ray diffraction analysis was utilized to confirm the crystal structures and to estimate the crystallite sizes of all adsorbents. The powdered sample was placed in a standard sample holder and examined by a Rigaku X-ray diffractometer system (RINT-2200) equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406 Å). The diffractometer was performed in the step-scan mode with a step size of 0.02 degree and a speed of 5 degree/min. Diffraction data were collected from 5° to 90° by an online microcomputer and analyzed by the PD-APD version 3.5B.

3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was employed to identify common structural features of the adsorbents. FTIR spectra were carried out on a FT-45A Bio-Rad Spectrophotometer with 16 scans at a resolution of 8 cm⁻¹ in the frequency range of 4000-400cm⁻¹. Approximately, 0.002 g of a dried sample

and 0.065 g of an optical-graded KBr powder used as a standard were mixed and ground together. Prior to the analysis, the specimens were hydraulically pressed to obtain a transparent thin pellet.

3.3.4 Energy-Dispersive X-Ray Spectrometer (EDS)

A Pentafet Link Oxford x-ray detector equipped with a scanning electron microscope JEOL JSM 5200 was used to analyze chemical elements and Si/Al ratio of adsorbents. The operating voltage was 20kV and micrographs of samples were taken at the magnification of 2000. Prior to the analysis, all specimens were hydraulically pressed to a thin pellet form, then the surface of all specimens was coated with a thin evaporated layer of gold under vacuum for 4 min in order to improve conductivity and prevent electron changing on the surface.

3.3.6 Thermogravimetric Analysis (TGA)

A Dupont TGA 2590 equipped with a thermal analyzer 2000 was used to determine water adsorption capacity and temperature at which an adsorbent started dehydration. Approximately 3 to 6 g of adsorbent after drying and outgassing at 200°C for 1 h was equilibrated with water vapor in a desiccator at room temperature for 24 h. Water adsorption capacity of the adsorbent was determined by heating the water saturated sample at the rate of 20°C/min from room temperature to 250°C. The sample was left at this temperature for 1 h.

3.4 Adsorption Experiments

The dynamic competitive adsorption of water and hydrocarbons on the pretreated and modified clinoptilolites was performed in this study. Dried and CO₂ free natural gas obtained from the Petroleum Authority of Thailand

(PTT) was used as the main hydrocarbon stream in this experiment. Composition of the natural gas was 67.82%vol methane, 13.27%vol ethane, 11.80%vol propane, 11.80%vol iso-butane, and 2.91%vol n-butane. Water and pentane vapors were introduced into the system by passing 99.99% nitrogen obtained from Thai Industrial Gas (Public) Co., Ltd. to the liquid water and pentane. The temperature of liquid water was constant at room temperature, but liquid pentane was placed in a constant temperature water bath at 3°C.

The experimental setup is shown in Figure 3.1. The setup can be classified into three major sections: gas blending system, the adsorption column, and gas chromatograph unit. In the gas blending system, all gaseous components were passed through a micron filter to avoid any solid particles going into the system. Mass flow controllers were employed to control flow rates of all the feed gases. A check valve was installed to prevent backflow. The gases were mixed in the mixing chamber before going to the bottom part of the adsorption column.

A Pyrex tube of 10 mm outside diameter was used as the adsorption column. The prepared adsorbent of known weight was packed in the center of the tube between 0.2 g of glass wool plugs. A heating tape was used to prevent water condensation. The temperature of the adsorbent bed inside the column was detected by a K-type thermocouple. The temperature of the electrical furnace was controlled within the range of 30-300±5°C by a PID temperature controller, Yamatake-Honeywell Instrument model SDC 16.

The outlet gas stream from the adsorption column was immediately analyzed for the total composition by a FISION 8340 gas chromatograph (GC) equipped with a TCD and PorapaxQ 50/80. The flow rate of the carrier gas, N₂, was 20 ml/min. Temperatures of the injector and detector were set at 150 and 180°C, respectively. The oven temperature was controlled by the temperature program; isothermal at 50°C for 2 minutes before going to 120°C with a heating rate of 10°C/min. After 2 minutes at 120°C, the oven

temperature was increased with the rate of 15°C/min until 200°C was reached and it was maintained at this temperature for 2 minutes. After the temperature program, oven temperature was cooled down to 50°C. The composition analysis was carried out with the Chrom-Card program.

