

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Background

There are many techniques for natural gas dehydration; an adsorptive separation technique is one of the best alternatives for water removal. The process is commonly performed in a packed-bed column. The principle of adsorption process and suitable solid adsorbents for drying natural gas are briefly described. Also, the adsorptive separation mechanisms will be discussed later. In addition, the adsorption column dynamic model consisting of a basic governing equation of the adsorption will be introduced. Furthermore a decrease in adsorbent capacity due to aging will be described. Finally, the related work on both adsorption experiments and mathematical modeling will be summarized.

2.1.1 Natural Gas Dehydration

To satisfy the water content specification in natural gas, the adsorption process is applied. Adsorption is a separation process by contacting and adhering of a liquid or gas molecule on the solid surface with reversible reaction. Generally, the fixed-bed column that contains a hydrophilic adsorbent has been applied to remove trace amount of moisture from natural gas. The main purposes of this process were to prevent the water freeze up in distillation process trains and to eliminate the condensation of water causing the hydrate formation in the processing and transportation facilities. Moreover, this process prevented the corrosion problem, caused by the combination of wet stream and acid gas.

2.1.2 Adsorption Equipments

In the most common cases, a two-bed dehydrator system consists of one bed on a adsorption mode and the other on regeneration mode. The schematic diagram of a typical two-bed system for natural gas drying is shown in Figure 2.1. The feed gas passes down through the packed-bed column. Downflow is preferred because upflow at high rate might fluidize the particles, causing attrition and loss of fine particles (McCabe *et al.*, 1993). The dried product natural gas, then, is delivered

to further downstream processings, such as distillation units. When the concentration of the adsorbate in the exit gas reaches a set-point value, breakthrough time or at a scheduled time, the saturated adsorption column will be switched to the regeneration mode while the other dry column will be replaced to the adsorption mode (McCabe *et al.*, 1993).

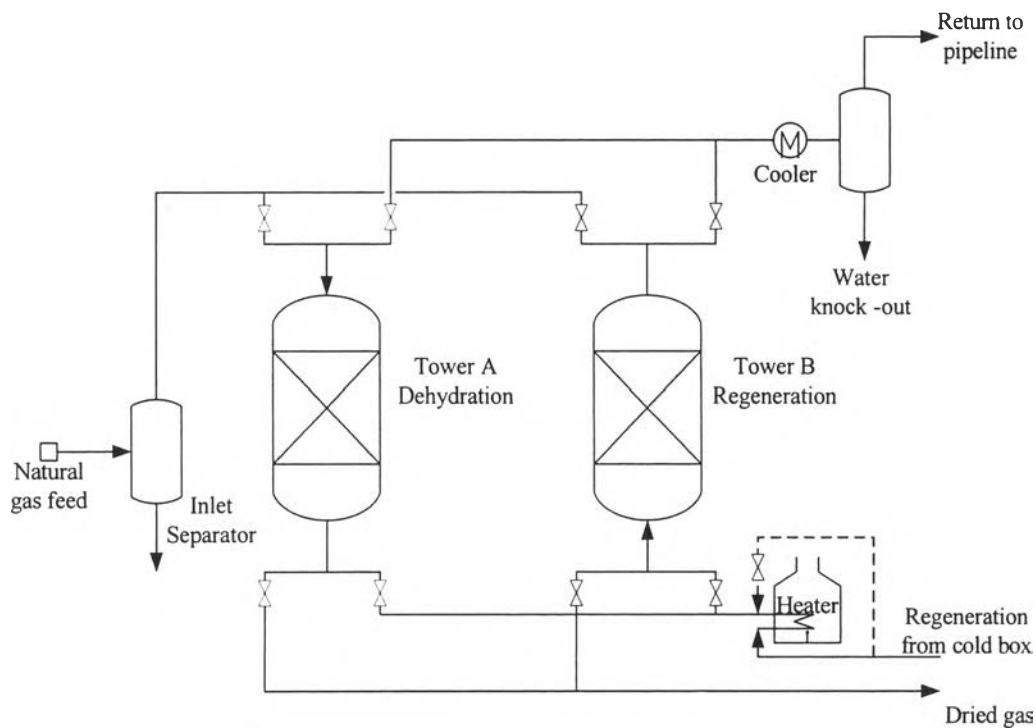


Figure 2.1 Molecular sieve natural gas dehydrator (Howe-Grant and Kroschwitz, 1992).

The process phenomena can be described by using the breakthrough curve. The time dependent concentration of an adsorbate in an effluent stream is shown in Figure 2.2. As show in Figure 2.2, LES (length of equivalent equilibrium section) is represented as the used capacity, and LUB (length of unused bed) is represented as the bed at the residual loading.

