

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Background

The adsorptive separation using solid adsorbents is used to remove water out of the natural gas stream. Both equilibrium and dynamic adsorption are needed to understand in the unit separation design. The equilibrium adsorption indicates the efficiency of an adsorbent for a particular adsorbate removal, and the dynamic adsorption in the adsorber is indicated as breakthrough analysis. In order to propose the dynamics adsorption model, the equilibrium adsorption is needed to studied together also the deactivation factor is important to consider because it always occur along the adsorption and regeneration process.

2.1.1. Natural Gas Components

Natural Gas is an essential component of the world's supply of energy. It is colorless, shapeless, and odorless in its pure form. Natural gas is a combustible mixture of hydrocarbon gases. While natural gas is formed primarily of methane, it can also include ethane, propane, butane and pentane. The composition of natural gas can vary widely, below is a chart outlining the typical makeup of natural gas before it is refined.

Table 2.1 Typical composition of natural gas^[1]

Composition	Chemical formula	%Mole
Methane	CH ₄	70-90%
Ethane	C ₂ H ₆	0-20%
Propane	C ₃ H ₈	
Butane	C ₄ H ₁₀	
Carbon Dioxide	CO ₂	0-8%
Oxygen	O ₂	0-0.2%
Nitrogen	N ₂	0-5%
Hydrogen Sulphide	H ₂ S	0-5%
Rare gases	Ar, He, Ne, Xe	trace
Water	H ₂ O	16-32 mg/m ³

^[1] www.uniongas.com

The final end-product of natural gas separation is a relatively homogeneous product, which is almost pure methane, so other impurities have to be removed from the stream. This work will focus on water removal because it causes many problems such as catalyst poisoning, corrosion, water freeze-up in the distillation column, and plugging by hydrate formation in the transportation facilities.

2.1.2 Natural gas dehydration

As known, water is one of the impurities in the natural gas stream and it causes many problems in natural gas processing, therefore, the dehydration unit is developed in order to reduce water content as much as possible. Nowadays there are many available separation technologies. The first one is adsorption with liquid triethyleneglycol (TEG) which water is removed by counter current contact in a tray type contactor with glycol solution. The next one is adsorption with solid adsorbents such as silica, molecular sieve or alumina. The other offered techniques are membranes, vortex tubes, supersonic separations and dew point control or Joule-Thomson expansion. The solid adsorptive separation is widely used because there are a lot of commercial adsorbents provided for several adsorption purposes and it is comfortable for the regeneration step.

2.1.3 Adsorption dehydration

Adsorption is one of the many separation technologies used in treating natural gas. The main description of gas-solid adsorption system is that molecules from the gas are held on the solid surface by surface force. There are two principal models of adsorption of molecules to surfaces: physical adsorption (physisorption) and chemical adsorption (chemisorption).

2.1.3.1 Physisorption: Physisorption occurs when vapors near their saturation pressures adsorb to a dry surface. The only bonding is by weak Van der Waals type forces. The heat of adsorption is in the neighborhood of a few hundred cal/deg.mol. It is a very rapid and reversible process with the equilibrium established quickly as the gas pressure varies. Note that physisorption is generally considered important only for vapors below their critical temperature.

2.1.3.2 Chemisorption: Chemisorption proceeds with a strong bonding of the molecules to the surfaces, often resulting in a change of both surfaces, and sorbate molecules chemical character. It results in strong binding forces, and is characterized by high adsorption energy. The reaction is likely to be slow and less reversible, so the equilibrium may take longer time to achieve.

Another gas-solid separation is based on size exclusion, where the molecules of the contaminant fit into the pores of the adsorbent and the rest passes by. Removal of N₂ or CO₂ with molecular sieves is one of the examples for this principle.

The chemisorption has limited applications in natural gas processing, and will not be discussed herein.

2.1.4 Adsorption equipment

Dehydration by adsorbent drying systems is typically operated in a regenerative mode with an adsorption half-cycle to remove water from the process gas stream and desorption half-cycle to remove water from the adsorbents and to prepare them for another adsorption half-cycle (Uttamaroop, 2004). The schematic diagram of a typical two-bed system for natural gas drying is shown in Figure 2.1.