Before starting the adsorption process, nitrogen at 30 ml/min was fed to the adsorption column at 250°C for 2 hours to desorb any contaminants from the adsorbents. The adsorbents were then cooled to 30°C for the gas adsorption step. A mixture of 6.44%vol methane, 1.26%vol ethane, 1.16%vol propane, 0.42%vol iso-butane, 0.29%vol n-butane, 1.35%vol n-pentane, and 1.12%vol water vapor at the total flow rate of 25 ml/min was then introduced into the system. The adsorption study was carried out until a constant gas composition was observed in the effluent.

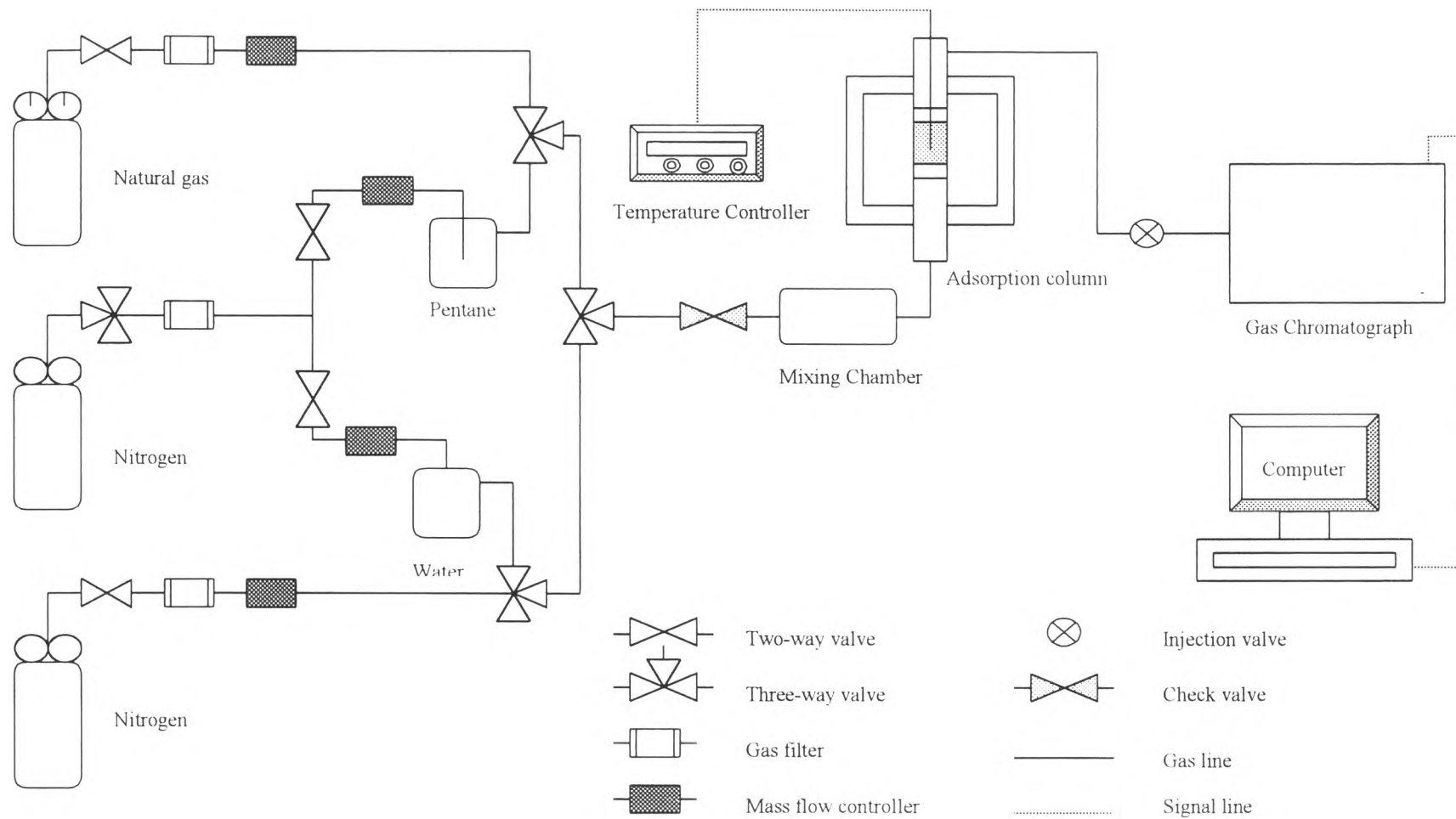


Figure 3.1 Schematic flow diagram of the equipment setup.