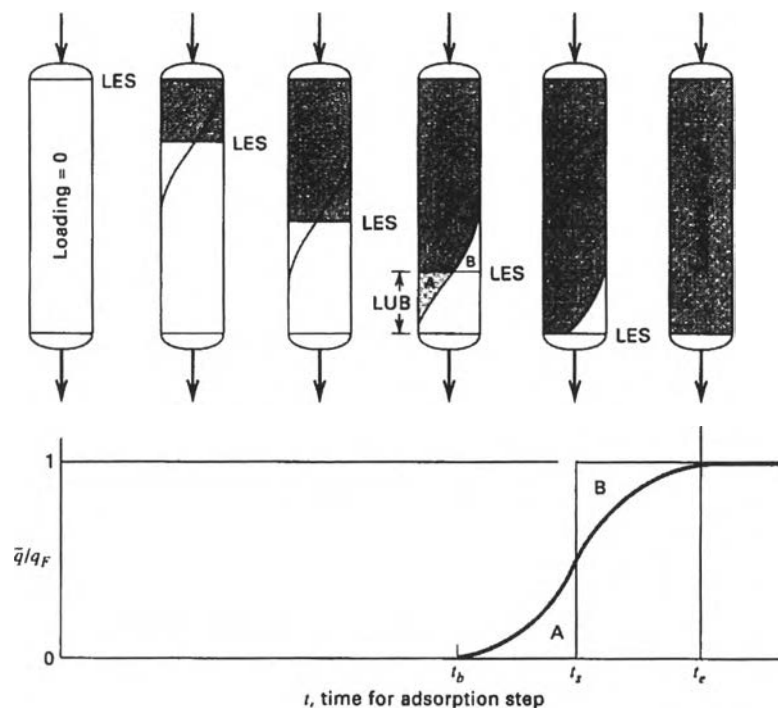


Figure 2.2 Progress of concentration profile and its corresponding effluent breakthrough curve (Seader and Henley, 1998).

An adsorbent can be regenerated by either thermal swing or pressure swing technique. Regeneration fluid can be hot inert gas or steam, but the most commonly used fluid is the product gas from the cold section of such a plant. The regeneration direction is generally performed counter-current to the drying direction, preventing the adsorbate to come in contact with the bottom part of the adsorbent.

If the demand for drying is intermittent, a single-bed system can also be used. In continuous system with high gas loading, more than two columns or multi-columns would be used. They could be in series flow or in parallel flow.

A multi-layer technology was developed based on the combination of the dominant properties of any adsorbent when dealing with the amount of contaminants in feed stream. As a result, multi-bed operation enhanced adsorption capacity of the whole system, improved the purification capability, and increased the lifetime of adsorbents.

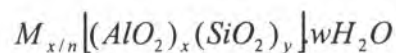
2.1.3 Adsorbents

The primary requirement for an economic separation process is an adsorbent with sufficiently high selectivity, capacity, and lifetime. Searching for a suitable adsorbent is generally the first step in the development of the adsorption separation process. Since the separation factor generally varies with temperature and also often with composition, the choice of suitable condition to maximize the separation factor is major consideration in process design (Ruthven, 1984).

There are four main types of commercial adsorbents: molecular-sieve zeolites, activated alumina, silica gel, and activated carbon. A high affinity and capacity for adsorption of moisture from a gas stream are simply the properties of adsorbent used as a solid desiccant. Therefore, the main requirements for an effective adsorbent are highly polar surface and high specific area (small pore). The most widely used adsorbents in gas drying are molecular-sieve zeolites (3A, 4A, and 13X), activated alumina, and silica gel.

Molecular-Sieve Zeolites

Molecular-sieve zeolites are the crystalline aluminosilicates with cations such as sodium, potassium, magnesium, and calcium. The structure formula of zeolite is based on the crystal unit cell, the smallest unit of structure, represented by



where n is the valence of cation M , w is the number of water molecules per unit cell, and x and y are the total numbers of tetrahedrals per unit cell (Rousseau, 1987).

Zeolites selectively adsorb or reject the molecules based on differences in molecular size, configuration of molecule (shape), and other properties such as polarity (Rousseau, 1987). Nearly most adsorption takes place inside the crystals (99%). The zeolites have high affinity and high capacity at low partial pressures. This makes them suitable to the gas streams, which have a very low humidity or dew point.

For drying application Molecular-sieve zeolite type 3A-potassium zeolite, 4A-sodium zeolite, 5A-calcium zeolite, and 13X-sodium zeolite are the most widely used. Although, the molecular-sieve zeolite type 4A has moderate

equilibrium water capacity, it is the most common type to apply for the natural gas dehydration. Figure 2.3 shows the framework structure of zeolite A and zeolite X.

