METHANE-NITROGEN SEPARATION
BY
PRESSURE SWING ADSORPTION

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SUMMARY

Natural gas, an important energy source, contains methane as its principal combustible component along with small amounts of higher hydrocarbons. Many natural gas reserves around the world remain unutilized due to high nitrogen contamination. In order to ensure a minimum calorific value per unit volume, there is a pipeline specification of less than 4% nitrogen for transmission to the consumers, which makes separation of nitrogen from methane a problem of significant commercial importance. Methane-nitrogen separation is also important in enhanced oil recovery, recovery of methane from coal mines as well as from landfill gas. A highly selective and cost effective methane-nitrogen separation process is, therefore, important for the utilization of methane from natural gas reserves and other aforementioned sources that are contaminated with unacceptable level of nitrogen.

Since natural gas emerges from gas well at a high pressure, a pressure swing adsorption (PSA) based separation process, in which purified methane is obtained as the high pressure raffinate product, is likely to enjoy favorable power cost advantage over the competing separation technologies. However, equilibrium selectivity favors methane over nitrogen on most known sorbents, such as activated carbon, zeolites, silica gel, activated alumina, etc., which will render methane as the extract product recovered at low pressure and thus destroy the natural advantage of a PSA process. Because of the small but workable difference in kinetic diameters of the two gases (3.8 Å for methane and 3.64 Å for nitrogen), the search for a new sorbent has been directed toward kinetic separation. Encouraging kinetic selectivity for the separation of nitrogen (as extract) from methane is known in the literature in carbon molecular sieve (CMS)
(Huang et al., 2003b) and strontium exchanged ETS-4 (Sr-ETS-4) (Marathe et al., 2004). There is also a contrasting claim of equilibrium selectivity of nitrogen with fast diffusion rates for both gases (Ambalavanan et al., 2004) in pore contracted Sr-ETS-4. In a more recent study completed in our laboratory, a nitrogen/methane kinetic selectivity of over 200 was reported from a single component study in a barium exchanged ETS-4 (Ba-ETS-4) sample dehydrated at 400 °C, which far exceeds the selectivity in CMS and Sr-ETS-4.

In this study, binary equilibrium and kinetics of methane and nitrogen in Ba-ETS-4 were measured. Ba-ETS-4 sample was prepared from previously synthesized Na-ETS-4 adsorbent by following a standard ion-exchange procedure and then dehydrating at 400 °C. Differential adsorption bed (DAB) method was used to carry out equilibrium and kinetic measurements on this sample named Ba400 for easy reference. Good agreement of single component methane isotherm with that obtained in a previous study confirmed reproducibility of the newly prepared Ba400 sample as well as adequacy of the DAB method. Binary adsorption equilibrium and uptakes of 50:50 and 90:10 mol ratio mixtures of methane and nitrogen were measured in the DAB apparatus. Multisite Langmuir model (MSL) and Ideal Adsorption Solution (IAS) theory predictions were compared with the experimental results. A binary bidispersed pore diffusional model with molecular diffusion in the macropores and micropore transport governed by the MSL isotherm and chemical potential gradient as the driving force for diffusion was in good agreement with the experimental uptake results.

Following the binary equilibrium and kinetic study, the next step was to develop a detailed numerical method to simulate a kinetically controlled Skarstrom PSA cycle.
for methane-nitrogen separation. In PSA simulation, the external fluid phase in the adsorber was represented by an axially dispersed plug flow model and the binary equilibrium and kinetics were represented by the models that were experimentally verified for methane-nitrogen mixture in Ba400. These equilibrium and kinetic models were also validated for adsorption and uptake of methane-nitrogen mixture in Sr-ETS-4 in an earlier study (Marathe et al., 2004). The kinetic model was modified appropriately to allow for dual transport resistance and stronger concentration dependence of the micropore transport coefficients in CMS according to the published results (Huang et al., 2003b). It should be noted that the binary equilibrium and kinetics models used parameters established from single component experiments and were, therefore, completely predictive. The PSA simulation model was used to carry out a comparative evaluation of the performances of CMS, Sr-ETS-4 and Ba-ETS-4 adsorbents for methane-nitrogen separation from a feed mixture that is representative of nitrogen contaminated natural gas reserves. The operating conditions favor high recovery while simultaneously meeting the required pipeline specification have been identified.
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# NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>- collocation matrix for the first derivative</td>
</tr>
<tr>
<td>$a$</td>
<td>- number of adsorption sites occupied by each molecule in the multi-site Langmuir isotherm</td>
</tr>
<tr>
<td>$B$</td>
<td>- collocation matrix for the second derivative</td>
</tr>
<tr>
<td>$b$</td>
<td>- Langmuir constant, cc/mol</td>
</tr>
<tr>
<td>$b_0$</td>
<td>- pre-exponential constant for temperature dependence of $b$, cc/mol</td>
</tr>
<tr>
<td>$c$</td>
<td>- gas phase concentration, mol/cc</td>
</tr>
<tr>
<td>$c_{im}$</td>
<td>- imaginary gas phase concentration, mol/cc</td>
</tr>
<tr>
<td>$c_p$</td>
<td>- gas phase concentration in macropores, mol/cc</td>
</tr>
<tr>
<td>$C$</td>
<td>- total concentration in the gas phase, mol/cc</td>
</tr>
<tr>
<td>$d_p$</td>
<td>- particle diameter, cm</td>
</tr>
<tr>
<td>$D_c$</td>
<td>- micropore diffusivity, cm$^2$/s</td>
</tr>
<tr>
<td>$D_{co}$</td>
<td>- limiting micropore diffusivity, cm$^2$/s</td>
</tr>
<tr>
<td>$D_{c_0}$</td>
<td>- pre-exponential constant for temperature dependence of diffusivity, cm$^2$/s</td>
</tr>
<tr>
<td>$D_L$</td>
<td>- axial dispersion, cm$^2$/s</td>
</tr>
<tr>
<td>$D_m$</td>
<td>- molecular diffusivity, cm$^2$/s</td>
</tr>
<tr>
<td>$D_p$</td>
<td>- macropore diffusivity, cm$^2$/s</td>
</tr>
<tr>
<td>$E_b$</td>
<td>- activation energy for diffusion across the barrier resistance at the pore mouth, kcal/mol</td>
</tr>
<tr>
<td>$E_d$</td>
<td>- activation energy for diffusion in the micropore interior, kcal/mol</td>
</tr>
<tr>
<td>$J$</td>
<td>- diffusion flux, mol cm$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$K$</td>
<td>- Henry’s constant, (-)</td>
</tr>
<tr>
<td>$k_b$</td>
<td>- barrier coefficient, s$^{-1}$</td>
</tr>
</tbody>
</table>
k_\text{b0} - pre-exponential constant for temperature dependence of barrier coefficient, s^{-1}

k_f - fluid phase mass transfer coefficient, s^{-1}

L - column length, cm

M - molecular weight, g/mol

m_t - mass of adsorbate adsorbed by adsorbent up to time t, g/g

m_\infty - mass of adsorbate adsorbed by adsorbent at equilibrium, g/g

n - total number of moles of adsorbate adsorbed by adsorbent, mol

P - pressure, bar

P_b - final pressure in the desorption system in DAB blank measurement, bar

P_D - final pressure in the desorption system in DAB set-up, bar

P_H - highest pressure in PSA system, bar

P_i - partial pressure of component i, bar

P_L - lowest pressure in PSA system, bar

P_i^0 - hypothetical pressure in the IAS theory that yield the same spreading pressure for every component in the mixture, bar

q - adsorbed phase concentration, mol/cc

q_c - adsorbed phase concentration based on micropore volume, mol/cc

q_p - adsorbed phase concentration based on particle volume, mol/cc

q_s - monolayer saturation capacity according to the Langmuir or multi-site Langmuir model, mol/cc

q_{si} - saturation capacity of each adsorbate component according to the multi-site Langmuir model, mol/cc

q_T - total adsorbed amount, mol/cc

q^* - equilibrium adsorbed amount based on microparticle volume, mol/cc

\bar{q} - average adsorbate concentration in the micropore, mol/cc
\( q \) - adsorbed phase concentration averaged over the adsorbent particle, mol/cc

\( q_i^0 \) - equilibrium adsorbed amount at pressure \( P_i^0 \), mol/cc

\( r \) - radial distance coordinate of microparticle, cm

\( r_c \) - microparticle radius, cm

\( R \) - radial distance coordinate in the macropores, cm

\( R_g \) - universal gas constant, 82.05 cm\(^3\) atm mol\(^{-1}\) K\(^{-1}\); 1.987 cal mol\(^{-1}\) K\(^{-1}\)

\( R_p \) - radius of adsorbent particle, cm

\( t \) - time, s

\( T \) - temperature, K

\( \Delta U \) - change of internal energy due to adsorption, kcal/mol

\( \Delta V \) - volume occupied by the adsorbent particles, cc

\( V_D \) - volume of the desorption system in DAB set-up, cc

\( V \) - interstitial gas velocity, cm/s

\( z \) - space dimension, cm

0(0\(^+,\)0\(^-\)) - column inlet (just inlet, just outlet)

L(L\(^+,\)L\(^-\)) - column outlet (just outside, just inside)

**Greek Letters**

\( \delta \) - dimensionless parameter \( \left( = \frac{k_f R_p}{\varepsilon_p D_p} \right) \), (-)

\( \gamma \) - dimensionless parameter \( \left( = \frac{D_{c0A}}{r_c^2 V_{01H}} \right) \), (-)

\( \varepsilon \) - bed voidage, (-)

\( \varepsilon_p \) - particle voidage, (-)

\( \eta \) - dimensionless parameter along the radius of micropore \( (= r/r_c) \), (-)
\( \rho \) - density of adsorbent, g/cc

\( \rho_g \) - gas density, g/cc

\( \tau \) - dimensionless time \( (= tD/\rho r_c^2) \), (-)

\( \chi \) - dimensionless parameter along the radius of macropore \( (= R/R_p) \), (-)

\( \mu \) - gas viscosity, g.cm\(^{-1}\).s\(^{-1}\)

\( \theta \) - fractional coverage of the adsorption sites, (-)

**Subscripts and Superscripts**

A - component A

B - component B

d - system dead volume

D - desorption system

e - net

H - high

i - component i (=A for component A and =B for component B)

im - imaginary

j - step j (=1 for pressurization, =2 for high pressure adsorption, =3 for blowdown and =4 for purge)

L - low

s - saturation capacity

t - time

T - total

0 - initial value

\( \infty \) - final value
CHAPTER 1
INTRODUCTION

Natural gas, a vital source of world’s supply of energy is one of the cleanest and safest fossil fuel. It is composed primarily of methane which when combusted produces carbon dioxide and water vapor. In contrast, other fossil fuels like coal and oil containing complex molecules with a higher carbon ratio and higher nitrogen and sulfur contents release toxic gases like sulfur dioxide, nitrogen oxides, carbon monoxide, carbon dioxide, etc. According to the 1998 report by Energy Information Administration (EIA) (shown in Table 1.1), the harmful emission levels of oil and coal are higher than that of natural gas. The global market for natural gas is much smaller than for oil because gas transport is difficult and costly. Proven global reserve of natural gas is 6,183 trillion cubic feet (Radler, 2006) or equivalent to 6,368,490 trillion BTU (British Thermal Units). The location of these reserves are distributed. The former Soviet Union and Middle East are the major suppliers of natural gas. Between these two regions, Middle East holds the largest reserves, over 40% of world total, as shown in Figure 1.1. World natural gas consumption, 100 trillion cubic feet in 2004, is increasing faster than of any other fossil fuel. Natural gas production rose by 3% in 2006 and is expected to grow even more in the near future as a result of new exploration and expansion of projects.
Table 1.1: Emission levels from fossil fuels (Pounds per Billion Btu of Energy Input).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Natural Gas</th>
<th>Oil</th>
<th>Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>117,000</td>
<td>164,000</td>
<td>208,000</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>40</td>
<td>33</td>
<td>208</td>
</tr>
<tr>
<td>Nitrogen Oxides</td>
<td>92</td>
<td>448</td>
<td>457</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>1</td>
<td>1,122</td>
<td>2,591</td>
</tr>
<tr>
<td>Particulates</td>
<td>7</td>
<td>84</td>
<td>2,744</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.000</td>
<td>0.007</td>
<td>0.016</td>
</tr>
</tbody>
</table>


Figure 1.1: Distribution of proven natural gas reserve in 2006 (Radler, 2006).

1.1 Demand and Growth Projection of Natural Gas

As already mentioned, the use of natural gas helps to reduce pollution and maintain a relatively cleaner environment. Therefore, the demand for fossil fuels has been directed toward natural gas. Industries, which utilize natural gas mainly as a heat source are the largest consumers of natural gas. In 2004, 44% of the total produced
natural gas was consumed by the industrial sector, while in 2030, the projected consumption by this sector is 43% of world total production, as shown in Figure 1.2. Continued growth in residential, commercial and industrial natural gas consumption will increase the global natural gas consumption from 100 trillion cubic feet in 2004 to 163 trillion cubic feet in 2030.


1.2 Natural Gas Upgrading

Natural gas consists primarily of methane but also contains higher hydrocarbons, nitrogen, moisture, carbon dioxide and sulfur components in varying amounts depending on its source. It’s main sources include oil fields, natural gas fields and coal mines. Landfill gas is a potential source of methane mixed with nitrogen and other contaminants. The contamination of nitrogen above a certain level makes many natural
gas reservoirs/sources unusable simply because they do not meet the pipeline specification (<4% nitrogen). The presence of nitrogen in natural gas also reduces the heating value of the fuel. If natural gas is produced continuously from a reservoir containing nitrogen below pipeline specification, the level of nitrogen concentration may progressively increase because of the accumulation of heavier nitrogen molecule at the bottom of the reservoir which will come out in large proportion as the reservoir depletes. In 2003, Gas Research Institute (GRI) estimated that 14% (or about 19 trillion cubic feet) of the natural gas reserves in the United States are sub-quality due to high nitrogen content (Hugman et al., 1993). In order to meet the long term demand for energy, these unused reservoirs will have to be used. Therefore, an energy efficient separation process is required for the utilization of natural gas reserves around the world.

A large majority of the existing nitrogen removal facilities utilize cryogenic distillation method. Cost of a cryogenic distillation process depends on the scale of operation. It is typically in the range $0.30-0.50/million standard cubic feet (MMscf) for plants handling 75 million standard cubic feet per day (MMscfd) and it increases to more than $1.0/Mscf for plants handling 2 MMscfd (Lokhandwala et al., 1996). Separation of methane-nitrogen mixture using conventional glassy polymeric membrane materials such as cellulose acetate and polysulfone, which separate gases based on the differences in the molecular sizes of gas molecules, has been attempted. However, as methane and nitrogen are of similar molecular sizes, these membranes did not offer sufficient selectivity to develop an effective separation process for this gas mixture. Therefore, membrane based separation for gas molecules having very close kinetic diameters has been pursued with membrane materials like silicone membranes that
separate gases on the basis of a difference in equilibrium affinity rather than a difference in their diffusion rates. However, purified methane from this membrane process is collected as the low pressure extract product, which must be recompressed before putting in the transmission line in order to deliver to the domestic and industrial end-users. Since natural gas emerges from the gas well at a high pressure, separation of methane from its mixture with nitrogen by a pressure swing adsorption (PSA) process is likely to enjoy a favorable power cost advantage. The main challenge of this separation is, therefore, to find a suitable adsorbent that is selective for nitrogen. A methane selective adsorbent, like the silicone membranes, will produce purified methane as the low pressure extract product in a PSA cycle, thus diminishing the energy advantage of the available high pressure natural gas feed. For this reason, an equilibrium controlled cycle using an adsorbent with stronger methane adsorption is not desirable. Hence, to capitalize on the availability of naturally occurring high performance feed, the search for a new adsorbent has been directed toward kinetic separation, where the objective is to exploit the available small but workable kinetic diameter difference between methane (3.8 Å) and nitrogen (3.64 Å) molecules (Ackley and Yang, 1990).

1.3 Pressure Swing Adsorption

The pressure swing adsorption (PSA) technology is a widely used unit operation for gas separation in chemical process industries. This technology has achieved wide acceptance for hydrogen purification, air drying and for small to medium scale air separation applications. Other industrial applications of PSA technology are separation of linear paraffins from branched hydrocarbons, solvent recovery and removal of pollutants such as SO$_2$ and H$_2$S from industrial gases. Potential areas where there are
significant efforts to make PSA an attractive option are air separation for personal medical application, methane-nitrogen and methane-carbon dioxide separation related to energy utilization, and olefin-paraffin separation. New adsorbents are expected to generate many novel PSA based separation applications.

A PSA separation process can be classified according to the nature of adsorption selectivity (equilibrium or kinetic). The selectivity can be achieved either by virtue of the difference in adsorption equilibrium (equilibrium controlled PSA separation) or by the difference in diffusion rates (kinetically controlled PSA separation). Air separation by PSA using zeolites (CaA, NaX, or CaX) is based on the preferential (equilibrium) adsorption of nitrogen. Carbon molecular sieve is known to offer significant kinetic
selectivity for oxygen-nitrogen, methane-carbon dioxide, methane-nitrogen mixtures. Other potential adsorbents like strontium exchanged ETS-4 dehydrated at 190 °C and 270 °C (Marathe, 2006) and barium exchanged ETS-4 dehydrated at 400 °C (Majumdar, 2004) provide a very high kinetic selectivity of nitrogen over methane. Therefore, these adsorbents can be used to separate methane-nitrogen mixture by kinetically controlled PSA separation process. The focus of the present work is, therefore, on kinetically controlled PSA process.

A typical PSA process involves a cyclic process where a number of connected vessels containing adsorbent/adsorbents undergo successive pressurization and depressurization steps in order to produce a continuous stream of purified product. The basic PSA cycle was developed and commercialized by Skarstrom in early 1960 (Skarstrom, 1960). A simple two-bed, four-step process was chosen to explain the steps involved in a PSA process. The steps include pressurization, high pressure adsorption, blowdown and desorption at low pressure. The four elementary steps, schematically shown in Figure 1.3, are described as follows:

Step 1: Bed 2 is pressurized to high pressure with feed from the feed end and at the same time, bed 1 is counter-currently blown down to a low operating pressure. During pressurization, enrichment of slower diffusing component in gas phase at product end is observed. The counter-current blowdown prevents contamination of the product end with more strongly adsorbed species.

Step 2: High pressure feed flows through the bed where strongly adsorbed (or faster diffusing) component is retained and a product stream enriched with less strongly
adsorbed component is collected as a high pressure raffinate product. A fraction of the purified effluent ($G > 0$) from bed 2 is used to pass through bed 1, countercurrent to the direction of feed flow. Alternatively, bed 1 can be left open ($G=0$, self-purge) at lower pressure for a period of time to diffuse out the adsorbed components.

Step 3: Same as step 1, the difference being that bed 2 is subject to blowdown, while bed 1 is subject to pressurization.

Step 4: This step is similar to step 2 but the beds are interchanged.

The Skarstrom cycle has become a common PSA cycle, although many modifications of this basic cycle have been made to increase product purity, recovery and productivity. The first major improvement in the Skarstrom cycle was the inclusion of cocurrent blowdown step (Cen and Yang, 1986) which is shown schematically in

![Figure 1.4: Schematic diagram of a 5-step PSA cycle for gas separation. Step 1: pressurization, step 2: high pressure adsorption, step 3: co-current blowdown, step 4: counter-current blowdown and step 5: purge/desorption.](image-url)
Figure 1.4. To incorporate this step into the Skarstrom cycle, the adsorption step is cut short before the breakthrough point. The cocurrent blowdown step is then followed by countercurrent blowdown and purge steps as required by the Skarstrom cycle. The net result of incorporating the cocurrent blowdown step is the enhancement of extract product purity as well as raffinate product recovery.

![Figure 1.5: Schematic diagram of modified Skarstrom PSA cycle with two packed adsorbent beds including pressure equalization step.](image)

Another modification over the Skarstrom’s original cycle proposed by Berlin (1966) was the introduction of a pressure equalization step. The sequence of operation is shown schematically in Figure 1.5. At the end of high pressure adsorption step of bed 2 and low pressure desorption step of bed 1, two beds are connected through their product ends to equalize pressure. As a result, bed 1 gets partially pressurized which in next step, is pressurized by feed and bed 2 is vented to complete blowdown after disconnecting the two beds. In addition to increasing product recovery, the pressure
equalization step conserves energy because of partial pressurization of low pressure bed by the compressed gas from high pressure bed. An improvement in separative work is also observed with inclusion of the equalization step.

![Schematic diagram of a 2-bed 4-step pressure vacuum swing adsorption cycle.](image)

Figure 1.6: Schematic diagram of a 2-bed 4-step pressure vacuum swing adsorption cycle.

To increase the recovery of the raffinate product, another cycle, namely, vacuum swing cycle was proposed. The idea of this cycle is same as Skarstrom cycle except that the low pressure purge step is replaced by a vacuum desorption step. By closing the product end, vacuum is pulled through the feed end, as shown in Figure 1.6. The loss of slower diffusing component in this case is less than the traditional Skarstrom cycle though the energy cost for this cycle is higher. For a cycle with high operating pressure slightly above the atmospheric pressure and with a very low desorption pressure, it is possible to enjoy energy savings by employing the vacuum swing cycle.
A new approach for producing two pure products from a binary mixture is the use of dual-reflux pressure swing adsorption (DR-PSA). Diagne et al. (1994, 1995a,b) experimentally investigated this cycle for removal of CO$_2$ from air. DR-PSA cycle steps are schematically shown in Figure 1.7. Different cycle configuration options can be made which are dependent on the bed to which feed gas is admitted and the pressure equalization mode. The feed can be sent to the high pressure or low pressure bed. For each case, the change in pressure (equalization, pressurization, and blowdown) can be made with either light (A) or heavy (B) product gas. Therefore, a total of four configuration options are possible. Here, only one configuration option (feed to low pressure bed and pressurization with light gas (A)) is shown for explaining the steps involved in a DR-PSA cycle.

Figure 1.7: Schematic diagram of a full cycle in a twin-bed dual reflux PSA system separating a binary feed mixture.
Each cycle contains two adsorbent beds. The bed to which feed is admitted undergoes feed step, while the other bed undergoes purge step. Two simultaneous pressure changing steps such as high pressure step (P\textsubscript{H}) and low pressure step (P\textsubscript{L}) are involved in the DR-PSA cycle. Pure light product (A) is collected from the top of bed 1, while pure heavy product (B) is taken from the bottom of bed 2. A fraction of product A is used to reflux bed 2 after compressing it to P\textsubscript{H}. Similarly, a fraction of product B is throttled to P\textsubscript{L} and refluxed to the low pressure bed. The other two steps are the pressure transposed steps which are accomplished by transferring the gas from one end of high pressure bed to the same end of low pressure bed. After pressure equalization, the bed initially at high pressure (P\textsubscript{H}) is blown down to make its pressure equal to P\textsubscript{L}. At the same time, pressure in the other bed initially at P\textsubscript{L} is raised to P\textsubscript{H} through pressurization.

### 1.4 Selectivity

Selectivity or separation factor is an important parameter for preliminary process assessment. Generally, two criteria, namely, equilibrium selectivity and kinetic selectivity, are used for process assessment. Equilibrium selectivity depends on the equilibrium capacity of the adsorbents. Kinetic selectivity stems from the differences in diffusion rates of different molecules. Selectivity is generally defined as (Ruthven, 1984):

\[
\eta_{AB} = \frac{q_A}{q_B} \cdot \frac{c_A}{c_B}
\]

where A, B denote two components, q\textsubscript{A} and q\textsubscript{B} are adsorbent loading of component A and B, respectively and c\textsubscript{A} and c\textsubscript{B} are gas phase concentrations of the two components.
For a binary system that follows the Langmuir isotherm, adsorbed amount of each component can be calculated from the following equation:

\[
\frac{q_A}{c_a} = \frac{\alpha_A}{1 + \beta_A c_A + \beta_B c_B} = \frac{K_A}{1 + \beta_A c_A + \beta_B c_B}
\]

\[
\frac{q_B}{c_B} = \frac{\alpha_B}{1 + \beta_A c_A + \beta_B c_B} = \frac{K_B}{1 + \beta_A c_A + \beta_B c_B}
\]

where \( q_s \) is the saturation capacity of the adsorbent and \( K_A \) and \( K_B \) are Henry’s constants of components A and B, respectively.

