CHAPTER III
EXPERIMENTAL

The experimental apparatus was constructed to study the adsorption of water vapor from natural gas on a multi-layer of three commercial adsorbents. The operating temperatures for the adsorption and for the regeneration were at 25 °C and heated up to 260 °C, respectively. However, both adsorption and regeneration processes were carried out under the same operating pressure of 1 atm. This section contains the details of materials used, experimental setup, and experimental procedure.

3.1 Materials

The natural gas sample collected from the upstream of dehydration unit of Gas Separation Plant Unit 1 (Rayong) of PTT Public Company Limited (PTTPLC) was used as the feed gas. The compositions of this natural gas sample are shown in Appendix A. Also, the highly purified nitrogen gas (99.999%), obtained from Thai Industrial Gas Public Company Limited, was used as a purge gas in the adsorbent pretreatment and regeneration steps. Three different types of commercial adsorbents were used: Silica gel, Molsiv 4A 1/8" and MolSiv 4A 1/16". These three adsorbents were packed in layers with the same volume ratio as in the commercial adsorption unit. The formula structures of these adsorbents are presented in Appendix B. In addition, the distilled deionized water was utilized as a water vapor source to mix with the natural gas in order to obtain a desired humidity level.

3.2 Experimental Setup

The experimental apparatus was designed and constructed, mainly consisting of a multi-bed adsorber and auxiliary equipment for preparation of water vapor-natural gas mixture, a gas mass flow controller, humidity analyzers, and a mobile electrical heater with a temperature controller. The experimental setup is schematically shown in Figure 3.1.

The Pyrex tube with an inside diameter of 33 mm and a height of 120 mm, or volume of about 75 ml was exploited as an adsorber (to obtain the adsorption breakthrough curve data.) The fixed volume ratio of adsorbents was divided by an adsorbent bulk density as to be mass basis. A simplified diagram of a layout of adsorbent layers is given in Appendix C.

In order to vary the water vapor contents of the feed inlet, the natural gas released from cylinder was split into two streams. One was humidified by passing through a two-stage chamber which contained the distilled deionized water. The other was a by-passed stream. Then, the humidity of the saturated and dry gas mixtures was analyzed using a portable humidity analyzer, Cole Parmer Tri-Sense® Relative Humidity/Air Velocity/Temperature Meter.

A constant flow rate of the natural gas supplied to the system was controlled by using a gas mass flow controller (GFC), AALBORG Instrument & Controls Inc., model GFC171S with a range between 0 to 500 sccm as calibrated for methane gas. A micron filter was added to the gas line before the mass flow controller to prevent the GFC from the damage due to small particles entrained in the gas. Moreover, check valves with 1 psig cracking pressure were added to the gas line after the GFC, and the inlet and outlet humidifiers to prevent a reverse flow.

The humidity of dried gas at the outlet from the adsorber was also measured by using the same model of the portable humidity analyzer as used at the feed inlet line.

The mobile electrical heater was fabricated and utilized as a heating source in the adsorbent pretreatment and regeneration steps. The temperature in the adsorber was monitored by using a J-type thermocouple, and was controlled to be constant by using the PID+FUZZY on the digital temperature controller, SIGMA model SF48 with a range of between 25-300°C (up to 1200 °C).