Two basic gas drying processes used in the plant are temperature swing adsorption (TSA) and pressure swing adsorption (PSA). The basic steps of a PSA gas drying process are:

- (1) The gas is flown over the adsorbents bed to adsorb the trace water vapor from the feed gas at an elevated pressure, and withdrawing a dry product gas at the pressure of the feed gas.
- (2) Countercurrent depressurization of the adsorber to near-ambient pressure and venting the effluent gas
- (3) The bed is countercurrent purged at a near-ambient pressure with a part of dry product gas from step 1 and discarding the effluent gas.
- (4) Countercurrent repressurization of the adsorber with a part of the dry product gas from step 1

The cycle is then repeated. Figure 2.1.4 illustrates the basic PSA unit to remove water vapor out of the air.

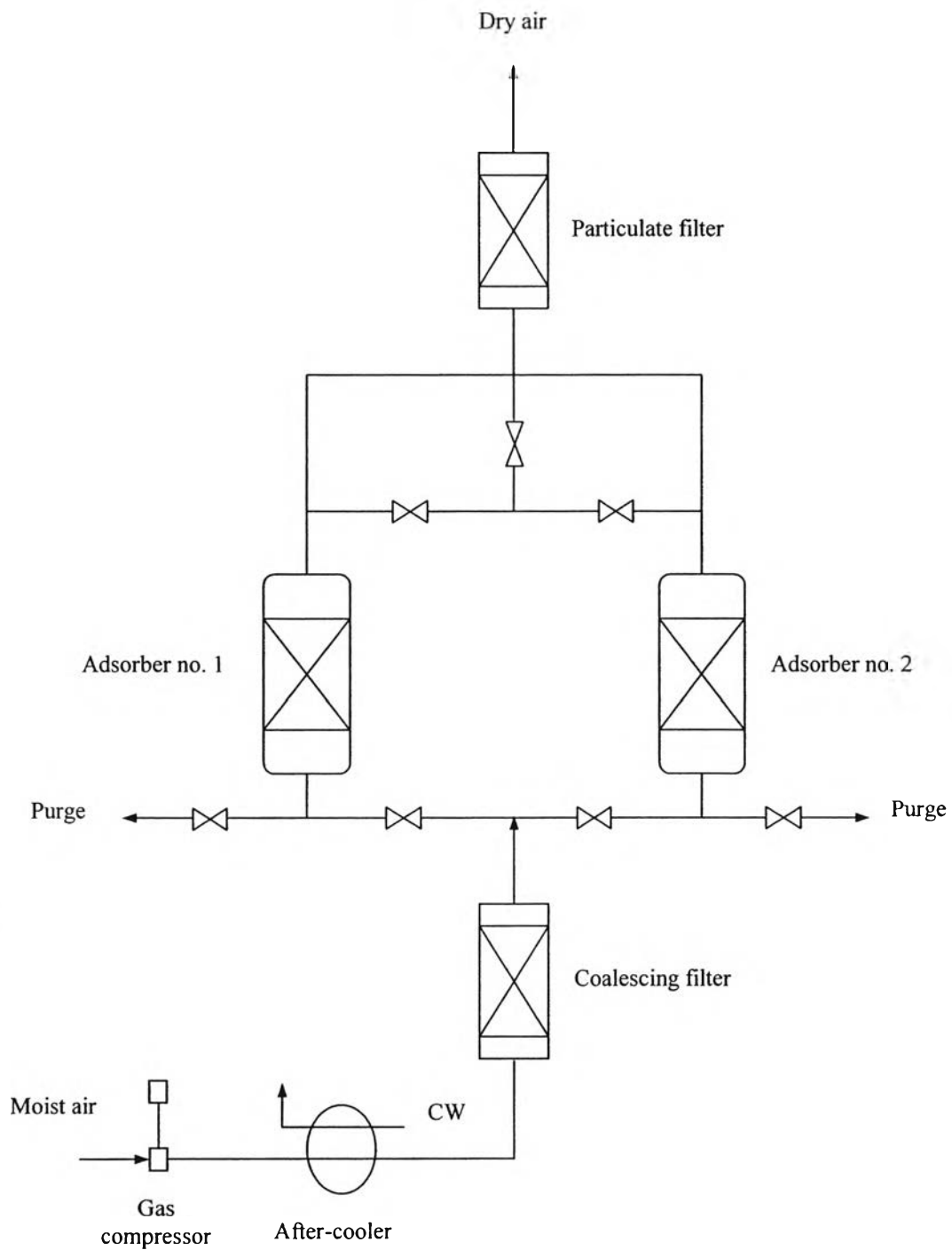


Figure 2.1 Pressure-swing adsorption for the dehydration process (Thomas, 1998).