For an equilibrium controlled process, using Eqs (1.1), (1.2) and (1.3), the following relation can be found:

\[
\frac{\eta_{E,AB}}{b_A q_s} = \frac{\alpha_A}{b_B q_s} = \frac{K_A}{K_B}
\]

In a kinetically controlled process, the selectivity depends on both equilibrium and kinetic effects. The analytical solution of the Fick’s law for a micropore diffusion controlled process with the assumptions of uniformly loaded adsorbent and constant boundary surface condition gives the following relation:

\[
\frac{\Delta q_t}{\Delta q_e} = \frac{m_t}{m_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_c t}{r_e^2}\right)
\]

where \( \frac{D_c}{r_e^2} \) is the diffusional time constant, \( \Delta q_t \) represents the change in adsorbent loading in time t and \( \Delta q_e \) represents the total change from initial condition to the new equilibrium.
At short contact times, Eq (1.5) can be written as:

\[
\frac{q_t}{q_\infty} = \frac{m_t}{m_\infty} = \frac{6}{\sqrt{\pi}} \frac{D_e t}{r_e^2}
\]  

(1.6)

In Henry’s Law region, \(q_\infty = K c\) where \(K\) is Henry’s constant. After substitution of this relationship, Eq (1.6) takes the following form:

\[
\frac{q_t}{c} = \frac{6K}{\sqrt{\pi}} \frac{D_e t}{r_e^2}
\]  

(1.7)

Therefore, when the kinetics is controlled by pore diffusion and equilibrium follows Henry’s law, kinetic selectivity at short contact time region can be written for an equimolar feed mixture as (Ruthven et al., 1994):

\[
\eta_{K,AB} = \frac{q_{tA}}{q_{tB}} \frac{c_{A0}}{c_{B0}} = \frac{K_A}{K_B} \frac{(D_e)_A}{(D_e)_B}
\]  

(1.8)

The effective selectivity can be calculated from the following equation:

\[
\text{Effective selectivity} = \frac{q_{Ap}(t)}{c_{A0}} \frac{c_{B0}}{q_{Bp}(t)}
\]  

(1.9)

where \(c_{A0}\) and \(c_{B0}\) are the feed concentrations of component A and B, respectively.

The procedure for calculating \(q_{Ap}(t)\) and \(q_{Bp}(t)\) is described in section 3.4.3.

![Figure 1.8: Two types of microporous adsorbents. (a) homogeneous and (b) composite adsorbents.](image)
1.5 Different Types of Adsorbents

The known adsorbents can be classified into two broad classes, namely, homogeneous and composite adsorbents. The homogeneous adsorbents have a continuous interconnected network of pores distributed over the particle and there is a continuous distribution in the pore size. In case of composite adsorbents, particles are made up of microporous crystals that are held together with or without any external binder. Hence, there is a clear bidispersity in the pore structure. The two types of adsorbents are schematically shown in Figure 1.8. Silica gel, activated carbon and activated alumina are homogeneous adsorbents, while carbon molecular sieves and zeolites are composite adsorbents. In carbon molecular sieves, the graphite crystallites show a narrow distribution in microporosity ranging typically from 4-10 Å with a mean between 5 to 6 Å. The inorganic zeolite crystals have uniform pore size (i.e., no distribution). In both the adsorbent types, the macropores show a pore size distribution range from 100 to $10^4$ Å. The SEM pictures of zeolite and carbon molecular sieve samples are shown in Figure 1.9 to illustrate the difference in crystal morphology of these two adsorbents.

Figure 1.9: SEM pictures of (a) zeolite crystal (Kuanchertchoo et al., 2006) and (b) carbon molecular sieve micropore structure (Li et al., 2005).
The transport of adsorbate molecules in adsorbent particles from bulk phase to the interior of adsorption sites are restricted by external film, macropore and micropore resistances (shown in Figure 1.10). The external film resistance is often very small under practical conditions of operation. Four different mechanisms have been suggested for transport of gases through the macropores. These are molecular diffusion, Knudsen diffusion, surface diffusion and poiseuille flow. The type of macropore diffusion acting on a particular adsorbent depends on pore size and nature of fluid-wall interaction. Surface diffusion is vital when the heat of adsorption is higher than the activation energy for diffusion. This type of diffusion is commonly found in homogeneous adsorbents. Poiseuille flow is important for the case where there is a significant gradient of pressure across the porous particle. Similarly, molecular and Knudsen diffusions are dominant transport mechanisms when the

Figure 1.10: Schematic diagram showing various resistances to transport of adsorbate gas in composite adsorbents.
distance between molecular collisions is smaller and greater than the pore diameter, respectively. In micropores, a force field of the surface is assumed to act on adsorbate molecules. Therefore, bulk properties are not valid for the fluid present in the micropores. In composite adsorbents, except in carbon molecular sieves, micropore diffusion is Fickian in nature. In carbon molecular sieves, transport mechanism in micropores can be described by a dual resistance, a combination of barrier resistance confined at the micropore mouth and a pore diffusional resistance distributed in the micropore interior (Huang et al., 2004), as shown in Figure 1.10. Depending on the nature of resistance in adsorbent particles, different models, namely, linear driving force (LDF) model, pore diffusion model, slit potential model, dual resistance model etc., have been proposed to represent adsorption kinetics in adsorbent particles.

1.5.1 Potential Adsorbents for CH₄/N₂ Separation

Zeolites, carbon molecular sieves, ETS-4 and its ion exchanged variant can be potential candidates for methane-nitrogen separation by pressure swing adsorption (PSA). The potentials of ETS-4, purified clinoptilolite (a naturally occurring zeolite) and ion-exchanged clinoptilolite for natural gas upgrading by PSA have been analyzed by Jayaraman et al. (2004). Extensive single component and mixture equilibrium and kinetic studies of N₂ and CH₄ in carbon molecular sieve and strontium exchanged ETS-4 adsorbents are available from previous studies conducted in the laboratory of the advisor of this thesis. For barium exchanged ETS-4 sample, only single component studies for N₂ and CH₄ are available and the result is promising. All these adsorbents show a favorable kinetic selectivity of nitrogen over methane, which makes these adsorbents potential candidates for natural gas cleaning using kinetically controlled pressure swing adsorption.
1.6 Objective and Scope

The main objective of this research was to evaluate the potential adsorbents mentioned in section 1.5.1 for methane-nitrogen separation by pressure swing adsorption (PSA). The scope of this intended objective involved the following steps:


2. Development of a suitable PSA model that complied with the binary equilibrium and kinetic study done in this work and those carried out earlier in our laboratory.

3. Comparative study to evaluate the performance of the mentioned potential adsorbents for natural gas upgrading.

1.7 Structure of the Thesis

The important stages of the research work are presented distinctly in various chapters of this thesis. A review of previous studies on gas adsorption and diffusion in different composite adsorbents, methane-nitrogen separation by PSA and dynamic modeling of a PSA process is presented in Chapter 2. Chapter 3 deals with the measurement and modeling of binary equilibrium and kinetics of methane-nitrogen mixture using a Ba-ETS-4 sample dehydrated at 400 °C. In Chapter 4, the equations constituting the simulation model for a two-bed, four-step, Skarstrom PSA cycle are introduced. The numerical solution procedure is also covered in this chapter. The simulation results are presented in Chapter 5 where comparison of the performances of various adsorbents for methane-nitrogen separation by PSA are included. Finally, the conclusions and recommendations are made in Chapter 6.
CHAPTER 2
LITERATURE REVIEW

In the previous chapter, the allowable limit of nitrogen level in natural gas transmission line and, therefore, the need to remove the excess amount have been discussed. The advantages and limitations of different separation processes for this kind of separation have also been highlighted. The importance of a suitable nitrogen selective adsorbent has emerged as the key element for developing an energy efficient process based on adsorption technology such as a pressure swing adsorption (PSA) process. In view of the aforementioned observations, the following two topics are reviewed in this chapter: (i) published results on adsorption and diffusion of methane and nitrogen in various adsorbents, and (ii) advances in dynamic modeling of a PSA process. The purpose of this review is to place the subsequent chapters in the proper context.

2.1 Adsorption and Kinetic Studies

There is a growing interest in the development of nitrogen selective adsorbents for methane-nitrogen separation, which has direct application in natural gas upgrading. In this section several studies reported on gas adsorption and kinetics of methane and nitrogen on some commercial and newly developed adsorbents have been summarized. The earliest study on methane-nitrogen adsorption dates back to 1958 when Habgood (1958a) attempted to separate this gas mixture using 4A zeolite. He used two gas mixtures (one having 10% and other having 50.9% nitrogen) for equilibrium and kinetics measurements. The kinetics of nitrogen in this material was faster than that of methane. The selectivity was defined as the ratio of the mole fraction of nitrogen to
methane in the adsorbed phase divided by the ratio of the mole fraction of nitrogen to methane in the gas phase. At short contact times, the selectivity, in case of 90/10 methane/nitrogen mixture, was about 3.5 which dropped to about 0.68 when equilibrium was achieved. At 193.7 K, there was a significant increase in selectivity that was sensitive to mixture composition with a lower percentage of nitrogen in the mixture giving higher initial selectivity. Because of fast uptakes of both gases at 273.1 K, the maximum selectivity attained was low and time to reach the maximum value was very short. The limiting forms of the definition of selectivity depending on whether the separation is equilibrium or kinetically controlled have been discussed in section 1.4.

Based on the above findings, Habgood filed a patent (Habgood, 1958b) claiming that natural gas could be upgraded by removing the faster diffusing nitrogen using 4A zeolite and a kinetically controlled separation process at a low sub-atmospheric temperature.

Simone et al. (2005) have studied the potential of CMS 3K adsorbent, manufactured by Takeda corporation for separating nitrogen from its mixture with methane. They investigated the adsorption equilibrium and kinetics of the aforementioned adsorbates and reported that there was a significant difference in the kinetics of adsorption of methane and nitrogen. But the amount of adsorbed nitrogen was much lower than that of methane, resulting in a low kinetic selectivity. At 308 K, in case of 53/47 methane/nitrogen mixture, the kinetic selectivity (see Eq 1.8) was only 1.9.
Ackley and Yang (1990) have also reported the possibility of using carbon molecular sieve, manufactured by Bergbau Forchung for air separation (N₂ production), to separate methane-nitrogen mixture by pressure swing adsorption. Pure gas adsorption isotherms and diffusion rates were measured gravimetrically and a kinetic separation factor (defined as the ratio of diffusional time constants (D/t²) of two gases) of 27 was reported. The kinetically controlled separation process (separation of methane-nitrogen mixture) was modeled using the method of characteristics. The linear driving force (LDF) model was used to represent mass transfer rate and equilibrium adsorbed amount was approximated by the extended Langmuir model. Using a traditional Skarstrom type PSA cycle, with evacuation replacing blowdown and purge, a product purity of about 90% was achieved from a feed mixture containing 50/50 methane/nitrogen.

To investigate the transport mechanism of gases in carbon molecular sieves (CMS), Huang et al. (2003a) measured the adsorption and diffusion of nitrogen, oxygen, carbon dioxide and methane using Bergbau-Forchung (BF) and Takeda (designated as Takeda I) CMS samples. A second Takeda CMS sample (Takeda II) was also used to perform similar measurements for oxygen and nitrogen. A dual resistance model was proposed and it was shown to be the desirable approach to capture the experimental results in the entire range covered in their study. Representative differential uptake results measured at various levels of adsorbent loading and fitted to the dual resistance model are shown in Figure 2.1. The two extracted micropore transport parameters were found to be functions of adsorbent loading, which surprisingly were stronger than the expected values calculated from the assumptions of chemical potential gradient as the driving force for diffusion and a constant intrinsic mobility. To account for this
stronger concentration dependence of the transport parameters, a simple empirical approach was proposed. Generally, in zeolites, where pore size is uniform, the limiting (thermodynamically corrected) transport parameters, $D_{c0}$ (limiting diffusivity) and $k_{b0}$ (limiting barrier coefficient) have been experimentally found to be independent of fractional coverage, $\theta$. However, in adsorbents like CMS where micropore sizes are
distributed and pore connectivities are unexplainable, it is realistic to assume that the limiting transport parameters are different in different pores. Hence, the following relations for $D_{c0}$ and $k_{b0}$ were proposed:

$$D_{c0} = D_{c0}^* \left( 1 + \beta_p \frac{\theta}{1-\theta} \right)$$  \hspace{1cm} (2.1)

$$k_{b0} = k_{b0}^* \left( 1 + \beta_b \frac{\theta}{1-\theta} \right)$$  \hspace{1cm} (2.2)

where the values of the fitting parameters $\beta_p$ and $\beta_b$ were obtained by fitting the experimental $D_c/D_{c0}^*$ vs. $\theta$ and $k_b/k_{b0}^*$ vs. $\theta$ data, respectively. $D_c$ and $k_b$ are related to...

Figure 2.2: Unary integral uptakes of (a) oxygen and (b) nitrogen in Takeda I CMS. Dual Model 1 represents solution with $\beta_p=0$, while Dual Model 2 represents solution with the fitted values of $\beta_p$ and $\beta_b$. Taken from Huang et al. (2003a).
\( D_{c0} \) and \( k_{b0} \) by the darkener equation \( D_{c}/D_{c0} = d\ln c/d\ln q \) and its equivalent for barrier coefficient \( k_{b}/k_{b0} = d\ln c/d\ln q \). \( q \) is the equilibrium adsorption phase concentration of \( c \). \( d\ln c/d\ln q \) is, therefore, related to the curvature of the equilibrium isotherm. \( \beta_p \) and \( \beta_b \) were introduced to take into account the effect of pore size distribution experienced by different adsorbates. The form of concentration dependence mentioned in Eqs (2.1) and (2.2) also ensured \( D_{c0} (or k_{b0}) = D^*_c (or k^*_b) \) as \( \theta \to 0 \). The proposed hypothesis was experimentally verified with single component integral uptake data for nitrogen and oxygen in Takeda I CMS, which are reproduced in Figure 2.2.

In a subsequent communication, Huang et al. (2003b) further validated Eqs (2.1) and (2.2) with integral uptake data for methane and carbon dioxide in BF and Takeda I CMS. They also proposed the following multicomponent extensions of Eqs (2.1) and (2.2):

\[
(D_{c0})_i = (D^*_c)_i \left(1 + \sum_{i=1}^{n} \beta_p \frac{\theta_i}{1 - \sum_{j=1}^{n} \theta_j}\right) \quad (2.3)
\]

\[
(k_{b0})_i = (k^*_b)_i \left(1 + \sum_{i=1}^{n} \beta_b \frac{\theta_i}{1 - \sum_{j=1}^{n} \theta_j}\right) \quad (2.4)
\]

where \( \theta_i = q_i/q_{si} \) and \( i = 1, 2, 3, ..., n \).

Eqs (2.3) and (2.4) were validated with binary integral uptake experiments for oxygen-nitrogen mixture in BF CMS, methane-carbon dioxide mixture in both BF and Takeda
CMS, and also ternary uptake of methane-carbon dioxide-nitrogen mixture in BF and Takeda CMS. Representative results are shown in Figures 2.3 and 2.4.

The above multicomponent extensions were based on the assumption that the contributions of components in a multicomponent systems are linearly additive. The input parameters were all obtained from unary differential uptake measurements and no additional fitting parameters were involved when the proposed empirical model was applied to predict binary and ternary integral uptake results.

Figure 2.3: Binary integral uptakes of carbon dioxide and methane in BF and Takeda CMS samples at 30 °C. Dual Model 1 represents solution with $\beta_{ip} = \beta_{ib} = 0$, while Dual Model 2 represents solution with the fitted values of $\beta_{ip}$ and $\beta_{ib}$. Taken from Huang et al. (2003b).
Figure 2.4: Ternary integral uptakes of nitrogen, carbon dioxide and methane in BF and Takeda CMS samples at 30 °C. Dual Model 1 represents solution with $\beta_{ip} = \beta_{ib}$=0, while Dual Model 2 represents solution with the fitted values of $\beta_{ip}$ and $\beta_{ib}$. Taken from Huang et al. (2003b).

Taking different adsorbents, namely, activated carbon, 13X zeolite, 5A zeolite and silica gel, Li et al. (2002) carried out a feasibility study of separating nitrogen from its mixture with methane by an adsorption process. They used breakthrough (chromatographic) method to calculate the adsorbed amount. Among all the adsorbents investigated, activated carbon AX-21 showed the highest selectivity for methane over nitrogen. This selectivity was clearly indicating that to make the process feasible, methane would have to be present as a contaminant in a nitrogen rich stream.
Extensive studies on methane and nitrogen adsorption have been reported on clinoptilolite, a naturally occurring zeolite belonging to the heulandite group. The general formula of clinoptilolite is $M_{6/n}Al_6Si_{30}O_{72}.24H_2O$, where $M$ is the exchangeable extra-framework cation with a valency of $n$. This extra-framework cation is required to compensate for the negatively charged framework composed of $\text{SiO}_4$ and $\text{TiO}_2$ tetrahedra. The unit cell of clinoptilolite is monolithic with $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ as the most charge balancing cations. This natural zeolite has been successfully synthesized by Goto (1977) and Chi and Sand (1983). Clinoptilolite has a two dimensional channel structure. The raw clinoptilolite and its partially exchanged $\text{Ca}^{2+}$ derivative were employed by Frankiewicz and Donnelly (1983) to measure both pure and binary diffusion of nitrogen and methane. Their studies provided an encouraging result to use this adsorbent as a potential candidate for methane-nitrogen separation. Later, Ackley and Yang (1991) conducted a series of experiments to measure the adsorption and diffusion of nitrogen and methane using pure natural clinoptilolite as well as samples fully exchanged with $\text{H}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$. They also presented a clear description of the role of the extra-framework cations and diffusion behavior of gases in the channels.

In the framework of clinoptilolite, three types of channels were identified and designated as A (10-member ring), B (8-member ring) and C (8-member ring). Among these channels, A and B are parallel to each other in [0 0 1] crystallographic direction. The third channel, C intersects the other two and moves in [1 0 0] crystallographic direction. Gas does not penetrate in [0 1 0] crystallographic direction due to the absence of channels. The selectivities and uptakes of the gases depend on the type, number and location of the charge balancing cations residing in the A, B and C
channels. Ackley and Yang (1991) have identified four sites within the channels that are occupied by cations. M(1) sites are located in the intersection of the channels A and C, while M(2) sites are at the intersection of the channels B and C. M(3) and M(4) are located at the mouths of channels C and A, respectively. The cationic location and channel system in clinoptilolite are shown in Figure 2.5.

![Figure 2.5: Location of M(1), M(2), M(3) and M(4) sites within the channel systems of clinoptilolite. From Ackley and Yang (1991).](image-url)
It can be seen from the above figure that Na\(^+\) and Ca\(^{2+}\) cations occupy the M(1) and M(2) sites, K\(^+\) occupies site M(3) and Mg\(^{2+}\) occupies M(4). Therefore, the most efficient channel blockers are Na\(^+\) and Ca\(^{2+}\) cations situated at the intersection of the channels. Complete blockage of channels A and C by K\(^+\) cation is possible but it has no effect on intersecting channels. The authors have concluded that the location of cation is more important than size or number and it is possible to tune the clinoptilolite structure through selected combination of cations to give effective separation of nitrogen from methane.

In another communication, Ackley et al. (1992) examined the role of cations in clinoptilolite for gas separation, particularly for methane-nitrogen separation. The analysis of the equilibrium capacity of ion-exchanged clinoptilolite showed that the order of the capacity was K\(^+\) > Mg\(^{2+}\) > Ca\(^{2+}\). However, the capacity of methane in Ca\(^{2+}\)-clinoptilolite was lower, giving an equilibrium reversal in favor of nitrogen and therefore, highest equilibrium selectivity of nitrogen among the other cation exchanged clinoptilolites. Also, analysis of the diffusion characteristics of the cation exchanged clinoptilolite revealed that the order of the uptake of nitrogen was Mg\(^{2+}\) > K\(^+\) > purified clinoptilolite > H\(^+\) > Ca\(^{2+}\) > Na\(^+\), while the order of methane uptake was K\(^+\) > H\(^+\) > Mg\(^{2+}\) > purified clinoptilolite > Ca\(^{2+}\) > Na\(^+\). The maximum kinetic selectivity in case of Mg\(^{2+}\)-clinoptilolite, was about 11. Chao et al. (1990) also reported an impressive rate selectivity of nitrogen over methane for various Mg\(^{2+}\)-clinoptilolites (Mg\(^{2+}\) content range from 5 to 49 wt%) . The kinetic selectivities ranged from 5 to 200 and were calculated from the uptake ratio at 24 s at a pressure of 1.0 atm.
To analyze the potential of purified, ion-exchanged and mixed ion-exchanged clinoptilolites, Jayaraman et al. (2004) measured isotherms and uptakes of methane and nitrogen both at low and high pressure levels. Purified clinoptilolite, containing various cations like Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\) and Fe\(^{3+}\) in different proportions, showed an impressive kinetic selectivity of nitrogen over methane, although the equilibrium selectivity marginally favored methane. Mg\(^{2+}\)-clinoptilolite showed the highest diffusivity ratio equal to 300 for nitrogen/methane. This was followed by purified-, K\(^+\)-, Li\(^+\), Na\(^+\)-, H\(^+\)- and Ca\(^{2+}\)- clinoptilolites in decreasing order. The highest equilibrium selectivity was observed in Ca\(^{2+}\)-clinoptilolite and it decreased in the order: Ca\(^{2+}\) > Na\(^+\) > Mg\(^{2+}\) > Purified- > K\(^+\) > Li\(^+\) > H\(^+\)-clinoptilolites.

Magnesium clinoptilolite structure offered lower resistance to nitrogen because Mg\(^{2+}\) cation occupied M(4) site causing the blockage of channel A (as shown in Table 2.1) and M(1), M(2) and M(3) sites were essentially unoccupied. Therefore, despite the drawback in equilibrium diffusivity, magnesium clinoptilolite could be employed for methane-nitrogen separation via a kinetically controlled PSA separation process. A modest kinetic selectivity as well as reduced equilibrium capacity of Na\(^+\)- and Ca\(^{2+}\)- clinoptilolites were the results of channel blockage and resultant molecular sieving. Like magnesium clinoptilolite, the potassium clinoptilolite showed equilibrium

Table 2.1: Channel blockage matrix for clinoptilolite (Ackley and Yang, 1991).

<table>
<thead>
<tr>
<th>Site</th>
<th>Channel A</th>
<th>Channel B</th>
<th>Channel C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH(_4)</td>
<td>N(_2)</td>
<td>CH(_4)</td>
</tr>
<tr>
<td>M(1)/M(2)</td>
<td>pb</td>
<td>pb</td>
<td>b</td>
</tr>
<tr>
<td>M(3)</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>M(4)</td>
<td>b</td>
<td>pb</td>
<td>o</td>
</tr>
</tbody>
</table>

b = blocked; pb = partially blocked; o = open
selectivity for methane. But the kinetic selectivity was somewhat lower compared to magnesium clinoptilolite. This was expected as one of the three channels in potassium clinoptilolite was blocked. H⁺-clinoptilolite showed a faster uptake, while the adsorption was strongly in favor of methane. The favorable uptake rate of nitrogen over methane made Li⁺-clinoptilolite a good candidate for natural gas upgrading by PSA via the kinetic mode. In the light of above discussion for all single ion-exchanged clinoptilolites, a conflict was observed between equilibrium selectivity and diffusivity ratio of nitrogen to methane. A particular exchange caused one to increase, while at the same time the other decreased. Therefore, the authors decided to develop mixed ion-exchanged clinoptilolites to optimize the kinetic selectivity.

In the aforementioned communication, Jayaraman et al. (2004) also investigated the adsorption and diffusion of nitrogen and methane in clinoptilolites containing mixed cations. Three different compositions, 20/80, 50/50 and 80/20 were developed for the following cation pairs: Mg²⁺/Ca²⁺, Mg²⁺/Na⁺ and K⁺/Na⁺. It was found that the equilibrium and kinetic properties differed significantly from those found in the case of single ion-exchanged samples. For Mg²⁺/Ca²⁺ cation combination, the equilibrium selectivity favoured nitrogen for all the three compositions. The behaviour was exactly opposite in the case of K⁺/Na⁺ combination. The 20/80 Mg²⁺/Na⁺ combination showed marginal equilibrium selectivity for nitrogen, while 80/20 composition showed very strong adsorption of methane over nitrogen. Mg²⁺/Na⁺ combination with 50/50 composition gave the best equilibrium selectivity and the capacity of nitrogen was fairly high in this material. Although Mg²⁺/Ca²⁺ combination gave high equilibrium selectivity, the slow diffusion rates of both the gases in these clinoptilolites made it unsuitable for methane-nitrogen separation using a pressure swing adsorption (PSA).
process. The 50/50 Mg\(^{2+}\)/Na\(^{+}\) clinoptilolite provided both high equilibrium selectivity and relatively large diffusivity ratio of nitrogen/methane. Therefore, 50/50 Mg\(^{2+}\)/Na\(^{+}\) clinoptilolite looked most promising for methane-nitrogen separation by PSA among the mixed cation exchanged clinoptilolite samples studied.