The nitrogen gas was used to serve two main purposes: (1) to attain humidity-free in the system, and (2) to purge the system in the regeneration step. The nitrogen flow rate was measured by using a rotameter with a range of between 0 to 400 ml/min. The nitrogen gas leaving from the top of the adsorber was delivered to a separatory funnel where the condensed water would be removed before the nitrogen gas was routed to the humidity analyzer for remaining water measurement.
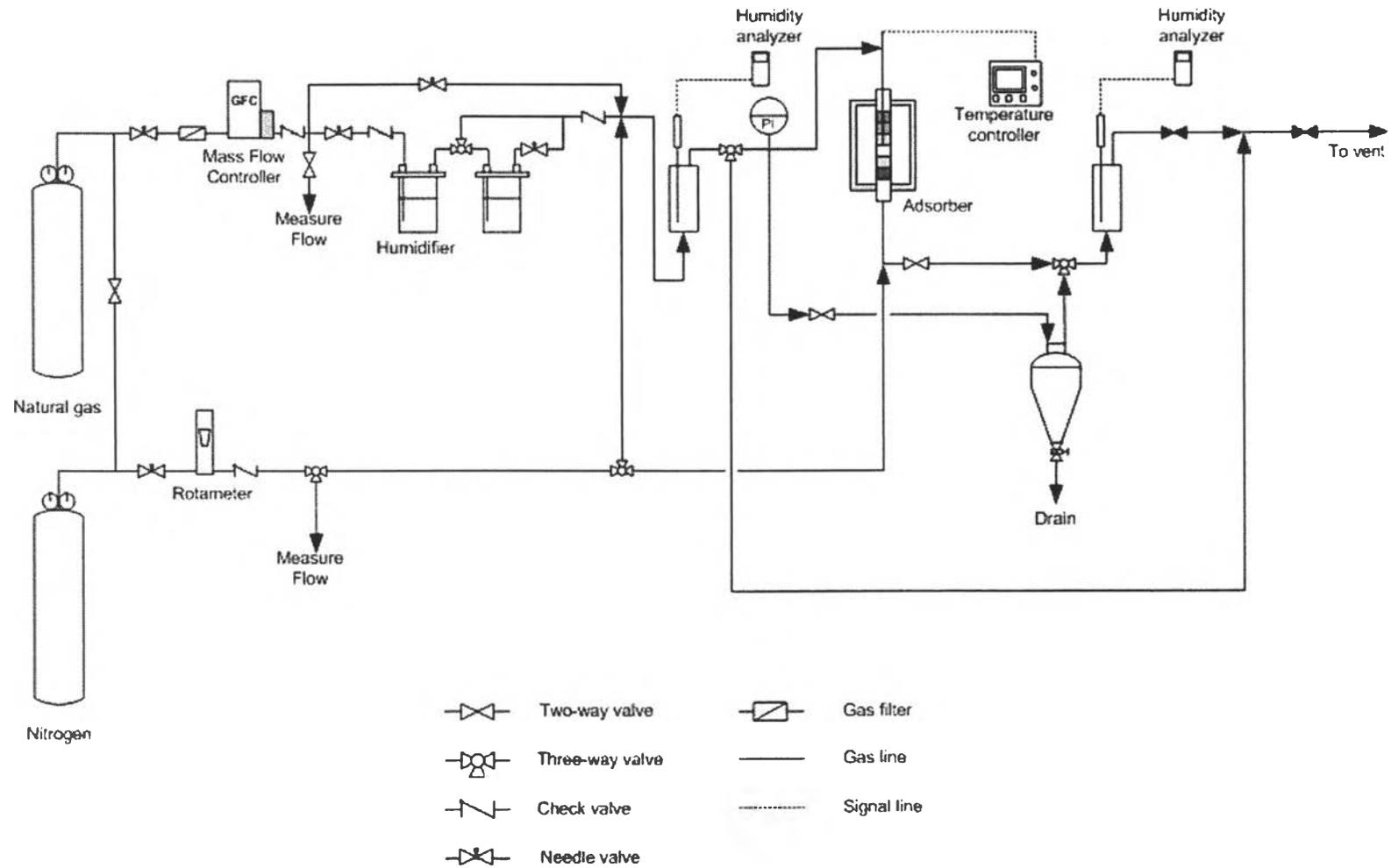
Figure 3.1 The schematic flow diagram for experimental setup.

3.3 Experimental Procedures

3.3.1 Adsorbent Characterization

Static Adsorption Capacity

The static adsorption capacity of adsorbents was evaluated using a thermogravimetric analysis (TGA), the Dupont TGA 2590 equipped with a thermal analyzer 2000. The nitrogen gas was used as a reactant gas and balance gas with the flow rates of 20 and 30 ml/min, respectively. The adsorbents were dried overnight in an oven at 110 °C. Then, they were saturated in the humidity control box by contacting with water vapor for about 1 week. After that, a pellet of saturated adsorbents was placed on a platinum dish, which was hung on the reference hook of TGA equipment. Before starting characterization, the starting weight of the adsorbents sample was measured and recorded.

The furnace was heated from the room temperature to 350 °C by 10 °C per min of ramping rate under the nitrogen flow. The weight of sample was continuously recorded with an increase in the temperature. A derivative weight loss due to the increasing of temperature was plotted, and the total weight loss in each temperature range was calculated. The static adsorption capacity of adsorbents was equal to a total weight loss accumulated from room temperature up to 260 °C divided by weight of dry adsorbent (weight remaining at 260°C).

