Dynamic Mixture Measurements of Commercial Adsorbents for Evaluating N\textsubscript{2} + CH\textsubscript{4} Separations by Pressure Swing Adsorption for Liquefied Natural Gas Production

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B.Nanotechnology Advanced (Honours I)

This thesis is presented for the degree of Doctor of Philosophy of The University of Western Australia

School of Mechanical and Chemical Engineering
Gas Process Engineering
Centre for Energy
2012
Abstract

The demand for liquefied natural gas (LNG) is forecast to grow substantially over the next three to four decades, particularly in the Asia-Pacific region. Impurities such as nitrogen in the natural gas feedstock used to produce LNG, pose a significant challenge to its efficient production, especially as high-quality natural gas fields are depleted and sub-quality gas needs to be utilised. Nitrogen is one of the most challenging contaminants to remove from unrefined natural gas because its inert properties make it difficult to separate from methane dominant gas streams.

A review of the current state of commercial N₂ + CH₄ separation technologies, with respect to LNG production, showed that although a small number of these technologies exist and are frequently used in LNG production, there are a number of specific opportunities for improvement. Pressure swing adsorption (PSA) was proposed as a technology that could improve N₂ + CH₄ separations in LNG production by utilising the low temperatures available in an LNG facility. The primary motivation for the research in this thesis is the improvement of LNG production efficiency through enhanced N₂ + CH₄ separations using low temperature PSA.

A dynamic column breakthrough apparatus was designed, constructed, and commissioned. This apparatus was capable of sorption measurements of multi-component mixtures with high adsorbate concentrations at temperatures from 190 to 498 K and pressures to 1000 kPa. The apparatus is not limited to the study of dilute adsorbates within inert carrier gases because the design and instrumentation allows the flow rate and composition of effluent mixtures to be measured accurately over a wide range. A mathematical framework was developed
to determine equilibrium adsorption capacities from the dynamic adsorption experiments and a method for quantitatively estimating the uncertainties of the measured capacities.

A screening investigation was conducted, targeted at commercially available, non-proprietary, adsorbent samples that had the potential for use in \( N_2 + CH_4 \) separations. Seven adsorbents were studied and compared based on equilibrium adsorption capacity, equilibrium selectivity, and kinetic behaviour, to identify the most promising \( CH_4 \) equilibrium selective and \( N_2 \) kinetically selective adsorbents for further investigation. The Norit RB3 activated carbon and MSC-3K-161 carbon molecular sieve were the adsorbents ranked highest for potential nitrogen clean-up and nitrogen rejection (front-end nitrogen rejection or end-flash upgrading) PSA processes within an LNG plant. For Norit RB3, the equilibrium adsorption capacities for each component and the equilibrium selectivity for \( CH_4 \) over \( N_2 \) increased at lower temperatures. The equilibrium capacity of MSC-3K-161 for both species also increased at lower temperatures; however, more importantly, the binary breakthrough curves showed \( N_2 \) kinetically selective behaviour, which also improved at lower temperatures.

The two most promising adsorbents (Norit RB3 and MSC-3K-161) were studied in increased detail over a range of temperatures, pressures, and flows. From these extended measurements, isotherm model parameters, heats of adsorption, and mass transfer coefficients (MTCs) were extracted for each adsorbent. The MTCs used to describe the adsorption kinetics in this work were derived from a linear driving force (LDF) model. The results showed that the Norit RB3 isotherm became more favourable at low temperatures: that is, in the pressure range where the isotherm follows Henry's law, the isotherm slope increased as the temperature decreased. Furthermore, the capacity and selectivity
improvements observed from the screening measurements were also confirmed. The MSC-3K-161 isotherm also became more favourable and capacity increases were also observed, but most importantly, the ratio of the N₂ to CH₄ MTCs increased from 30 at 903 kPa 303 K, to 1087 at 902 kPa 244 K. This result showed that the difference in uptake rates, which gives rise to kinetic selectivity, increased significantly at reduced temperature. The fundamental sorption data measured for the two adsorbents provide evidence that improvements to N₂ + CH₄ separations can be made through low temperature adsorption, and provide a basis for the development of improved N₂ + CH₄ separations based upon low temperature PSA processes.
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Contributions to jointly authored work incorporated into this thesis

1. P. S. Hofman, T. E. Rufford, K. I. Chan, and E. F. May, “A Dynamic Column Breakthrough Apparatus for Adsorption Capacity Measurements with Quantitative Uncertainties,” Published in Adsorption vol. 18 pp. 251-263, 2012. This manuscript is predominantly my own work and is included as Chapter 3 in this thesis. I appear as the first author and was responsible for initiation of this work, the apparatus design and construction—apart from machining and welding of some components by technical staff, the computer programming of both the control and analysis software, and commissioning of the apparatus. I was responsible for the experimental design and execution, data analysis, and writing the manuscript. Dr Thomas Rufford contributed to the mathematical analysis required to determine equilibrium capacities from the dynamic column data and provided limited editing assistance. Professor Eric May contributed to the development of the mathematical description of the uncertainty estimation, provided project guidance, and edited the manuscript. Additional minor contributions made by those who are not co-authors are recognised in the manuscript acknowledgements.

2. P. S. Hofman and E. F. May, “Improved LNG production through the advancement of N₂ + CH₄ separations using pressure swing adsorption,” Published in the APPEA Journal, vol. 52. pp. 55-66, 2012. This publication is included as Chapter 2 in this thesis and is wholly my own work, apart from advisory and editorial contributions made by Professor Eric May and minor contributions made by those who are not co-authors, but are recognised in the publication acknowledgements.
Other contributions to this thesis

The chabazite measurements contained in Chapter 4 were performed by Dr Thomas Rufford and Mr Thomas Saleman. I was responsible for the experimental design and analysis of these measurements. This thesis was professionally proofread by Kate van Dooren of Elite Editing Writing and Research.

Additional published work relevant to this thesis but not forming part of it


Contents

Abstract................................................................................................................................................. i

Declaration..................................................................................................................................... iv

List of Tables..................................................................................................................................... xii

List of Figures ............................................................................................................................. xv

Acknowledgements.......................................................................................................... xxv

Nomenclature........................................................................................................................ xxvii

Chapter 1 ............................................................................................................................................ 1

1.1 Project overview......................................................................................................................... 2

1.2 Goals and objectives .................................................................................................................. 4

1.3 Thesis structure......................................................................................................................... 5

Chapter 2 ............................................................................................................................................ 7

2.1 Foreword....................................................................................................................................... 8

2.2 Abstract..................................................................................................................................... 8

2.3 Introduction............................................................................................................................... 9

2.4 Importance of energy supply through natural gas and LNG........................................ 10

2.4.1 Process overview of a typical LNG production facility ................................................. 14

2.4.2 Conventional nitrogen rejection in LNG production..................................................... 16

2.5 Opportunities for improved N₂ + CH₄ separations in LNG production ...... 18

2.5.1 Front-end nitrogen rejection............................................................................................ 18

2.5.2 End-flash upgrading........................................................................................................... 19

2.5.3 Nitrogen clean-up............................................................................................................... 21
Chapter 4

4.1 Overview

4.2 Adsorbent selection

4.3 Experimental adsorbent screening program

4.3.1 Selection of experimental conditions

4.3.2 Experimental measurements

4.4 Adsorbent screening results and discussion

4.4.1 Experimental measurement observations

4.4.2 Adsorbent equilibrium capacities

4.4.3 Comparison of selectivities

4.4.4 Examination of binary breakthrough curves

4.5 Conclusions

Chapter 5

5.1 Overview

5.2 Development of a process model of the dynamic column breakthrough apparatus

5.2.1 Description of the apparatus section to be modelled

5.2.2 Modelling software used for the process model

5.2.3 Implemented model

5.2.4 Solution of the implemented model

5.3 Extra-column void volume

5.4 Norit RB3 activated carbon

5.4.1 Adsorption equilibria and heats of adsorption

5.4.2 Extraction of mass transfer coefficients

5.4.3 Correlation of mass transfer coefficients
5.4.4 Parameter testing with binary adsorbate experiments ............... 154