Another study on naturally occurring clinoptilolite and acid treated natural clinoptilolite was conducted by Aguilar-Armenta et al. (2002). They investigated the kinetics of CO\(_2\), N\(_2\) and CH\(_4\) at different temperatures. It was reported that at 20 °C, the uptake rate of CO\(_2\) was the fastest among the gases studied which was attributed to the interactions of its quadrupole \((0.64 \text{ Å}^3)\) with the charge field of the cations present in the zeolite. The activation energies of the gases increased in the sequence CO\(_2\) > N\(_2\) > CH\(_4\) which were in the order of their molecular size. Exchange of bigger cations such as Na\(^{+}\), K\(^{+}\) and Ca\(^{2+}\) with a smaller one such as H\(^{+}\) by acid treatment of the natural zeolite was reported to offer less resistance to the diffusing gas molecules into the pores. This was due to the increase of free pore aperture after the exchange. Capacity of the exchanged clinoptilolite was, however, found to decrease compared to the original sample. This might have happened due to the change in electrostatic force field. As nitrogen kinetics was fast and methane diffusion was very slow, clinoptilolite was seen as a good candidate for the separation of methane-nitrogen mixture.

Kuznicki et al. (1990) first reported the use of titanium silicate molecular sieves for upgrading the natural gas. In this patent, they reported the synthesis of a family of titanium silicate molecular sieves, named Engelhard Titanium Silicate, ETS-4, from a synthesis gel containing sodium oxide, titanium oxide, silicon oxide and de-ionized water. In a later patent, Kuznicki et al. (2000) showed the development of ion-
exchanged ETS-4 with pores that could be tuned up to angstrom level to give the commercially important separation of gas mixtures with similar molecular size such as N₂/CH₄, Ar/O₂, N₂/O₂ etc. The as-synthesized ETS-4 containing the exchangeable charge balancing Na⁺ cation (designated as Na-ETS-4) was ion exchanged with bivalent Sr²⁺ cation to produce strontium exchanged ETS-4 (Sr-ETS-4). The authors have presented the equilibrium capacities of methane and nitrogen in Sr-ETS-4 at various dehydration temperatures which are reproduced in Figure 2.6. It is obvious from the figure that the capacities of both adsorbates decreased with increasing dehydration temperature. A significant drop in equilibrium capacity of methane at a temperature over 250 °C was observed, while that of nitrogen was considerably small. Similarly, the capacity of methane dropped sharply after the dehydration temperature of 290 °C, while the capacity of nitrogen was less affected. The equilibrium capacity of the adsorbent for methane and nitrogen diminished after the dehydration temperature of 300 °C and 340 °C, respectively. The authors attributed this loss of capacity to the reduction in pore size caused by dehydration temperature.

Figure 2.6: Effect of dehydration temperature on the equilibrium capacity of N₂ and CH₄ at 25°C and 100 psi in Sr-ETS-4. From Kuznicki et al. (2000).
In another communication, Kuznicki et al. (2001) studied the adsorption and structural properties of ETS-4. They reported shrinkage in the pore structure in all three crystallographic directions, along with the gradual loss of crystallinity with progressive increase in regeneration temperature. Also, the molecular gate effect of different molecules in partially (75%) exchanged Sr-ETS-4 was demonstrated. The effect was that larger molecules like methane, ethane etc., were totally excluded in the sample regenerated at 270 °C, while the smaller molecules like nitrogen, oxygen etc., could still penetrate. Similarly, the sample dehydrated at 300 °C turned into an oxygen selective adsorbent in which only oxygen could enter.

Marathe et al. (2005) carried out a systematic study of adsorption and uptake of oxygen, nitrogen and methane on as-synthesized ETS-4 (Na-ETS-4) and heat treated Sr-ETS-4 samples. The Sr-ETS-4 sample were dehydrated at 190, 240, 270 and 310 °C. A dehydrated sample was designated as Srxxx where xxx indicates the dehydration temperature. For example, Sr270 means an Sr-ETS-4 sample dehydrated at 270 °C. It was shown that exchanging monovalent Na⁺ with bivalent Sr²⁺ resulted in a faster uptake of nitrogen without affecting the uptake of methane, thus creating a larger difference in diffusion rates of gas molecules, while the equilibrium was in favor of methane. As a result, the high diffusivity ratio in favor of nitrogen did not result in a high kinetic selectivity. There was progressive pore contraction with increasing dehydration temperature, which was evident from the reduction in uptake rates of the gases. Pore contraction also decreased the pore potential for adsorption of gas molecules. Between methane and nitrogen, the drop was more for marginally bigger methane and eventually there was a reversal in adsorption affinity. Figure 2.7
shows that there was a reversal in the equilibrium selectivity of nitrogen over methane in Sr-ETS-4 sample changing from 0.34 to 2.11 when dehydrated in the range 190 to 270 °C. However, in this dehydration temperature range, the diffusivity ratio decreased from 375 to 31 since the pore contraction appeared to have a larger effect on nitrogen kinetics. Therefore, the combined effect of equilibrium selectivity and diffusivity ratio resulted in a maximum kinetic selectivity of ~12 in Sr270.

Figure 2.7: Effect of dehydration temperature on (a) equilibrium selectivity, (b) diffusivity ratio and (c) kinetic selectivity of nitrogen over methane in Sr-ETS-4. From Marathe et al. (2005).
Single component equilibrium and kinetics of nitrogen and methane in barium exchanged ETS-4, Ba-ETS-4, have been studied by Majumdar (2004). It was shown that the diffusivity ratio was in favour of nitrogen, while the equilibrium selectivity was initially in favour of methane. Similar to Sr-ETS-4, reversal in equilibrium selectivity was also observed in Ba-ETS-4 with dehydration at progressively increasing temperature. The effect of dehydration temperature on equilibrium selectivity, diffusivity ratio and kinetic selectivity observed by Majumdar (2004) is reproduced in Figure 2.8. The diffusivity ratio of nitrogen/methane was initially very high but then dropped significantly as the dehydration temperature was increased.
beyond 400 °C. However, in contrast to Sr-ETS-4, the diffusivity ratio here was still very high when the equilibrium reversal took place. As such, the maximum selectivity attained in this study was over 200 at a dehydration temperature of 400 °C. This selectivity is the highest selectivity reported so far in the literature. Following the same nomenclature used for the dehydrated Sr-ETS-4 sample, the Ba-ETS-4 sample dehydrated at 400 °C was designated as Ba400.

2.2 Review of Methane-Nitrogen Separation by PSA

Many researchers have extensively studied the separation of methane from its mixture with nitrogen by pressure swing adsorption. Dolan et al. (2002) used a two-bed PSA separation unit- one packed with a hydrocarbon selective adsorbent, while other was packed with a nitrogen selective adsorbent. Different hydrocarbon selective adsorbents namely, crystalline alluminosilicate zeolite (13X), high aluminum X zeolite having a silicon to aluminum ratio of about 1 and amorphous adsorbent such as silica gel or carbon were considered and silica gel was chosen because of its higher adsorption capacity for heavier hydrocarbons and lower affinity for methane. CTS-1 zeolite, a heat treated ETS-4 developed by Engelhard corporation described by Kuznicki et al. (2000), was chosen as the nitrogen selective adsorbent in the second bed. The natural gas stream was passed through the first bed where heavier hydrocarbons were preferentially adsorbed. The product stream from the first bed, enriched with methane and nitrogen, entered the second bed. The product stream from second bed was heated to a temperature sufficient to regenerate the adsorbent. A temperature of over 150 °C was capable of desorbing the co-adsorbed methane and regenerating the nitrogen adsorption capacity. The purity of the product was found to decrease with time.
Another report on PSA separation process for natural gas cleaning came from Fatehi et al. (1995). They used a two-bed set-up packed with a carbon molecular sieve adsorbent. The four-step PSA cycle used in this study was able to produce a product purity of 76% for 40/60 nitrogen/methane mixture, while the maximum purity was limited to 96% for 8/92 nitrogen/methane mixture. Simulation studies were performed to interpret the experimental results using a linear driving force (LDF) dynamic model. The model used in their study was able to capture the observed experimental trends.

Warmuzinski and Sodzawiczny (1999) carried out experimental studies and computer simulations to investigate the performance of a two-bed PSA process for the separation of methane and nitrogen using a carbon molecular sieve adsorbent. They investigated the effect of adsorption pressure, feed concentration and duration of cycle on the methane content in the low pressure product. The methane concentration in the product stream showed a distinct maximum with respect to the operating pressure of the adsorption step. It was shown that the location of the maximum was also dependent on the cycle length and gas flow rate. The probable reason for the appearance of the maximum in methane product purity was linked to the isotherm curvature that resulted in an equilibrium selectivity varying with the adsorption pressure.

Ambalavanam et al. (2005) have reported the development of cation exchanged clinoptilolites, and have used the single component equilibrium and kinetic results to numerically investigate the influence of various cations on methane-nitrogen separation by PSA. It was mentioned that mixed ion-exchanged clinoptilolites opened up a wide range of possibilities for controlling the channel dimensions to achieve desired separation. The cations used in this study included Sr$^{2+}$, Ce$^{3+}$, Na$^+$, Li$^+$, and
Mixed forms of ion-exchanged clinoptilolites were prepared by sequential ion exchange and the samples were analyzed through neutron activation analysis. The equilibrium selectivity as well as diffusivity ratio were influenced by the extent of cation exchange. It was claimed that the clinoptilolite sample partially exchanged with Ce$^{3+}$ showed a reversal of equilibrium selectivity from nitrogen to methane with an increase in the extent of exchange. In case of Na/Li clinoptilolite, higher equilibrium selectivity (2.22) was observed in the sample with high Na/Li ratio. The diffusivity ratio of nitrogen/methane declined from 277 to 6.7 with increase in Na/Li ratio from 0.25 to 4. The diffusion rate of nitrogen in 26.5% exchanged Ce-clinoptilolite was faster than that in Na/Li (80/20) clinoptilolite, while that of methane was reversed. Clearly, extent of ion exchange and combination of cations constituted a challenging selectivity optimization problem.

PSA simulations were conducted for a two-stage PSA process for various tailored clinoptilolite samples and ETS-4. Both the stages operated on a five-step cycle, namely, pressurization, high pressure adsorption, cocurrent depressurization, countercurrent blowdown and countercurrent desorption. It was shown that at a pressure of 7 atm and a feed containing 80/20 methane/nitrogen mixture, the highest recovery attained with ETS-4 was 96.2%. In purified and Mg/Na (50/50) clinoptilolites, the maximum recovery values were 95.4% and 93.6%, respectively. The recovery was the lowest (92.6%) in Ce-clinoptilolite. For all the samples, the purity was kept constant around 96%. Lastly, the product throughput decreased in the order Ce-clinoptilolite $>$ Mg/Na(50/50) clinoptilolite $>$ Purified clinoptilolite $>$ ETS-4. The authors claimed that at 40 atm the overall process performance of the mixed clinoptilolites would be better than purified clinoptilolite and ETS-4 because of their
higher nitrogen selective, less favorable isotherms. However, no results were presented that could support this claim.

Butwell et al. (2001) in their patent, have reported the selective removal of nitrogen from natural gas by pressure swing adsorption. The schematic diagram of their process is reproduced in Figure 2.9 for easy reference. The feed gas containing 75% methane was introduced into a bed containing 60 ft$^3$ of nitrogen-selective CTS-1 or Ba-ETS-4 adsorbent for a period of 80 s at a pressure of about 400 psia. At the end of 80 s, the feed gas supply was stopped and the bed was depressurized co-currently to another bed for pressure equalization. Two pressure equalization steps, each having a duration of approximately 20 s, were introduced to reach a pressure of 240 psia after the first equalization and 120 psia after the second equalization. The bed was then co-currently depressurized to 75 psia to provide purge gas to another bed. Thereafter, it was counter-currently depressurized (blowdown) to 5 psia for about 10 s. At the end of the blowdown step, the bed was purged counter-currently for about 100 s with gas from another bed undergoing a co-current depressurization step. The methane recovery from the first stage unit was about 80%. The gas from the blowdown step and the gas leaving the bed during purge step were combined to create the stream designated as W. The gas stream W1, created by compressing the waste gas stream, W, released at a pressure of 50 psia, was fed to a second PSA unit containing a methane selective adsorbent. The effluent gas from the second unit contained 4% methane. Next, the bed was depressurized in a similar manner to the first stage. After compressing, the stream W2 from the second stage was recycled back to the feed to bring the overall plant recovery to 98.74%.
2.3 Review of Dynamic PSA Models

Theoretical modeling of a PSA process has been studied over the years. This process can be modeled on the basis of either equilibrium theory or dynamic theory. Although the equilibrium theory approach is restricted to idealized systems where there are no dispersive effects, it still provides a preliminary design guidance and useful insight into the system behavior. The latter theory, which takes into account the effect of axial mixing and mass transfer resistance, is more realistic. In this section, the gradual development in dynamic PSA models over the years is reviewed.

One of the earliest PSA models was one reported by Mitchell and Shendalman (1973). They modeled equilibrium controlled purification of helium by removing trace CO₂ on
silica gel. A very simple model based on the linear driving force (LDF) mass transfer approximation was used for the sorption of trace concentration of an adsorbable species (CO₂) from an inert carrier (He), subject to the assumptions of isothermality, plug flow, constant velocity along the column and linear equilibrium relationship. The model equations were solved by the method of characteristics. However, the model provided a poor representation of the experimental data.

Like Mitchell and Shendalman (1973), Chihara and Suzuki (1983a and 1983b) developed a similar model for the sorption of a trace concentration of moisture from air, which was approximated as an inert carrier. Major differences between the former and later models were the inclusion of heat effects and use of a different numerical method namely, finite difference method.

Raghavan et al. (1985) first reported a comparative study of PSA simulation using finite difference and orthogonal collocation methods. They used the experimental results of Mitchell and Shendalman (1973) to compare the theoretical results obtained by using two different numerical methods. Unlike the model of Mitchell and Shendalman (1973), they included the axial dispersion at constant velocity along the column and LDF mass transfer model was assumed to be molecular diffusion controlled with a constant value of Ω chosen as 15. However, the simplified assumptions like linear equilibrium isotherm and isothermality were retained. It was shown that at cyclic steady state, the two methods agreed well, but for similar accuracy collocation method required much less computational time. The model showed a good quantitative agreement when the effective mass transfer coefficient was allowed to
vary inversely with operating pressure of the step in progress, which is expected for molecular diffusion controlled mass transfer and was ignored in the previous study.

Hassan et al. (1985) extended the model developed by Raghavan et al. (1985) to a non-linear trace system. They studied purification of helium by removing trace $\text{C}_2\text{H}_4$ on 4A and 5A zeolites. The model equations were solved by the method of orthogonal collocation. Experiments were conducted to validate the simulation results. The model provided a good representation of experimental results. Hence, it was suggested that the model could be used to study more complex multi-bed PSA cycles, used in commercial hydrogen purification process.

The restriction discussed above, that the more strongly adsorbed component was present at a trace level, was relaxed by Yang and Doong (1985). They reported the experimental and theoretical studies for the separation of 50/50 $\text{H}_2/\text{CH}_4$ mixture using activated carbon. They were also the pioneers in considering the velocity variation through the bed, which is significant in bulk separation, and a pore diffusing model for mass transfer in the adsorbent particles. Finite difference method was used and the solution was simplified by assuming a parabolic concentration profile within the particle. Another important development was the use of loading ratio correlation in stead of linear isotherm as the equilibrium model for this bulk separation. They also included the energy balance equations in their model. Many researchers have reported that LDF approximation is equivalent to solving the pore model with parabolic profile assumption. Hence, the importance of using the pore model when mass transfer is macropore diffusion controlled cannot be assessed by this study.
The system chosen in the modeling studies mentioned above were equilibrium controlled separations. One of the first studies on kinetically controlled separation was done by Raghavan and Ruthven (1985). They presented simulation studies for the production of nitrogen from air on a carbon molecular sieve in which both kinetic effects and axial dispersion were included. It was a simple model with the assumptions of linear equilibrium isotherms and LDF mass transfer rate expressions for the two adsorbate components. The model was solved numerically by the method of double collocation. The model appeared to provide a reasonable representation of the behavior of a two-bed PSA adsorption system, although the use of linearized rate expression in lieu of full diffusion equations to represent the sorption kinetics was a major approximation.

The above model was later extended by Hassan et al. (1986) to systems having nonlinear binary equilibrium isotherm instead of linear equilibrium isotherm. Also, the LDF constant, \( \Omega \), was assumed to be cycle time dependent. The model, solved by the orthogonal collocation method, was shown to provide a good representation of the experimentally observed behavior over a wide range of operating conditions.

Using a modified Skarstorm cycle with pressure equalization and no external purge, Hassan et al. (1987) further extended their earlier study. The model was similar to the previous one but with some modifications in the boundary conditions to accommodate the self-purge and approximations to simplify the pressure equalization step. The model provided a good quantitative prediction of the performance of a small scale laboratory unit over a wide range of operating conditions.
Doong and Yang (1986) developed a model for the separation of a gas mixture containing more than two components and applied it to PSA separation of H₂-CH₄-CO₂ mixture on activated carbon. To predict the experimental results, three models were formulated for the cyclic process: equilibrium, surface diffusion and surface plus Knudsen diffusion. The later provided a better representation of the experimental data due to the important contribution of the surface flux to the total flux.

An important issue in the modeling of a PSA process is the consideration of adsorption during the pressure changing steps (like the pressurization and depressurization steps). Unfortunately, in all the studies discussed so far, except the studies by Yang and Doong (1985) and Doong and Yang (1986), this was neglected and a frozen solid approximation and square wave change in column pressure were adopted. This frozen solid approximation may be a valid assumption for applications involving trace adsorbates in a carrier. But for bulk gas separation like air separation, this is not a reasonable assumption. Shin and Knaebel (1987) proposed a general model by considering the mass transfer between the fluid and solid under changing pressure during pressurization and depressurization steps. They used a pore diffusion model with constant diffusivity to account for mass transfer resistance. They presented a theoretical study for the production of nitrogen from air on 4A zeolite.

In a later study, Shin and Knaebel (1988) experimentally verified their previous model (Shin and Knaebel, 1987). The system studied was nitrogen production from air using RS-10, a modified 4A zeolite. A good agreement between theory and experiment was obtained over a wide range of pressures by fitting the micropore diffusion coefficient. The fitted diffusivity values were significantly different from the experimental values.
measured in the linear range. This was due to the concentration dependence of micropore diffusivity. Farooq and Ruthven (1991) thereafter developed a full diffusion model for a binary bulk kinetic separation taking into account isotherm non-linearity represented by the Langmuir isotherm, and concentration dependence of micropore diffusivity according to the gradient of chemical potential as the true driving force for diffusion. In a subsequent study, Farooq et al. (1993) applied their model to the system studied by Shin and Knaebel (1988) with independently estimated single component equilibrium and kinetic parameters. Their model showed an improved ability to replicate the experimental data. The model was then extended to include the transport resistance in the macropores (Gupta and Farooq, 1999). The pore diffusion model with bidispersed pore structure was further modified to include the dual transport resistance in the micropores, in which a barrier resistance confined at the micropore mouth was assumed to act in series with pore diffusional resistance distributed in the micropore interior (Huang et al., 2001).

2.4 Chapter Summary

The significant adsorption and diffusion studies of methane and nitrogen in small pore zeolite, carbon molecular sieve and ion-exchanged ETS-4 adsorbents have been reviewed. Available equilibrium and kinetic studies involving methane-nitrogen mixture are limited to CMS and Sr-ETS-4 samples, most of which were carried out in the laboratory of the advisor of this thesis. A review of the published dynamic models for simulating a PSA process has also been presented. In the next chapter, measurement and modeling of binary equilibrium and kinetics of methane-nitrogen mixture in a Ba-ETS-4 sample carried out in the present study will be discussed in detail.
An essential requirement for the design of an adsorption separation process is complete information on adsorption equilibrium and kinetics of the involved adsorbates on the chosen adsorbent. Reliable equilibrium and kinetic data must be obtained over a wide range of temperature, pressure and composition. Several techniques for the measurement of adsorption kinetics, namely, time lag method, diffusional cell method, gravimetric method, volumetric method, dynamic column breakthrough (DCBT) method, pulse chromatographic method, zero length column (ZLC) method, NMR pulsed feed gradient method, semi batch constant molar flow rate method and differential adsorption bed (DAB) method have been reported in the literature. Among these experimental methods gravimetric, volumetric, DCBT, chromatographic, ZLC and DAB methods can also be used for extracting the equilibrium information. Each method has its own advantages and disadvantages. Comprehensive reviews of these experimental techniques have been given by Kärger and Ruthven (1992) and Do (1998). In the present study, DAB method was used to measure binary equilibrium and kinetics of methane-nitrogen mixture in a barium exchanged ETS-4 (Ba-ETS-4) sample. The equilibrium measurements were carried out over a wide range of pressure, while the kinetic measurements were carried out at a high pressure where the interaction between the diffusing molecules of the two species are expected to be pronounced. Two different mixture compositions were used. This sample was short listed in a recently completed M.Eng. study from our laboratory (Majumdar, 2004), the salient features of which have been detailed in section 2.1. The sample, named Ba400
for easy identification, was dehydrated at 400 °C and it gave a kinetic selectivity of more than 200 for nitrogen over methane based on single component equilibrium and kinetics of these two gases measured in the linear range of the isotherm. It should be recalled that this selectivity value is the highest reported so far in any adsorbent for methane-nitrogen separation. The measured mixture equilibrium results are compared with predictions from the Multisite Langmuir model (MSL) and Ideal Adsorption Solution (IAS) theory. The IAS theory calculations use single component equilibrium data fitted to the Langmuir isotherm model. A bidispersed binary diffusion model based on the chemical potential gradient theory as the driving force is used to predict the measured kinetic data.

### 3.1 Ion Exchange

As already mentioned, a very high kinetic selectivity of nitrogen over methane in barium exchanged ETS-4 (Ba-ETS-4) sample dehydrated at 400 °C was reported from a single component study by Majumdar (2004). Ba-ETS-4 sample used to measure mixture equilibrium and kinetics, was prepared again in this study by ion exchange from previously synthesized Na-ETS-4 sample. The ion-exchange procedure is detailed in the next paragraph. The benefits of using a new sample will be discussed later. It is important to note that bivalent cation exchanged variants of Na-ETS-4 show enhanced thermal stability as well as improved adsorption and catalytic properties (Kuznicki, 1999 and Marathe et al., 2004).

Barium chloride dihydrate (BaCl$_2$.2H$_2$O, Merck) was used for exchange. About 10 g of Na-ETS-4 powder was mixed with 500 ml of 0.5 M solution of BaCl$_2$.2H$_2$O, which was prepared by dissolving 122.16 g of the salt in 1 liter of deionised water. The
mixture was stirred continuously with the help of a mechanical stirrer for about 1 hour at a temperature of 85 °C. The solution was cooled down to room temperature to allow ETS-4 crystals to settle and clear liquid from the top was decanted. The degree of exchange depends on the duration of heating and the available driving force (i.e., concentration of exchangeable cation, Ba\(^{2+}\), present in the solution) which decreases with time. The boiling-cooling-supernatant decanting cycle was, therefore, repeated five times to ensure maximum exchange. The exchanged sample was dried at 100 °C. The degree of exchange achieved was confirmed by Energy Dispersive X-Ray (EDX) analysis and the results are shown in Table 3.1. It is clear from Table 3.1 that sodium was not detected in the ion exchanged sample. It is well known that EDX gives accurate elemental composition at particle surface up to a depth of a few nanometers. A more accurate elemental analysis that is representative of the bulk particle is obtained from Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). Marathe (2006) compared elemental composition from EDX and ICP-OES for Na-ETS-4 and Sr-ETS-4 samples and found good consistency between the two sets of results, and was able to attain complete exchange of Na\(^+\) with Sr\(^{2+}\) by repeating the ion-exchange procedure five times using temperature, heating duration and salt concentration that were similar to those adopted in the present study. Hence, the Ba-ETS-4 sample prepared in this study was assumed to have achieved complete ion exchange based on EDX results.