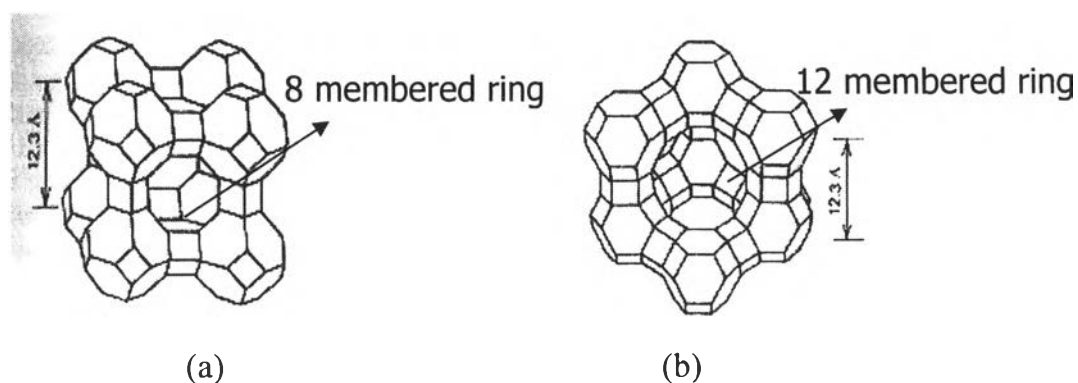


Figure 2.3 Schematic representation of the framework structure of (a) zeolite A, and (b) zeolite X (Ruthven, 1984).

Activated Alumina

Activated alumina adsorbents are amorphous or “transition aluminas” whose chemical composition is Al_2O_3 . Their fine pore structure and surface chemistry provide the adsorption selectivity. They have a high affinity for water, not as high as that of molecular-sieve zeolites, but they can produce dried gas with less than 1 ppm moisture content. Although, they are more robust than zeolites and less sensitive to deactivation by organics, they are less suitable when applied at a very low humidity stream (Rousseau, 1987).

Silica Gel

Silica gel adsorbents are composed of rigid three-dimensional spherical particles of amorphous colloidal silica (SiO_2). The silica gel surface has an affinity for water and organics, although water is preferred. Even though the affinity of the silica gel adsorbents for moisture is lower than that of either alumina or the zeolites, they have good capacity at high relative humidity, and relative low regeneration temperature is required (Rousseau, 1987).

Additionally, the typical adsorption equilibrium isotherms of water on these three types of adsorbents are shown in Figure 2.4. The 4A zeolites display

higher water adsorption capacity at relatively low humidity. While activated alumina and silica gel have higher adsorption capacity at high humidity. Therefore, the selection of suitable adsorbent depends on the application requirement and economics. In case of a very low humidity required as in petrochemical plant, 4A zeolite is the most suitable to achieve that specification.

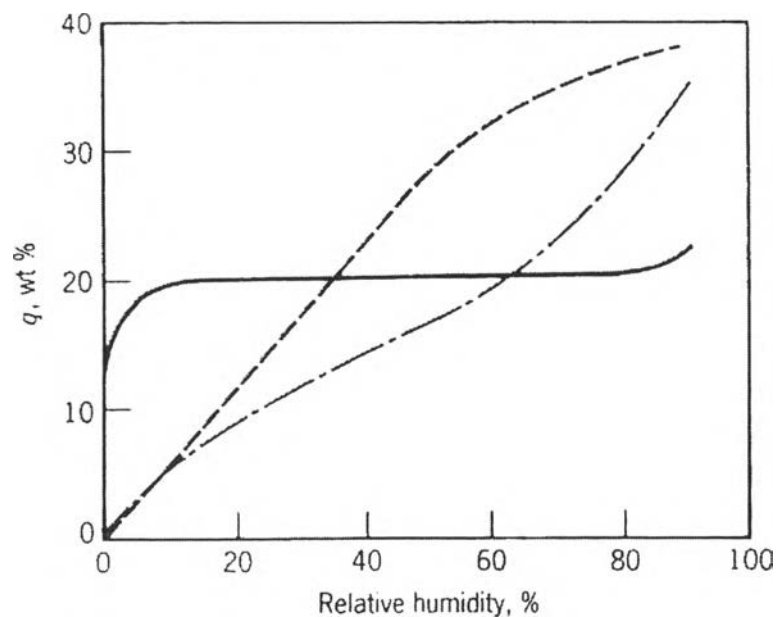


Figure 2.4 Adsorption equilibrium isotherms for moisture on three commercial adsorbents: palletized 4A zeolite (—), Silica gel (---) and, a typical activated alumina (- · - ·) (Howe-Grant and Kroschwitz, 1992).