5.5 MSC-3K-161 .................................................................................................................. 158

5.5.1 Adsorption equilibria and heats of adsorption .................. 158

5.5.2 Extracted mass transfer coefficients ........................................... 160

5.5.3 Correlation of mass transfer coefficients ......................... 168

5.5.4 Parameter testing with binary adsorbate experiments ........... 175

5.6 Conclusions ................................................................................................................... 179

Chapter 6 .......................................................................................................................... 181

6.1 Conclusions .................................................................................................................. 182

6.2 Recommendations for future research .............................................. 184

References ......................................................................................................................... 187

Appendix A ......................................................................................................................... 203
**List of Tables**

**Table 2-1:** Opportunities for N\(_2\) + CH\(_4\) separations in a typical LNG production facility (> 1 MTPA) ..............................................................................................................................................................................22

**Table 3-1:** Component uncertainties associated with the dynamic breakthrough apparatus .................................................................................................................................................................................65

**Table 3-2:** Equilibrium excess (\(q^\text{ex,i}\)) and absolute (\(q^\text{abs,i}\)) adsorption capacities of N\(_2\) + CH\(_4\) on mordenite at 301.9 K measured on the DCB apparatus with pure fluids. The uncertainty \(u(q^\text{ex,i})\) in the adsorption capacity measurement is also reported........................................................................................................................................................................................69

**Table 3-3:** Equilibrium excess (\(q^\text{ex,i}\)) and absolute (\(q^\text{abs,i}\)) adsorption capacities of N\(_2\) + CH\(_4\) on zeolite 13X at 301.9 K and 229.2 K measured on the DCB apparatus with pure fluids. The uncertainty \(u(q^\text{ex,i})\) in the adsorption capacity measurement is also reported........................................................................................................................................................................................69

**Table 3-4:** Excess (\(q^\text{ex,i}\)) and absolute (\(q^\text{abs,i}\)) adsorption capacities determined from the DCB measurements with N\(_2\) + CH\(_4\) mixtures and predicted with the Ideal Adsorbed Solution Theory (\(q^\text{IAST,i}\)) using pure fluid Toth model parameters for mordenite and 13X reported by Delgado et al. [91] and Cavenati et al. [37], respectively. Also listed are the adsorption selectivities (\(\alpha_{\text{CH}_4,N_2}\)) of CH\(_4\) over N\(_2\) on mordenite and 13X measured with N\(_2\) + CH\(_4\) mixtures on the DCB (\(\alpha_{\text{CH}_4,N_2}\)\(_\text{meas}\)) and predicted with the IAST models (\(\alpha_{\text{CH}_4,N_2}\)\(_\text{IAST}\)). The average uncertainties in (\(\alpha_{\text{CH}_4,N_2}\)\(_\text{meas}\)) for mordenite and 13X are ± 0.4 and ± 0.2, respectively..............................................70

**Table 4-1:** Adsorbents selected for screening measurements............................................83
Table 4-2: Screening experiment conditions used for each adsorbent..............87
Table 4-3: Adsorbents ranked in order of N₂ equilibrium adsorption capacity from highest to lowest........................................................................................................................................93
Table 4-4: Adsorbents ranked in order of CH₄ equilibrium adsorption capacity from highest to lowest........................................................................................................................................94
Table 4-5: Adsorbents ranked in order of total equilibrium adsorption capacities for the binary mixture of N₂ + CH₄ from highest to lowest ..........................................................95
Table 4-6: Pure gas Sips parameters calculated for each selected adsorbent......104
Table 4-7: Measured capacities and selectivities for binary mixtures of 0.5N₂ + 0.5CH₄ together with values predicted using the extended Sips models .106
Table 5-1: Parameters implemented into Aspen Adsorption model for each adsorbent........................................................................................................................................127
Table 5-2: Solver and parameters implemented into Aspen Adsorption..........129
Table 5-3: Measured extra-column void volumes........................................129
Table 5-4: Parameters of the Sips model fitted to pure gas adsorption capacities on Norit RB3 ........................................................................................................................................136
Table 5-5: Extracted N₂ MTCs on Norit RB3.............................................140
Table 5-6: Extracted CH₄ MTCs on Norit RB3.............................................141
Table 5-7: Modelled Norit RB3 N₂ MTCs.....................................................151
Table 5-8: Modelled Norit RB3 CH₄ MTCs.....................................................151
Table 5-9: Norit binary experimental measurement compared with model, including the calculated MTCs used in the model and the NRMSE of each of the fits ........................................................................................................................................154
Table 5-10: Pure gas Sips parameters calculated for MSC-3K-161............158
Table 5-11: Extracted N₂ MTCs on MSC-3K-161.......................................160
Table 5-12: Extracted CH₄ MTCs on MSC-3K-161.......................................160
Table 5-13: Modelled N₂ MTCs on MSC-3K-161 ................................................................. 171

Table 5-14: Modelled CH₄ MTCs on MSC-3K-161 .............................................................. 172

Table 5-15: MSC-3K-161 binary experimental measurement compared with model, including the calculated MTCs used in the model and the NRMSE of each of the fits ..................................................................................................................................................... 176

Table A-1: Norit pure N₂ experimental measurements ....................................................... 203

Table A-2: Norit pure CH₄ experimental measurements ................................................... 204

Table A-3: Norit binary experimental measurements ....................................................... 205

Table A-4: MSC-3K-161 pure N₂ experimental measurements ....................................... 206

Table A-5: MSC-3K-161 pure CH₄ data from Watson et al. [38] used for fitting ........ 207
List of Figures

Figure 2-1: Past (blue) and predicted (red) global energy consumption [2] ........... 11

Figure 2-2: Annual total of LNG ships around the world (* includes ships on order) [7] .................................................................................................................................................. 13

Figure 2-3: Typical unit operations in an LNG production facility [4, 5]. The locations of the N₂ + CH₄ separation opportunities that have been identified are also highlighted: 1. front-end nitrogen rejection; 2. end-flash upgrading; and 3. nitrogen clean-up .................................................................................................................................................................................. 14

Figure 2-4: Two pairs of cryogenic nitrogen rejection units (highlighted red), showing the large size relative to the gas plant [13] ................................................................................................................. 17

Figure 2-5: Vapour pressure curves of N₂ and CH₄, illustrating that the difference of boiling points grows as pressure is increased facilitating greater separation by distillation [17] .................................................................................................................................................................................. 23

Figure 2-6: Two bed micro-scale nitrogen rejection PSA system [31] ..................... 29

Figure 2-7: Type-I isotherms, illustrating changes in adsorption with both temperature for TSA and pressure for PSA .................................................................................................................................................................................. 30

Figure 2-8: Shows the progression of the MTZ through the bed. (a) Illustrates how a small MTZ results in a small amount of unused bed; and (b) a large MTZ results in a large amount of unused bed [15] .................................................................................................................................................................................. 31

Figure 2-9: Development pathway of a PSA technology ........................................ 36

Figure 3-1: Schematic diagram of the dynamic column breakthrough (DCB) apparatus .................................................................................................................................................................................. 50

Figure 3-2: Dynamic breakthrough profile for the adsorption of CH₄ on mordenite at 104 kPa, 301.9 K. (a) Column feed and effluent flow rates. (b) Effluent mole
fraction compositions. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 3-3: Temperatures measured by the column thermometers PRT-1, PRT-2, and PRT-3 (see Figure 3-1) during the dynamic adsorption of CH₄ on mordenite at 104 kPa, 301.9 K, corresponding to the data shown in Figure 3-2. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 3-4: Adsorption capacity of N₂ + CH₄ on mordenite at 302 K measured with pure fluids using the DCB apparatus. (a) Equilibrium capacities measured in this work and by Jensen et al. [89] are shown together with capacities calculated using the Toth isotherm parameters reported by Delgado et al. [91]. (b) Deviations between the measured capacities and those calculated using the Toth isotherm models.

Figure 3-5: Adsorption capacity of N₂ + CH₄ on 13X at 302 K and 229 K measured with pure fluids using the DCB apparatus. The data points were measured in this work. Toth parameters from Cavenati et al. [37] were used to calculate the model curves: the dashed curves correspond to an extrapolation of the models, which were regressed to data measured in the range 298 K to 323 K.

