MODELLING CONCENTRATED GAS MIXTURE ADSORPTION IN DYNAMIC BREAKTHROUGH COLUMN EXPERIMENTS

Thomas Saleman, Guillaume C.Y. Watson, Thomas E. Rufford, and Eric F May

Centre For Energy, School of Mechanical and Chemical Engineering, The University of Western Australia, 35 Stirling Highway, Crawley WA 6009, Australia
Email address: tsaleman@mech.uwa.edu.au, Eric.May@uwa.edu.au

ABSTRACT

This paper reports the equilibrium and kinetic parameters for N\textsubscript{2} and CH\textsubscript{4} adsorption on the zeolite H\textsuperscript{+} mordenite measured at 303 K and pressures up to 900 kPa using a dynamic column breakthrough (DCB) apparatus. The equilibrium capacities of mordenite measured for pure gases were 1.56 mmol/g CH\textsubscript{4} and 0.85 mmol/g N\textsubscript{2} at 900 kPa from which a pure gas selectivity of 1.8 can be inferred. Our DCB apparatus was equipped with instrumentation to allow measurement of effluent flow rate and composition, so that experiments could be conducted with concentrated N\textsubscript{2} and CH\textsubscript{4} mixtures representative of industrial process streams in the LNG plant. The use of concentrated gas affects temperature and gas velocities across the bed. We describe here a numerical model of the DCB used to extract mass transfer coefficients (MTCs) from pure and 50% diluted N\textsubscript{2} and CH\textsubscript{4} measurements.

INTRODUCTION

The conventional technology to separate N\textsubscript{2} and CH\textsubscript{4} in liquefied natural gas plants is cryogenic distillation. An emerging technology which has the potential to compete with cryogenic distillation is pressure swing adsorption (PSA). One of the challenges in designing PSA systems is obtaining the necessary adsorbent properties required to evaluate existing and novel adsorbents.

A common method for measuring the kinetics of adsorption is to use a dynamic column breakthrough (DCB) apparatus. This type of experiment involves gas flowing through a column packed with the adsorbent of interest and measuring the composition signal at the column outlet. During adsorption the gas flow at the column outlet decreases due to material being adsorbed into a liquid phase of the solid surface. This causes a velocity drop which has to be modeled, complicating the analysis. Many previous studies avoid this complexity by using a gas that has been diluted with a non-adsorbing component (helium) so that the velocity drop is negligible and a constant velocity assumption is reasonable. In this work a DCB apparatus was used that had a novel way of accurately measuring the column outlet flow rate when the composition is varying.

EXPERIMENTAL

Materials

The adsorbent H\textsuperscript{+}-Mordenite reported in this paper was selected as it is representative of a typical micropore zeolite. The H\textsuperscript{+}-Mordenite (HSZ-640HOA) was provided by TOSOH Corporation (Japan) in the form of 1 mm diameter extruded pellets with an average length of 4 mm; approximately 30 g was loaded into the apparatus. Prior to loading the H\textsuperscript{+}-Mordenite to the adsorption column for the DCB measurements, the adsorbent was heated under vacuum (10 Pa) at 573 K for 24 h to remove any adsorbed
water and other contaminants. All gases used in this work were supplied by BOC who stated the flowing fractional purities: He 99.999 %, CH4 99.995%, and N2 99.999 %.

**Apparatus and Procedure**

We constructed a Dynamic Column Breakthrough (DCB) apparatus (Fig. 1) capable of measuring adsorption capacity and kinetic of gas mixtures, for total gas pressures from (100 to 900) kPa, with adsorbate partial pressures down to 20 kPa and for temperature in the range (243 to 303) K. The DCB system consisted of a stainless steel column with an internal diameter of 22.3 mm and length of 130.8 mm. The system used high quality flow meters (20 to 200 sccm), back pressure regulators and a residual gas analyser (RGA, Stanford Research Systems QMS-100) for analysing composition of flowing gas mixtures. Helium was used as carrier gas during the DCB runs and was assumed to not adsorb within our range of conditions (Malbrunot et al. 1997). The flow meter was an orifice type meter that used the pressure drop and viscosity of the gas to calculate the flowrate. As the viscosity varies with the composition a correction was applied to measured flowrate to convert this to the true flow. Details on the construction and operation of this apparatus, including description of the instruments used for the measurements of flow rate, pressure, temperature and molar composition, are described in detail in elsewhere (Hofman 2012). The adsorption column was submerged in a stirred water-glycol bath to control the temperature in the range 243 - 353 K.