2.1.4 Mechanism of Separation

The adsorptive separation can be achieved by one of the following mechanisms: steric, kinetic, or equilibrium effect. The *steric* separation is unique with zeolites because of their uniform aperture size in the crystalline structure. In this case, only small and properly shaped molecules can diffuse into the adsorbent whereas other molecules are excluded. The *kinetics* separation can be achieved by the feature of the differences in diffusion rate of various molecules in pores. The kinetic selectivity can be controlled by the adjustment of the pore size. A large majority of process operates through the equilibrium adsorption of the mixture, which is called *equilibrium* separation processes. The separation is based on the

difference in equilibrium capacity of each of the components in the gas mixture. This equilibrium selectivity is generally controlled by adjusting the balance between electrostatic and Van der Waals forces. All the separation mechanism aforementioned is described in Yang (1987).

2.1.5 Mathematical Models

Adsorptive gas separation processes are, in general, carried out in fixed-bed columns, which contain the porous adsorbent particles or pellets. The mathematical models are needed to understand the dynamic of such systems. Mass and heat balance as well as the equilibrium isotherm should be accounted for the adsorptive gas separation model. Therefore, both mass and heat transfer resistance inside and outside the adsorbent pellets are significant. Since the local rate of adsorption is assumed instantaneous and much greater than that of the transport process, thus, the model equation can be the coupling of the equilibrium isotherm and the continuity of flux at the surface of the pellet (Yang, 1987).

The flow pattern can commonly be adequately represented by the axial dispersion plug flow model, according to a mass balance of the column. The basic differential equation governing the dynamic behavior is illustrated as the following (Howe-Grant and Kroschwitz, 1992):

$$-D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z}(vc) + \frac{\partial c}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon} \right) \frac{\partial \bar{q}}{\partial t} = 0 \quad (2.1)$$

where

D_L = axial dispersion coefficient

c = adsorbate concentration in fluid phase

v = interstitial velocity of fluid

z = distance measured from column inlet

t = time

ε = bed void fraction, and

\bar{q} = adsorbed phase concentration average over a particles.

The term $\frac{\partial \bar{q}}{\partial t}$ represents the overall rate of mass transfer for adsorbed component average over a particle. The mass balance for an adsorbent particle yields the adsorption rate expression, which may be written as

$$\frac{\partial \bar{q}}{\partial t} = f(q, c) \quad (2.2)$$

This rate equation must satisfy the boundary conditions imposed by the equilibrium isotherm, and it must be thermodynamically consistent so that the mass transfer rate falls to zero at the equilibrium. It may be a linear driving force model. In this model, it is assumed that the driving force for mass uptake in the particle is proportional to the difference between the equilibrium adsorbate concentration and the actual uptake in the particle. The model expression can be written as

$$\frac{\partial \bar{q}}{\partial t} = k(q^* - \bar{q}) \quad (2.3)$$

where $q^* = f(c)$ represents the equilibrium adsorbed phase concentration, or it may be a set of diffusion equations with their associated boundary condition (Howe-Grant and Kroschwitz, 1992).

For an isothermal system, the simultaneous solution of Equation 2.1 and 2.2 is subject to the boundary conditions imposed on the column provides the expressions for the concentration profiles $c(z, t)$, $\bar{q}(z, t)$ in both phases (Howe-Grant and Kroschwitz, 1992).

2.1.6 Deactivation

Aging of an adsorbent causes a decrease in adsorption capacity. Two types of aging include:

1) Hydrothermal aging is an irreversible change of adsorbent structure caused by hydrothermal treatment during regeneration, resulting in a decrease in active area. The slow loss of crystallinity is the common problem in thermal swing

cycles where the sieve is used as a desiccant, or water present as an impurity in the feed is adsorbed in the first few layers of the adsorbent bed. During thermal regeneration, the sieve is exposed to a combination of high temperature and high humidity. Under these conditions, a slow and irreversible breakdown of the crystal structure may occur. Aging is, therefore, dependent on the number of cycles and quality of adsorbent.

2) Aging through contamination is caused by coadsorption of undesired species and coke formation on the active surface of the adsorbent. This phenomenon is not completely reversible, and the carbon deposit increases at each regeneration.

2.2. Literature Survey

The previous work related to both experiment and mathematical modeling for adsorption of the component from fluid phase onto solid adsorbent is summarized in this section.