Figure 3-6: Dynamic adsorption of 0.53N₂ + 0.47CH₄ on mordenite at 792 kPa, 301.9 K. (a) Column effluent flow rate (left axis) and pressures at each end of column (right axis). (b) Effluent mole fraction compositions. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 3-7: Adsorption capacities for yN₂ + (1-y)CH₄ gas mixtures, with y = 0.51 ± 0.02, in equilibrium with mordenite at 301.9 K.
Figure 4-1: Difference between inlet flow rate and outlet flow rate CH$_4$ adsorption on MSC-3K-161 at 105.9 kPa and 302.9 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.........................90

Figure 4-2: Difference between inlet flow rate and outlet flow rate for CH$_4$ adsorption on Linde 4A at 104.6 kPa and 213.5 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz ...................................................................................................................................................................... 91

Figure 4-3: Adsorption capacity of N$_2$ and CH$_4$ on 4A at 301.8 K. The N$_2$ and CH$_4$ data points were measured in this work. Toth parameters from Jensen et al. [89] were used to calculate the model curves, which are extrapolated at pressures above 120 kPa........................................................................................................................................................................ 98

Figure 4-4: Adsorption capacity of N$_2$ on MSC-3K-161 at 244.1 and 302.9 K using Toth parameters from Watson et al. [38]. The N$_2$ data points at 244.1 and 302.9 K were measured in this work........................................................................................................... 99

Figure 4-5: Adsorption capacity of (a) N$_2$ and (b) CH$_4$ on chabazite at 301.6 and 238.6 K. The 301.6 and 238.6 K data points were measured in this work. Toth parameters from Jensen et al. [89] were used to calculate the model curves, which are extrapolated at pressures above 120 kPa........................................................................................................... 100

Figure 4-6: Adsorption capacity of N$_2$ + CH$_4$ on Norit R1 Extra using dual-site Langmuir parameters from Dreisbach et al. [108] at 298 K. The N$_2$ + CH$_4$ data points were measured in this work on Norit RB3 at ~302 K......................................................... 102

Figure 4-7: Breakthrough Curve for 0.5N$_2$ + 0.5CH$_4$ feed on 13X at 106.0 kPa and 302.1 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz ...................................................................................................................................................................... 108
Figure 4-8: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on Norit RB3 at 105.3 kPa and 230.1 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-9: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on Clinoptilolite at 792.7 kPa and 302.1 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-10: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on 4A at 792.5 kPa and 301.8 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-11: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on 4A at 792.1 kPa and 237.6 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-12: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on MSC-3K-161 at 107.2 kPa and 302.8 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-13: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on MSC-3K-161 at 901.5 kPa and 302.9 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-14: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on MSC-3K-161 at 901.6 kPa and 243.7 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 5-1: Flow path components that contribute to the experimental breakthrough curve for the DCB apparatus, with the sections under different pressures highlighted.

Figure 5-2: Flow sheet of DCB apparatus implemented into Aspen Adsorption.
Figure 5-3: Comparison of experimental blank measurements at 108.6 and 793.0 kPa, at 302.0 K, with blank profiles modelled in Aspen Adsorption. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 5-4: (a) Equilibrium adsorption capacity of N₂ on Norit RB3 measured using the DCB apparatus with fitted Sips model. (b) Deviations between the measured capacities and those calculated using the Sips isotherm model.

Figure 5-5: (a) Equilibrium adsorption capacity of CH₄ on Norit RB3 measured using the DCB apparatus with fitted Sips model. (b) Deviations between the measured capacities and those calculated using the Sips isotherm model.

Figure 5-6: (a) Equilibrium adsorption capacities of N₂ and CH₄ on Norit RB3 at 302.4 K with a 0.5N₂ + 0.5CH₄ feed measured using the DCB apparatus, and predicted isotherms using IAST with Sips isotherms. (b) Deviations between the measured capacities and those predicted using IAST with Sips isotherms.

Figure 5-7: (a) Equilibrium adsorption capacities of N₂ and CH₄ on Norit RB3 at 273.3 K with a 0.5N₂ + 0.5CH₄ feed measured using the DCB apparatus, and predicted isotherms using IAST with Sips isotherms. (b) Deviations between the measured capacities and those predicted using IAST with Sips isotherms.

Figure 5-8: (a) Equilibrium adsorption capacities of N₂ and CH₄ on Norit RB3 at 243.7 K with a 0.5N₂ + 0.5CH₄ feed measured using the DCB apparatus, and predicted isotherms using IAST with Sips isotherms. (b) Deviations between the measured capacities and those predicted using IAST with Sips isotherms.

Figure 5-9: Dynamic adsorption of N₂ on Norit RB3 at 108.2 kPa, 302.2 K. (a) Column effluent flow rate of He and N₂ with fitted model to 300 seconds. (b) Bed temperature profiles with fitted model to 600 seconds. The number of data points...
shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.......................... 143

**Figure 5-10:** Dynamic adsorption of N\textsubscript{2} on Norit RB3 at 504.8 kPa, 273.8 K. (a) Column effluent flow rate of He and N\textsubscript{2} with fitted model. (b) Bed temperature profiles with fitted model. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.......................... 144

**Figure 5-11:** Dynamic adsorption of CH\textsubscript{4} on Norit RB3 at 504.7 kPa, 274.2 K. (a) Column effluent flow rate of He and CH\textsubscript{4} with fitted model. (b) Bed temperature profiles with fitted model. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.......................... 145

**Figure 5-12:** Dynamic adsorption of CH\textsubscript{4} on Norit RB3 at 900.8 kPa, 244.5 K. (a) Column effluent flow rate of He and CH\textsubscript{4} with fitted model. (b) Bed temperature profiles with fitted model. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.......................... 146

**Figure 5-13:** Packed column cross-section showing random packing of adsorbent in contact with a temperature sensor and the column wall. ........................................ 147

**Figure 5-14:** Correlation of MTC on $v_g$ for N\textsubscript{2} and CH\textsubscript{4}, which displays a linear dependence ............................................................................................................................................... 149

**Figure 5-15:** Deviations between the measured N\textsubscript{2} MTCs and those calculated using Equation (5.12) .................................................................................................................................................. 152

**Figure 5-16:** Deviations between the measured CH\textsubscript{4} MTCs and those calculated using Equation (5.12) .................................................................................................................................................. 152

**Figure 5-17:** Comparison between 0.51N\textsubscript{2} + 0.49CH\textsubscript{4} experiment on Norit RB3, at 107.6 kPa, 302.3 K, and modelled component flow rates of He, N\textsubscript{2}, and CH\textsubscript{4}, with fitted model using derived isotherm and MTC parameters. The number of data
points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

**Figure 5-18:** Comparison between 0.51N₂ + 0.49CH₄ experiment on Norit RB3, at 902.9 kPa, 302.2 K, and modelled component flow rates of He, N₂, and CH₄, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

**Figure 5-19:** Comparison between 0.51N₂ + 0.49CH₄ experiment on Norit RB3, at 106.3 kPa, 244.8 K, and modelled component flow rates of He, N₂, and CH₄, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

**Figure 5-20:** Comparison between 0.51N₂ + 0.49CH₄ experiment on Norit RB3, at 902.8 kPa, 241.9 K, and modelled component flow rates of He, N₂, and CH₄, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

**Figure 5-21:** (a) Equilibrium adsorption capacity of N₂ on MSC-3K-161 measured using the DCB apparatus with fitted Sips model. (b) Deviations between the measured capacities and those calculated using the Sips isotherm model.