![Fig. 1: Schematic representation of the adsorption column from the DCB apparatus](image)

**EQUILIBRIUM ADSORPTION RESULTS**

The equilibrium adsorption capacity of pure CH₄ and N₂ on H⁺-Mordenite were measured at 303 K for partial pressures from (50 to 900) kPa. These data are shown in Fig. 2. Details of the method to determine the equilibrium capacities and their uncertainties are reported by Hofman (Hofman 2012). The shape of these isotherms corresponds to Type 1 in IUPAC classification (Brunauer et al. 1940). A least squares regression analysis was used to determine the best-fit parameters of the Langmuir isotherm (Equation 1 with n=1) to describe the equilibrium adsorption capacities by minimizing the standard deviation of the measured pure gas data from the
prediction of the correlation. The best fit values reported in Table 1 predict an adsorption capacity at 900 kPa that is within 5% of the prediction using the isotherm proposed by Delgado et al. (2006), which is within our experimental uncertainty. The Extended Langmuir model was used to describe the equilibrium adsorption capacity of components in a gas mixtures measured in the DCB apparatus. This model is adequate for the purpose of engineering design calculations as it contains only three parameters for each gas adsorbed and provides an analytical expression for $Q_i^*$ that is an explicit function of temperature, T, and gas partial pressure, $P_i$.

$$Q_i^* = \frac{Q_{\text{max}} b_i P_i}{1 + \sum_j^n b_j P_j} \quad \text{with} \quad b_i = b_{0,i} \exp \left( \frac{-\Delta H_i}{RT} \right)$$

Equation 1

Fig. 2: Measured adsorption capacities of pure CH₄ (red triangles) and pure N₂ (green squares) on H⁺-Mordenite from this work: (A) Adsorption capacities measured (points) and calculated (lines) by the Langmuir model (Equation 1) (B) Deviations between the measured and the calculated capacities.
Table 1: Parameters of the Langmuir Model Fitted to the Adsorption Capacities for Each Pure Gas Measured at 303 K and Pressures up to 900 kPa.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$Q_{\text{max}}$ [mmol.g$^{-1}$]</th>
<th>$10^6 K_{0,i}$ [kPa$^{-1}$]</th>
<th>rms deviation [mmol.g$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>2.33</td>
<td>0.59</td>
<td>0.048</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.18</td>
<td>0.38</td>
<td>0.014</td>
</tr>
</tbody>
</table>

**ANALYSIS OF DYNAMIC DATA**

Fig. 3 shows a characteristic set of dynamic effluent flow rate data measured during a DCB experiment with pure N$_2$. A mathematical model was developed to describe the adsorption in the packed-bed of the DCB apparatus and the model consisted of a set of coupled material, energy and momentum balances. Similar models have been reported previously by several workers such as Farooq and Ruthven (1990), Guntauuka et al. (2008) and Mulgundmath et al. (2012). The key assumptions of the DCB model include:

1. The gas phase was ideal.
2. There were no mass, heat and momentum gradients transfer in the radial direction.
3. The bed hydrodynamics were represented as plug flow with axial mass dispersion.
4. The rate of mass transfer between the gas and adsorbed phases was described by the linear driving-force approximation (LDF) with a lumped mass transfer coefficient (MTC).
5. The adsorption of helium was neglected under the conditions studied.
6. The column operated under isobaric and isothermal condition.

The primary partial differential equations (PDE) describing an adsorption column are the total material balance and the component material balances, shown in **Equation 2** and **Equation 3** below.

\[
\frac{\partial C}{\partial t} = -\frac{\partial \left(v_x C\right)}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \rho_i \sum_{i=1}^{n} \frac{\partial Q_i}{\partial t} \quad \text{Equation 2}
\]

\[
\frac{\partial c_i}{\partial t} = D_{ax} \frac{\partial^2 c_i}{\partial z^2} - \frac{\partial \left(v_x c_i\right)}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \rho_i \frac{\partial Q_i}{\partial t} \quad \text{Equation 3}
\]

The mass transfer rate for each solute $i$ to the solid phase (adsorbent) was modeled using the linear-driving-force approximation (LDF) with a lumped MTC (Yang 1987):

\[
\frac{\partial q_i}{\partial t} = MTC_i \left(Q^* - Q_i\right) \quad \text{Equation 4}
\]
Fig. 3: Data (green) vs. model prediction (black) for pure N\textsubscript{2} at 108 kPa using the MTC extracted from the effluent N\textsubscript{2} flow rate (MTC = 0.044 s\textsuperscript{-1}, RMS\textsubscript{N2} = 0.8 µmol.s\textsuperscript{-1})

**Model of extra column effects**

To mathematically describe breakthrough curves generated from the DCB apparatus used in this study required consideration of the extra-column components. This is because the extra-column components contribute to the retention time and band broadening of the experimental breakthrough curve, and therefore must be accounted for to accurately compare experimental results with the models simulation (Rajendran et al. 2008). There is approximately the same gas volume in the extra column components than in the adsorption column. The extra column volume was simulated from a mixture of plug flow reactors and continuous stirred tank reactors.

**Numerical method**

The model was implemented in LabVIEW V9.0 (National instruments, Texas). LabVIEW has an inherent parallel architecture and is therefore highly suited towards solving large numbers of coupled equations. The finite element method was used to reduce the set of partial differential equations (PDE’s) into ordinary differential equations (ODE’s). The spatial domain was discretised over a uniform grid of 100 points by the central differencing scheme (CDS). For systems that include axial dispersion, the CDS is more accurate than the commonly used upwind differencing scheme (UDS) for a reasonable CPU requirement time. The time integration was performed with the Runge Kutta 4-5 algorithm, with variable step size of $1.10^{-12}$ to 1 s.

