

## **CHAPTER III**

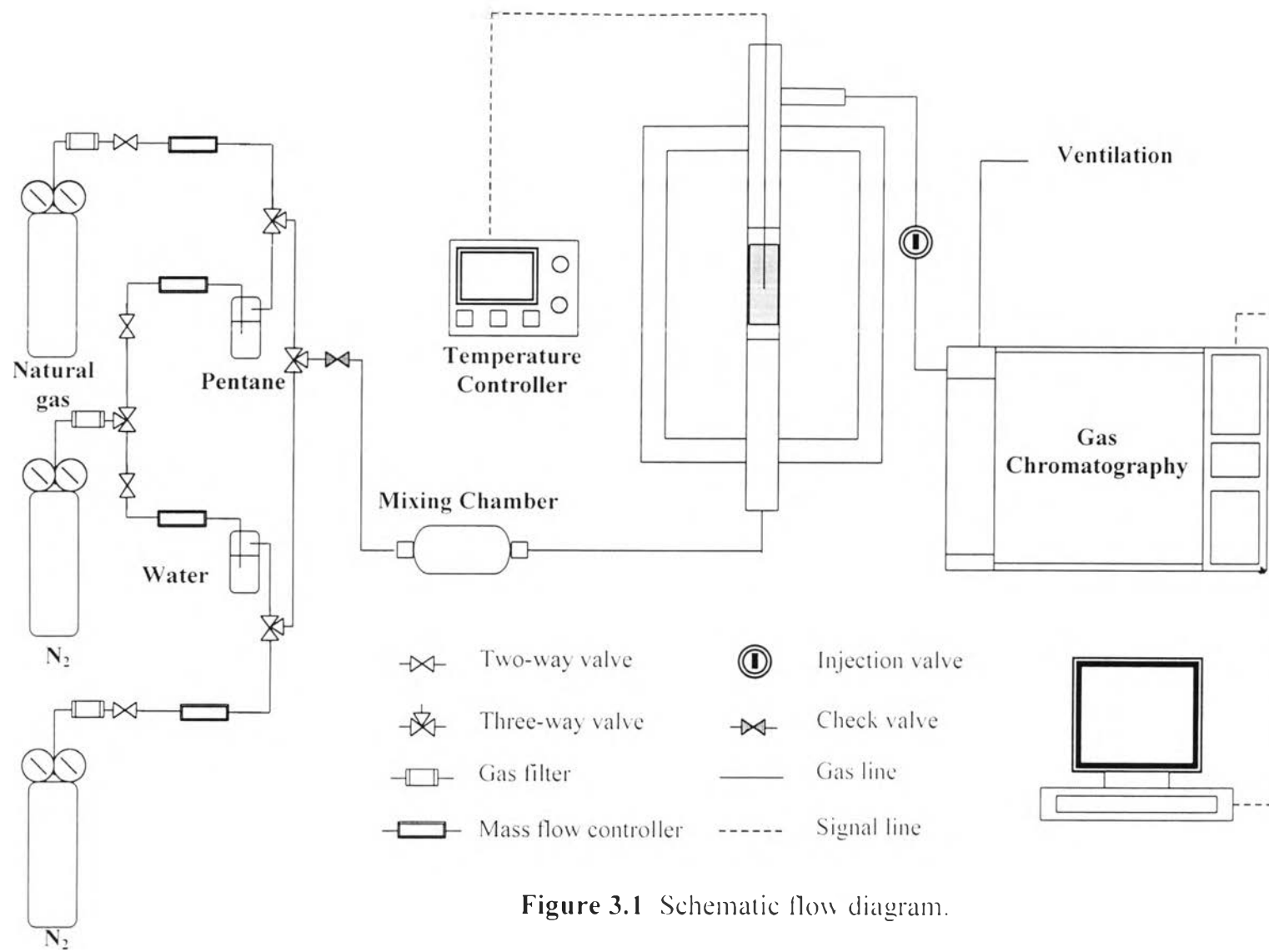
### **EXPERIMENTAL SECTION**

The experiment of the water adsorption from natural gas was performed using alumina prepared by the sol-gel technique in a packed-bed reactor at 1 atm and 30°C. Illustration of the complete reaction system is shown in Figure 3.1. The experimental section is divided into two separated parts; experimental setup and experimental procedure. More details of each part will be discussed in this chapter.