**Figure 5-22:** Dynamic adsorption of N₂ on MSC-3K-161 at 106.9 kPa, 302.9 K. (a) Column effluent flow rate of He and N₂ with fitted model and (b) bed temperature profiles with fitted model; both to 800 seconds. The number of data points shown here has been reduced for clarity; however, the experimental sampling rate was 1 Hz.
Figure 5-23: Dynamic adsorption of N\textsubscript{2} on MSC-3K-161 at 108.7 kPa, 244.2 K. (a) Column effluent flow rate of He and N\textsubscript{2} with fitted model to 1500 seconds and (b) bed temperature profiles with fitted model to 4000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz ........................................................................................................................................... 163

Figure 5-24: Dynamic adsorption of N\textsubscript{2} on MSC-3K-161 at 900.8 kPa, 302.9 K. (a) Column effluent flow rate of He and N\textsubscript{2} with fitted model and (b) bed temperature profiles with fitted model; both to 3000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz ........................................................................................................................................... 164

Figure 5-25: Dynamic adsorption of N\textsubscript{2} on MSC-3K-161 at 902.4 kPa, 244.1 K. (a) Column effluent flow rate of He and N\textsubscript{2} with fitted model and (b) bed temperature profiles with fitted model; both to 3000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz ........................................................................................................................................... 165

Figure 5-26: Dynamic adsorption of CH\textsubscript{4} on MSC-3K-161 at 105.9 kPa, 302.9 K. (a) Column effluent flow rate of He and CH\textsubscript{4} with fitted model to 500 seconds and (b) bed temperature profiles with fitted model to 2000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz ........................................................................................................................................... 166

Figure 5-27: Dynamic adsorption of CH\textsubscript{4} on MSC-3K-161 at 901.3 kPa, 244.1 K. (a) Column effluent flow rate of He and CH\textsubscript{4} with fitted model and (b) bed temperature profiles with fitted model; both to 8000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz ........................................................................................................................................... 167
**Figure 5-28:** Comparison of $N_2$ and $CH_4$ MTCs on MSC-3K-161 with $v_g$, not showing any obvious dependence ................................................................................................................ 168

**Figure 5-29:** The MTC pressure dependence of $N_2$ (left axis) and $CH_4$ (right axis) at three temperatures for MSC-3K-161 ........................................................................................................ 169

**Figure 5-30:** Deviations between the MTCs measured for $N_2$ and those calculated using the Arrhenius MTC model; Equation (5.13) .................................................................................. 172

**Figure 5-31:** Deviations between the MTCs measured for $CH_4$ and those calculated using the pressure dependent Arrhenius MTC model; Equation (5.14) ...................... 173

**Figure 5-32:** The modelled MTCs of $N_2$ and $CH_4$ with temperature at a pressure of 900 kPa. The difference between the $N_2$ and $CH_4$ MTCs significantly increases with reduced temperature ....................................................................................................................... 175

**Figure 5-33:** Comparison between $0.51N_2 + 0.49CH_4$ experiment on MSC-3K-161, at 107.2 kPa, 302.8 K, and modelled component flow rates of He, $N_2$, and $CH_4$, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz................................................................................................................................................. 177

**Figure 5-34:** Comparison between $0.51N_2 + 0.49CH_4$ experiment on MSC-3K-161, at 901.5 kPa, 302.9 K, and modelled component flow rates of He, $N_2$, and $CH_4$, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz................................................................................................................................................. 178

**Figure 5-35:** Comparison between $0.51N_2 + 0.49CH_4$ experiment on MSC-3K-161, at 106.7 kPa, 243.8 K, and modelled component flow rates of He, $N_2$, and $CH_4$, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz................................................................................................................................................. 178
Figure 5-36: Comparison between $0.51N_2 + 0.49CH_4$ experiment on MSC-3K-161, at 901.6 kPa, 243.4 K, and modelled component flow rates of He, N$_2$, and CH$_4$, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Acknowledgements

I firstly want to say thank you to my family and close friends, you mean everything to me. You are the only ones who truly know how hard this journey has been for me and without your support, continuous encouragement, and unswerving faith, this thesis would never have come to be.

Thank you to my primary supervisor Professor Eric May for taking me on as your first PhD student and providing me the opportunity to undertake this project. I appreciate your guidance, support, and suggestions throughout the course of this project; you have never given up on me and have always given your all.

Thanks to my secondary supervisor Professor Mark Trebble for your input in the early stages of the project. I extend my thanks to all the members of the PSA and PVT research groups, and broader fluid science group, for all the discussions, suggestions, and camaraderie throughout the course of this project. A special thanks to Dr Guillaume Watson for helping me in all aspects of the project right from day one and Nathan Jensen who has also supported me along the way. Thank you to Dr Thomas Rufford, I especially appreciate you helping me over a sticking point in the project; your appearance came at just the right time. I extend my appreciation to David Zhang and Thomas Saleman for working with me to navigate the modelling software and underlying mathematics. I would like to thank Dr Mohamed Kandil for the many lunch-time conversations while running experiments and your general supportive nature.

I would like to extend my sincere appreciation for the scholarships I received from Chevron Corporation, the Western Australian Energy Research Alliance (WA:ERA), and the Australia-China Natural Gas Technology Partnership Fund. This extra financial support was instrumental in relieving financial pressures, allowing
me to concentrate solely on this project. A special thank you to the Australian Petroleum Production and Exploration Association (APPEA) for granting me the KA Richards Memorial Scholarship. This award has provided several opportunities throughout my PhD and created opportunities that I can see will extend beyond. I also want to thank Jill Stajduhar and Colin Beckett for supporting my research and application for the APPEA scholarship.

My appreciation is extended to all the technical staff in the Physics workshop, in particular Craig Grimm for always having a ‘drop everything’ attitude towards helping me with my project, for being a source of refuge when needed, and for just being a great guy. A special thanks to Dave McPhee for helping with various odd jobs saving me lots of time, and especially for filling the liquid nitrogen Dewar early each morning so I could start experiments each day.

Thanks to the administration staff at The University of Western Australia, in particular Dr Sato Juniper and Dr Krystyna Haq from the graduate research school for helping me through some tough times and providing the extra push and positive thinking needed to keep going and finish.

To everyone who has made this thesis possible, thank you!
Nomenclature

\( a \) empirical fitting parameter in Equation (3.1)

\( a_p \) specific particle surface area per bed unit volume (m)

\( \text{Å} \) Angstrom \((1 \times 10^{-10} \text{ m})\)

\( b \) empirical fitting parameter in Equation (3.1)

\( C \) gas phase concentration \((\text{mol m}^{-3})\)

\( C_{vg} \) specific gas phase heat capacity at constant volume \((\text{J mol}^{-1} \text{K}^{-1})\)

\( C_{ps} \) adsorbent specific heat \((\text{J mol}^{-1} \text{K}^{-1})\)

\( C_{pai} \) adsorbed phase specific heat \((\text{J mol}^{-1} \text{K}^{-1})\)

\( C_{pw} \) wall specific heat \((\text{J mol}^{-1} \text{K}^{-1})\)

\( D_B \) bed diameter (m)

\( D_c \) intracrystalline diffusivity \((\text{m}^2 \text{s}^{-1})\)

\( D_L \) axial dispersion coefficient \((\text{m}^2 \text{s}^{-1})\)

\( D_m \) molecular diffusivity \((\text{m}^2 \text{s}^{-1})\)

\( D_p \) pore diffusivity \((\text{m}^2 \text{s}^{-1})\)

\( E_{act} \) activation energy of the Arrhenius relationship \((\text{J mol}^{-1})\)

\( E_{act,IP} \) activation energy of the inverse pressure dependent Arrhenius relationship \((\text{J mol}^{-1})\)

\( E_{act,P} \) activation energy of the pressure dependent Arrhenius relationship \((\text{J mol}^{-1})\)

\( f \) component molar flow rate \((\text{mol s}^{-1})\)

\( F \) total molar flow rate \((\text{mol s}^{-1})\)

\( H_{amb} \) wall to ambient heat transfer coefficient \((\text{W m}^{-2} \text{K}^{-1})\)

\( H_l \) heat of adsorbed phase rate \((\text{J m}^{-3} \text{s}^{-1})\)

\( H_w \) gas-wall heat transfer coefficient \((\text{W m}^{-2} \text{K}^{-1})\)
HTC  gas-solid heat transfer coefficient (W m\(^{-2}\) K\(^{-1}\))

\(k_0\)  pre-exponential factor (s\(^{-1}\))

\(k_{0,IP}\)  inverse pressure dependent pre-exponential factor (Pa m s\(^{-1}\))