Table 3.1: Elemental composition of Ba-ETS-4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Technique</th>
<th>Elemental composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Na</td>
</tr>
<tr>
<td>Ba-ETS-4</td>
<td>EDX</td>
<td>0.0</td>
</tr>
</tbody>
</table>
3.2 Pelletization and Dehydration of Ba-ETS-4 Sample

Ba-ETS-4 adsorbent particles used in the measurement of binary equilibrium and kinetics were prepared by pressure binding of the powdered sample at a pressure of eight tons. The steps involved in the preparation of adsorbent particles are clearly described in Figure 3.1. It is evident from the figure that the adsorbent particles had a bidispersed pore structure contributed by intercrystalline macropores and intracrystalline micropores. Like in other zeolitic adsorbents, the main adsorption is in the micropores (of molecular dimension) and macropores contain adsorbates having same pressure and composition as in the bulk phase. Since Majumdar (2004) reported the highest kinetic selectivity in Ba-ETS-4 adsorbent dehydrated at 400 °C, the ion exchanged sample prepared in this study was also dehydrated at this temperature in a furnace for 15-16 hours with a small flow of helium, as recommended in the previous
study. According to the naming procedure discussed in section 2.1, the Ba-ETS-4 sample after dehydrating at 400 °C was called Ba400 and was ready for carrying out the equilibrium and kinetic measurements.

3.3 Differential Adsorption Bed (DAB) Method

An existing differential adsorption bed (DAB), which was designed and fabricated in a previous study completed in our laboratory (Huang, 2002), was employed to measure binary equilibria and integral uptakes in the aforementioned Ba400 sample. The DAB method can provide both equilibrium and kinetic data simultaneously for any number of components. Also, by using a high gas flow rate heat effect of adsorption can be kept to a minimum and the experiment can be assumed to proceed isothermally. However, the DAB method is time consuming since a series of regeneration, adsorption and desorption steps, and blank correction are needed to get just one point of equilibrium or uptake data.

A schematic diagram of this set-up is shown in Figure 3.2. The apparatus consisted of two main parts: gas adsorption system and desorption system. The main component of the gas adsorption system was the adsorber, which was constructed from a 3/8-in. stainless steel Swagelok connector about 4 cm in length. The following description of the experimental set-up has been adapted from the study of Huang (2002) referred earlier where it was first used.

The adsorbent particles were placed inside the adsorber supported by a 200 μm mesh screen. The adsorber was connected directly to two 3-way valves, TWV-1 and TWV-2, using 1/8″ stainless steel tube and quick connectors. A 1/8″ K type thermocouple was
mounted inside the adsorber to measure temperature and the adsorber was placed
directly in a digitally controlled constant temperature water bath (Polyscience, Model
9101) to maintain a steady temperature during the experiment. The inlet line consisted
of 40 meters long 1/8” stainless steel tube upstream of the 3-way valve, TWV-1,
which was coiled and immersed in the same constant temperature bath to ensure
negligible temperature gradient between the feed gas from the cylinder and the
adsorber. The bath controller could accurately maintain the experimental temperature
within ± 0.1 °C. A heating mantle (HORST Gmbh, 3L and 800 W) was used to heat
silicon oil contained in a beaker which in turn was used as the heating fluid that heated
the adsorber and desorbed adsorbate from the adsorbent particles. The oil bath was
heated up to 240 °C to ensure complete desorption of the adsorbate gas. The flow rate

Figure 3.2: Schematic representation of the DAB set-up. From Huang et al. (2002).
of the feed gas and inert (helium) to the adsorber was controlled using two mass flow controllers, MFC1 and MFC2 (Brooks 5850E, 12 SLPM and 2 SLPM, respectively). A small inert flow was used while heating the adsorber after the adsorption step ended. This facilitated complete transfer of the desorbing adsorbate to the desorption bomb. A pressure controller (Brooks 5866RT, 10000 SCCM, 1500 psig maximum operating pressure), PC, at the system outlet maintained the system pressure at the desired value and allowed high-pressure measurements. An absolute pressure transducer (TransInstruments, Type 6100F, Range 0-25 bar) measured the system pressure and provided the feedback signal to the pressure controller. The pressure controller modulated the gas flow through the control valve to change or maintain the pressure. The two mass flow controllers and the pressure controller were independently connected to three secondary electronic units (Brooks Instrument, Model 0151E) which provided digital readouts of the flowrates and the pressure. The control valves could be kept fully open or fully closed, or their opening could be set by keying-in the desired set-point in the electronic controller units in order to control the flow rate or pressure.

In Figure 3.2, the units to the right of the TWV2 constituted the desorption system. At the end of an adsorption measurement run, the desorbing adsorbate was collected in a cylinder called the desorption bomb, DB. Suitable cylinder volume allowed to keep the adsorbate concentration high enough to ensure reliable mass balance from chromatographic analysis. A 1/8” K type thermocouple mounted inside the desorption bomb read the bomb temperature. The pressure in the bomb was measured by an absolute pressure transducer (TransInstruments, Type 6100F, Range 0-5 bar). A digital pressure calibrator (Fluke, Model 700P07) was used to periodically calibrate the
pressure transducer to ensure reliability of pressure measurement. The voltage signal from the absolute pressure transducer was read directly on a multimeter (Hewlett Packard, Model 34401A) that can read up to 0.1 mV accurately. A vacuum pump (HANNING, Model E8CD4B1-162) was also used to ensure thorough regeneration of adsorbent particles and removal of any adsorbate retained in the system before starting a new experiment. After every experimental run, heating the adsorber together under vacuum and intermittent flushing with helium ensured effective regeneration.

The desorption bomb outlet was connected to a 6-port valve in which a sample loop having an internal volume of 0.5 cc was mounted. The gas in the sample loop was sent directly to a gas chromatograph (Perkin Elmer GC, Autosystem) using an inert carrier gas (helium) flow for composition analysis. Alternatively, the gas in the desorption bomb could be vented to the atmosphere via a silicone oil trap. The oil trap ensured a constant pressure in the sample loop and prevented back-flow of the ambient air into the loop. A thermal conductivity detector (TCD) analyzed the contents of the gas sample. A 2M × 1/8″ stainless steel column packed with 80/100 Carboxen-1000 (Supelco, Lot no. 35102765-10) was used for separating nitrogen and methane.

3.3.1 Preliminary Steps for Binary Measurements

3.3.1.1 Calibration of TCD

In chromatographic analysis, area of the measured detector response to a pulse input is required to relate to the concentration of the adsorbate. Prior to the adsorption measurements, the thermal conductivity detector (TCD) in the gas chromatograph (GC) was calibrated using pure gas which was diluted to several known concentrations by mixing with known amounts of inert (helium) gas in the desorption bomb. The gas
was then injected via the 6-port valve (mentioned in Figure 3.2) to the GC for analysis. Helium was used on the reference side of the GC and as the carrier gas as well. An offset of 0.005 V was used as the base line. A digital data acquisition card (National Instruments DAQ, BNC 2110) and a LabView data acquisition software were used to read the response from the GC. A minimum of three injections were analyzed for each composition. Representative TCD responses recorded by the aforementioned data acquisition system are shown in Figure 3.3. Interestingly, in all the cases the response to the first injection was somewhat shorter in height compared to the remaining responses, which were very reproducible. The mystery of the first response could not be explained. The TCD responses were integrated to get areas and the mean of the values from second and third responses were then plotted against the known mole fractions. A linear relationship was observed in the range of compositions covered in this study. The calibration curves for nitrogen and methane are shown in Figure 3.4. In order to further confirm the accuracy of the results, gas mixtures with known concentrations were generated by mixing known amounts of pure nitrogen, pure methane and pure helium in the desorption bomb. Representative TCD responses from
mixture injection are shown in Figure 3.5. The known mixture responses were in good agreement with the individual calibrations, which is expected in case of good baseline separation and non-interference of the mixture components. The calibration lines in Figure 3.4 can be described by the following linear equation: $y = b_1x + b_0$ where $y$ is the response area, $x$ is the mole fraction of component $i$, and $b_0$ and $b_1$ are the regression coefficients. The values of the regression coefficients are shown in Figure 3.4. Particular care was taken to stabilize the TCD signal i.e., to get a stable, non-drifting baseline signal. This was achieved by switching the TCD on a few hours before performing any calibration or actual experiment, and by adjusting the current and signal attenuation to keep the sensitivity to a modest level. A drifting baseline would introduce error in the calculated response area and the corresponding mole fraction. Calculation of the equilibrium and kinetic data depends on the system volume. So the system volume like volume of the desorption system, $V_d$, the volume of the desorption bomb including the associated tubes was carefully measured and good accuracy was ensured by checking reproducibility a few times.

![Figure 3.4: Calibration curves of TCD for (a) nitrogen and (b) methane.](image)

Figure 3.4: Calibration curves of TCD for (a) nitrogen and (b) methane.
Figure 3.5: Representative TCD responses for three injections of a 50/50 methane/nitrogen mixture. The first response in each pair is for nitrogen and the second one is for methane.

3.3.2 Adsorbent Regeneration

The amount of adsorption in an adsorbent is affected by the degree of regeneration. Therefore, prior to the experimental run, the adsorbent placed in the adsorber was regenerated by immersing the adsorber in the silicone oil bath and heating it to the desired temperature (240 °C). The temperature of the silicon oil bath was controlled by varying the power to the heating mantle. The power input to the heating mantle was controlled using a variable voltage transformer (VOLTAC, range 0-260V, 5A). Once the temperature was reached, vacuum was pulled through valve V5 for 2 hours and the adsorber was flushed intermittently, each time for 10 min, with helium.

3.3.2 Experimental Measurement of Binary Equilibrium & Uptake

About 1.0 g Ba400, having density (based on external contour volume) of 1.7173 g/cc was used in the experiments. Before starting the experiment, the desorption bomb was repeatedly purged with helium and evacuated to ensure that no residual adsorbate gas remained. Pre-mixed bottled gas (with known component mole fractions) was used for
the experiments. All the gas streams were passed through beds of 3A zeolite to remove any trace moisture which, if present, could affect measured equilibrium capacity and interfere with the chromatographic analysis. The binary isotherm and kinetic measurements involved the following steps which was similar to those discussed by Huang (2002) and Marathe (2006).

(1) The adsorbent was effectively regenerated by heating, evacuating, and flushing periodically with helium as, discussed in section 3.3.1.2. The adsorber was then placed in the constant temperature water bath set at the desired experimental temperature. The adsorption system was pressurized to the desired level with helium. This was done by putting the Pressure Controller, PC, on AUTO mode and entering the appropriate set-point. When the pressure signal from the Pressure Transducer, PT1, stabilized, the adsorber was isolated by closing the two 3-way valves, TWV1 and TWV2. A steady temperature reading from the thermocouple mounted inside the adsorber was taken as the indication of thermal equilibrium between the adsorber and the bath. This usually took about 60-75 min. Then, TWV-1 was opened to the pressure controller and the adsorbate gas mixture was introduced into the system (upstream of the TWV1). The PC was set to OPEN and the adsorbate flow was maintained long enough to drive off all residual helium remaining in the tube and the length between the mass flow controllers and the 3-way valve. The PC was then set to AUTO to maintain the system (upstream of TWV1) pressure to the desired level with the adsorbate gas mixture.

(2) At time t = 0, the two 3-way valves were operated (TWV1 opened to the adsorber and TWV2 opened to the PC) swiftly and simultaneously to introduce gas into the adsorber for some exposure time. The swift operation was necessary to ensure that
the mass flow controller was not disturbed, that any small pressure variations were short-lived, and that the system pressure was restored to the set value in the shortest possible time. For kinetic measurements, starting from a short exposure time (25 s), the duration was progressively increased until equilibrium was attained. For equilibrium measurements, the equilibrium was ensured by checking that the adsorbed amount did not change by a further increase in exposure time. A high flow of adsorbate gas was not important for equilibrium measurements, but it was very important for kinetics experiment. A high adsorbate gas flow ensured practically negligible gradient in gas concentration across the adsorber. Also, though the heat released during adsorption was small, it was effectively removed by the fast flowing adsorbate gas mixture. In the present study, 2 LPM of the adsorbate gas was used, while the helium flow was 0.5 LPM.

(3) At the end of desired duration, TWV-1 was closed and TWV-2 was switched towards the desorption bomb simultaneously. The adsorber was instantly depressurized when connected to the evacuated desorption bomb, which helped to immediately stop further adsorption. The duration of exposure to adsorbate flow was recorded. The TWV1 was then opened towards the pressure controller, PC, which was set to OPEN in order to vent out the adsorbate gas remaining in the system volume upstream of the adsorber. A helium flow of about 0.5 LPM was used for this flushing step.

(4) Following the flushing of adsorbate in the line upstream of the adsorber, a small flow of helium was introduced towards the adsorber to purge the desorbing adsorbate gas into the desorption bomb. At the same time, the adsorber was heated (to 220-240 °C) by immersing it in the silicone oil bath for about 90 min. Simultaneous heating and purge ensured complete desorption of the gas from the
adsorber to the desorption bomb. The helium flow was regulated in such a way that the final pressure in the bomb would not exceed 3-4 bar. This pressure level was sufficient to enable the gas from the bomb to flow readily to the GC for analysis, while ensuring that the gas mixture in the bomb would not be too dilute to be reliably analyzed by the TCD. After the desorption was complete, TWV-2 was closed to isolate the desorption bomb. The pressure and temperature of the desorption bomb were recorded from the pressure transducer, PT2 and thermocouple, T2, respectively.

(5) A small amount (corresponding to about 500-600 mbar pressure) of the gas in the desorption bomb were bled out to the small silicone oil beaker through the screw down valve, SV. This flushed out any residual gas in the adsorption sample loop. A steady stream of bubbles in the silicone oil also indicated a steady flow of the adsorbate out of the bomb. The gas concentration in the desorption bomb was analysed using the gas chromatograph prepared earlier. The analysis was repeated at least three times to ensure reproducibility. As already mentioned in relation to TCD calibration in section 3.3.1.1, the average of at two three results, typically the second and third responses, which were within ±0.5 % of one another, was taken as the final result for each uptake or equilibrium data point.

(6) Blank experiments were carefully performed in the same adsorber to determine the volume of the adsorber voids and the volume of the tubing between the two 3-way valves, TWV1 and TWV2 which constituted the dead volume in the system. The volume occupied by the adsorbent sample, calculated from its known weight and particle density, which was duly accounted in blank correction.

(7) The adsorbed amount during a given duration of exposure was calculated from the total amount of adsorbate collected in the desorption bomb on heating and helium
flushing minus the contribution from the system dead volume. A complete uptake curve for a particular experimental condition was obtained by repeating steps (1)-(6), each time gradually increasing the exposure time of the adsorbent sample to the feed flow.

3.3.3 Processing of Experimental Equilibrium and Kinetic Data

The number of moles, \( n_{di} \) in the system dead volume was:

\[
 n_{di} = \frac{y_{ib} P_{Db} V_D}{R_g T} - \frac{y_{ib} P_{Db} \Delta V}{R_g T} \quad (3.1)
\]

In the above equation, \( V_D \) is the desorption bomb volume, \( \Delta V \) is the volume occupying by the adsorbent particles, \( P_{Db} \) is the total pressure in the bomb after flushing the adsorbate gas from the empty adsorber, \( y_{ib} \) is the mole fraction of component \( i \) in the desorption bomb obtained from GC analysis, \( R_g \) is the gas constant, and \( T \) is the bomb temperature. Since the final pressure in the desorption bomb was always in the range of 3-4 bar, the ideal gas law was assumed to hold.

Similarly, the number of moles in the macro- and micro-pores of the adsorbent and the system dead volume during each run of the adsorption experiment was calculated as:

\[
 n_i = \frac{y_i P_D V_D}{R_g T} \quad (3.2)
\]

where \( y_i \) and \( P_D \) are the mole fraction of component \( i \) and the total pressure in the desorption bomb, respectively, at the end of the desorption step. The net amount adsorbed during the experimental run, \( n_{ei} \), was obtained by subtracting Eq. (3.1) from Eq. (3.2) as given below:

\[
 n_{ei} = n_i - n_{di} \quad (3.3)
\]

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Then the amount adsorbed based on macroparticle volume \( q_{ip} \) was calculated from the weight and density of adsorbent used in the measurement. The experimental fractional uptake was equal to the ratio \( q_{ip}/q_{ip}^* \) where \( q_{ip}^* \) was the measured equilibrium adsorbed amount of component \( i \) based on the particle volume, which is related to the crystal volume based equilibrium capacity, \( q_{ic} \), according to the following relation:

\[
q_{ip}^* = \varepsilon_p c_{i0} + (1 - \varepsilon_p)q_{ic} \tag{3.4}
\]

where \( \varepsilon_p \) is the particle voidage and \( c_{i0} \) is the gas phase concentration of component \( i \).

### 3.4 Model Development

Detailed single component isotherms for methane and nitrogen in Ba-ETS-4 sample used in this study was measured and analyzed by Majumdar (2004). Both Langmuir and multisite Langmuir models were fitted to the experimental isotherms. The model parameters obtained in this study are reproduced here in Table 3.2. It is clear from the last column of the Table 3.2 that multisite Langmuir model gave a much better fit compared to the Langmuir model.

#### 3.4.1 Binary Equilibrium

Based on the fit of the single component equilibrium data, comparing the predictions of the multicomponent multisite Langmuir model with the measured methane-nitrogen binary equilibrium data was an obvious choice. In addition, prediction from Ideal adsorption Solution theory using Langmuir isotherm fitted individually to the two components was used and also calculated for comparison. It is important to note that the extended Langmuir model is not thermodynamically consistent when the
components in the mixture differ in size and, therefore, in the saturation capacity (Rao and Sircar, 1999).

Table 3.2: Equilibrium isotherm parameters for nitrogen and methane on Ba-ETS-4 dehydrated at 400°C (Majumdar, 2004).

<table>
<thead>
<tr>
<th>Model</th>
<th>Adsorbate</th>
<th>$b_0$</th>
<th>$(-\Delta U)$</th>
<th>$q_s$</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>N$_2$</td>
<td>0.00785</td>
<td>4.448</td>
<td>2.3974</td>
<td>0.12305</td>
</tr>
<tr>
<td></td>
<td>CH$_4$</td>
<td>0.06794</td>
<td>3.248</td>
<td>0.8599</td>
<td>0.0322</td>
</tr>
<tr>
<td>Multi-site</td>
<td>N$_2$</td>
<td>0.007589</td>
<td>4.1627</td>
<td>3.327</td>
<td>4.4143</td>
</tr>
<tr>
<td>Langmuir</td>
<td>CH$_4$</td>
<td>0.12282</td>
<td>2.3051</td>
<td>5.540</td>
<td>2.6510</td>
</tr>
</tbody>
</table>

3.4.1.1 Multisite Langmuir Model

Unlike Langmuir model, Multisite Langmuir model, derived by Nitta et al. (1984), takes into account the relative size difference of the adsorbate molecules. Therefore, according to this model, an adsorbent has a fixed number of adsorption sites and an adsorbate molecule can occupy more or less than one site depending on its size and orientation in the adsorbed phase. For a multicomponent system it has the following form:

$$b_i c_i = \frac{q_{ic}}{q_{si}} a_i^{n-\sum_{i=1}^{n} \frac{q_{ic}}{q_{si}}}$$  (3.5)

where $a_i$ is the number of adsorption sites occupied by a molecule of adsorbate $i$. $q_{si}$ is the saturation capacity of adsorbate $i$. Both $a_i$ and $q_{si}$ are independent of temperature. $c_i$ is the gas phase concentration of component $i$. $b_i$ is the adsorption affinity parameter of component $i$, which is a function of temperature according to the Arrheniuse equation:

$$b_i = b_0_i e^{-\frac{-\Delta U_i}{RT}}$$  (3.6)
where $b_{0i}$ is the pre-exponential factor and $\Delta U_i = \Delta H_i + RT$. $\Delta H_i$ is the differential heat of adsorption and $\Delta U_i$ is the change in internal energy of adsorbate due to adsorption.

### 3.4.1.2 Ideal Adsorption Solution (IAS) Theory

IAS theory using individually fitted Langmuir model was described in detail and applied for the prediction of binary isotherm of oxygen and nitrogen in carbon molecular sieves by Huang et al. (2003b). A brief description of the IAS theory is repeated here for easy reference. IAS theory is applicable for multicomponent equilibrium prediction even when the individual components have unequal $q_i$ (Do, 1998). Myers and Praunitz (1965) developed this theory on the basis of solution thermodynamics. IAS theory uses Roult’s law to describe mixture adsorption equilibrium.

$$P_{yi} = P_i^0 x_i$$  \hspace{1cm} (3.7)

where $P$ is the total gas phase pressure, $P_i^0$ is the equilibrium gas phase pressure corresponding to the adsorption of pure component $i$ at the same spreading pressure, $\pi$ and at the same temperature as for the adsorbed mixture. $x_i$ and $y_i$ are the mole fractions of the component $i$ in adsorbed phase and the gas phase, respectively. The spreading pressure, $\pi$, can be found from the Gibbs adsorption isotherm:

$$\frac{\pi A}{R_g T} = \int_0^{P_i^0} \frac{q_i}{P_i} dP_i$$  \hspace{1cm} (3.8)

where $A$ is the surface area per unit mass of adsorbent and $P_i (= P_{yi})$ is the partial pressure of component $i$. $q_i$ is the measured adsorption isotherm of component $i$. It can be calculated from Langmuir isotherm. After replacing $q_i$, Eq (3.8) takes the following form:
\[
\frac{\pi A}{R_g T} = \Pi = q_{ai} \ln \left( 1 + \frac{b_i P_i^0}{R_g T} \right)
\]  

(3.9)

On the adsorbed surface, the sum of the mole fraction of the every gas is equal to unity.

\[
\sum_{i=1}^{n} x_i = 1 \tag{3.10}
\]

Using Eqs (3.7), (3.9) and (3.10)

\[
\sum_{i=1}^{n} \left( b_i P_i x_i \frac{1}{R_g T \left( e^{q_i} - 1 \right)} \right) = 1 \tag{3.11}
\]

Nonlinear equation solver subroutine, NEQNF in IMSL can be used to solve Eq (3.11) to find the only unknown Π. Once Π is known, \( P_i^0 \) and \( x_i \) can be calculated from Eqs (3.9) and (3.7), respectively. The total adsorbed amount, \( q_T \) can be calculated from the definition of the ideal adsorbed solution (Do, 1998).

\[
\frac{1}{q_T} = \sum_{i=1}^{n} \frac{x_i}{q_i^0} \tag{3.12}
\]

where \( q_i^0 \) is the pure component adsorbed amount of component \( i \) at a pressure \( P_i^0 \), which is calculated from Langmuir isotherm:

\[
q_i^0 = \frac{q_{ai} b_i P_i^0}{1 + \frac{b_i P_i^0}{R_g T}} \tag{3.13}
\]

So, in a multicomponent mixture, the adsorbed amount of each component can be calculated from the following equation:

\[
q_i = x_i q_T \tag{3.14}
\]
3.4.2 Binary Integral Uptake

The model equations for calculating binary integral uptake in Ba-ETS-4 are presented in this section. The model is based on the following assumptions:

1. Ideal gas law applies and the system is considered isothermal.
2. The fluid phase and the adsorbent solid phase are linked through an external film resistance. The value of this resistance is relatively small under high adsorbate flow rate and can be neglected. Keeping the external film resistance term and assigning a large value to approximate a negligible effect is often numerically more advantageous than the alternative approach of applying the equilibrium boundary condition at the adsorbent solid surface.
3. Both macro- and micro-pores are assumed spherical.
4. The adsorbate transport in the macropores is by molecular diffusion.
5. Gradient of chemical potential is the driving force for diffusion in the micropores.

Macropore mass balance for component i

\[
\varepsilon_p \frac{\partial c_{ip}}{\partial t} + (1 - \varepsilon_p) \frac{\partial \overline{q}_{ic}}{\partial t} = \varepsilon_p D_p \left[ \frac{\partial^2 c_{ip}}{\partial R^2} + \frac{2}{R} \frac{\partial c_{ip}}{\partial R} \right]
\]

where \( \overline{q}_{ic} \) is the average adsorbed concentration of component i in the micropore.