Lertviriyakijskul (2000) studied the competitive adsorption between the hydrocarbons and water on activated alumina prepared by sol-gel technique. Also, he studied the effects of calcination temperature on the water adsorption capacity of alumina. It was found that at the beginning the hydrocarbons were adsorbed and, then, desorbed by the replacement of water, since alumina preferred to adsorb water from natural gas because of higher affinity between water molecule and alumina surface. In addition, these sol-gel aluminas provided a high water adsorption capacity and low desorption temperature of 100°C. The highest adsorption capacity of sol-gel alumina was 19.9 g water/100 g alumina.

In year 2001 Bamrunget followed the works accomplished by Lertviriyakijskul by changing the adsorbent from activated alumina to modified clinoptilolite. The results showed the same trend of competitive adsorption between water and hydrocarbons. The water adsorption capacity of the modified clinoptilolite was about 7.34-10.04 g water/100 g clinoptilolite.

Thipkhunthod *et al.* (2001) developed the mathematical model for predicting the competitive adsorption between the hydrocarbon and water on

activated alumina (mentioned above on the experiment done by of Lertviriyakijkskul). The model was established based on unsteady state mass transfer and Langmuir-Freundlich equilibrium adsorption equations. The adjustable parameters in the equilibrium adsorption model were determined from equilibrium adsorption data of single component. FORTRAN programming language was used to solve the set of mathematical equations. With the pre-determined parameters, the equilibrium adsorption model can be used to well predict the water and hydrocarbon adsorption. The dynamic adsorption capacity of water from the experiment was about 4.49 g water/100g of alumina, while the predicted value was about 4.05 g/100g of alumina.

In addition, the experimental and theoretical breakthrough curves of volatile organic compounds (VOC) on zeolite were studied by Brosilion *et al.* (2001). They proposed simulations of breakthrough curves based on the Linear Driving Force model (LDF). The experiments were performed on fixed beds of hydrophobic commercial zeolites. A good agreement between experimental and numerical results was found when an adjustable value of the internal mass-transfer coefficient was used. A constant value of effective diffusivity was found independent of the nature and the amount of VOCs adsorbed. A relation linking intrapellet mass-transfer coefficient and equilibrium constant was proposed, including the average effective diffusivity, in order to make predictions of breakthrough curves for any kind of volatile organic pollutant in gaseous effluents.

Moreover, the development of a gas purifier to remove butane from air using ZSM-5 facilitated adsorption has been developed by Sundry *et al.* (2001) in order to reduce the concentration of butane in air. The laboratory-scale purifier was tested and employed both ideal and rigorous modeling to characterize the adsorption of butane on ZSM-5. The experimental breakthrough curve differed from Klinkenberg model expectation because of the effect of incomplete activation and channeling during the experiment. And also, in year 2002 Dicken *et al.* investigated the adsorption of toluene on ZSM-5. The breakthrough results were compared with the model predictions, and sensitivity analysis was performed on the model to account for the relative model. The investigation showed that the adsorption model was very sensitive to the bed length, bed void fraction, gas flowrate, and pellet diameter.

The adsorption technique onto solid adsorbents was also applied with the adsorption of component in liquid phase. The adsorption isotherms of benzoic acid onto activated carbon and breakthrough curves in fixed-bed columns were investigated by Chern *et al.* (2001). The adsorption isotherms of benzoic acid onto granular activated carbon at varied solution temperatures and pHs from an aqueous solution were experimentally determined by batch tests. The Toth model was found to fit well with all of the experimental data. A series of column tests were performed to determine the breakthrough curves with varying bed depths and water flow rates. The results showed that the half breakthrough time increased proportionally with increasing bed depths, but decreased inverse proportionally with increasing velocity. The constant-pattern wave approach using the Freundlich isotherm model fit the experimental breakthrough curves quite successfully. A correlation was proposed to predict the volumetric mass-transfer coefficient in the liquid phase.

Since the adsorption of water vapor contaminated in natural gas through the fixed-bed column is mostly used in the real application. In order to improve the industrial design and to find the optimal operating condition, the adsorption phenomena of a fixed-bed process need to model. So, this work was focused on the water removal from natural gas through the multi-layer adsorber. The experimental was set up to investigate the effect of feed concentration and contact time on the characteristics of breakthrough curve. Furthermore, a theoretical breakthrough curve was obtained by solving the set of mathematical equations. The adsorption was based on an axial dispersion plug flow and Linear Driving Force (LDF) models. The adsorption isotherm of adsorbents was obtained from the dynamic adsorption of the mixed adsorbents through the multi-layer adsorber. The isotherm equation was applied to complete the mathematical model. The method of lines (MOL) combined with the finite difference and computer programming were utilized to obtain the theoretical breakthrough curve.