\(k_{0,P}\)  pressure dependent pre-exponential factor (Pa\(^{-1}\) s\(^{-1}\))

\(k_a\)  empirical fitting parameter (m\(^{-1}\)) in Equation (5.12)

\(k_f\)  external fluid film mass transfer coefficient (m s\(^{-1}\))

\(k_g\)  gas phase thermal conductivity (W m\(^{-1}\) K\(^{-1}\))

\(k_s\)  solid phase thermal conductivity (W m\(^{-1}\) K\(^{-1}\))

\(k_w\)  wall thermal conductivity (W m\(^{-1}\) K\(^{-1}\))

\(K\)  Henry's law equilibrium constant

\(m\)  mass of adsorbent (kg)

\(M\)  molecular weight (kg mol\(^{-1}\))

\(MTC\)  mass transfer coefficient (s\(^{-1}\))

\(n\)  number of moles (mol)

\(N\)  number of data points

\(P\)  pressure (Pa)

\(Pe_\infty\)  limiting value of the Peclet number

\(q\)  adsorbent loading (mol kg\(^{-1}\))

\(q^*\)  adsorbent loading at equilibrium (mol kg\(^{-1}\))

\(r_c\)  crystal or microparticle radius (m)

\(r_p\)  particle radius (m)

\(R\)  universal gas constant (8.314, J K\(^{-1}\) mol\(^{-1}\))

\(t\)  time (s)

\(t_0\)  time at initiation (s)

\(t_{eq}\)  time at equilibrium (s)

\(T\)  temperature (K)
\(T_{amb}\) ambient temperature (K)

\(T_g\) gas phase temperature (K)

\(T_s\) solid phase temperature (K)

\(T_w\) wall temperature (K)

\(u\) absolute uncertainty

\(u_r\) relative uncertainty

\(v_g\) gas phase superficial velocity (m s\(^{-1}\))

\(V_{gas}\) volume of gas phase (m\(^3\))

\(W_r\) column wall thickness (m)

\(x\) adsorbed phase mole fraction

\(X_{\text{experiment}}\) value of the experimental point

\(X_{\text{model}}\) value of the modelled point

\(y\) gas phase mole fraction

\(y^*\) gas phase mole fraction at equilibrium

\(z\) axial coordinate (m)

**Greek Letters**

\(\alpha\) equilibrium selectivity

\(\beta\) radial dispersion factor

\(\gamma_i\) inverse tortuosity (\(\tau^{-1}\))

\(\varepsilon_b\) total bed voidage

\(\varepsilon_i\) interparticle voidage

\(\varepsilon_p\) intraparticle voidage

\(\eta\) viscosity (Pa s)

\(\mu\) dynamic viscosity (N s m\(^{-2}\))

\(\rho_g\) density of the gas (kg m\(^{-3}\))
\( \rho_w \) density of the wall (kg m\(^{-3}\))

\( \rho_s \) adsorbent bulk density (kg m\(^{-3}\))

\( \tau \) tortuosity

\( \Psi \) sphericity factor

\( \Omega \) Ohm

**Abbreviations**

APCI Air Products and Chemicals, Inc.

APPEA Australian Petroleum Production and Exploration Association

AUD Australian dollars

BET Brunauer-Emmett-Teller

BPR back-pressure regulator

C3MR Propane (C3) Mixed-Refrigerant

CMS carbon molecular sieve

COPOC ConocoPhillips Optimised Cascade

CSTR constantly stirred tank reactor

DCB dynamic column breakthrough

IAST ideal adsorbed solution theory

ICL inlet cooling loop

ITS-90 International Temperature Scale of 1990

IUPAC International Union of Pure and Applied Chemistry

LDF linear driving force

LNG liquefied natural gas

MCHE main cryogenic heat exchanger

MFC mass flow controller

MFM mass flow meter
MMSCFD  million standard cubic feet per day
MPV    multi-position valve
MS     mass spectrometer
MTPA   million tonnes per annum
MTR    Membrane Technology and Research
MTZ    mass transfer zone
NRMSE  normalised root mean square error
NRU    nitrogen rejection unit
OHL    outlet heating loop
ODE    ordinary differential equation
OMC    organo-metallic complex
PDE    partial differential equation
PFTR   plug flow tube reactor
ppm    parts per million
ppmv   part per million by volume
PRT    platinum resistance thermometer
PSA    pressure swing adsorption
QPT    quartz-crystal pressure transducer
RMSE   root mean square error
SCCM   standard cubic centimetres per minute
TGPE   Tucker Gas Processing Equipment, Inc.
TSA    thermal swing adsorption
UDS    upwind differencing scheme
WA     Western Australia
WA:ERA Western Australian Energy Research Alliance
Chapter 1

Introduction
1.1 Project overview

One of the most captivating aspects of liquefied natural gas (LNG) production is the enormous scale of production. In 2010, the average global production of LNG was over 600,000 tonnes per day, which constitutes a market value of approximately $300 million per day (calculated using average Japanese Cost-Insurance-Freight prices of LNG) [1]. The magnitude of this production means that even the slightest improvements in production efficiency can result in substantial decreases in energy usage (lowering the environmental impact through reduced CO₂ emissions) and increased production revenue. The primary motivation for the research in this thesis is to improve LNG production efficiency through enhanced N₂ + CH₄ separations.

The requirement of an engineer to deliver solutions to problems is sometimes achieved through the development of completely new structures, devices, machines, or processes. However, often the most innovative, practical, and efficient solutions are provided through the application of existing technologies in novel ways. With this in mind, the proposed method for enhancing N₂ + CH₄ separations in LNG production is to use pressure swing adsorption (PSA), a well-established, industry-proven separation technology; but to operate the process at the low temperatures available in a LNG production facility.

While PSA is widely used for gas separations, the commercial realisation of a low temperature PSA process to improve LNG production efficiency is a challenging task that requires a series of developmental hurdles to be overcome. Designing a PSA process first requires the selection of an adsorbent with suitable properties for the intended application. The fundamental equilibrium and kinetic data for the selected adsorbent can then be used to complete process designs to
optimise the process for implementation in the final working facility. While this sequence appears to be a fairly straightforward progression, the difficulties associated with selecting an adsorbent and obtaining the thermodynamic data are amplified for the proposed low temperature process. Although hundreds of adsorbent materials are available for gas separation applications, the property data needed to compare and select an appropriate adsorbent are generally scarce and often unavailable for common adsorbents at general conditions—the adsorbent property data for \( \text{N}_2 + \text{CH}_4 \) mixtures at low temperatures and high pressures are exceedingly rare. This presents two of the major obstacles that need to be overcome:

- To identify adsorbent materials suitable for the proposed low temperature \( \text{N}_2 + \text{CH}_4 \) PSA separation process.

- To generate the fundamental sorption data needed to enable the design of the proposed process.

To overcome these challenges requires quality adsorption data, to compare and identify adsorbent materials for the proposed application and enable process design; however, experimental apparatus capable of making measurements at the high pressure, low temperature conditions required are expensive or non-existent for some specialised cases. This presents another, more immediate obstacle to be overcome:

- To develop the tools required to effectively compare adsorbents and generate the fundamental sorption data needed for initial process design.
In this thesis, the obstacles described above are addressed and a method is provided by which the foundation work needed to develop low temperature PSA processes for enhanced N\textsubscript{2} + CH\textsubscript{4} separations can be conducted.

1.2 Goals and objectives

The overarching theme of this research is to inform the development of a low temperature N\textsubscript{2} + CH\textsubscript{4} PSA separation process to improve the efficiency of LNG production. To achieve this, several major developmental steps must be undertaken, each requiring considerable time and effort. The research contained in this thesis represents the first steps to reaching this longer-term goal. The specific aims of this research are to:

- Review the current state of N\textsubscript{2} + CH\textsubscript{4} separations with respect to LNG processing and identify the specific opportunities for improvement through the integration of low temperature PSA processes, the advantages of such systems, and the challenges associated with their development.

- Design, construct, and commission an apparatus capable of testing and comparing adsorbents under conditions that are as close to process conditions as practicable, and that is also capable of generating the fundamental sorption data required for initial process design.