Boundary conditions

\[
\frac{\partial c_{ip}}{\partial R} \bigg|_{R=0} = 0 \quad (3.16a)
\]

\[
\varepsilon_p D_p \frac{\partial c_{ip}}{\partial R} \bigg|_{R=R_p} = k_f (c_i - c_{ip}) \bigg|_{R=R_p} \quad (3.16b)
\]
Rate of change in adsorbate accumulation in the micropore volume is equal to the flux at the micropore surface. Hence,

$$\frac{\partial q_{le}}{\partial t} = -\frac{3}{r_c} J_i \bigg|_{r=r_c} \quad (3.17)$$

where $J_i$ is the diffusional flux of component $i$ in the microparticles. It is derived from the chemical potential gradient theory by introducing an imaginary gas phase concentration (Hu and Do, 1993).

$$J_i = (D_{co})_i \frac{q_{le}}{c_{im}} \frac{\partial c_{im}^{*}}{\partial r} \quad (3.18)$$

where $c_{im}^{*}$ is the imaginary gas phase concentration in equilibrium with the adsorbed phase concentration. This concentration is considered as imaginary because there is no gas inside the micropores. In other words, the adsorbate molecules inside the micropores of molecular dimension are always within the strong force-field of adsorbent wall which keeps these molecules in a phase that is much denser than the gas phase.

Mass balance for component $i$ in the micropores:

$$\frac{\partial q_{le}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( (D_{co})_i \frac{q_{le}}{c_{im}} \frac{\partial c_{im}^{*}}{\partial r} \right) \right] \quad (3.19)$$

Boundary conditions

$$\frac{\partial c_{im}^{*}}{\partial r} \bigg|_{r=0} = 0 \quad (3.20a)$$

$$c_{im}^{*} \bigg|_{r=r_c} = c_{ip} \quad (3.20b)$$

Here, multisite Langmuir model was used to calculate the imaginary gas phase concentration, $c_{im}^{*}$, corresponding to the $q_{le}$ in a location along the microparticle radius and it was explicitly obtained from the following equation:
where \( q_{si} \) and \( a_i \) are the saturation capacity and the relative size factor of the respective components in the adsorbate mixture.

### 3.4.3 Model Solution

The model equations described in the previous section were written in dimensionless form. Orthogonal collocation method was used to reduce the set of coupled partial (dimensionless) differential equations to a set of ordinary differential equations, which were then integrated in the time domain using Gear’s variable step integration routine in the FORSIM (1976) integration package.

Figure 3.1 shows how the adsorbent particles used in the measurements were prepared from the synthesized powder crystals, which gave rise to a bidisperse pore structure consisting of interparticle macropores and intracrystalline micropores of the order of a few angstroms. The fractional uptake at any given time was obtained by integrating the radial concentration profiles in the macro- and micro-pores over the respective volumes according to the following equation:

\[
\frac{q_{ip}(t)}{q_{ip}^*} = \frac{\epsilon_p \int \int 3c_{ip}(t)\chi^2 d\chi + (1 - \epsilon_p) \int \int 3\overline{q}_{ic}(t)\chi^2 d\chi}{\int \int q_{ip}^* \chi^2 d\chi} \tag{3.22}
\]

where the average concentration of component \( i \), \( \overline{q}_{ic} \) in the micropore is given as follows:

\[
\overline{q}_{ic}(t) = \int \int q_{ic}(t)\eta^2 d\eta \tag{3.23}
\]
In the above equation, \( q_{ip} \) is the adsorbed amount of component \( i \) at a certain time based on particle volume. \( \chi (= R/R_p) \) and \( \eta (= r/r_c) \) are the dimensionless distances along macroparticle and microparticle radii, respectively.

### 3.5 Results and Discussions

#### 3.5.1 Reproducibility of Measured Single Component Isotherm Data

Prior to the binary equilibrium and kinetics measurements, single component isotherms of methane were measured at 283.15 K on the newly prepared Ba400 adsorbent using DAB method and the results are shown in Figure 3.6. The pure component isotherms measured by Majumdar (2004) by the constant volume method are also included for comparison. The initial DAB runs were conducted without putting any guard bed of 3A zeolite in the gas line necessary to remove any trace moisture that might be present in the gas cylinders containing the experimental and carrier gases. When a reduced capacity was observed, as shown in Figure 3.6, the measurements were repeated after installing a bed of 3A zeolite to dehydrate the incoming gas when the equilibrium values of methane adsorption showed excellent agreement with the previous results of Majumdar (2004). The DAB method being a continuous flow process, any trace moisture, if present, in the adsorbate gas can significantly affect the equilibrium capacity. Good agreement between the results obtained from two different measurement methods gave confidence that DAB method was working properly. It also confirmed that Na-ETS-4 synthesized nearly two years ago did not deteriorate during long storage.
3.5.2 Binary Equilibrium

The experimental binary equilibrium isotherms for 50:50 and 90:10 CH$_4$:N$_2$ mixtures on Ba400 measured at 10 $^\circ$C, according to the procedure detailed in section 3.3.2, are shown in Figure 3.7. Repeat runs have been included, which show excellent reproducibility. Multisite Langmuir (MSL) and Ideal Adsorption solution (IAS) theory predictions using single component parameters given in Table 3.2 are also shown in Figure 3.7. For 50:50 CH$_4$:N$_2$ mixture, the deviations between the experimental data and model predictions are rather large. While the nitrogen isotherm is over-predicted, the methane isotherm is grossly under-predicted. The situation is somewhat better for 90:10 CH$_4$:N$_2$ mixture. Here, prediction by MSL is marginally closer to the methane data than that by IAS theory, whereas the two models predict equally well for nitrogen.

Incidentally, natural gas upgrading typically involves methane-nitrogen mixture containing 10-15% nitrogen. Moreover, Huang et al. (2003b) have experimentally established that the MSL isotherm can effectively predict mixture equilibrium on BF and Takeda CMS using binary and ternary data of oxygen, nitrogen, methane and...
carbon dioxide. Marathe (2006) also arrived at a similar conclusion using binary methane-nitrogen adsorption data on Sr-ETS-4 dehydrated at 190 and 270 °C (i.e., Sr190 and Sr270). Hence, it should be quite reasonable to choose MSL as the isotherm model to study binary uptake of methane-nitrogen mixture in Ba400 in the next section and ultimately to develop a PSA simulation model to study natural gas upgrading in the next chapter.

Figure 3.7: Experimental results and theoretical predictions for binary isotherms of (a) 50:50 and (b) 90:10 CH4:N2 mixtures in Ba400 at 283.15 K. Repeated runs are shown for reproducibility check.

3.5.3 Binary Integral Uptake

Binary integral uptake of 50:50 and 90:10 CH4:N2 mixtures in Ba400 were measured at 7 bar and at a temperature of 283.15 K. In order to confirm reproducibility, a couple of experiments were repeated. The experimental results along with the repeat runs are shown in Figure 3.8. The predicted uptakes according to the model presented in section 3.4.2 are also shown in Figure 3.8. The features of the diffusion model are bidispersity in pore structure having molecular diffusion in the macropore, concentration dependent micropore diffusion with chemical potential gradient as the driving force for diffusion, and adsorption equilibrium at the micropore surface following multisite Langmuir isotherm. The equilibrium and diffusion parameters
are given in Tables 3.2 and 5.1, respectively. Despite the large deviation in equilibrium prediction for 50:50 mixture in Figure 3.7(a), it is indeed very encouraging that uptake of both the mixtures are reasonably well predicted by the model including the roll-up of nitrogen beyond a fractional uptake level of 1, which indicates maximum uptake for binary equilibrium. Since nitrogen is the faster diffusing component, it reaches the micropore interior much ahead of methane and attains a loading higher than the limit of binary equilibrium. The excess is eventually displaced by the slower diffusing methane giving rise to the roll-up of nitrogen.

Figure 3.8: Experimental results and theoretical predictions for binary uptakes of (a) 50:50 and (b) 90:10 CH₄:N₂ mixtures in Ba400 at 283.15 K and 7 bar. Repeated runs are shown for reproducibility check.

3.5.4 Selectivity for Methane-Nitrogen Separation

The simplest approach to screen kinetically selective adsorbents is to use ideal kinetic selectivity and that is commonly done in the literature (Ruthven et al., 1994). A proper definition of separation factor (or selectivity) in a kinetically controlled process is given by Eq (1.9). Ideal kinetic selectivity assumes short contact time, uncoupled diffusion, and a linear or a Langmuir isotherm. In addition to these assumptions, ideal kinetic selectivity only accounts for the loading in the micropores and completely ignores the non-selective storage capacity of the micropore. The time dependent,
effective selectivity of nitrogen over methane in Ba400 according to Eq (1.9) for the
two methane-nitrogen mixtures studied are compared with experimental results
measured at 10 °C in Figure 3.9. The ideal selectivity (i.e., uncoupled selectivity)
obtained from a previous study (Majumdar, 2004) is also included in the figure for
comparison. It is evident from the figure that for both mixtures, the selectivity passes
through a maxima at a short contact time and then it gradually approaches the
equilibrium selectivity limit. The theoretical maximum value attained is higher for the
90:10 CH4:N2 mixture, although it is still far below the ideal selectivity value which is
expected since the former takes into account the non-selectivity capacity of the
adsorbent macropores. As for the experimental results, the first few data points give
infinite selectivity since methane adsorption was undetectable in the early part of the
uptake. This, most likely was due to the limitation of the GC analysis system. These
points in the early part of the uptake are, therefore, not shown in Figure 3.9(b). The
large deviation between the experimental and predicted results in Figure 3.9(a) is due
to a similar deviation in methane uptake in Figure 3.8(a). Like the ideal selectivity of
200, the maxima in the effective selectivity showing a value over 30 for 90:10 CH4:N2
mixture is also considered very high compared to other known adsorbents. Moreover,
the decay in the effective selectivity beyond the peak value is very slow for over 1600
s shown in Figure 3.9(b), which means that Ba400 will enjoy some flexibility with
cycle time.
Figure 3.9: Experimental results and theoretical predictions for effective N₂/CH₄ separation selectivity for (a) 50:50 and (b) 90:10 CH₄:N₂ mixtures at 283.15 K and 7 bar in Ba400. Ideal selectivity is also shown for reference.

3.6 Chapter Summary

Ba-ETS-4 was prepared from powdered Na-ETS-4 sample synthesized in a previous study. The ion exchanged sample was then dehydrated at 400 °C to get Ba400. After checking reproducibility of the single component isotherm of methane in Ba400, binary equilibrium and uptakes of two different mixtures of methane and nitrogen were measured in this sample using DAB method. Suitable models for representing binary equilibrium and uptake have been identified for the development of a PSA simulation model.
CHAPTER 4

DETAILED MODELING OF A KINETICALLY CONTROLLED PSA PROCESS

Pressure swing adsorption is a complex process due to its transient nature and the equations describing the system dynamics are complex, particularly for a kinetically controlled separation. The performance of this process depends on several process variables as well as on the detailed transport mechanism of the adsorbates in the adsorbent micropores, which reduce the possibility of simulating a kinetically controlled PSA cycle using a simple approach. The dynamic PSA simulation models can be differentiated based on the form of the mass transfer rate equations chosen to describe adsorbate uptake in the adsorbent from the fluid phase, which have been detailed in Chapter 1. Five adsorbents, namely, barium exchanged ETS-4 dehydrated at 400 °C (Ba400), strontium exchanged ETS-4 dehydrated at 190 °C (Sr190) and 270 °C (Sr270), Bergbau-Forchung carbon molecular sieve (BF CMS) and Takeda carbon molecular sieve (Takeda CMS) have been selected for simulation study. Choice of these adsorbents is discussed further in Chapter 5. The transport mechanism of gases in CMS and ETS-4 adsorbents are different. In ETS-4 adsorbent, where a regular pore network with uniform micropores on a relative scale is present, the gas transport is controlled by pore diffusional resistance distributed in the micropore interior (Marathe et al., 2005). In contrast, in CMS the gas transport is controlled by a combination of barrier resistance at the entrance of micropore mouth followed by a distributed pore interior resistance acting in series (Huang et al., 2003a, 2003b). A detailed PSA simulation model operated on a Skarstrom cycle is developed in this chapter to cater for the transport of adsorbates (methane and nitrogen in present study) in the
micropores of both ETS-4 and CMS adsorbents. The performances of the adsorbents can be enhanced to some extent by choosing different types of cyclic configurations, presented in section 1.3. But a preliminary simulation study using the basic Skarstrom cycle would provide a primary idea of selecting a potential adsorbent for separating a particular gas mixture. Therefore, a 2-bed, 4-step Skarstrom cycle is chosen for this study.

4.1 Common Assumptions for Models

To develop a more detail mathematical model for the PSA process, the following simplified assumptions are made, many of which are common with many published PSA models (Huang et al., 2003b):

(1) The system is considered isothermal.
(2) The ideal gas law applies.
(3) Frictional pressure drop along the bed is negligible.
(4) The flow pattern is described by axial dispersed plug flow model.
(5) Velocity along the bed is assumed to vary due to adsorption/desorption.
(6) Mass transfer between gas and adsorbed phase is accounted for in all steps i.e., pressurization, high pressure adsorption, blowdown and purge steps.
(7) The total column pressure remains constant during high pressure adsorption and purge steps. During pressurization and blowdown, the pressure profiles are assumed to change exponentially with time.
(8) Gas is considered containing two components only. In this case, it is N₂ and CH₄.
(9) Adsorption equilibrium is represented by the Multisite Langmuir model.
(10) Adsorbent particles are spherical.
In addition to the approximations mentioned above, any additional approximations required for specific models will be discussed separately.

4.2 Bidispersed PSA Model

The following assumptions are introduced in addition to the earlier assumptions discussed in section 4.1.

1. Molecular diffusion dominates in the macropores.
2. Micropore surface is in equilibrium with the macropore gas.
3. The gradient of chemical potential is taken as the driving force for micropore diffusion.

4.2.1 Model Equations

Generally, the PSA model is represented by a series of material balance equations. The equations are written in general terms for component \( i (= A \) for slower diffusing component and \( = B \) for faster diffusing component) and step \( j (= 1 \) for pressurization, \( = 2 \) for high pressure adsorption, \( = 3 \) for blowdown and \( = 4 \) for purge). The \( (\pm) \) sign is used to indicate the flow direction. The term with \((+)\) sign represents the flow from feed end \((0)\) to the product end \((L)\). Flow from \(L\) to \(0\) is indicated by \((-)\) sign.

4.2.1.1 Gas Phase Mass Balance

Gas phase component mass balance:

The axial dispersed plug flow model is used to represent the flow pattern through an adsorption column in a PSA system. For component \( i \), a mass balance over a differential volume element yields:
\[-D_L \frac{\partial^2 c_{ij}}{\partial z^2} \pm \frac{\partial c_{ij} V_j}{\partial z} + \frac{\partial c_{ij}}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \frac{\partial q_j}{\partial t} = 0\]  

(4.1)

where values of \( j \) are positive for \( j = 1 \) and \( 2 \) and negative for \( j = 3 \) and \( 4 \). \( c_i \) is the fluid phase concentration of component \( i \), \( V \) is the interstitial gas velocity, \( q \) is the average loading of the adsorbent particle, \( \varepsilon \) is the bed voidage, \( z \) is axial distance and \( t \) is time.

The first three variables are the functions of time, \( t \) and space, \( z \). In the equation shown above, the effects of all mechanisms that contribute to axial mixing are lumped together into a single axial dispersion coefficient, \( D_L \). The axial dispersion term can be neglected for the case where mass transfer resistance is significantly greater than the axial dispersion. For large industrial units, axial dispersion is generally not important. But for small laboratory columns, axial mixing may be more significant due to the tendency of the particles to stick together to form clusters that act effectively as a single particle in front of the fluid flow. Generally, the four terms in the above equation are a combination of dispersion, convection, accumulation in the gas phase and accumulation in the adsorption particles, respectively, for component \( i \).

The standard (Danckwerts) inlet and exit boundary conditions are used to represent the boundary conditions for a dispersed plug flow system.

For \( j = 1 \) and \( 2 \)

\[D_L \frac{\partial c_{ij}}{\partial z} \bigg|_{z=0} = -V_j \bigg|_{z=0} \left( c_{ij} \bigg|_{z=0} - c_{ij} \bigg|_{z=0^{-}} \right);\]

\[\frac{\partial c_{ij}}{\partial z} \bigg|_{z=L} = 0\]  

(4.2a)

For \( j = 3 \)
\[ \frac{\partial c_{ij}}{\partial z} \bigg|_{z=0} = 0; \]

\[ \frac{\partial c_{ij}}{\partial z} \bigg|_{z=L} = 0 \]  \hspace{1cm} (4.2b)

For \( j = 4 \)

\[ D_L \frac{\partial c_{ij}}{\partial z} \bigg|_{z=L} = -V_j \bigg|_{z=L} \left( c_{ij} \bigg|_{z=L} - c_{ij} \bigg|_{z=L^-} \right); \]

\[ D_L \frac{\partial c_{ij}}{\partial z} \bigg|_{z=L} = 0 \]  \hspace{1cm} (4.2c)

where for \( j = 1 \) and 2, \( c_{ij} \bigg|_{z=0} \) is the inlet concentration of \( i \)th component that is known, and for \( j = 4 \), \( c_{ij} \bigg|_{z=L^-} \) is the inlet concentration of the bed undergoing purge which is calculated from the following expression:

\[ c_{ij} \bigg|_{z=L^-} = \frac{P_L}{P_{l1}} (c_{i2} \bigg|_{z=L}) \]  \hspace{1cm} (4.2d)

Here, \( j = 2 \) indicates that other bed is under high pressure adsorption. This relation is not applicable for self-purge cycle.

Continuity condition:

Based on the continuity condition assuming negligible pressure drop through the bed due to frictional losses, we can write:

\[ \sum_i c_{ij} = c_{A_j} + c_{B_j} = C_j \]  \hspace{1cm} (4.3)

where \( C \) is the total concentration in the gas phase. Based on the assumptions 1, 2 and 3 in section 4.1, it is independent of \( z \). In the light of the assumption 7, it remains constant during high-pressure adsorption (\( j = 2 \)) and purge (\( j = 4 \)) steps and changes during pressurization (\( j = 1 \)) and blowdown (\( j = 3 \)) steps.
Overall material balance:

A detailed analysis to account for the variation of velocity through the bed is required for the feed mixture containing more adsorbable component (or components). Overall material balance equation is required to capture this variation of velocity through the bed. Therefore, under constant pressure condition \((j = 2 \text{ and } 4)\):

\[
\pm C_j \frac{\partial V_j}{\partial z} + \frac{1 - \varepsilon}{\varepsilon} \sum_i \frac{\partial q_{ij}}{\partial t} = 0
\]

\([j = 2 \text{ and } 4; (+) \text{ when } j = 2 \text{ and } (-) \text{ when } j = 4]\)

and, for variable pressure condition \((j = 1 \text{ and } 3)\):

\[
\pm C_j \frac{\partial V_j}{\partial z} + \frac{\partial C_j}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \sum_i \frac{\partial q_{ij}}{\partial t} = 0
\]

\([j = 1 \text{ and } 3; (+) \text{ when } j = 1 \text{ and } (-) \text{ when } j = 3]\)

Velocity boundary conditions are written based on flow features of different steps. The product ends remain closed during pressurization and blowdown steps. In case of high pressure adsorption step, the feed velocity is considered as an operating parameter. The boundary conditions are given as follows:

For \(j = 1\)

\[
V_j \big|_{z=0} = V_{0j} = f(P);
\]

\[
\frac{\partial V_j}{\partial z} \bigg|_{z=L} = 0
\]

\((4.5a)\)

For \(j = 2\),

\[
V_j \big|_{z=0} = V_{0j};
\]

\[
\frac{\partial V_j}{\partial z} \bigg|_{z=L} = 0
\]

\((4.5b)\)
For \( j = 3 \),

\[
V_j\bigg|_{z=0} = 0; \\
\frac{\partial V_j}{\partial z} \bigg|_{z=L} = 0
\]  \hspace{1cm} (4.5c)

For \( j = 4 \),

\[
V_j\bigg|_{z=0} = GV_{0j}; \\
\frac{\partial V_j}{\partial z} \bigg|_{z=L} = 0
\]  \hspace{1cm} (4.5d)

For a self-purging cycle, \( G = 0 \).

For a binary system, Eqs (4.1), (4.3) and (4.4a) or (4.4b) are used to solve \( V, c_A \) and \( c_B \) as a function of time, \( t \) and space, \( z \). During constant pressure operations, namely high pressure adsorption and purge steps, the total concentration, \( C \) is a known constant. In case of variable pressure steps, two methods can be used to solve \( C \) as a function of time. The commonly used method is to directly provide the experimental pressure-time history, normally expressed in exponential forms (Farooq et al., 1993) as shown in equations below:

\[
P = f(t) = P_H - (P_H - P_L)e^{-a_1 t} \) (For \( j = 1 \)) \hspace{1cm} (4.6)
\]

\[
P = f(t) = P_L + (P_H - P_L)e^{-a_2 t} \) (For \( j = 3 \)) \hspace{1cm} (4.7)
\]

where \( P_H \) and \( P_L \) are the high and low pressures of the PSA operation, respectively, \( a_1 \) and \( a_2 \) are the constants to be empirically determined. In the light of the assumptions of ideal gas and isothermal system, \( C \) is directly proportional to \( P \) and is no longer an unknown once pressure-time history is given. The other method is to relate the pressurization and blowdown flow rates with column pressure.
4.2.1.2 Mass Balance in Adsorbent Particles

Mass transfer rate across the external film:

The adsorbate gas crosses the external film and penetrates into the porous structure during adsorption and travels the same paths in reverse direction during desorption. Therefore, accumulation in the particle is given by the amount transferred across the external film, which can also be expressed as the flux at the surface of the macropores.

\[
\frac{\partial q_{ij}}{\partial t} = \frac{3}{R_p} k_f \left( c_{ij} - c_{prij} \right) \bigg|_{R_p = R_p} = \frac{3}{R_p} \varepsilon_p D_p \frac{\partial c_{prij}}{\partial R} \bigg|_{R_p = R_p_p}
\]  

(4.8)

where \( k_f \) is the fluid phase mass transfer coefficient, \( D_p \) is the macropore diffusivity, \( c_{pi} \) is the macropore concentration and \( \varepsilon_p \) is the particle voidage.

Macropore mass balance:

Bulk gas equations are followed by macropore mass balance equation, which is given by the following form:

\[
\frac{\partial c_{prij}}{\partial t} + \frac{1 - \varepsilon_p}{\varepsilon_p} \frac{\partial q_{ij}}{\partial t} = D_p \left[ \frac{\partial^2 c_{prij}}{\partial R^2} + \frac{2}{R} \frac{\partial c_{prij}}{\partial R} \right]
\]  

(4.9)

where \( \overline{q_{ij}} \) is the average adsorbed concentration of component \( i \) in the micropore which is calculated from the following relation:

\[
\frac{\partial \overline{q_{ij}}}{\partial t} = -\frac{3}{r_c} J_i \big|_{r = r_c}
\]  

(4.10)

where \( J \) is the diffusion flux of component \( i \) in the microparticles which is derived from the chemical potential theory by introducing an imaginary gas phase concentration (Hu et al., 1993).

\[
J_i = -\left(D_{ci0}\right) \frac{q_{ij}}{c_{ij}^{im}} \frac{\partial c_{ij}^{im}}{\partial r}
\]  

(4.11)
where $c_{ij}^{im}$ is the imaginary gas phase concentration in equilibrium with the adsorbed phase concentration and $D_{c0}$ is the limiting diffusivity. The imaginary gas phase concentration is calculated from the multisite Langmuir model.

**Boundary conditions for macropore balance:**

\[
\frac{\partial c_{ij}}{\partial R} \bigg|_{R=0} = 0 
\quad \text{(4.12a)}
\]

\[
\varepsilon_f D^{\pi}_{pi} \frac{\partial c_{pij}}{\partial R} \bigg|_{R=R_y} = k_f \left( c_{ij} - c_{pij} \bigg|_{R=R_y} \right) 
\quad \text{(4.12b)}
\]

**Micropore mass balance:**

In the light of the assumption 3 in section 4.2, the particle mass balance equation takes the following form:

\[
\frac{\partial q_{ij}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( D_{c0} q_{ij} \frac{\partial c_{ij}^{im}}{\partial r} \right) \right] 
\quad \text{(4.13)}
\]

The limiting diffusivity $D_{c0}$ is dependent on temperature according to the following equation:

\[
\frac{D_{c0}}{r_c^2} = \frac{D_{c0}^{r_e}}{r_c^2} \exp \left( \frac{E_d}{R_t T} \right) 
\quad \text{(4.14)}
\]

where $E_d$ is the activation energy for diffusion in the micropore interior and $D_{c0}^{r_e}$ is the pre-exponential constant.