Adsorbent Crystallinity

The X-Ray Diffraction (XRD) technique was applied to observe the crystallinity patterns of fresh adsorbents. These patterns were obtained by using a Rikagu X-Ray diffractometer system (RINT-2200) equipped with a graphite monochromator and a copper tube for generating a CuK_α radiation. A sample was prepared by grinding adsorbents to very fine homogenous powders and putting them over an aluminum slide holder. This prepared sample was scanned from 3 degree to 90 degrees (2Θ) with scanning speed of 0.02 degrees/min. The digital output of the proportional X-Ray detector and the geniometer angle measurements were recorded via an on-line computer for subsequent analysis.

3.3.2 Adsorption Isotherm of Water on Multi-layer Adsorbents

The adsorbents were dried overnight at 110 °C, then weighted and packed in a column with the approximate weight as shown in Table 3.1. The pretreatment step was further performed with the flow of nitrogen gas at the temperature of 260 °C. The remaining adsorbed water was monitored using a humidity analyzer, which also measured the relative humidity of outlet nitrogen gas from the adsorber. The pretreatment step was ceased, when the relative humidity was down to zero. The nitrogen gas flow was remained to cool down the adsorber to the room temperature. The adsorber was carefully removed from the system and sealed with paraffin at the front end and at the rear end. After that, the net dried weight adsorbent was determined before resuming the adsorption step.

Table 3.1 Approximate weight of adsorbents in each layer

Adsorbent type	Actual volume ratio*	Weight of adsorbents (g) [£]	
		Column ∅14mm †	Column ∅33mm [#]
Silica gel	0.0426	0.2617	2.9643
MolSiv 1/8"	0.6231	2.9146	33.0121
MolSiv 1/16"	0.3343	1.8237	20.6566
Total	1.0000	5.0000	56.6330

* Basis volume equal 1.0

[£] Volume of each layer converted to mass

† Small column to determine the adsorption isotherm

[#] Large column to study the breakthrough curve

The humidity level of the feed gas was adjusted by mixing dry gas with saturated gas to obtain the desired value before the feed gas was introduced to the top of the adsorber. The adsorption step continued until the humidity of the outlet gas was equal to that of the inlet gas. Then, the adsorber was removed to measure the weight for saturated adsorbents. The amount of water adsorbed on the adsorbents per gram could be calculated as follows:

(Weight of saturated sample – Weight of dry sample)/ (Weight of dry sample).

The adsorption isotherm curve was achieved by plotting the ratio of the amount of adsorbed water to the weight of dry adsorbents versus the water inlet concentration or humidity, which was obtained from running the adsorption at various humidity levels.

3.3.3 Adsorption Experimental Procedure

The following experiment steps were to be done to obtain an adsorption breakthrough curve:

(1) All adsorbents, Silica gel, MolSiv 4A 1/8", MolSiv 4A 1/16", were dried at 110 °C for overnight.

(2) Each adsorbent and ceramic balls were weighted. The approximate weights are shown in Table 3.1

(3) Each adsorbent was packed into the column (Pyrex tube) one by one as multiple layers according to designed volume ratios. The order of packing is shown in Appendix C.

(4) The pretreatment step was performed with the same procedure as referred to the adsorption isotherm of water on multi-layer adsorbents section.

(5) The system was purged with N_2 gas until the humidity level was down to zero.

(6) A portion of natural gas was introduced through the humidifier chamber and mixed with the dry natural gas to obtain the desired humidity level, which was continuously detected using an on-line humidity analyzer.

(7) The humidified natural gas was passed to the top of the adsorber. The water content in the outlet gas from the bottom of the adsorber was immediately analyzed using an on-line humidity analyzer.

(8) The adsorption experiment was continuously performed, and the data were gathered until the adsorbents were totally saturated at the point where the water contents in the inlet and the outlet were equal.

(9) The adsorption experiment was stopped.

(10) The regeneration step was started with the same procedure as pretreatment procedure.

(11) The Steps (6) to (10) were repeated with different flow rates and/or humidity levels. The breakthrough curve could be obtained by plotting the outlet water and inlet water concentration ratio (C/Co) versus time. The ranges of experimental conditions are shown in Table 3.2.

Table 3.2 Ranges of experimental conditions

Parameters	Ranges
Operating pressure (constant pressure)	1 atm
Operating temperature (Isothermal condition)	25 $^{\circ}$C
Humidity of natural gas feed	
- Adsorption isotherm	5-75 %RH
- Breakthrough curve study	60 and 75%RH
Natural gas feed flow rate	130 and 260 ml/min
Contact time (based on the feed flow rate)	17 and 34 sec
Bed volume (for breakthrough curve study)	75 ml