The basic steps of a TSA gas drying process are:

- (1) The wet gas is flown over a packed bed of the adsorbents at near-ambient temperature and withdrawing a dry product gas.

(2) The adsorbents are then heated by the countercurrent flow of a hot, dry gas through the bed while rejecting the water-loaded effluent gas, and

(3) The bed is subsequently cooled by countercurrent flowing of a dry gas through the bed at feed temperature. The effluent gas from this step is rejected or used in step 2 after reheating

A part of the dry product gas from the step 1 is often used as the regeneration gas for step 2 and 3.

2.1.5 Adsorption isotherms

The measurement of the amount of gas adsorbed over range of bulk partial pressure at a single temperature results in a graph known as adsorption isotherm. The adsorption isotherms describe the equilibrium relationship between an adsorbate in the gas stream and the moles adsorbed on the solid surface at a constant temperature.

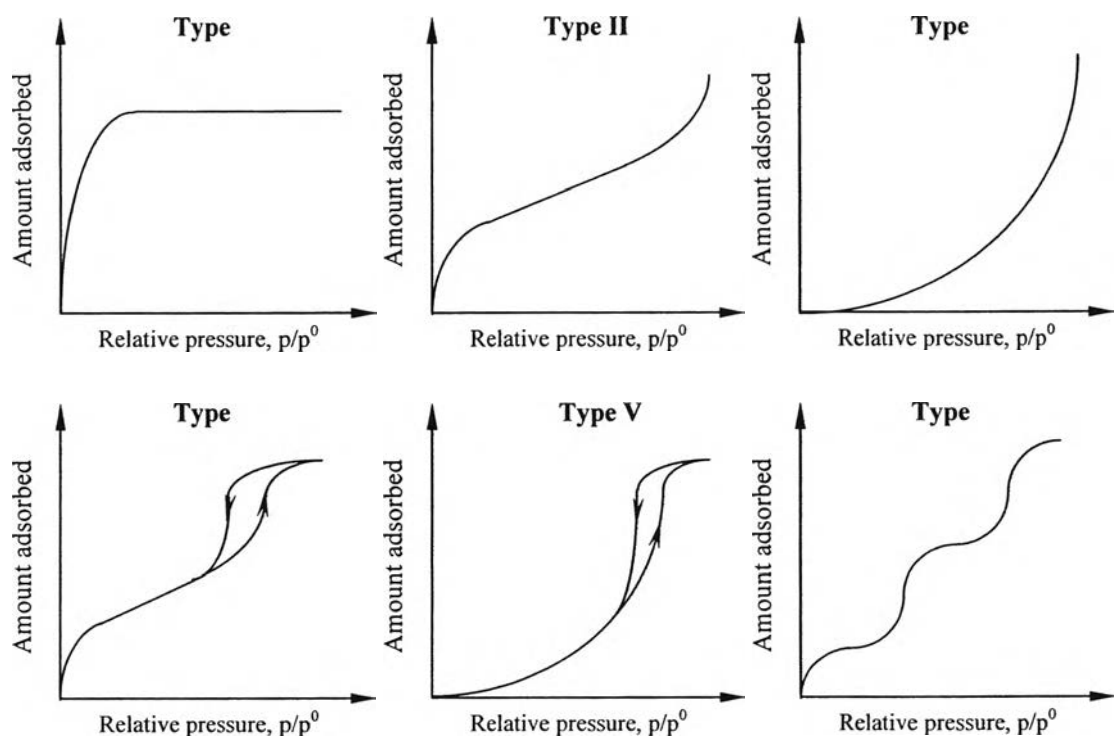


Figure 2.2 IUPAC classifications of gas adsorption isotherms (IUPAC, 1994)

There are many types of isotherms observed in the literature, and the different types depend on the type of adsorbents, the type of adsorbate, and

intermolecular interactions between the gas and the surface. Brunauer, et al. (1940) described 5 general types of gas-solid sorption isotherms. Type I is isotherm for microporous adsorbents, this type of isotherm is similar to Langmuir isotherm, which assumes that only gas is being adsorbed, and the coverage of the surface is a monomolecular layer. Types II and III give adsorption isotherms on macroporous adsorbents with strong and weak affinities, respectively. Type IV and V characterize mesoporous adsorbents with strong and weak affinities, respectively, and also show hysteresis effect. Brunauer's classification has become the core of the modern IUPAC classification of adsorption isotherms by addition of one last type or type VI, which shows steps in adsorption, as illustrated in Figure 2.2.