- Identify potential commercial adsorbents for N\textsubscript{2} + CH\textsubscript{4} separations at low temperatures through experimental screening measurements of a selection of potential adsorbents.
• Generate fundamental adsorption data for initial process design by performing detailed adsorption experiments on adsorbents identified from the screening measurements.

• Examine the fundamental sorption data generated to forecast the likelihood of a low temperature PSA process for enhanced N₂ + CH₄ separations.

1.3 Thesis structure

This thesis is presented in a hybrid format in accordance with the requirements of The University of Western Australia. Chapters 1, 4, 5, and 6 are presented in a traditional format, Chapter 2 as journal publication, and Chapter 3 as a submitted manuscript. The publication and manuscript have been formatted to the style of overall thesis; however, the content is presented as it appears in the publication and manuscript. The outline of the thesis is as follows:

• **Chapter 1** introduces the central theme of the research, methodology used, specific goals and objectives of the research contained in this thesis; and outlines the structure of the thesis.

• **Chapter 2** presents a literature review highlighting the importance of this research, and identifies the specific opportunities for improvement to N₂ + CH₄ separations in LNG processing using a low temperature PSA process, the advantages of its development, and the challenges associated with its development.

• **Chapter 3** describes the constructed dynamic column breakthrough apparatus and its operation, the data analysis techniques used, and results to demonstrate the capability of the system.
• **Chapter 4** outlines principles, procedures, and outcomes from experiments designed to identify adsorbents that could be used to complete a preliminary evaluation of the proposed low temperature PSA process.

• **Chapter 5** covers the generation and analysis of the fundamental sorption data required for initial process design and the examination of this data to forecast the likelihood of a low temperature PSA process for N₂ + CH₄ separations.

• **Chapter 6** presents the general research conclusions, highlights the original contributions made by this research, and discusses future research directions.
Chapter 2

Improved LNG production through the advancement of 

$\text{N}_2 + \text{CH}_4$ separations using pressure swing adsorption

P. S. Hofman and E. F. May
2.1 Foreword

This article is published in the APPEA Journal, vol. 52. pp. 55-66, 2012. This chapter is primarily a review, focusing on the overarching motivation for the work in this thesis: that is, to improve $N_2 + CH_4$ separations in LNG processing using low temperature PSA. This chapter highlights the importance of subsequent chapters of the thesis with respect to developing such a process. Key points highlighted in this chapter and the subsequent chapters that address them are:

- Experimental tools for conducting adsorption measurements need to be developed (Chapter 3).
- Potential adsorbent materials for the proposed application need to be investigated and adsorbents for a preliminary investigation identified (Chapter 4).
- Fundamental sorption data are needed to conduct preliminary process modelling (Chapter 5).

2.2 Abstract

The majority of global energy analysts predict that the demand for liquefied natural gas (LNG) is set to grow substantially during the next three to four decades, particularly in the Asia-Pacific region. Impurities in the natural gas feedstock used to produce LNG pose a significant challenge to its efficient production, especially if high-quality natural gas fields are depleted and sub-quality gas needs to be used. One of the most challenging contaminants to remove from unrefined natural gas is $N_2$ as its inert properties make it difficult to separate from $CH_4$ dominant gas streams. Although a small number of $N_2 + CH_4$ separation technologies exist for
this purpose, economies of scale dictate that cryogenic distillation, although costly, is the only technique economically viable for flows above 25 MMSCFD at this point.

In this study, the present state of commercial \( \text{N}_2 + \text{CH}_4 \) separation technologies with respect to LNG production and present opportunities for improvement is examined. The potential that pressure swing adsorption (PSA) has over competing technologies through the use of the low temperature conditions available in an LNG gas processing facility is illustrated. Finally, the challenges associated with developing the proposed low temperature PSA process and the status of the research now underway to address them is discussed.

2.3 Introduction

LNG is now a major growth industry particularly in the Asia-Pacific region, and presents key opportunities for technical contributions as the industry expands. During the past few decades there has been a significant amount of research directed toward the improvement of various \( \text{N}_2 + \text{CH}_4 \) separation technologies, specifically for improving pipeline natural gas production. While some of the \( \text{N}_2 + \text{CH}_4 \) separation technologies developed from this section of the natural gas industry have been applied to the rapidly growing LNG industry, it has generally been older, established separation technologies that have been used for these new developments. There is now an opportunity to exploit new technologies for \( \text{N}_2 + \text{CH}_4 \) separations in LNG production. Many publications describe new and improved \( \text{N}_2 + \text{CH}_4 \) gas separations and occasionally their application to natural gas production; however, now there is a need to research and evaluate new \( \text{N}_2 + \text{CH}_4 \) separation technologies suitable for LNG production.

In this work, the major unit processes and most common \( \text{N}_2 + \text{CH}_4 \) separations found in a typical LNG production facility are described. The general
compositional makeup and basic separation requirements of \( N_2 + CH_4 \) streams in an LNG facility are defined to identify where improved separation technologies could potentially be used. Firstly, the present state of the main commercial technologies available for \( N_2 + CH_4 \) separations for pipeline natural gas, their existing limitations for use in LNG processing, and their potential for future expansion into the LNG industry are briefly reviewed. Secondly, the development of a PSA process that takes advantage of the low temperatures inherent in LNG production is proposed. Finally, the primary steps required to develop the proposed process and some of the present research being undertaken to achieve this are listed.

2.4 Importance of energy supply through natural gas and LNG

The importance of natural gas is set to grow during the coming decades as the world continues to require energy at an ever increasing rate. The global demand for energy has been steadily increasing and is predicted to continue growing for several decades, as shown in Figure 2-1 [2]. The present demand and predicted growth are both expected to be met predominantly by primary non-renewables (oil, coal, and natural gas) [2]. In 2010, 87.8 % of global energy demands were satisfied by oil, coal, and natural gas, with natural gas accounting for 28.1 % of this share [1]. The forecast growth of natural gas use reflects some of its key benefits over the use of oil and coal. Compared with oil and coal when combusted, natural gas produces 23.9 % and 40.7 % less carbon dioxide per kWh, respectively [3].
These reductions are significant as many nations around the globe aim to achieve lower carbon emissions targets. The reduction of CO\textsubscript{2} emissions through the use of natural gas can be achieved rapidly; for example, by having it replace coal use in industrial electricity generation or by using it in place of gasoline to power combustion engines.

In addition to carbon emission reductions, the use of natural gas in place of oil or coal helps reduce the emissions of other pollutants. The stringent processing and quality specifications of saleable natural gas mean produced sulphur dioxides, nitrogen oxides, mercury, and particulates responsible for acid rain and degradation in air quality are also lower for natural gas compared with oil and coal [4]. Therefore, if global energy demand continues to grow as predicted, natural gas will be an increasingly important component of world energy supply.

If natural gas is to meet the predicted share of the energy market, then methods for its global distribution will be of high importance. Presently, the primary distribution of natural gas is through pipelines; however, increasingly
natural gas is being transported as LNG. LNG is produced by reducing the
temperature of natural gas to -161 °C at 1 atmosphere, reducing the volume by a
factor of about 600, and thereby producing a liquid product with high energy
density [5]. This increase in energy density means transoceanic shipping of LNG
often becomes more cost effective than distribution through a pipeline [6]. While
distance does influence the choice between LNG shipping and pipeline
construction, there are other key factors increasingly making LNG a preferable
option [6]:

- There is flexibility in redirecting LNG shipments from decreasing to increasing
  markets worldwide.

- The construction of international gas pipelines can involve crossing a number of
countries and borders entailing negotiations in unstable political environments,
  which may be avoided by shipping routes.

- LNG storage tanks take up less space than compressed gas, and can be used to
  store gas during low use periods with a relatively small footprint area.

- Liquefaction technologies are continually improving, reducing the cost of LNG
  production.