**Boundary conditions:**

\[
\frac{\partial c_{ij}^{im}}{\partial t} \bigg|_{r=0} = 0 
\quad \text{(4.15a)}
\]

\[
c_{ij}^{im} \bigg|_{r=r_t} = f(c_{pij}) 
\quad \text{(4.15b)}
\]
Equilibrium isotherm:

The equilibrium relationship for both components is represented by the binary Multisite Langmuir model. This model is an extension of the Langmuir model for single component and multi-component equilibrium on microporous adsorbents that has created provision for taking variation of adsorbate sizes into account (Nitta et al., 1984). The model has the following form:

\[
b_{ij}c_{ij} = \frac{q_{ij}}{q_{ai} s_i} \left\{ 1 - \sum_{i=1}^{n} q_{ai} \right\}
\]

(4.16)

where \( b_{ij} \) is the affinity constant, \( q_{ai} \) is the saturation capacity of component \( i \) and \( q_{ij} \) is the distributed concentration in the micropore.

### 4.3 Dual Resistance Model

Dual resistance model is an extension of the bidispersed model. In some adsorbents like carbon molecular sieves, gas diffusion is controlled by a combination of barrier resistance confined at micropore mouth and a pore diffusional resistance distributed in micropore (Huang et al., 2003a, 2003b) interior. A detail description of associated resistances in CMS is given in Chapter 1 and Chapter 2.

In addition to the earlier assumptions (1)-(10) discussed in section 4.1, the following assumptions are also made.

(1) The transport mechanism in the micropores is observed as a series of combination of barrier resistance confined at the micropore mouth followed by the pore diffusional resistance in the interior of the micropores.
(2) The chemical potential gradient is the driving force for diffusion across the micropore mouth and in the micropore interior. The limiting micropore transport parameters are assumed to be increasing functions of adsorbent loading according to Eqs (2.3) and (2.4).

(3) Molecular diffusion dominates in the macropores.

The equations discussed for bidispersed model are also applicable for the dual resistance model, but the boundary condition at the micropore mouth i.e., Eq (4.12b) changes to the following equation:

\[
\frac{3(D_{c0})}{r_c} \frac{\partial c_{im}}{\partial r} \bigg|_{r=r_c} = \left( k_{b0} \right) \frac{\partial c_{im}}{\partial q_{ij}} \left( q_i^* - q_{ij} \right)_{r=r_c}
\] (4.17)

Here limiting diffusivity, $D_{c0}$ and limiting barrier coefficient, $k_{b0}$ can be calculated from Eqs (2.3) and (2.4), respectively. The concentration dependence of the transport parameters ($D_{c0}$ and $k_{b0}$) has been elaborately described in section 2.1. The temperature dependence of the limiting diffusivity can be calculated from Eq (4.14). Again, the temperature dependence of limiting barrier coefficient can be calculated from the following equation:

\[
k_{b0} = k_{b0}' e^{-\frac{E_b}{R_s T}}
\] (4.18)

where $E_b$ is the activation energy for diffusion across the barrier resistance at pore the mouth and $k_{b0}'$ is pre-exponential constant.

$q_i^*$ in Eq (4.17) is the equilibrium adsorbed phase concentration based on micropore volume corresponding to the macropore gas concentration.

\[
q_i^* = f(c_{p0})
\] (4.19)
The pore diffusion model is actually an extreme case of dual model. The dual model solution reduces to that of the pore diffusion model when a large value is assigned to the barrier coefficient.

### 4.4 Calculation of Performance Indicators

The performance of a PSA process is calculated in terms of purity, recovery and productivity. In this study, these are defined as follows:

**Product purity**

\[
\text{product purity} = \left( \text{volume averaged mole fraction of CH}_4 \text{ in the product from the high pressure adsorption step} \right) = \frac{\left( \frac{t_{\text{adsorption}}}{A} \int_0^L \frac{c_{\text{CH}_4}}{C} \, V_2 \bigg|_{z=L} \, dt \right)}{\left( \frac{t_{\text{adsorption}}}{A} \int_0^L V_2 \bigg|_{z=L} \, dt \right)}
\]

\[\text{(4.20)}\]

**Product recovery**

\[
\text{product recovery} = \frac{\left( \text{moles of CH}_4 \text{ from the high pressure adsorption step} \right) - \left( \text{moles of CH}_4 \text{ used in the purge step} \right)}{\left( \text{moles of CH}_4 \text{ fed during the pressurization and high pressure adsorption steps} \right)} = \frac{\left( \frac{t_{\text{adsorption}}}{A} \int_0^L \frac{c_{\text{CH}_4}}{C} \, V_2 \bigg|_{z=L} \, dt \right) - \left( \frac{t_{\text{adsorption}}}{A} \int_0^L \frac{c_{\text{CH}_4}}{C} \, V_2 \bigg|_{z=L} \, dt \right)}{\left( \frac{t_{\text{pressurization}}}{A} \int_0^L P(t) \frac{c_{\text{CH}_4}}{C} \bigg|_{z=0} \, V_1 \bigg|_{z=0} \, dt + \frac{t_{\text{adsorption}}}{A} \int_0^L \frac{c_{\text{CH}_4}}{C} \bigg|_{z=0} \, V \bigg|_{z=L} \, dt \right)}
\]

\[\text{(4.21)}\]

**Productivity**

\[
\text{productivity} = \frac{\left( \text{volume of CH}_4 \text{ produced} \right)}{\left( \text{volume of adsorbent used in the bed} \right) \times \text{cycle time}} = \frac{\left( \frac{t_{\text{adsorption}}}{A} \int_0^L \frac{c_{\text{CH}_4}}{C} \, V_2 \bigg|_{z=L} \, dt \right) - \left( \frac{t_{\text{adsorption}}}{A} \int_0^L \frac{c_{\text{CH}_4}}{C} \, V_2 \bigg|_{z=L} \, dt \right)}{\left( \frac{t_{\text{adsorption}}}{A} \int_0^L \frac{c_{\text{CH}_4}}{C} \, V_2 \bigg|_{z=L} \, dt \right) \times (1 - \epsilon) \times \text{cycle time}}
\]

\[\text{(4.22)}\]

where A is cross sectional area of the bed and L is length of the bed.
4.5 Input Parameters

A summary of the input parameters such as equilibrium and kinetic parameters are summarized in Table 5.1 and other parameters like bed characteristics, particle characteristics, and feed gas conditions are summarized in Table 5.2.

In this study, the axial dispersion coefficient, $D_L$ was calculated from the following equation (Ruthven, 1984):

$$D_L = 0.7D_m + 0.5V_0d_p$$

(4.23)

where $V_0$ is the interstitial velocity, $d_p$ is the diameter of the adsorbent particle and $D_m$ is the molecular diffusivity, which can be calculated by using the Chapman-Enskog equation:

$$D_m = \left(1.86 \times 10^{-3}\right)T^{3/2} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}$$

$$\frac{P\sigma_{AB}^2\Omega_{AB}}{}$$

(4.24)

where $T$ is the temperature, $M_A$ and $M_B$ are the molecular weights of gases A and B, $P$ is the total pressure, $\Omega_{AB}$ is the collision integral which is dependent on temperature and $\sigma_{AB}$ is a constant in the Lenard-Jones potential energy function for pair AB and is calculated from the following expression:

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$$

(4.25)

where $\sigma_A$ and $\sigma_B$ are the collision diameters of gases A and B calculated from Lenard-Jones potential. The mass transfer coefficient, $k_f$ was calculated from the correlation given by Wakao and Funazkri (1978):

$$Sh = 2.0 + 1.1Sc^5Re^{0.6}$$

(4.26)
where,

\[ Sh = \text{Sherwood No.} = \frac{k_d d_p}{D_m} \]
\[ Sc = \text{Schmidt No.} = \frac{\mu}{D_m \rho_g} \]
\[ Re = \text{Reynolds No.} = \frac{d_p \nu \epsilon \rho_g}{\mu} \]

**4.6 Method of Solution**

All the equations shown above were written in dimensionless form (discussed in Appendix A) and the set of partial differential equations were then converted to a set of coupled algebraic (linear and non-linear) and ordinary differential equations by discretizing all the special variables (dimensionless forms of \( z, R \) and \( r \)) using Orthogonal Collocation scheme with 15, 5 and 15 internal collocation points along the bed, macropores and micropores, respectively. The way of fixing these collocation points is described in the section 4.8. The initial bed condition is known which is normally in equilibrium with the feed mixture at either high or low operating pressure. The algebraic and ordinary differential equations were then solved by using Gear’s variable step integration routine in the FORSIM (1976) integration package to obtain the gas phase concentration as a function of dimensionless bed length (\( z/L \)) and adsorbed phase concentration as a function of both the dimensionless bed length and dimensionless macropore (\( R/R_p \)) and micropore (\( r/r_c \)) particle radius for various values of time. A personal computer with Intel® Core™2 CPU 6600 @ 2.40 GHz and 2 GB of RAM was used to solve the bidispersed PSA model which took 410-615 CPU minutes to complete 40 cycles.
4.7 Transient Behavior Leading to Cyclic Steady State

All the simulation runs were conducted at cyclic steady state condition. Therefore, for one set of operating conditions (run no. 7 in Table 4.1 and bed characteristics in Table 5.2), the concentration profiles of methane in the gas phase and that in the micropores at a representative location are plotted as functions of dimensionless bed length and dimensionless micropore radius in Figures 4.1(a) and 4.1(b), respectively, which show the approach to cyclic steady state. Again, in order to obtain the number of cycles required to approach cyclic steady state, mole fraction of methane in product gas is plotted as a function of cycle number in Figure 4.1(c). Initial change in concentration profile is much steeper. It is evident from the figure that cyclic steady state was reached in about 35 cycles. The changes were very rapid in the first few cycles followed by a slow approach to cyclic steady state. It was noted that, the number of cycles required to reach steady state differed slightly depending on the exact operating conditions. Hence, in order to investigate the performance of a PSA process in the cyclic steady state region at different operating conditions, all the simulations were run up to 40 cycles and the performance indicators were calculated using results from the 41\textsuperscript{st} cycle.

4.7.1 Material Balance Error

Overall material balance error is also an important measure of cyclic steady state. The error may start from a non-zero value, but decrease should through the transient state to reach a value of zero at steady state. A representative error in overall material balance vs. cycle number plot is shown in Figure 4.2. The error reduced to ~0.5\% at steady state which is very good for a numerical simulation of this rather complex
model executed using single precision. The cyclic steady state behavior is significantly affected by the number of collocation points which is discussed in the next section.

Figure 4.1: (a) Mole fraction of methane in gas phase as a function of dimensionless bed length, (b) mole fraction of methane in micropore as a function of dimensionless micropore radius (at z/L=0.5 and R/R_p=0.68) and (c) mole fraction of methane in product gas during high pressure adsorption step as a function of cycle number. The results are for Ba400 sample. See Table 5.1 for equilibrium and kinetic parameters and Run 7 in Table 4.1 for other operating conditions.
4.8 Fixing the Number of Collocation Points

Fixing the number of collocation points is important for accurate numerical solution. The bidispersed PSA model was solved numerically by using orthogonal collocation to discretize the partial differential equations (Finlayson, 1972; Raghavan and Ruthven, 1983). This discretization was made for spatial variables, resulting in a set of time dependent ordinary differential equations. Number of collocation points was kept at an essential minimum level that would ensure convergence of the solution and at the same time prevent the overall computational time from becoming exceptionally long. For solving this bidispersed PSA model using orthogonal collocation scheme, collocation points were varied in three spatial dimensions: along the bed, along the macropore radius and along the micropore radius. The operating conditions and equilibrium and kinetic parameters were kept fixed at the values given in Table 4.1. It can be seen from Figure 4.3 that the concentration profiles of both adsorbates near the micropore mouth are sharper than that of micropore interior. Also, the micropore concentration profile significantly affect the overall performance of a PSA process when the number of collocation points is inadequate. Therefore, the selection of collocation points was
started from the micropores. By gradually increasing the internal collocation points along the micropore radius from 13, while keeping the other two collocation points at random values of 17 and 7 respectively, it was found that beyond 15 points there was no more change in any of the profiles, as may be seen from Figures 4.4-4.6. It is evident from Figure 4.7 that the concentration profile in the macropore is flat, indicating negligible resistance in the macropore. Hence, fewer internal collocation points along the macropore radius were used. As shown in Figures 4.8-4.10, the macropore profiles were practically indistinguishable when the number of internal collocation points along the macropore was increased from 5 to 7. Therefore, the number of internal collocation points was fixed at 5. In the same way and based on the results in Figures 4.11-4.13, the appropriate number of internal collocation points along the bed was chosen to be 15. Negligible change in purity, recovery and productivity was observed with changing the internal collocation points along the bed and macropore radius, as shown in Table 4.1.
Table 4.1: Effect of number of various collocation points on purity, recovery and productivity.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Collocation point</th>
<th>Cycle no.</th>
<th>( P_L ) (atm)</th>
<th>( P_H ) (atm)</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( L )</th>
<th>( V_0 )</th>
<th>PR (s)</th>
<th>HPA (s)</th>
<th>Purity (%)</th>
<th>Recovery (%)</th>
<th>Productivity (cc/cc-ads/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17-7-13</td>
<td>40</td>
<td>1</td>
<td>9</td>
<td>0.1</td>
<td>0.2</td>
<td>50</td>
<td>1.5</td>
<td>50</td>
<td>50</td>
<td>96.78</td>
<td>47.24</td>
<td>144.66</td>
</tr>
<tr>
<td>2</td>
<td>17-7-14</td>
<td>40</td>
<td>1</td>
<td>9</td>
<td>0.1</td>
<td>0.2</td>
<td>50</td>
<td>1.5</td>
<td>50</td>
<td>50</td>
<td>96.67</td>
<td>47.21</td>
<td>144.65</td>
</tr>
<tr>
<td>3</td>
<td>17-7-15</td>
<td>40</td>
<td>1</td>
<td>9</td>
<td>0.1</td>
<td>0.2</td>
<td>50</td>
<td>1.5</td>
<td>50</td>
<td>50</td>
<td>96.52</td>
<td>47.21</td>
<td>144.66</td>
</tr>
<tr>
<td>4</td>
<td>17-7-16</td>
<td>40</td>
<td>1</td>
<td>9</td>
<td>0.1</td>
<td>0.2</td>
<td>50</td>
<td>1.5</td>
<td>50</td>
<td>50</td>
<td>96.45</td>
<td>47.16</td>
<td>144.65</td>
</tr>
<tr>
<td>5</td>
<td>17-5-15</td>
<td>40</td>
<td>1</td>
<td>9</td>
<td>0.1</td>
<td>0.2</td>
<td>50</td>
<td>1.5</td>
<td>50</td>
<td>50</td>
<td>96.5</td>
<td>47.22</td>
<td>144.75</td>
</tr>
<tr>
<td>6</td>
<td>16-5-15</td>
<td>40</td>
<td>1</td>
<td>9</td>
<td>0.1</td>
<td>0.2</td>
<td>50</td>
<td>1.5</td>
<td>50</td>
<td>50</td>
<td>96.5</td>
<td>47.22</td>
<td>144.72</td>
</tr>
<tr>
<td>7</td>
<td>15-5-15</td>
<td>40</td>
<td>1</td>
<td>9</td>
<td>0.1</td>
<td>0.2</td>
<td>50</td>
<td>1.5</td>
<td>50</td>
<td>50</td>
<td>96.5</td>
<td>47.23</td>
<td>144.77</td>
</tr>
<tr>
<td>8</td>
<td>14-5-15</td>
<td>40</td>
<td>1</td>
<td>9</td>
<td>0.1</td>
<td>0.2</td>
<td>50</td>
<td>1.5</td>
<td>50</td>
<td>50</td>
<td>96.5</td>
<td>47.23</td>
<td>144.79</td>
</tr>
</tbody>
</table>

PR: pressurization/blowdown time; HPA: high pressure adsorption/ purge (self) time; \( L/V_0 \): bed length to velocity ratio; \( P_L \): purge gas pressure; \( P_H \): adsorption pressure; \( a_1 \) and \( a_2 \): constants to present the pressure profiles during pressurization and blowdown steps respectively. Feed composition: 90% CH\(_4\) and 10% N\(_2\) on molar basis. Temperature: 300 K. The results are for Ba400. See Table 5.1 for equilibrium and kinetic parameters.
Figure 4.3: Effect of number of various collocation points on the micropore concentration profiles as a function of dimensionless micropore radius at the end of a) pressurization (PR) b) high pressure adsorption (HPA) c) blowdown (BD) and d) self -purge (SP) steps after reaching cyclic steady state.

Figure 4.4: Effect of number of micropore collocation points on the concentration profile of methane as a function of dimensionless bed length at the end of a) pressurization (PR) b) high pressure adsorption (HPA) c) blowdown (BD) and d) self-purge (SP) steps after reaching cyclic steady state.
Figure 4.5: Effect of number of micropore collocation points on the velocity profile as a function of dimensionless bed length at the end of a) pressurization (PR) b) high pressure adsorption (HPA) c) blowdown (BD) and d) self-purge (SP) steps after reaching cyclic steady state.

Figure 4.6: Effect of number of micropore collocation points on a) exit methane mole fraction and b) inlet/exit flow rate as a function of time at the end of pressurization (PR), high pressure adsorption (HPA), blowdown (BD) and self-purge (SP) steps. The results completely overlap in many cases. This applies to all plots where the differences cannot be seen.
Figure 4.7: Effect of number of collocation points on the macropore concentration profiles as a function of dimensionless macropore radius during a) pressurization (PR) b) high pressure adsorption (HPA) c) blowdown (BD) and d) self-purge (SP) steps after reaching cyclic steady state.

Figure 4.8: Effect of number of macropore collocation points on the concentration profile of methane as a function of dimensionless bed length at the end of a) pressurization (PR) b) high pressure adsorption (HPA) c) blowdown (BD) and d) self-purge (SP) steps after reaching cyclic steady state.
Figure 4.9: Effect of number of macropore collocation points on the velocity profile as a function of dimensionless bed length at the end of a) pressurization (PR) b) high pressure adsorption (HPA) c) blowdown (BD) and d) self-purge (SP) steps after reaching cyclic steady state.

Figure 4.10: Effect of number of macropore collocation points on a) exit methane mole fraction and b) flow rate as a function of time at the end of pressurization (PR), high pressure adsorption (HPA), blowdown (BD) and self-purge (SP) steps after reaching cyclic steady state.
Figure 4.11: Effect of number of collocation points along the bed on the concentration profile of methane as a function of dimensionless bed length at the end of a) pressurization (PR) b) high pressure adsorption (HPA) c) blowdown (BD) and d) self-purge (SP) steps after reaching cyclic steady state.

Figure 4.12: Effect of number of collocation points along the bed on the velocity profile as a function of dimensionless bed length at the end of a) pressurization (PR) b) high pressure adsorption (HPA) c) blowdown (BD) and d) self-purge (SP) steps after reaching cyclic steady state.
Figure 4.13: Effect of number of collocation points along the bed on a) exit methane mole fraction and b) flow rate as a function of time at the end of pressurization (PR), high pressure adsorption (HPA), blowdown (BD) and self-purge (SP) steps.
4.9 Simulated Pressure Profiles

As discussed in section 4.1, the total column pressure remains constant during high pressure adsorption and purge steps, while the profiles are assumed to change exponentially with time during pressurization and blowdown steps. The value of the exponential constants were taken as 0.1 and 0.2 for pressurization and blowdown steps, respectively. The PSA simulation study was carried out with these assumptions using the bidispersed pore model and the simulated pressure profiles are presented in Figure 4.14. It should be mentioned here that the constant pressure assumption during high pressure adsorption step gives a conservative prediction of PSA performance. However, it is reasonable for parametric study presented in the next chapter.

![Simulated pressure profiles](image)

Figure 4.14: Simulated pressure profiles as a function of time at the end of pressurization (PR), high pressure adsorption (HPA), blowdown (BD) and purge (SP) steps after reaching cyclic steady state. The results are for Ba400. See Table 5.1 for equilibrium and kinetic parameters. See Run 7 in Table 4.1 for other operating conditions.
Figure 4.15: Computed steady state gas phase profiles at the end of (a) pressurization (PR) (b) high pressure adsorption (HPA) (c) blowdown (BD) and (d) purge (SP) steps. The results are for Ba400 adsorbent. See Table 5.1 for equilibrium and kinetic parameters. See Run 7 in Table 4.1 for other operating conditions.

4.10 Simulated Concentration Profiles

An essential requirement to understand the PSA cycle is to know the shape and movement of concentration profiles at cyclic steady state along the bed during each of elementary steps. The profiles shown in Figure 4.15 were calculated for (a) pressurization with feed gas, (b) high pressure adsorption (c) blowdown and (c) purge steps. The direction of flow of the first two steps is from feed to product end, while that for later two is from product to feed end. During pressurization step, the gas in the bed is pushed toward the closed end of the bed, while in high pressure adsorption step, the concentration wave front travels down the column, and a high pressure raffinate product is collected from product end of the bed. A plateau is formed in high pressure adsorption profile. The region before the plateau is nothing but the penetration of the feed gas. In blowdown and purge steps, the concentration profiles are pushed back and a relatively clean bed is found for the next cycle.
4.11 Chapter Summary

In this chapter, a detailed description of the bidispersed PSA model that takes into account the diffusion of gases both in the macropores and micropores has been presented. A dual resistance model, in which the controlling resistance confined at the micropore mouth is assumed to act in series with the pore diffusional resistance in the micropore interior, has also been discussed. The models are based on the Multisite Langmuir equilibrium isotherm and chemical potential gradient was taken as the driving force for micropore diffusion. A solution method based on the Orthogonal Collocation scheme has also been placed. Finally, a series of simulation results has been presented for fixing the number of various collocation points, which is necessary to reduce the magnitude of oscillation in the solution of differential equations.
CHAPTER 5

PSA SIMULATION RESULTS

The model equations necessary to simulate a kinetically controlled PSA process operated on a Skarstrom cycle for methane-nitrogen separation are detailed in Chapter 4. Axially dispersed plug flow is assumed for the external fluid phase. A bidispersed pore diffusion model is chosen in which transport of gases in the macropores and micropores are separately recognized. The features that distinguish transport of gases in the micropores of carbon molecular sieve and cation exchanged ETS-4 adsorbents have been discussed in Chapters 2 and 3, and are duly incorporated in the PSA process simulation. The multisite Langmuir isotherm is chosen to represent binary equilibrium. Adequacy of the binary equilibrium and kinetic models have been verified with mixture experiments using parameters extracted from independent single component experiments. A comparative evaluation of methane-nitrogen separation by PSA on five adsorbents, namely Ba400, Sr190, Sr270, Takeda CMS and BF CMS is presented in this chapter.

5.1 Selection of Adsorbents

Takeda and BF carbon molecular sieves are extensively used in industrial PSA air separation process for nitrogen production in which kinetic selectivity of oxygen over nitrogen is exploited. These adsorbents have also been recommended as potential candidates for methane-nitrogen separation based on linear driving force (LDF) mass transfer model based PSA simulation (Ackley and Yang, 1990), which is not appropriate for a kinetically controlled separation process governed by a difference in micropore diffusion. A detailed evaluation of pure component and mixture equilibrium
and kinetics in these CMS adsorbents by Huang et al. (2003a, 2003b) revealed new features that were previously not recognized. A reassessment of these adsorbents for methane-nitrogen separation by incorporating the new features in the PSA simulation was, therefore, felt necessary. Ba400 and Sr270 were chosen because these are the best candidates among the dehydrated Ba-ETS-4 and Sr-ETS-4 samples in terms of ideal kinetic selectivity. In case of Sr190, although the nitrogen to methane diffusivity ratio was very high, the adverse equilibrium selectivity favoring methane reduced the kinetic selectivity. Nevertheless, this sample was chosen to examine how much of the high diffusivity ratio can be exploited in a kinetically controlled PSA process despite the adverse equilibrium. In fact, based on binary uptake of methane-nitrogen mixture in Sr190, Marathe (2006) suggested that this sample could be suitable for a PSA cycle with a short cycle time. Dominance of the high diffusivity ratio was also discussed in relation to the results shown in Figure 3.7.