There are many adsorption equations which have been proposed to explain the adsorption behavior of adsorbate onto adsorbents. Each model has the different parameters that can be found from the experimental data. Table 2.2 presents some of the conventional adsorption isotherm models applied in the literatures (Gobrach *et al.*, 2003).

Table 2.2 Names and equations of applied conventional adsorption isotherm models

Model	Equation	Parameters
Langmuir	$q = q_s \frac{b_p}{1 + b_p}$ $b(T) = b_\infty \exp(b_T / T)$	2
LangmuirT	$q = q_s(T) \frac{b(T)p}{1 + b(T)p}$ $b(T) = b_0 \exp(b_T (T_0 / T - 1))$	3
Langmuir2T0	$q_s = q_{s0} \exp(q_{sT} (1 - T / T_0))$	4
HenryLangmuir	$q = Kp + q_s \frac{bp}{1 + bp}$	4

Model	Equation	Parameters
HenryLangmuir2T	$q = K(T)p + q_s \frac{b(T)p}{1 + b(T)p}$ $b(T) = b_\infty \exp(b_T / T)$	3
FreundlichV	$q = K\Phi^n$	2
FreundlichDubinin AstakhovV	$q = K\Phi^m + q_s \exp\left(- (a \log(1/\Phi))^n\right)$	5
DubininAstakhovV	$q = q_s \exp\left(- (a \log(1/\Phi))^n\right)$	3
DubininAstakhovVT	$q = q_s \exp\left(- (aT \log(1/\Phi))^n\right)$	3
Dubinin RadushkevichVT	$q = q_s \exp\left(- (aT \log(1/\Phi))^2\right)$	3
Toth	$q = q_s \frac{bp}{(1 + bp')^{1/i}}$	3
TothV	$q = q_s \frac{b\Phi}{(1 + b\Phi')^{1/i}}$	2
Sips	$q = q_s \frac{(bp)^n}{(1 + (bp)^n)}$	2
BETV	$q = q_s c \frac{\Phi}{(1 - \Phi)(1 + (c - 1)\Phi)}$	2
AranovichV	$q = q_s c \frac{\Phi}{(1 - \Phi)^{0.5}(1 + c\Phi)}$	2
D-A equation ^[3]	$q = q_s \exp\left\{- \left(\frac{R_g T}{E}\right)^n \left[\ln\left(\frac{P_o(T)}{P}\right)\right]^n\right\}$	4
DMAP equation ^[3]	$q = q_{s1} \left(\frac{P}{P_o(T)}\right)^{\frac{R_g T}{E_1}} + (q_{s2} - q_{s1}) \left(\frac{P}{P_o(T)}\right)^{\frac{R_g T}{E_2}}$	5
UNILAN ^[4]	$q = \frac{q_m}{2s} \ln \left[\frac{c + Pe^{+s}}{c + Pe^{-s}} \right]$	3
Henry's isotherm (Linear isotherm)	$q = Hp \text{ or } q = H \frac{P}{P^o}$	1

^[3] Moore, 2004

^[4] Kim, 2005

2.1.6 Adsorbents

Most solids are able to adsorb species from gases or liquids. Only a few exhibit sufficient selectivity and capacity that make them suitable for commercial uses. Adsorbents should have a large specific surface area. Any commercial adsorbent normally have a total surface area of 500 to 800m²/g (Campbell, 1992). This range is usually achieved by the method of adsorbent synthesis. Commercial adsorbents may be acquired either as a powder, a granular, a flake, a sphere, and a cylindrical pellet, or as a fiber.