The 22.6 % increase in LNG shipping movements seen from 2009 to 2010 and the
spike in the number of constructed LNG ships in the last decade (Figure 2-2),
further illustrate that distribution of natural gas as LNG is of growing global
importance [1, 7].
For geographically isolated countries like Australia to reach major export markets, LNG is the only viable option. In 2010, Australia was the fourth largest LNG producer in the world, exporting about 18.8 million tonnes of LNG, mostly to its largest customers—China and Japan [1]. There has been considerable development of the Australian LNG export industry, highlighted by the announcement of several major capital LNG projects between 2009 and 2011. These projects will see well over $100 billion worth of LNG exported during the next 30 years, illustrating the importance of LNG to Australia’s economy now and into the future. The scale of the LNG industry in Australia presents significant opportunities for cost reductions through improvements to LNG production. Only relatively small cost reductions are required to make a huge impact on these projects; for example, a 1% reduction in LNG production costs would correspond to around $1 billion in the value of Australian LNG projects announced through 2009 and 2011.
2.4.1 Process overview of a typical LNG production facility

Figure 2-3 shows the typical processing stages in an integrated LNG production facility with the gas pre-treatment section highlighted. Many of the operations shown in the pre-treatment section are common to those used in pipeline natural gas processing. Inlet processing to separate bulk solids and liquids, acid gas removal, dehydration, and mercury removal are examples of unit processes used in both LNG and natural gas processing [4, 5]. Although there are commonalities in the use of these units, compared with natural gas processing LNG production requires tighter unit operating conditions to more stringently pre-treat inlet gas before entering the cryogenic section of the plant. For example, components such as H₂O and CO₂ are generally removed to fractions below 0.1 ppmv and 50 ppmv, respectively. This is done to prevent damage to cryogenic equipment through blockages caused by freezing of these components, or reduced thermal (refrigeration) efficiencies caused by solid film accumulation on heat exchanger surfaces [4].

Figure 2-3: Typical unit operations in an LNG production facility [4, 5]. The locations of the N₂ + CH₄ separation opportunities that have been identified are also highlighted: 1. front-end nitrogen rejection; 2. end-flash upgrading; and 3. nitrogen clean-up.
While there are operational differences between the pre-treatment sections of natural gas and LNG facilities, the key difference between a natural gas and LNG plant is the addition of the cryogenic processing section required to produce LNG. This section typically accounts for 30 to 40% of the capital cost of the overall plant depending on the liquefaction technology used [8]. While several patents exist describing different processes for LNG liquefaction, only two processes have gained widespread commercial acceptance. The Air Products and Chemicals, Inc. (APCI) C3MR process is by far the most widely used and proven technology, accounting for 84% of LNG plants built to 2007; however, the ConocoPhillips Optimised Cascade (COPOC) process—which already makes up an additional 11%—is increasingly being used in new developments [5]. While advances in expanding capacities have been made, such as APCI’s AP-X® process (7.8 MTPA on a single train), this process and others are all primarily based around a main cryogenic heat exchanger (MCHE) module using various pure or mixed gas refrigerants [5, 9]. To generate the large amount of refrigeration needed to produce LNG, substantial compression work is required. The industry minimum is 280 kWh of specific compression work to produce 1 tonne of LNG [5]. A typical 4 MTPA plant produces LNG at a rate of about 460 tonnes per hour, thus the power required amounts to 130 MW, which is more than the power consumption of 170,000 average Australian homes [10]. The operating power requirements and the large capital costs of the liquefaction technologies significantly add to the overall cost of LNG production.

The main unit processes contained in the cryogenic gas processing section of an LNG facility are: pre-cooling and heavy hydrocarbon removal, refrigeration and liquefaction, and, if required, nitrogen rejection. Feed gas from the pre-treatment section is initially pre-chilled between -30 to -40 °C using propane refrigerant.
before the heavy hydrocarbons are removed; this prevents freeze out and plug formation of heavy hydrocarbons in downstream cryogenic equipment [5]. After heavy hydrocarbon removal, the pre-cooled, predominantly CH₄ gas stream is further refrigerated and completely condensed through heat exchange with a refrigerant stream in the MCHE. The sub-cooled liquid product leaving the MCHE then undergoes a single flash or a series of flashes to separate the vapour and liquid fractions. During pressure let down, N₂ in the main feed gas is rejected to the vapour phase; this vapour phase is commonly referred to as end-flash gas and is often used as plant fuel. Nitrogen rejection through this end-flash is essentially built in to the liquefaction process. The final liquid fraction, now low pressure LNG, is pumped through an LNG rundown line to LNG storage tanks to await shipping.

2.4.2 Conventional nitrogen rejection in LNG production

In the majority of LNG plants, nitrogen rejection through the described end-flash is sufficient to achieve the 1 % N₂ quality specification attached to the LNG product. This is generally required to meet both heating value requirements and prevent rollover of the product during shipping [5]. Rollover is the sudden mixing of stratified liquid layers, resulting in rapid release of vapour, which can destabilise the containment vessel [11]. The need for a dedicated nitrogen rejection unit (NRU) is sometimes required where feed gas from the reservoir contains high levels of N₂ (>4 %). Hence, the use of dedicated NRUs may become increasingly common as more sub-quality gas resources are used. Dedicated NRUs could be particularly relevant to many gas developments off the west coast of Australia, which contain sub-quality gas comprising upward of 4 % N₂.

The capital-intensive nature of establishing an LNG project generally means only high-volume (>1 MTPA) projects are developed, which means nitrogen
rejection through cryogenic distillation is the only economical choice available. This is because although the capital cost of cryogenic distillation is high, it is the only nitrogen rejection technology economical for flows above 25 MMSCFD (0.17 MTPA) [12]. Figure 2-4 illustrates the large size of a cryogenic NRU in a gas plant. While other commercial nitrogen rejection technologies exist—membrane separation, solvent absorption extraction, and physical adsorption (discussed in Section 2.6)—presently, these are all suited to modest flows from small scale fields; flows too small to justify LNG production on the scale of 1 MTPA or larger.

![Figure 2-4](image)

**Figure 2-4:** Two pairs of cryogenic nitrogen rejection units (highlighted red), showing the large size relative to the gas plant [13].

In an LNG plant, the cryogenic distillation process couples particularly well with the MCHE, as cryogenic distillation requires additional cooling of product from the MCHE to achieve separation of the $\text{N}_2 + \text{CH}_4$. The required cooling can be provided through integration into the refrigeration loops that already exist in the LNG facility, simplifying additional infrastructure requirements. Furthermore, higher recovery of $\text{CH}_4$ can be achieved with cryogenic distillation than with
alternative commercial technologies—membrane separation, solvent absorption extraction, and physical adsorption—and through a conventional end-flash. Higher recovery means more CH₄ can be converted to LNG, which generates more saleable LNG product and less CH₄ remaining in the vapour phase. Higher conversions and reduced end-flash vapour are increasingly important in maximising LNG production.

2.5 Opportunities for improved N₂ + CH₄ separations in LNG production

There are three primary opportunities for improved N₂ + CH₄ separation technologies in an LNG production facility. Figure 2-3 indicates the location of the opportunities that will now be discussed in detail.

2.5.1 Front-end nitrogen rejection

Front-end nitrogen rejection involves the removal of N₂ from the CH₄ dominant primary production stream prior to the MCHE to achieve a certain product specification; commonly 1 % N₂ in the LNG product, for example. Typical initial N₂ fractions range anywhere from 1 to 50 %, which means front-end nitrogen rejection technologies often need to remove large fractions of N₂ to meet tight specifications.

Improvements to front-end nitrogen rejection in LNG processing present the greatest opportunities for enhancing LNG production; however, such technologies are also likely to be the most difficult to develop. Conventionally, N₂ is only separated from the CH₄ once it has been carried through the entire production process, including the MCHE. Nitrogen rejection through conventional techniques is performed as the last major process, meaning every prior process encounters
the $N_2$ fraction present in the gas. The presence of the $N_2$ fraction increases the capital and operating costs of the LNG plant through such additions as higher processing volume and energy consumption in each unit process. Essentially, the $N_2$ is unwanted ballast in the process stream that increases the capital and operating costs as the $N_2$ content rises.