5.2 Input Parameters

The single component equilibrium and kinetic parameters used in the PSA simulation for the five adsorbents chosen in this study are given in Table 5.1. Other common parameters including the range of those process conditions that were varied are summarized in Table 5.2. The axial dispersion coefficient were calculated from Eq (4.23) and binary molecular diffusivity of methane-nitrogen pair was estimated from Chapman-Enskog equation detailed in section 4.5.

5.2.1 Operating Temperature

Raw natural gas emerges from well at high pressure. It is then taken to the gas processing plant through pipeline for producing a clean natural gas by separating
impurities and various non-methane hydrocarbons and fluids. The temperature of the raw natural gas in that pipeline is roughly same as ambient temperature. Depending on the location of the well, the gas temperature varies. An ambient temperature of 300 K was chosen as the operating temperature in this study.

Table 5.1: Equilibrium and kinetic parameters used in simulation†.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Ba400</th>
<th>Sr190</th>
<th>Sr270</th>
<th>Takeda CMS</th>
<th>BF CMS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Equilibrium Isotherm Parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_s$ for CH$_4$ (mmol/cc)</td>
<td>2.651</td>
<td>7.94</td>
<td>8.56</td>
<td>7.32</td>
<td>6.00</td>
</tr>
<tr>
<td>$Q_s$ for N$_2$ (mmol/cc)</td>
<td>4.4143</td>
<td>9.88</td>
<td>9.06</td>
<td>7.40</td>
<td>6.20</td>
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<tr>
<td>$\Delta U$ for CH$_4$ (kcal/mol)</td>
<td>2.3051</td>
<td>3.50</td>
<td>0.91</td>
<td>5.98</td>
<td>6.31</td>
</tr>
<tr>
<td>$\Delta U$ for N$_2$ (kcal/mol)</td>
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<td>2.40</td>
<td>2.33</td>
<td>4.72</td>
<td>4.61</td>
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<td>$a$ for CH$_4$</td>
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<td>2.90</td>
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</tr>
<tr>
<td>$a$ for N$_2$</td>
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<td>2.56</td>
<td>2.76</td>
<td>3.51</td>
<td>3.36</td>
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<tr>
<td>$b_0$ for CH$_4$ (cc/mmol)</td>
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<td>0.012</td>
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<td>3.37E-04</td>
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<td>$b_0$ for N$_2$ (cc/mmol)</td>
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<td>8.04E-04</td>
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<td></td>
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<tr>
<td>$(Dc_0/r^2)$ for CH$_4$ (1/s)</td>
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<tr>
<td>$E_d$ for CH$_4$ (kcal/mol)</td>
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<td>8.43</td>
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<td>10.43</td>
<td>8.42</td>
<td>7.32</td>
</tr>
<tr>
<td>$\beta_p$ for CH$_4$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>5.52</td>
<td>5.52</td>
</tr>
<tr>
<td>$\beta_p$ for N$_2$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2.28</td>
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<td>468.74</td>
<td>7310.0</td>
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<tr>
<td>$k_{b0}$ for N$_2$ (kcal/mol)</td>
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<td>--</td>
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<td>819.83</td>
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<td>$E_b$ for CH$_4$ (kcal/mol)</td>
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<td>$E_b$ for N$_2$ (kcal/mol)</td>
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<td>5.62</td>
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<td>$\beta_b$ for CH$_4$</td>
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<td>$\beta_b$ for N$_2$</td>
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<td>--</td>
<td>--</td>
<td>7.93</td>
<td>7.93</td>
</tr>
</tbody>
</table>

†Equilibrium and kinetic parameters, and adsorbent properties of Sr190 and Sr270 from Marathe et al. (2005), BF CMS and Takeda CMS from Huang et al. (2003a and 2003b) and Ba400 from Majumdar (2004).
5.2.2 Nitrogen Content in Natural Gas

Natural gas is a gaseous natural resource, consisting mainly of methane and small amount of higher hydrocarbons. The composition of natural gas varies from region to region. Some natural gas reserves contain high percentage of nitrogen as well as carbon dioxide and hydrogen sulfide. At the natural gas well head, nitrogen content of 5 to 20 mol% are more typical (Cavenati et al., 2005). Therefore, an intermediate nitrogen concentration of 10 mol% was chosen for the comparative evaluation study.

Table 5.2: Some common parameters used in simulation.

<table>
<thead>
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<th>Bed Characteristics</th>
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<tr>
<td>Bed length (cm)</td>
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<tr>
<td>Bed radius (cm)</td>
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<tr>
<td>Bed voidage (-)</td>
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</table>

<table>
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<tr>
<td>Particle radius (cm)</td>
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<tr>
<td>Particle voidage (-)</td>
<td>0.4 (Sr190, Sr270, Ba400); 0.33(CMS)</td>
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</table>

<table>
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<th>Feed Gas Conditions</th>
<th></th>
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</thead>
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<td>CH₄ in feed gas (mol %)</td>
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</tr>
<tr>
<td>N₂ in feed gas (mol %)</td>
<td>0.1</td>
</tr>
<tr>
<td>Feed gas temperature (K)</td>
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</tr>
</tbody>
</table>

Other Parameters

<table>
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</thead>
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<td>Pressure (atm)</td>
<td>0.2-9</td>
</tr>
<tr>
<td>Pressurization/blowdown time (s)</td>
<td>75-150</td>
</tr>
<tr>
<td>Adsorption/purge time (s)</td>
<td>75-150</td>
</tr>
<tr>
<td>L/V₀ ratio (s)</td>
<td>25-45</td>
</tr>
<tr>
<td>Purge to feed ratio (G)</td>
<td>0-0.6</td>
</tr>
</tbody>
</table>
5.3 Effect of Various Operating Parameters on PSA Performance

The effects of various independent process variables such as velocity, bed length, feed gas pressure, purge gas pressure, configuration of the process steps etc., on the process performance indicators such as purity, recovery and productivity have been evaluated. The operating parameters for each runs are tabulated in Appendix B. Several different combinations of the PSA process variables can be used to produce high purity methane as well as high recovery and productivity. The sensitivity of PSA process performance to the aforementioned process variables is analyzed for different adsorbents in the following sections. The product purity, recovery and productivity were calculated from Eqs (4.20), (4.21) and (4.22), respectively.

Figure 5.1: Effect of length to velocity (L/V0) ratio on methane a) purity b) recovery and c) productivity. The legends used in the last figure apply to all figures. See Appendix B for other operating conditions.
5.3.1 Effect of L/V₀ Ratio

Figure 5.1 summarizes the net results for CH₄ purity, recovery and productivity as a function of L/V₀ ratio for different adsorbents. The general trend is that recovery and productivity increase with decreasing L/V₀, but the trend is opposite for purity. For a fixed column length, a decrease in L/V₀ ratio means an increase in inlet velocity (or flow rate) to the bed. It is evident from the Figure 5.2 (a) that a decrease in L/V₀ from 45 to 25 s results in a change of exit flow rate of about 40 to 75 cm³/s calculated at 1 atm and 300 K. With increasing feed velocity, there is less residence time in the bed for adsorption and more methane is collected during the given period of high pressure adsorption step. As a result, recovery is improved. However, it is clear from Figure 5.3 that an increase in velocity (or decrease in L/V₀ ratio) also causes more nitrogen to travel to the product end which contaminates the product. Therefore, a reduced concentration of methane in the product during the high pressure adsorption step is observed, as shown in Figure 5.2(b), which in turn diminishes the product purity.

Figure 5.2: (a) Flow rate and (b) mole fraction of CH₄ at the column exit as a function of time during high pressure adsorption step for three different L/V₀ ratios. The results are for Ba400. See Runs 1, 2 and 3 in Appendix B for other operating conditions.
Figure 5.3: Mole fraction of CH\textsubscript{4} in the gas phase as a function of dimensionless bed length at the end of high pressure adsorption step for three different L/V\textsubscript{0} ratios. The results are for Ba400. See Runs 1, 2 and 3 in Appendix B for other operating conditions.

Figure 5.4: Effect of pressurization time on a) purity b) recovery and c) productivity. The legends used in the last figure apply to all figures. See Appendix B for other operating conditions.
5.3.2 Effect of Pressurization/Blowdown Step Duration

In the present study, traditional Skarstrom cycle is used where pressurization and blowdown times are equal. Hence, the effect of a change in pressurization time should be analyzed together with a simultaneous change in blowdown time. From the results shown in Figure 5.4, it appears that pressurization/blowdown time has very little effect on methane purity and recovery. Since the direction of mass transfer is from gas to solid during pressurization and vice versa during blowdown and the two steps have equal duration, a likely explanation for the observed trends in purity and recovery is the additional mass transfer due to a larger duration of one step gets cancelled by an approximately equal effect in opposite direction during other step. Support for this explanation may be obtained from the respective gas phase methane concentration profiles in the bed at the end of pressurization and blowdown steps of different duration shown in Figure 5.5. Longer blowdown time allows more of the slower diffusing methane to desorb from the adsorbent and hence at the end the gas phase has more methane, which is evident from Figure 5.5(b). The subsequent pressurization step, which has equal duration as the blowdown step, provides the necessary extra time.
for readsorption of the additional amount of methane desorbed during the longer blowdown. The gas phase methane concentration profile along the bed, therefore, remains practically the same as what is attained with a shorter pressurization/blowdown time, as may be seen from Figure 5.5(a). Increasing pressurization/depressurization time increases the total cycle time without significantly affecting the methane product purity and flow rate, which decreases the productivity seen from Figure 5.4(c).

Figure 5.6: Effect of adsorption time on a) purity b) recovery and c) productivity. The legends used in the last figure apply to all figures. See Appendix B for other operating conditions.
5.3.3 Effect of Duration of High Pressure Adsorption /Purge Step

In a traditional Skarstorm cycle, both high pressure adsorption and purge steps have equal duration like the pressurization and blowdown steps. Therefore, it is not possible to independently vary the high pressure adsorption and purge durations. The combined effect of equally changing the adsorption and purge steps on the performance of a PSA process is presented in Figure 5.6. For all five adsorbents, purity decreases, while recovery and productivity increase with increasing adsorption/purge step duration. This process variable appears to be an effective way of increasing methane recovery when there is some room to sacrifice methane purity in the product.

The representative methane concentration profiles in the gas phase along the adsorber length at the end of high pressure adsorption and self-purge steps shown in Figure 5.7 will help to explain the underlying mechanism that leads to the effects seen in Figure 5.6. Longer adsorption time means that the feed concentration front penetrates deeper into the bed, which is well captured in Figure 5.7(a). Progress of the concentration front in the gas phase gives a measure of how much of the bed has been equilibrated with respect to the feed composition. Since we are dealing with a kinetically controlled process, the rate of change of concentration is directly related to the time spent in the adsorption step. Therefore, increasing the adsorption time results in a deeper penetration of the concentration front, indicating a more thorough equilibration of the bed. This, in turn, leads to a higher purity of the product stream.
separation where the mass transfer resistance is high, there is a decrease in the adsorption rate as the bed length available for further adsorption decreases. Hence, the product flow rate increases with increasing high pressure adsorption time, and the productivity increases. Since other operating parameters such as L/V₀ ratio, high and low operating pressures, etc., do not change, the total input of methane to the system during pressurization and high pressure adsorption remains practically the same and, therefore, methane recovery also increases.

A decreasing in adsorption rate with increasing penetration of the feed concentration front causes more nitrogen to flow to the product end. As discussed in section 5.3.1, this increased flow of nitrogen to the product end can contaminate the methane product. However, in order to fully understand the reason for drop in methane purity one also needs to take into consideration the profiles in Figure 5.7(b) where it is shown that the bed contains more nitrogen at the end of a longer self-purge step compared to a shorter one. The area above each line in the figure gives the average mole fraction of nitrogen remaining in the bed after self-purge step of corresponding duration. This residual nitrogen is pushed to the product end during the next pressurization step and is released with the high pressure product. The drop in methane product purity with increasing adsorption time is, therefore, a combined effect of a decreasing adsorption rate and insufficiency of self-purge for methane-nitrogen PSA separation on the adsorbents under investigation. The issue is further discussed in section 5.3.4.

5.3.4 Effect of Purge to Feed Ratio (G)

In an equilibrium controlled PSA separation operated on a conventional Skarstrom cycle, a part of the high pressure raffinate product is used to execute a counter-current
purge step following blowdown to the low operating pressure. The step is necessary to sufficiently remove the stronger adsorbate from the bed and ensure high raffinate product purity in the subsequent high pressure adsorption step. The purge step is analogous to the light component reflux in distillation or a similar counter-current mass transfer operation. In a kinetically controlled PSA cycle, the idea of self-purge (G=0, in Eq (4.5d)) is effective when the slower desorbing component (for example, nitrogen in case of air separation using CMS) is in sufficient amount to effectively push out the faster desorbing component from the bed voids, which could otherwise contaminate the high pressure raffinate product in the next cycle. The effect of purge to feed ratio on methane-nitrogen separation is compared for different adsorbents in
Figure 5.8. The observed trends may be explained by closely looking at the results presented in Figure 5.9 and 5.10.

Figure 5.9: Mole fraction of methane in the gas phase as a function of dimensionless bed length at the end of (a) blowdown and (b) self-purge (G=0) steps showing inadequacy of self-purge in most cases. See Appendix B for other operating conditions.

The gas phase concentration profiles along the bed length at the end of blowdown and self-purge (G=0) steps shown in Figure 5.9 clearly show the inadequacy of self-purge for most adsorbents considered in this study. The shift in corresponding profiles in Figures 5.9(a) and 5.9(b) is a measure of how much nitrogen is pushed out of the voids in the bed by the slower diffusing methane. Except for Sr190, the residual amount of faster diffusing nitrogen in the gas phase at the end of the self-purge step is quite high in case of all other four adsorbents, namely, Ba400, Sr270, BF CMS and Takeda CMS. For these adsorbents, introduction of external purge (G=0.6) brings about significant changes to the methane concentration profiles at the end of the purge step, which is best appreciated by comparing the profiles in Figure 5.10(b) with those in Figure 5.9 (b). In case of Sr190, self-purge is adequate and further improvement by introducing external purge is negligible. Hence, external purge leads to better regeneration and, therefore, increased methane purity when the self-purge is inadequate. External purge,
however, means that less high pressure raffinate gas is available for withdrawal as product, which lowers the recovery and productivity.

Figure 5.10: Mole fraction of methane in the gas phase as a function of dimensionless bed length at the end of (a) blowdown and (b) purge (G=0.6) steps showing the improvements after introducing external purge. See Appendix B for other operating conditions.

5.3.5 Effect of Adsorption Pressure

Figure 5.11 shows the effect of adsorption pressure on the performance of methane-nitrogen separation by PSA for the five adsorbents. It is clear from the figure that productivity gradually increases as the adsorption pressure is increased. On the other hand, except in case of Sr190, recovery remains practically constant and there is a modest increase in purity with increasing adsorption pressure for the other adsorbents. In case of Sr190, purity drops and recovery increases as adsorption pressure in increased. When the adsorption pressure is increased in a self-purged Skarstrom cycle without changing L/V₀ ratio, low operating pressure and duration of various steps, it implies two things: (i) an increase in the bed capacity for adsorption and (ii) an increase in the input molar flow rate to the bed. Favorable equilibrium isotherm and dominance of mass transfer resistance both contribute to a deeper penetration of the concentration front with increasing adsorption pressure and there is an increase in the
Figure 5.11: Effect of adsorption pressure on a) purity b) recovery and c) productivity. The legends used in the last figure apply to all figures. See Appendix B for other operating conditions.

product flow rate for reasons that have already been discussed in section 5.3.3 in connection with the effect of high pressure step duration. This explains the monotonic increase in methane productivity seen in Figure 5.11(c). In this case, however, moles of feed gas (and therefore, methane) entering the adsorber during pressurization and high pressure adsorption also increase with increasing adsorption pressure. Since recovery is defined as the ratio of methane output in product gas to that entering during pressurization and high pressure adsorption, constant recovery implies that these quantities are linearly related to the high operating pressure. This is indeed the case, which is evident from Figure 5.12. Increase in purity with high operating pressure is a consequence of increased bed capacity for adsorption, which allows more adsorption
of faster diffusing nitrogen compared to the slower diffusing methane. This results in purer methane at the product end, as may be seen from Figure 5.13.

Figure 5.12: Volume of CH₄ in (a) product gas, (b) feed gas during high pressure adsorption and (c) feed gas during pressurization. The results are for Takeda CMS. See Runs 2, 4 and 5 in Appendix B for other operating conditions.

Figure 5.13: Mole fraction of methane as a function of dimensionless bed length at the end of high pressure adsorption (HPA) step. The results are for Ba400. See Runs 2 and 5 in Appendix B for other operating conditions.
5.3.6 Effect of Desorption Pressure

An adsorption bed is better regenerated by lowering the purge pressure. The capacity of the bed is increased for both adsorbates, but nitrogen being the faster component, is adsorbed more relative to the slower methane. Hence, an increase in product purity at the expense of some drop in product recovery is expected with decreasing purge step pressure. The results in Figure 5.14 are consistent with these expectations. It is obvious that sub-atmospheric purge step pressure can be very effective for attaining high purity methane product, but the practical limitation of running an industrial column at a very high vacuum should also be taken into consideration.

Figure 5.14: Effect of desorption pressure on a) purity b) recovery and c) productivity. The legends used in the last figure apply to all figures. See Appendix B for other operating conditions.
5.3.7 Effect of Methane Diffusivity in Ba400 on a Self-purge Cycle

It is clear from the discussion in section 5.3.4 that the effectiveness of a self-purge step in a kinetically controlled PSA process depends on the amount of slower component desorbed during this step. The amount desorbed depends firstly on the amount adsorbed on the first place during the high pressure step and secondly on how fast it can come out over the duration of the self-purge step. Effect of the diffusivity of methane in Ba400 on the performance of a self-purge PSA cycle was, therefore, investigated and the results are shown in Figure 5.15. There seems to be an optimum methane diffusivity value at which the self-purge cycle will be most effective and will give maximum methane purity in the high pressure product. Increased methane diffusivity will, however, result in a drop in recovery, which makes the overall effect comparable with introduction of external purge. Hence, a modified Ba-ETS-4 with somewhat higher methane diffusivity may not be advantageous over Ba400.

Figure 5.15: Effect of diffusivity of methane on purity and recovery in Ba400 sample.
The operating conditions are: $P_H = 9$ atm, $P_L = 0.5$ atm, $L/V_0$ ratio = 35 s, pressurization/blowdown time = 75 s, high pressure adsorption/purge time = 150 s. See Table 5.1 for equilibrium and kinetic parameters.
5.4 Comparative Study of Ba-ETS-4, Sr-ETS-4 and CMS Adsorbents

The effects of several operating parameters on the performance of methane-nitrogen separation by PSA have been investigated for all five adsorbents. The following general observations can be summarized in the light of above discussions:

(i) It is very easy to attain >96% methane purity in Ba400 and Sr190.

(ii) The performances in terms of purity, recovery and productivity attained with two CMS samples are consistently lower than those of the other samples.

(iii) Given the low enrichment attained using the CMS samples, it is not surprising that these samples give high methane recovery in all the cases. What is noteworthy is the comparable high recovery achieved with Ba400 simultaneously with methane purity consistently above 96%. Sr190 gives the lowest recovery in all the cases.

(iv) The samples do not seem to differ significantly in terms of productivity.

Having studied one by one the sensitivity of the process performance to various operating parameters, the next step is to find how these operating parameters can be optimally chosen to maximize both purity and recovery. To achieve this goal, purity of methane is plotted as a function of recovery of methane for six different parameters in Figures 5.16 to 5.18, each plot representing one of the five adsorbents. The arrows in the figures indicate the increasing directions of the respective operating parameters. Here the target is set to produce, starting from a 90:10 CH₄:N₂ mixture, a product of at least pipeline quality natural gas, at highest possible recovery. It is clear that for the four-step cycle operation with no purge, the most efficient way to increase purity is to reduce desorption pressure since corresponding loss of recovery is relatively low as
compared to other cases. But reducing desorption pressure will increase energy consumption and hence the operating cost. The product purity may also be significantly improved by regenerating the adsorbent bed with product purge. However, the recovery is reduced by introducing purge. It is also evident from the figures that the best parameters to increase the recovery are high pressure adsorption time and length to velocity ratio, although these parameters adversely affect the purity. Hence, longer high pressure step, high L/V₀ ratio, sub-atmospheric desorption pressure together with product purge are the desirable conditions to attain the pipeline specification of methane concentration without a severe drop in its recovery.

Figures 5.16 to 5.18 show that the overall performances of the adsorbents decrease in the order Ba₄₀₀ > Sr₁₉₀ > Sr₂₇₀ > Takeda CMS > BF CMS. The BF CMS sample cannot meet the pipeline specification at least when Skarstrom cycle is used. It is possible to reach 96% methane purity with Takeda CMS sample by resorting to a desorption pressure below 0.2 atm or introducing a small product purge at a desorption pressure of 0.2 atm. Sr₁₉₀ and Sr₂₇₀ adsorbents can still be used for methane-nitrogen separation by PSA, but Ba₄₀₀ adsorbent appears to be the best choice. In addition to giving high purity, it also gives a high recovery. The high sensitivity (indicated by sharp changes in purity or recovery) of some parameters seen in Figure 5.18 also confirms that these can be manipulated to further increase purity as well as recovery. In this study, a higher productivity of Ba₄₀₀ is observed (although the difference with the other adsorbents is not large) indicating that this sample will require a relatively smaller bed for the same separation. Therefore, a considerable savings in both capital and operating cost may be expected for a PSA process designed for separating nitrogen from its mixture with methane using Ba₄₀₀.
Figure 5.16: Plot of methane purity vs. recovery showing the effects of different parameters on the performance of a PSA system on a) BF CMS and b) Takeda CMS samples. The arrows indicate the increasing directions of the operating parameters. The legends used in the first figure apply to all figures. \( P_H \): the adsorption pressure (5-9 atm); \( L/V_0 \): ratio of column length to feed velocity (25-45 s); \( P_L \): desorption pressure (0.2-1 atm); PR: pressurization step (75-150 s); HPA: high pressure adsorption step (75-150 s) and G: purge to feed ratio (0-0.6). For column dimension, see Table 5.2.

Figure 5.17: Plot of methane purity vs. recovery showing the effects of different parameters on the performance of a PSA system on a) Sr270 and b) Sr190 samples. The arrows indicate the increasing directions of the operating parameters. The legends used in the first figure apply to all figures. \( P_H \): the adsorption pressure (5-9 atm); \( L/V_0 \): ratio of column length to feed velocity (25-45 s); \( P_L \): desorption pressure (0.3-2 atm); PR: pressurization step (75-150 s); HPA: high pressure adsorption step (75-150 s) and G: purge to feed ratio (0-0.6). For column dimension, see Table 5.2.
Figure 5.18: Plot of methane purity vs. recovery showing the effects of different parameters on the performance of a PSA system on Ba400 sample. The arrows indicate the increasing directions of the operating parameters. P_H: the adsorption pressure (5-9 atm); L/V_0: ratio of column length to feed velocity (25-45 s); P_L: desorption pressure (0.3-2 atm); PR: pressurization step (75-150 s); HPA: high pressure adsorption step (75-150 s) and G: purge to feed ratio (0-0.6). For column dimension, see Table 5.2.