Desirable characteristics at an adsorbent include (Campbell, 1992):

- a. Large surface area for high capacity to minimize the amount of adsorbent needed,
- b. High selectivity for the components to be removed,
- c. High mass transfer rate for rapid adsorption,
- d. Easy and economic regeneration,
- e. Good activity retention with time,
- f. Small resistance to gas flow with free-flowing tendency for ease of filling or emptying vessels,
- g. High mechanical strength to resist crushing, dust formation, and erosion,
- h. Chemical and thermal stability, including low solubility in the contacting fluid, to preserve the amount of adsorbent and its properties,
- i. No tendency to promote undesirable chemical reactions and no appreciable change in volume during adsorption and desorption, and strength preservation toward wetting, and
- j. Relatively low cost.

The widely-used solid desiccants are activated alumina (Al₂O₃), silica gel, carbon (activated and molecular-sieve carbon), and molecular-sieve zeolites.

- Activated alumina, Al₂O₃ is made from removing water from hydrated colloidal alumina. It has a moderately high specific surface area, with a

capacity for water adsorption sufficient to dry gases to less than 1 ppm moisture content.

- Silica gel, SiO_2 is made from colloidal silica. It has high surface area and high affinity for water and other polar compounds, so it is highly desirable for water removal. Types of silica gel are divided by pore size. Both small-pore and large-pore types are available.

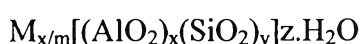
- Carbon or charcoal is treated and activated to have adsorptive capacity. The partial oxidation of a number of materials such as coconut shells, fruit nuts, wood, coal, lignite, peat, petroleum residue and bones is conducted to make the activated carbon. The high specific surface area and hydrophobic nature of most activated carbons make them particularly useful for processes involving non-polar and weakly polar organic molecules. The low bonding strength of adsorption by activated carbons results in a low heat of adsorption and ease of regeneration of the adsorbent. Types of activated carbon are also divided by pore size. The molecular sieve carbon typically has a pore size in the range 0.2 to 1.5 nm, making it possible to separate N_2 from air.

Table 2.3 Properties and applications of zeolites^[5]

Designation	Cation	Unit cell formula	Aperture size. nm	Typical applications
3A	K^+	$\text{K}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$	0.29	Drying of reactive gases
4A	Na^+	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$	0.38	H_2O , CO_2 removal; air separation
5A	Ca^{2+}	$\text{Ca}_5\text{Na}_2[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$	0.44	Separation of air; linear paraffins
10X	Ca^{2+}	$\text{Ca}_{43}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}]$	0.80	Separation of air; removal of mercaptans
13X	Na^+	$\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}]$	0.84	

^[5] <http://www.zeoponix.com/zeolite.htm>

- Molecular sieve zeolites have the general stoichiometric unit cell formula as;



Where M is the cation with valence m , z is the number of water molecules in each unit cell, and x and y are integers such that $y/x \geq 1$. The cations balance the charge of the AlO_2 groups, each having a net charge of -1 . These adsorbents contain very narrow pore size distributions offering highly selective physical properties. The properties and applications of 5 of the most commonly used molecular sieve zeolites are summarized in Table 2.3. The properties of commercial adsorbents are listed in Table 2.4.

Table 2.4 Representative properties of commercial porous adsorbents ^[6]

Adsorbent	Nature	Pore diameter, d_p , nm	Surface area, S_g , m^2/g	Capacity for H_2O vapor at 25 °C and 4.6 mmHg, Wt %, (dry basis)
Activated alumina	Hydrophilic, amorphous	1.0 – 7.5	320	7
Silica gel: Small pore Large pore	Hydrophilic – hydrophobic, amorphous	2.2 – 2.6 10.0 – 15.0	750 – 850 300 – 350	11 —
Activated carbon: Small pore Large pore	Hydrophobic, amorphous	1.0 – 2.5 > 3.0	400 – 1200 200 – 600	1 —
Molecular-sieve carbon	Hydrophobic	0.2 – 1.0	400	—
Molecular-sieve zeolite	Polar-hydrophilic, crystalline	0.3 – 1.0	600 – 700	20 – 25
Polymeric adsorbents	—	0.4 – 2.5	80 – 700	—

^[6] <http://www.zeoponix.com/zeolite.htm>

2.1.7 Deactivation

Catalyst deactivation is a result of a number of unwanted chemical and physical changes leading to the loss of catalytic activity and/or selectivity over time. Along the dehydration process, the deactivation of the adsorbents commonly occurs. The causes of deactivation are classically divided to three categories: chemical, thermal and mechanical (Butt and Petersen, 1988; Bartholomew, 2001). There are three major categories of deactivation mechanisms sintering, poisoning, and coke formation or fouling (Forzatti and Lietti, 1999). They may occur separately

or in combination, but the net effect is always the removal of active sites from the catalytic surface.