The pressure drop along the column has been measured to be, at most, 2% of the total pressure, rendering the isobaric assumption plausible. Due to the exothermic nature of adsorption, the local temperature in the column can rise by up to 5 K, which is assumed to not break the isothermal assumption. The model has been compared to a commercial software package, which has a model that includes rigorous energy and momentum balances of the DCB, and in general the two models produce consistent results.
Extraction of Mass Transfer Coefficients

The value and the uncertainty of the MTC for each run were estimated by fitting the outlet flow rate of the adsorbable species, using the approximation method of non-linear fitting (Bevington P. R. 1992). The MTC was estimated by minimising the goodness-of-fit parameter $\chi^2$ (the chi squared):

$$\chi^2 = \frac{1}{N_p} \sum_{i} \left( \frac{F_{i,\text{meas}} - F_{i,\text{mod}}}{u(F_{i,\text{meas}})} \right)^2$$

Equation 5

where $N_p$ is the number of data point for each run. For convenience the uncertainty $u(F)$ was related to the inlet total flowrate. From Hofman et. al. (2012), $u(F) = 1.2$ sccm for a 100 sccm flowrate. The error in the fitting parameter (here the MTC) was estimated by varying the MTC to increase $\chi^2$ by 1 from the minimum value.

The example shown in Fig. 3 is a pure N$_2$ experiment carried out at 108 kPa. This figure shows the data versus the model prediction using the best fit MTC. The fitting technique for this experiment is shown in Fig. 4, which shown the best fit MTC to be 0.044 s$^{-1}$ with a confidence range of (0.03934 to 0.05060) s$^{-1}$ or (-11 to +15) %. In general, fittings had a better resolution in the lower range of confidence for MTC. For the runs with pure gas the lower and the upper range were typically 5-15% and 10-20%.

Several runs were also performed with the adsorbate 50% diluted with inert helium. In general the fitting were good (low $\chi^2$) but the sensitivity of the data to the MTC was much lower. The lower and the upper range of confidence for the MTCs extracted from dilution adsorbate data were typically -25% and +40% respectively. The MTC values extracted are displayed in Fig. 5 and appear to follow a linear trend with inverse partial pressure.
Fig. 5: Extracted MTCs for CH₄ (red triangles) and N₂ (green squares). The plot shows the values extracted for pure fluids (closed) and 50% He diluted fluids (open).

CONCLUSIONS

In this work we used a dynamic breakthrough column, designed to operate with concentrated gas mixtures, and a mathematical model to measure adsorption capacities and kinetic parameters for sorption of CH₄ and N₂ on the zeolite H⁺-Mordenite. This adsorbent has equilibrium selectivity for CH₄ over N₂. The adsorption capacity was measured in the total pressure range (100 to 900) kPa with partial pressure as low as 1 kPa with the measured capacities being adequately described by the Langmuir isotherm. Mass transfer coefficients were extracted for pure fluids in the same range including several 50% dilution experiments, and appear to follow a linear trend with inverse partial pressure. In ongoing work, the DCB model is being improved to better predict the separation of gas mixtures by adsorption. Modifications to the model will include incorporating a full dynamic energy balance on the system to allow prediction over a wider range of operating temperatures and pressures.

NOMENCLATURE

b  Langmuir fitting parameter [kPa⁻¹]
c  component gas phase concentration [mol.m⁻³]
C  total gas phase concentration [mol.m⁻³]
Dₐx  axial dispersion [m² s⁻¹]
Dₜ  micropore diffusivity [m² s⁻¹]
Dₚ  macropore diffusivity [m² s⁻¹]
F  mass flowrate [mol s⁻¹]
k_f  film mass transfer coefficient [m s⁻¹]
k_b  barrier mass transfer resistance [s⁻¹]
K  dimensionless Henry's coefficient [ ]
MTC  lumped mass transfer coefficient [s⁻¹]
N_p  Number of experimental points
P     pressure [Pa]
Q^*   equilibrium amount adsorbed [mmol g^{-1}]
Q     average amount adsorbed [mmol g^{-1}]
Q_{max}  Langmuir fitting parameter [mmol g^{-1}]
r_p    pore radius  [m]
r_c    crystal radius  [m]
t     time [s]
v_g   gas phase superficial velocity [m/s]
z     axial coordinate [m]

Greek letters
\( \varepsilon \) interparticle voidage [m^3 void /m^3 bed]
\( \varepsilon_p \) intraparticle voidage [m^3 pore /m^3 particle]
\( \rho_s \) adsorbent skeleton density [kg m^{-3}]
\( \mu \) dynamic viscosity [Pa s]
\( \chi^2 \) chi squared [ ]

REFERENCES
Mulgundmath, V.P., Jones, R.A., Tezel, F.H., Thibault, J.: Fixed bed adsorption for the removal of carbon dioxide from nitrogen: Breakthrough behaviour and