Figure 5.19: Plot of purity vs. recovery of methane for Ba400, clinoptilolite and ETS-4 adsorbents. The arrows indicate the increasing directions of the operating parameters. For Ba400: L/V_0: ratio of column length to feed velocity (25-45 s); P_L: desorption pressure (0.3-2 atm) HPA: high pressure adsorption step (75-150 s) G: purge to feed ratio (0-0.6). Total pressurization time: 75 s. For clinoptilolite and ETS-4: L/V_0: ratio of column length to feed velocity (10-40 s). Desorption pressure: 0.4 atm; adsorption pressure: 7 atm; pressurization time: 30 s; high pressure adsorption time: 60 s; cocurrent blowdown time: 10 s; countercurrent blowdown time: 30 s; desorption time: 60 s. Data for clinoptilolite and ETS-4 from Jayaraman et al. (2004).
5.5 Comparison with Published Performance

Having established the Ba400 as the best adsorbent for natural gas cleaning, the performance of this adsorbent is compared with that of purified clinoptilolite and ETS-4 studied by Jayaraman et al. (2004). A fair comparison of the sorbent performance can be made by using similar conditions for all the sorbents. The simulation results for clinoptilolite and ETS-4 summarized in Figure 5.19 were reported for 85/15 methane/nitrogen mixture. Therefore, new results were computed for Ba400 using the same feed composition. It is evident from the figure that at the highest recoveries attain for clinoptilolite and ETS-4 samples, the product purity was below pipeline specification of ≥96% methane (or ≤4% nitrogen). In contrast, Ba400 sample, in addition to meeting the pipeline specification, is also able to attain up to 75% recovery. For Ba400 sample, there is enough room to further increase purity by tuning some parameters like G and P_L, as shown in Figure 5.19. By increasing the high pressure adsorption (HPA) time, it is also possible to increase the recovery beyond 75%, but the purity falls below the minimum limit. Another way to increase recovery without significant loss of purity is to use a five-step PSA cycle as used by Jayaraman et al. (2004) to produce the results shown in Figure 5.19. The steps involved in the cycles shown in Figure 5.20 were: (I) pressurization with feed gas; (II) high-pressure adsorption; (III) cocurrent depressurization to produce additional CH₄-rich product; (IV) countercurrent blowdown to a low pressure and (V) low pressure countercurrent desorption step. The inclusion of cocurrent blowdown step in the five-step cycle contributes to higher methane recovery. Therefore, by using this cycle and Ba400 adsorbent, it is also possible to significantly increase recovery of methane. It is important to note that part of the methane rich product from the five-step cycle is released at low pressure product and needs to be repressurized for combining with high
pressure product. Hence, the additional recovery comes at the expense of additional compression energy.

Figure 5.20: Steps in five-step PSA cycle used in simulation (Jayaraman et al., 2004).

5.6 Chapter Summary

From the comparative evaluation of five adsorbents for methane-nitrogen separation by PSA operated on a Skarstrom cycle, the performance of Ba400 appears most promising. The performance of this sample also compares well that the results reported in the literature.
CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

The aim of the project was to identify suitable adsorbents for methane-nitrogen separation by PSA where purified methane was recovered as the high pressure raffinate product. The study encompassed (i) measurement and modeling of binary equilibrium and kinetics of methane-nitrogen mixture in a barium exchanged ETS-4 sample that had earlier shown very high ideal kinetic selectivity of nitrogen over methane, and (ii) a systematic PSA simulation study where performances of various adsorbents were compared.

6.1 Conclusions

The major conclusions are summarized here:

1. Single component equilibrium of methane was measured in a newly prepared Ba-ETS-4 sample dehydrated at 400 °C (Ba400) using differential adsorption bed (DAB) method. The results found from this study were similar to the results obtained in a previous study (Majumdar, 2004). The importance of removing moisture, even if present in trace amount, from feed gas of a flow process was clearly demonstrated.

2. Measurements of binary equilibrium and kinetics were carried out in Ba400 using DAB method for 50:50 and 90:10 CH₄:N₂ feed mixtures. Two different models such as Ideal Adsorption Solution (IAS) theory using individually fitted Langmuir parameters and multisite Langmuir model (MSL) were used to predict binary equilibrium results. A considerable deviation between experimental data and model predictions were observed for 50:50 CH₄:N₂.
mixture. However, MSL model was marginally better in predicting experimental data of 90:10 CH₄:N₂ mixture, which is a representative composition for natural gas wells. The MSL model was also the preferred choice for predicting methane-nitrogen equilibrium in CMS and Sr-ETS-4 adsorbents. A bidispersed pore diffusional model with MSL isotherm and chemical potential gradient as the driving force for diffusion was used to predict the binary uptake results. The model predictions were found to be very encouraging for both mixtures despite the mismatch found in equilibrium prediction for 50:50 CH₄:N₂ mixture.

3. A detailed PSA simulation model was developed based on axially dispersed plug flow in fluid phase, MSL isotherm to represent binary equilibrium and bidispersed pore diffusion to represent adsorption kinetics including the features that correctly capture the binary transport of gases in the micropore of carbon molecular sieve and ion exchanged ETS-4 adsorbents. Using this simulation model, an extensive study was conducted to compare the performances of five adsorbents, namely, BF CMS, Takeda CMS, Sr190, Sr270 and Ba400 for methane-nitrogen separation by PSA. Among the adsorbents investigated, Ba400 and Sr190 were found to easily attain pipeline quality natural gas (≥96% methane). The overall performance of Ba400 was, however, better than that of Sr190. The performance of the PSA system was very sensitive to process variables like high pressure adsorption time and length to velocity ratio were identified as the significant parameters to tune recovery. The purge to feed ratio as well as desorption pressure were found most sensitive for tuning purity.
4. The performance of the best sample for methane-nitrogen separation by PSA found from the simulation study, Ba400, was compared with published performances of ETS-4 and clinoptilolite. It was found that, in addition to meeting pipeline specification, Ba400 also provided higher recovery, thus making this adsorbent a promising candidate for further exploration.

6.2 Recommendations

The following recommendations are put forward for consideration in future studies:

1. It is desirable to conduct PSA experiments in order to validate the simulation results. The main challenge will be to synthesize enough material to fill up a laboratory size adsorption column.

2. Neglecting temperature variation was one of the major assumptions of the PSA model. The heat balance equation can be included to the current model to assess its effect on purity, recovery and productivity.

3. To make the simulation results more realistic with respect to industrial processes, it is recommended to take into account the pressure drop through the bed. Darcy’s equation can be used to take the pressure drop through the bed into account.

4. To reduce the long computation time faced with the in-house simulator, a new simulation tool, namely, COMSOL Multiphysics, can be used to solve the dynamic PSA model.
REFERENCES


APPENDIX A
SOLUTION OF THE PSA MODEL USING ORTHOGONAL COLLOCATION METHOD

The model equations for bidisperse PSA model shown in Chapter 4 are formulated in their dimensionless and collocated forms in sections A.1 and A.2, respectively.

A.1 Dimensionless Form of PSA Model Equations

Following dimensionless variables are defined:

\[ X_A = \frac{c_A}{C_T}, \quad X_{Ap} = \frac{c_{Ap}}{C_L}, \quad X_{Bp} = \frac{c_{Bp}}{C_L}, \quad Y_A = \frac{q_A}{q_{As}}, \quad Y_B = \frac{q_B}{q_{Bs}}, \quad Y_A^* = \frac{q_A^*}{q_{As}}, \quad Y_B^* = \frac{q_B^*}{q_{Bs}} \]

\[ z = \frac{z}{L}, \quad \chi = \frac{R}{R_p}, \quad \eta = \frac{r}{r_c}, \quad \tau = \frac{t V_{0H}}{L}, \quad u = \frac{V}{V_{0H}}, \quad X_A^{im} = \frac{c_A^{im}}{C_L}, \quad X_B^{im} = \frac{c_B^{im}}{C_L} \]

\[ Pe = \frac{V_{0H} L}{D_L}, \quad \delta = \frac{k_f R_p}{\varepsilon_p D_p}, \quad \beta = \frac{D_p L}{R_p^2 V_{0H}}, \quad \gamma_A = \frac{D_{c0A} L}{r_c^2 V_{0H}}, \quad \gamma_B = \frac{D_{c0B} L}{r_c^2 V_{0H}} \]

(A.1……A.19)

Step 1: Pressurization of bed 2 and high pressurization adsorption of bed 1.

The modeling procedure for this step is same as step 2 which is discussed next. The only difference is that in this case the column pressure of both beds is a function of time.

Step 2: High pressure adsorption in bed 2 and desorption at low pressure in bed 1.
Fluid phase equation:

External fluid phase in bed 2:

\[
\frac{\partial X_{A2}}{\partial \tau} = \frac{1}{Pe_H} \frac{\partial^2 X_{A2}}{\partial Z^2} - u_2 \frac{\partial X_{A2}}{\partial Z} + 3 \left( \frac{1 - e}{e} \right) \frac{P_L}{P} \left( X_{A2} - 1 \right) \frac{\partial X_{Ap2}}{\partial \chi} \bigg|_{\chi=1.0} + X_{A2} \frac{\partial X_{Bp2}}{\partial \chi} \bigg|_{\chi=1.0}
\]  \quad (A.20)

boundary conditions:

\[
\left. \frac{\partial X_{A2}}{\partial Z} \right|_{z=0} = -Pe_H \left( X_{A2} \bigg|_{\text{feed}} - X_{A2} \bigg|_{z=0} \right)
\]  \quad (A.21)

\[
\left. \frac{\partial X_{A2}}{\partial Z} \right|_{z=1.0} = 0
\]  \quad (A.22)

overall mass balance:

\[
\frac{\partial u_2}{\partial Z} = -3 \left( \frac{1 - e}{e} \right) \frac{P_L}{P} \left( \frac{\partial X_{Ap2}}{\partial \chi} \bigg|_{\chi=1.0} + \frac{\partial X_{Bp2}}{\partial \chi} \bigg|_{\chi=1.0} \right)
\]  \quad (A.23)

boundary conditions:

\[
\left. u_2 \right|_{z=0} = \frac{V_{2}}{V_{0H}}
\]  \quad (A.24)

\[
\left. \frac{\partial u_2}{\partial Z} \right|_{z=1} = 0
\]  \quad (A.25)

For high pressure adsorption, \( u_2 \bigg|_{z=0} = 1 \)

Macropore equation:

\[
\frac{\partial X_{Ap2}}{\partial \tau} = \beta_H \nabla^2 X_{Ap2} - 3 \gamma_H \frac{1 - e_p}{e_p} q_{Ax} C_L \left[ \frac{Y_{A2}}{X_{A2}^m} \frac{\partial X_{A2}^m}{\partial \eta} \right]_{\eta=1.0}
\]  \quad (A.26)

\[
\frac{\partial X_{Bp2}}{\partial \tau} = \beta_H \nabla^2 X_{Bp2} - 3 \gamma_H \frac{1 - e_p}{e_p} q_{Bm} C_L \left[ \frac{Y_{B2}}{X_{B2}^m} \frac{\partial X_{B2}^m}{\partial \eta} \right]_{\eta=1.0}
\]  \quad (A.27)
boundary conditions:
\[ \frac{\partial X_{A2}}{\partial \eta} \bigg|_{\eta=0} = 0 \]  \hspace{1cm} (A.28)
\[ \frac{\partial X_{A2}}{\partial \eta} \bigg|_{\eta=1.0} = \delta_H \left[ \frac{p}{p_L} X_{A2} - X_{A2,0} \right] \]  \hspace{1cm} (A.29)
\[ \frac{\partial X_{B2}}{\partial \eta} \bigg|_{\eta=0} = 0 \]  \hspace{1cm} (A.30)
\[ \frac{\partial X_{B2}}{\partial \eta} \bigg|_{\eta=1.0} = \delta_H \left[ \frac{p}{p_L} X_{B2} - X_{B2,0} \right] \]  \hspace{1cm} (A.31)

Macropore equation:
\[ \frac{\partial Y_{A2}}{\partial \tau} = \left( \gamma_A \frac{Y_{A2}}{X_{A2}^{\text{im}}} \right) \nabla^2 X_{A2}^{\text{im}} + \frac{\partial X_{A2}^{\text{im}}}{\partial \eta} \frac{\partial}{\partial \eta} \left( \gamma_A \frac{Y_{A2}}{X_{A2}^{\text{im}}} \right) \]  \hspace{1cm} (A.32)
\[ \frac{\partial Y_{B2}}{\partial \tau} = \left( \gamma_B \frac{Y_{B2}}{X_{B2}^{\text{im}}} \right) \nabla^2 X_{B2}^{\text{im}} + \frac{\partial X_{B2}^{\text{im}}}{\partial \eta} \frac{\partial}{\partial \eta} \left( \gamma_B \frac{Y_{B2}}{X_{B2}^{\text{im}}} \right) \]  \hspace{1cm} (A.33)

\[ X_{A2}^{\text{im}} = \frac{Y_{A2}}{C_l b_A (1 - Y_{A2} - Y_{B2})^\alpha} \]  \hspace{1cm} (A.34)
\[ X_{B2}^{\text{im}} = \frac{Y_{B2}}{C_l b_B (1 - Y_{A2} - Y_{B2})^\alpha} \]  \hspace{1cm} (A.35)

boundary conditions:
\[ \frac{\partial X_{A2}^{\text{im}}}{\partial \eta} \bigg|_{\eta=0} = 0 \]  \hspace{1cm} (A.36)
\[ X_{A2}^{\text{im}} \bigg|_{\eta=1.0} = X_{A2,0} \]  \hspace{1cm} (A.37)
\[ \frac{\partial X_{B2}^{\text{im}}}{\partial \eta} \bigg|_{\eta=0} = 0 \]  \hspace{1cm} (A.38)
\[ X_{B2}^{\text{im}} \bigg|_{\eta=1.0} = X_{B2,0} \]  \hspace{1cm} (A.39)
For dual resistance model

\[
\frac{\partial X_{im}^{A_2}}{\partial \eta} \bigg|_{\eta=0} = 0
\]

\[
3 \left( \frac{(D_{c0})_A}{r_c^2} \right) C_L \frac{\partial X_{im}^{A_2}}{\partial \eta} \bigg|_{\eta=1.0} = \frac{1}{b_A (1 - Y_{A2} - Y_{B2})^{\alpha_A+1}} \times \\
\left[ k_{AA} (Y_{A2} - Y_{A2}) + k_{AB} (Y_{B2}^* - Y_{B2}^*) \right]_{\eta=1.0}
\]

\[
\frac{\partial X_{im}^{B_2}}{\partial \eta} \bigg|_{\eta=0} = 0
\]

\[
3 \left( \frac{(D_{c0})_A}{r_c^2} \right) C_L \frac{\partial X_{im}^{B_2}}{\partial \eta} \bigg|_{\eta=1.0} = \frac{1}{b_B (1 - Y_{A2} - Y_{B2})^{\alpha_B+1}} \times \\
\left[ k_{BA} (Y_{A2}^* - Y_{A2}) + k_{BB} (Y_{B2}^* - Y_{B2}) \right]_{\eta=1.0}
\]

where

\[
k_{AA} = (k_{b0})_A \left[ 1 + (a_A - 1)Y_{A2} - Y_{B2} \right] \\
k_{AB} = (k_{b0})_A a_A Y_{A2} \\
k_{BA} = (k_{b0})_B a_B Y_{B2} \\
k_{BB} = (k_{b0})_B [1 - Y_{A2} + (a_B - 1)Y_{B2}]
\]

External fluid phase in bed 1:

\[
\frac{\partial X_{A1}}{\partial \tau} = \frac{1}{P_e L} \frac{\partial^2 X_{A1}}{\partial Z^2} + u_1 \frac{\partial X_{A1}}{\partial Z} \\
+ 3 \left( \frac{1 - e}{e} \right) \epsilon_p \beta_p \left[ \frac{P_L}{p} \right] \left( X_{A1} - 1 \right) \frac{\partial X_{Apl}}{\partial \chi} \bigg|_{\chi=1.0} + X_{A1} \frac{\partial X_{Bpl}}{\partial \chi} \bigg|_{\chi=1.0}
\]

boundary conditions:

\[
\frac{\partial X_{A1}}{\partial Z} \bigg|_{Z=0} = -P_e L \cdot G \left( X_{A1} \bigg|_{Z=-L_1} - X_{A1} \bigg|_{Z=L_1} \right)
\]

\[
\frac{\partial X_{A1}}{\partial Z} \bigg|_{Z=1.0} = 0
\]
overall mass balance:

\[
\frac{\partial u_i}{\partial z} = -3 \frac{1 - \varepsilon}{\varepsilon} e^{\beta_i} \frac{p_t}{p} \left( \frac{\partial X_{Ap}}{\partial \chi} \bigg|_{z=1,0} + \frac{\partial X_{Bp}}{\partial \chi} \bigg|_{z=1,0} \right) \tag{A.48}
\]

boundary conditions:

\[
\frac{\partial u_i}{\partial z} \bigg|_{z=0} = 0 \tag{A.49}
\]

\[
u_i \bigg|_{z=1} = G \tag{A.50}
\]

Macropore and micropore equations do not change with step. But to maintain similarity with the above discussion for bed 1, the subscripts 2 and H used for bed 2 are replaced by 1 and L, respectively.

Step 3: Same as step 1. The only difference in this case is that bed 1 is subjected to pressurization and bed 2 is subjected to blowdown.

Step 4: Same as step 2 but the beds are interchanged.

**A.2 Collocation Form of Model Equations**

The collocation form for the set of equations discussed above is written as follows:

Eq (A.20)

\[
\frac{\partial X_{A2} (j)}{\partial \tau} = \sum_{i=1}^{M_2} \left[ \frac{1}{Pe_H} Bx(j, i) - u(j)Ax(j,i) \right] X_{A2} (i) \\
+ 3 \left( \frac{1 - \varepsilon}{\varepsilon} e^{\beta_i} \frac{p_t}{p} \right) \left[ (X_{A2} (j) - 1) \sum_{i=1}^{N_I} A(Nl,i)X_{Ap2} (j,i) + X_{A2} (j) \sum_{i=1}^{N_I} A(Nl,i)X_{Bp2} (j,i) \right]
\]

Eq (A.21)

\[
\sum_{i=1}^{M_2} Ax(1,i)X_{A2} (i) = -Pe_H [X_{A2} (0) - X_{A2} (1)] = -Pe_H [X_{Afeed} - X_{A2} (1)]
\]

Eq (A.22)

\[
\sum_{i=1}^{M_2} Ax(M2, i)X_{A2} (i) = 0
\]
Eq (A.23)

\[
\sum_{i=1}^{M_2} A_x(j,i) u_2(i) = -3 \left( 1 - \varepsilon \right) \frac{p_{L}}{p} \beta_H \left[ \sum_{i=1}^{N_1} A(N_l,i) X_{Ap_2}(j,i) + \sum_{i=1}^{N_1} A(N_l,i) X_{Bp_2}(j,i) \right]
\]

Eqs (A.24) and (A.25)

\[ u_2(1) = 1.0 \]

\[
\sum_{i=1}^{M_2} A_x(M_2,i) u_2(i) = 0
\]

Eq (A.26) and (A.27)

\[
\frac{\partial X_{Ap_2}(j,k)}{\partial \tau} = \beta_H \sum_{i=1}^{N_1} B(k,i) X_{Ap_2}(j,i) - 3 \gamma_A \frac{1 - \varepsilon}{\varepsilon} p_{Ax} \frac{q_{Ax}}{C_L} \times \left[ Y_{A_2}(j,k,N_l) X_{A_2}^{im}(j,k,N_l) \sum_{i=1}^{N_1} A(N_l,i) X_{A_2}^{im}(j,k,i) \right]
\]

\[
\frac{\partial X_{Bp_2}(j,k)}{\partial \tau} = \beta_H \sum_{i=1}^{N_1} B(k,i) X_{Bp_2}(j,i) - 3 \gamma_B \frac{1 - \varepsilon}{\varepsilon} p_{Bx} \frac{q_{Bx}}{C_L} \times \left[ Y_{B_2}(j,k,N_l) X_{B_2}^{im}(j,k,N_l) \sum_{i=1}^{N_1} A(N_l,i) X_{B_2}^{im}(j,k,i) \right]
\]

Eq (A.28) and (A.29)

\[
\sum_{i=1}^{N_1} A(l,i) X_{Ap_2}(j,i) = 0
\]

\[
\sum_{i=1}^{N_1} A(N_l,i) X_{Ap_2}(j,i) = \delta_H \left[ \frac{p_{L}}{p} X_{A_2}(j) - X_{Ap_2}(j,N_l) \right]
\]

Eq (A.30) and (A.31)

\[
\sum_{i=1}^{N_1} A(l,i) X_{Bp_2}(j,i) = 0
\]

\[
\sum_{i=1}^{N_1} A(N_l,i) X_{Bp_2}(j,i) = \delta_H \left[ \frac{p_{L}}{p} X_{B_2}(j) - X_{Bp_2}(j,N_l) \right]
\]
Eq (A.32) and (A.33)

\[
\frac{\partial Y_{A2}(j,k,l)}{\partial \tau} = \left[ \gamma_A \frac{Y_{A2}(j,k,l)}{X_{A2}^{im}(j,k,i)} \right] \sum_{i=1}^{N1} B(l,i)X_{A2}^{im}(j,k,i) + \left[ \sum_{i=1}^{N1} A(l,i)X_{A2}^{im}(j,k,i) + \gamma_A \sum_{i=1}^{N1} A(l,i) \frac{Y_{A2}(j,k,i)}{X_{A2}^{im}(j,k,i)} \right]
\]

\[
\frac{\partial Y_{B2}(j,k,l)}{\partial \tau} = \left[ \gamma_B \frac{Y_{B2}(j,k,l)}{X_{B2}^{im}(j,k,i)} \right] \sum_{i=1}^{N1} B(l,i)X_{B2}^{im}(j,k,i) + \left[ \sum_{i=1}^{N1} A(l,i)X_{B2}^{im}(j,k,i) + \gamma_B \sum_{i=1}^{N1} A(l,i) \frac{Y_{B2}(j,k,i)}{X_{B2}^{im}(j,k,i)} \right]
\]

Eq (A.34) and (A.35)

\[
X_{A2}^{im}(j,k,i) = \frac{Y_{A2}(j,k,i)}{C_L b_A \left( 1 - Y_{A2}(j,k,i) - Y_{B2}(j,k,i) \right)^{\alpha_a}}
\]

\[
X_{B2}^{im}(j,k,i) = \frac{Y_{B2}(j,k,i)}{C_L b_B \left( 1 - Y_{A2}(j,k,i) - Y_{B2}(j,k,i) \right)^{\alpha_a}}
\]

Eq (A.36) and (A.37)

\[
\sum_{i=1}^{N1} A(l,i)X_{A2}^{im}(j,k,i) = 0
\]

\[
X_{A2}^{im}(j,k,N1) = X_{Ap2}(j,k)
\]

Eq (A.38) and (A.39)

\[
\sum_{i=1}^{N1} A(l,i)X_{B2}^{im}(j,k,i) = 0
\]

\[
X_{B2}^{im}(j,k,N1) = X_{Bp2}(j,k)
\]
## APPENDIX B

**OPERATING CONDITIONS AND SIMULATION RESULTS FOR VARIOUS ADSORBENTS**

Table B.1: Simulation results for Ba400.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>PR (s)</th>
<th>HPA (s)</th>
<th>(P_L) (atm)</th>
<th>(P_H) (atm)</th>
<th>L/V(_0) (s)</th>
<th>G</th>
<th>Recovery (%)</th>
<th>Purity (%)</th>
<th>Productivity (cc/hr/cc ads)</th>
<th>Vol(_m) of (\text{CH}_4) in product gas (cm(^3))</th>
<th>Vol(_m) of (\text{CH}_4) in pressurization gas (cm(^3))</th>
<th>Overall material balance error (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.2</td>
<td>75</td>
<td>150</td>
<td>0.5</td>
<td>9</td>
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Table B.2: Simulation results for Sr190.

<table>
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<tr>
<th>Run no.</th>
<th>a₁</th>
<th>a₂</th>
<th>PR</th>
<th>HPA</th>
<th>Pₗ</th>
<th>Pₜ</th>
<th>L/V₀</th>
<th>G</th>
<th>Recovery (%)</th>
<th>Purity (%)</th>
<th>Productivity (cc/hr/cc ads)</th>
<th>Vol&lt;sup&gt;m&lt;/sup&gt; of CH₄ in product gas (cm&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Vol&lt;sup&gt;m&lt;/sup&gt; of CH₄ in pressurization gas (cm&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Overall material balance error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.2</td>
<td>75</td>
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Table B.4: Simulation results for BF CMS.

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Table B.5: Simulation results for Takeda CMS.

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### Table B.6: Simulation results for Ba400 using 85/15 CH₄/N₂ mixture.

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<th>P_L (atm)</th>
<th>P_H (atm)</th>
<th>L/V₀ (s)</th>
<th>G</th>
<th>Recovery (%)</th>
<th>Purity (%)</th>
<th>Productivity (cc/hr/cc ads)</th>
<th>Volume of CH₄ in product gas (cm³)</th>
<th>Volume of CH₄ in pressurization gas (cm³)</th>
<th>Overall material balance error (%)</th>
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