- Sintering is a common problem in processes running at high temperatures. Metal atoms or small crystallites may migrate and form larger aggregates. This causes the loss of active surface area and the deactivation of the catalyst.

- Poisoning is caused by substances that adsorb more or less irreversibly to the active sites of the catalyst. Common examples are: lead, sulfur, carbon monoxide and strong bases. Whether or not a substance is a poison depends on the catalyst and its ability to adsorb and desorb the substance.

- Coke formation is the last cause of catalyst deactivation. It takes place during many hydrocarbon processes.

Some other deactivation mechanisms, such as pore blockage, volatilization of active component, destruction of the active surface and incorporation of the active component into the washcoat in an inactive form can also cause a decline in the catalyst's activity (Butt and Petersen 1988, Bartholomew 2001).

2.1.8 Mathematical model

In order to fulfill the breakthrough model proposed by Uttamarop (2003), a deactivation model for the adsorption of water vapor from natural gas onto the activated alumina and molecular sieve zeolites in a packed bed adsorber was developed in this work.

The mass balance equation of the adsorber developed by Uttamaroop

$$-D_L \frac{\partial^2 c_i}{\partial z^2} + \frac{v \partial c_i}{\partial z} + \frac{\partial c_i}{\partial t} + \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial \bar{q}}{\partial t} = 0 \quad (2.1)$$

The change of adsorption due to the change of adsorption capacity of deactivated adsorbents was studied, and the correlation of the change was developed in this work for each adsorbent. The equilibrium adsorption isotherm was next developed for each fresh and deactivated adsorbent, and subsequently employed in

the dynamic adsorption model to predict the breakthrough time of various adsorbents packed with various layer series of fresh and deactivated adsorbents.

2.2 Literature Survey

Jong-Hwa *et al.* (2003) studied adsorption equilibria of water vapor on alumina, zeolite 13X and zeolite X/activated carbon composite. The effect of temperature and pressure were studied. The results showed that at a low temperature of 293.2 K, the plots of adsorption isotherm from the experimental data were classified as the Type II Brunauer isotherm for all adsorbents. At the higher temperatures from 313.2 to 353.1 K, the adsorption isotherm was matched with the Type I Brunauer isotherm. Also the order of the adsorption capacity for water vapor was zeolite 13X, Zeocarbon, and Al₂O₃, except at 293.2 K and in the high-pressure region. In addition, the prediction of equilibrium adsorption is accomplished by comparing between Aranovich and Donohue (A-D) model and *n*-layer BET model. The experimental equilibrium data were satisfactorily correlated with the A-D equation.

Correlation of adsorption equilibrium data for water vapor on F-200 activated alumina was determined by Moore, *et al.* (2004). Two isotherm equations were used to predict the adsorption equilibrium data. The first one was Dubinin-Astakhov (D-A) equation, and the second one was DMAP equation obtained from a methodology proposed by Kotoh *et al.* (1993).

$$q = q_s \exp \left\{ - \left(\frac{R_g T}{E} \right)^n \left[\ln \left(\frac{P_o(T)}{P} \right) \right]^n \right\} \quad \text{D-A equation}$$

$$q = q_{s1} \left(\frac{P}{P_o(T)} \right)^{\frac{R_g T}{E_1}} + (q_{s2} - q_{s1}) \left(\frac{P}{P_o(T)} \right)^{\frac{R_g T}{E_2}} \quad \text{DMAP equation}$$

DMAP equation is referred as a dual mechanism adsorption potential equation because it is a linear combination of two Freundlich isotherms. In a result, DMAP model provided a better fit for the adsorption data than the D-A model, while

neither model described the adsorption data well. Also the experimental isotherms at various temperatures (5-35 °C) fitted with the Type II Brunauer.

Lertviriyakijskul (2000) studied the competitive adsorption between the hydrocarbon and water on activated alumina prepared by sol-gel technique. It was found that sol-gel alumina had high affinity for water than hydrocarbons. In addition, this sol-gel alumina provided a high water adsorption capacity and low desorption temperature of 100°C. Also the adsorption isotherm of water vapor on sol-gel alumina was of the Type II Brunauer isotherm. Bamrunget (2001) followed Lertviriyakijskul's work by changing the adsorbent from activated alumina to modified clinoptilolite. The result showed the same trend of competitive adsorption between water and hydrocarbon.