#### **3.1 Experimental Setup**

The experimental setup of this study was shown in Figure 3.1. The setup can be classified into three major sections; gas blending system, the adsorption column, and gas chromatography unit. In the gas blending system, all gaseous components were passed through a micron filter to avoid any solid particles passing into the system. Mass flow controllers with a constant pressure were employed to keep flow rates of all gases at desired values. A high purity nitrogen gas stream was separated into two lines, which were passed through liquid water and pentane to vaporize these two components into the system. The mixture gas was then fed to the bottom part of the adsorption column. Another pure nitrogen line was used for the pretreatment and regeneration of the alumina bed. A check valve was installed to prevent the backflow.

The Pyrex tube of 10 mm outside diameter was used as an adsorption column. The prepared adsorbent of known weight was packed in the center of the tube between constant weight glass wool plugs. A heating tape was used to wrap around at the upper path of adsorption column to prevent water



**Figure 3.1** Schematic flow diagram.

condensation. A type-K thermocouple was used to detect the temperature of the adsorbent bed inside the column. The temperature of the electrical furnace was control with the range between 30-300°C by a PID temperature controller, Yamatake-Honeywell Instrument model SDC 16. The variation of the reaction temperature was  $\pm 5^\circ\text{C}$ .

The outlet gas stream from the adsorption column was immediately analyzed for the total composition by a gas chromatograph (GC) instrument. The model of this gas chromatography was FISONs 8340 Series equipped with a TCD and, Porapax Q 50/80. The temperature of the injector, oven, and detector were set at 150°C, 100°C, and 200°C, respectively. The flow rate of the carrier gas,  $\text{N}_2$ , was set constant at 20 ml/min. The evaluation of all the data, including peak position, peak area, and composition of total detected gases, was done with Chrom-Card program.

## 3.2 Experimental Procedure

### 3.2.1 Adsorbent Preparation

The sol-gel technique by the hydrolysis of metal alkoxide was used in this study for the preparation of adsorbent, alumina. Fibrillar aluminum hydroxide sols solution was prepared by dissolving the calculated weight of aluminum isopropoxide ( $\text{Al}(\text{OC}_3\text{H}_7)_3$ ) of 98% purity to hot water at 85°C with a small amount of 65% nitric acid; obtained from Labscan Co., Ltd. The solution was then mixed with 99% purity 1,3-butanediol. Both aluminum isopropoxide (AIP) and 1,3-butanediol were supplied by Fluka Co., Ltd. The temperature of the mixed solution was controlled at 85°C for one hour and then cooled the solution down to room temperature with constant stirring. After the sol solution was stirred at room temperature for 24 hours, the solvents were eliminated by drying at 110°C under reduced pressure for one day. Finally, calcination of the adsorbent alumina was done by placing the

dried adsorbent, which was ground to appropriate particle size, in the oven at high temperature between 400-700°C. The prepared sol-gel alumina was stored in a vacuum desiccator.

### 3.2.2 Adsorbent Characterization

#### *Surface Area Measurement*

The Brunauer-Emmer-Teller (BET) method was used as a method to determine surface areas of the prepared adsorbents. The characterization is based on the physical adsorption of nitrogen gas through the Autosorb-1 Gas Sorption system (Quantachrome Corporation) at the liquid nitrogen temperature (77 K). The quantity of gas adsorbed onto or desorbed from a solid surface at some equilibrium vapor pressure is measured.

The characterization started with out-gassing the adsorbent of known weight in the flowing helium stream at 300°C for 2 hours. Then, the net dried weight of adsorbent was calculated through the difference between the weight of sample before and after the out-gassing. Based on the net dried weight of adsorbent, the specific surface area was obtained from five points nitrogen adsorption isotherm.

#### *Thermogravimetric Analysis (TGA)*

The determination of total water adsorption capacity was performed through the thermogravimetric analysis. The Dupont TGA 2590 equipped with the thermal analyzer model 2000 was applied in this experiment. There were two inlet nitrogen lines entering the TGA, the reactant line and balance line. Flow rates of the reactant and balance line were adjusted to 20 and 30 ml/min, respectively. The reactant line was connected to a water vaporizer, which was used to introduce water vapor into system to determine the water adsorption capacity.