Adsorption equilibrium of water vapor on activated carbon and DAY zeolite was studied by Kim, *et al.* (2005). The experiments were conducted at various temperatures, and a statistic volumetric method was used. The experimental adsorption isotherms of water vapor on DAY zeolite at 293 K were correlated with linear isotherm equation. At high temperatures from 313 to 373 K, the experimental adsorption isotherms were classified as the Type I Brunauer and satisfactorily correlated with the Sips, Toth, and UNILAN equations.

Lee, *et al.* (2003) studied adsorption of water vapor on mesoporous materials, zeolite types of which have different pore sizes and shapes at various temperatures. At 293 K constant temperature, the experimental adsorption isotherm data exhibited the unusual Type V isotherms for every zeolite adsorbents. Also a hybrid isotherm model composed of a Henry isotherm and a Sips isotherm was applied to the analysis of water adsorption on mesoporous including its surface adsorption and capillary condensation. The results showed the proposed isotherm nicely simulated measured adsorption data over the whole range at these experimental conditions.

In year 2002, Chaikasetpaiboon developed mathematical model of breakthrough curves for a multi-layer gas adsorber. The model was based on the assumption that the uptake rate of water vapor by the adsorbent pellet is linearly proportional to a driving force, and the driving force was defined as the difference between the equilibrium water concentration and the actual uptake on the particle.

The isotherm equations were obtained by fitting the experimental data, and found to fit with Langmuir and the linear model. The equilibrium adsorption isotherm was obtained from the adsorption of the entire bed consisting of four different materials in layers at various humidity levels. Furthermore the developed mathematical adsorption models predicted the adsorption capacity quite accurately, and gave acceptable prediction (with 27% error) of the breakthrough time for water adsorption from natural gas onto the multi-layer adsorber. Uttamaroop (2003) followed Chaikasetpaiboon's work. The sensitivity analysis was performed to improve the breakthrough models. The results showed the interstitial velocity and the effective bed voidage were more sensitive to the theoretical breakthrough curves than the effective axial dispersion coefficient. But since the water concentration in the natural gas feed was very small, the decrease in the interstitial velocity can be neglected. Therefore, the assumption of constant fluid velocity was applied in the mathematical model. The successful result of the model was received with the deviation value of just only 3-5 %.

Measurement and modeling of water vapor adsorption on zeolite 4-A was accomplished by Gorbrach *et al.* (2002). The equilibrium and kinetics adsorption were examined. The equilibrium was measured in a wide range of partial pressure and temperature, and was modeled by several conventional approaches and a new type isotherm model. Kinetics was determined by measuring breakthrough curves. The results showed that several conventional isotherm equations were fitted to the experimental data, and a new type of isotherm was presented due to their lack of fit especially in the very low pressure range and matched all experimental data well.

Firstly, the adsorption isotherm equations of fresh adsorbents and hydrothermal aged adsorbents will be determined. Then, the correlation between fresh and deactivated adsorption isotherm is examined, and the deactivation model for adsorption isotherm of deactivated adsorbents used in natural gas dehydration process will then be developed. Also, this model is related and used in prediction of the breakthrough time for the adsorber.

From all background and literature reviews mentioned in the first part, in order to establish the mathematical model of overall mass transfer of the adsorber,

the adsorption isotherms of the adsorbents have to be developed for being used in the dynamic adsorption model for the prediction of breakthrough time.

In this work, the adsorbents were deactivated by hydrothermal steaming technique. Static adsorption was performed to develop the adsorption isotherms. The experimental dynamic adsorption was conducted to determine the breakthrough curve of the adsorbents, and the experimental breakthrough time was compared with that predicted from the mathematical dynamic model for various types of packed beds. The scopes of this work were the followings. The adsorbents were prepared in deactivated forms by hydrothermal steaming at the temperature range of 300 to 550°C and the aging time of 1 to 3 days. The static and dynamic adsorptions were accomplished using the apparatus set by Chaikasetpaiboon (2002) and Uttamaroop (2003). The wet natural gas at a constant contact time of 9.83 seconds was passed through the packed bed adsorber at 25°C and 1 atm.