An alumina sample with a constant weight was placed on a platinum dish suspended on the reference hook of the TGA equipment. The

starting weight of sample was recorded. The weight of the sample in a controlled atmosphere was continuously recorded as a function of temperature or time as the temperature of the sample changed. The thermograms were obtained under the nitrogen flow, which was heated from room temperature to 250°C at the rate of 20°C/min. The temperature was maintained at 250°C for 60 min. Finally, the sample was cooled down to 30°C by the flowing of humidified nitrogen flow. The sample sited under this controlled atmosphere until the monitored weight was read constant. The difference between the starting and finished weights was the total water adsorption capacity of the adsorbent sample.

#### *X-ray diffraction (XRD)*

The XRD technique was used to identify the internal structure, bulk phase, and composition of the crystalline material. The XRD pattern was obtained by using a Rikagu X-ray diffractometer system equipped with a graphite monochromator and a Cu tube for generating a CuK radiation. The adsorbent sample was ground to a very fine homogenous powder and held in the beam in a thin-walled glass container. Constructive interference could be achieved with monochromatic irradiation by varying the angle of incidence from 5 to 90 degrees. The digital output of the proportional X-ray detector and the goniometer angle measurements were sent to an online computer to record and subsequently analyze by PC-APD version 3.5B.

#### 3.2.3 Adsorption Experiment

The dynamic competitive adsorption between water and hydrocarbons on alumina surface was performed in this study. Simulated natural gas comprising of moisture content and pentane was passed through the packed-bed of high surface area alumina and the leaving gas stream composition was continuously detected by the gas chromatographic instrument.

Dried and CO<sub>2</sub> free natural gas obtained from the Petroleum Authority of Thailand (PTT) was used as a main hydrocarbon stream in this experiment. Composition of this natural gas is shown in Appendix. Nitrogen stream of 99.999% purity obtained from Thai Industrial Gas (Public) Co., Ltd. was introduced into two lines, which were passed through liquid water and pentane to vaporize these two components to obtain the mixed gas containing the desired composition. The liquid water and pentane were placed in a constant temperature water bath to keep the temperature of both liquids constant. Another pure nitrogen line was applied as a diluent gas and also used for the pretreatment and regeneration of the alumina bed. The composition of each gas was varied to observe their effects on alumina adsorption capacity; 2-5% vol. for natural gas, 0.05-1% vol. for water vapor, and 0.1-0.5% vol. for pentane. Total flow rate of the mixed gas was 100 ml/min. A gas-mixing chamber was used to mix all gaseous components before entering the adsorption column.

Typically, 3 g of alumina with the range of particle size between 0.125 to 0.212 mm was packed in the adsorption column equipped with 0.2 g of glass wool on both top and bottom of the adsorbent bed. Before starting the adsorption process, the adsorbent was pretreated by passing pure nitrogen through the adsorbent bed, in which, at the same time, was heated to 250°C and remained at this temperature for 2 hours. After 2 hours of the pretreatment, the adsorbent was cooled down to 30°C. The adsorption step was then proceeded by passing the mixed gas upward through the adsorbent bed.

As soon as the adsorption experiment started, the gas outlet composition was regularly measured. A gas sampling valve was used to pass the constant volume of the sample gas to the gas chromatographic unit. The chromatogram was obtained continuously as a function of time. The experiment was terminated when the composition of the outlet stream was the

same as the composition of the inlet stream. The regeneration of the adsorbent was then carried out using the same procedure as the pretreatment method as mentioned before.

The total adsorbed quantity of each gas was determined by the integration of the plot between the amount of adsorbed gas versus time recorded. Plotting of all these values against the gas concentration yielded the adsorption isotherms of that gas on interested adsorbent. The breakthrough curve of every gases was also determined by plotting of  $C_t/C_i$  ratio against adsorption time ( $C_t$  is the concentration of the interested gas at any adsorption time and  $C_i$  is the concentration of this gas at the initial state).