The development of a front-end NRU located upstream of the MCHE would significantly reduce the cost of LNG production by reducing the size of the required MCHE and eliminating the need for a cryogenic NRU—resulting in large reductions in capital and operating costs. Furthermore, removing $N_2$ early would result in a high CH$_4$ content end-flash, which could potentially be recycled directly to the MCHE to increase LNG product. This could be especially important in large developments where end-flash gas production exceeds the fuel requirements of the LNG plant. The challenge to performing front-end nitrogen rejection is in developing technologies that can operate cost effectively at flow rates $>150$ MMSCFD (~1 MTPA) in comparison with cryogenic distillation.

A potential avenue for the development of front-end nitrogen rejection technologies could be to take advantage of the pre-cooled (-30 to -40 °C) gas feed to the MCHE. Many separation processes have been shown to improve at decreased temperatures—adsorption capacity increases at decreased temperatures, for example [14]. This provides a specific example where a separation process could be inserted into an LNG facility to enhance an $N_2 + CH_4$ separation.

### 2.5.2 End-flash upgrading

End-flash upgrading is the process of raising or upgrading the heating value of end-flash gas, normally to make it suitable for use as plant fuel. While increasing
the heating value can be achieved through blending with a higher heating value gas, reducing the N₂ content in the end-flash is progressively more desirable, especially in installations where the quantity of end-flash exceeds plant fuel requirements. This task is significantly less challenging than front-end nitrogen rejection for two main reasons:

1. The volume of gas to be treated from the end-flash vent is only a portion of the main production stream.

2. The required reduction in N₂ content from the end-flash stream to meet fuel requirements is often quite modest.

For example, the N₂ content limit on common gas turbine generators is 30 %; therefore, end-flash gas initially containing 50 % N₂ would only require its N₂ content to be reduced by 40 %. This is essentially a bulk gas separation. While there are always examples outside this general description, for the purposes of this work end-flash upgrading refers to bulk N₂ separations from a CH₄ dominant end-flash vent stream.

Technologies developed to improve front-end nitrogen rejection may also be applied to the upgrading of end-flash gas; however, end-flash upgrading does present slightly different opportunities. Particularly, the lower volume of end-flash to be treated increases the suitability of alternative separation technologies to cryogenic distillation, such as adsorption. Furthermore, the temperature of the end-flash leaving the MCHE is around -160 °C, which again could be used to enhance the separation. In this case, some of the cold would likely be recovered to raise the temperature to optimise the separation, and to improve the efficiency of the plant refrigeration cycle.
2.5.3 Nitrogen clean-up

Nitrogen clean-up arises from the need to remove small fractions of CH₄ (1 to 5 %) from the N₂ dominant vent stream from a cryogenic NRU. Nitrogen clean-up generally serves two important functions:

1. Reduction of the CH₄ content in the N₂ vent stream to meet environmental specifications.
2. The recovery of valuable CH₄ to be recycled into the production stream.

Although rejecting N₂ before the MCHE would provide the most benefit, this is likely to take some time and be difficult to develop. Until then, some new and existing LNG production facilities using cryogenic distillation may require nitrogen clean-up of vent streams from cryogenic NRUs. This presents another opportunity for the development of N₂ + CH₄ separations to treat these vent streams. These N₂ dominant vent streams leave the cryogenic distillation towers near atmospheric pressure and at temperatures around -160 °C (they are heated prior to atmospheric venting), which provides the same opportunities for enhanced separations using low temperatures.

2.5.4 Summary of opportunities for improved N₂ + CH₄ separations in LNG production

The common theme for the described separations is that in an LNG facility each of the streams discussed is at a reduced temperature, which could be used to improve N₂ + CH₄ separations. A summary is shown in Table 2-1, which lists the N₂ + CH₄ separation opportunities, includes an assessment of the potential gains to be made, as well as an estimate of anticipated development difficulty and where the low temperature process would likely be located.
Table 2-1: Opportunities for N$_2$ + CH$_4$ separations in a typical LNG production facility (> 1 MTPA)

<table>
<thead>
<tr>
<th>Required N$_2$ + CH$_4$ separation improvement</th>
<th>Expected impact on LNG production</th>
<th>Anticipated Difficulty</th>
<th>Potential position of technology in LNG facility</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Front-end nitrogen rejection</td>
<td>High</td>
<td>High</td>
<td>Between heavy hydrocarbon removal and the MCHE</td>
</tr>
<tr>
<td>2. End-flash upgrading</td>
<td>Moderate</td>
<td>Moderate</td>
<td>At the outlet of the MCHE</td>
</tr>
<tr>
<td>3. Nitrogen clean-up</td>
<td>Moderate</td>
<td>Moderate</td>
<td>At the outlet of the cryogenic NRU</td>
</tr>
</tbody>
</table>

2.6 The present state of industry-proven N$_2$ + CH$_4$ gas separation technologies and their potential to improve LNG production

The following section briefly discusses the basic operation of the four commercialised N$_2$ + CH$_4$ separation technologies, their present industry status, most recent advances, and future directions with respect to the LNG industry.

2.6.1 Cryogenic distillation

Gas separations by cryogenic distillation operate principally through the separation of components, by taking advantage of the differing volatilities of components at cryogenic temperatures. Cryogenic distillation is particularly useful for the separation of N$_2$ + CH$_4$ because the similar molecular sizes of N$_2$ (3.6 Å) and CH$_4$ (3.8 Å) combined with the lack of selective reactivity of the molecules, make any other separation technique technically difficult [15]. Typically, the distillation columns operate at high pressures (~2500 to 3000 kPa) to increase the difference between component boiling points (Figure 2-5), facilitating the separation process [12]. Key advantages of cryogenic distillation are the highly selective separations
possible (product impurities at levels between 0.5 and 2 mol %) and the ability to
design processes to operate over a wide range of N₂ feed contents (1 to 50 %) [16].

![Graph showing vapour pressure curves of N₂ and CH₄, illustrating that the difference of boiling points grows as pressure is increased facilitating greater separation by distillation [17].](image)

Cryogenic NRUs are designed and supplied by many companies in the natural
gas industry who often hold patents for their specific process configurations. While
each supplier will generally implement a unique design for an application, these
designs will be based around three main cryogenic NRU processes:

1. The single column process.

2. The ‘classical’ double column process.

3. The two or three column process.

The choice between these main process configurations is primarily
determined by the N₂ content in the feed gas; however, the subtleties of the final
design and implementation are ultimately based on capital and operating costs.
These are in turn driven by process considerations, such as product specifications, operating pressure, and flow rate [16, 18].

Cryogenic distillation is a mature technology and has undergone several process refinements in the configurations mentioned. Advancements in technology will surely be applied to cryogenic distillation and improvements are likely to continue; however, with more than a century of development it would be reasonable to propose that less mature technologies have more potential for further refinement and development.

### 2.6.2 Solvent absorption extraction

While rarely used in the natural gas industry, nitrogen rejection through absorption has been commercialised through the selective absorption of CH₄ gas into a liquid solvent—generally hydrocarbon oil [19-21]. These hydrocarbon oils usually have a low capacity for CH₄ absorption, which is undesirable for nitrogen rejection with a generally large CH₄ component. To achieve substantial recovery of the CH₄, the inventory and circulation rate of the solvent required are high, which increases costs. After absorption of the CH₄, the saturated hydrocarbon oil needs to be regenerated to retrieve the CH₄ component and restart the process. The regeneration is performed through either a series of flashes or a thermally-driven distillation, both of which result in the CH₄ being desorbed near atmospheric pressure. Normally, the desorbed CH₄ then requires recompression for further use, adding to the operating costs of the process. The costs associated with the inventory and circulation of the absorbent liquid—and the CH₄ regeneration and recompression—limit the use of CH₄ selective absorption for nitrogen rejection to flow rates to <30 MMSCFD. Nevertheless, even though absorption may be
economical at these flow rates, the inherent complexity of the process further limits the use of this technology.

The most likely advancement required for absorption to be used in large-scale nitrogen rejection applications would be through further development of N₂ selective solvents. While the system would still retain much of its complexity, the system itself could potentially be scaled to almost 1/20th of a CH₄ selective process, assuming only about 5% of the gas (the N₂ content) were absorbed rather than the existing 95%. Some organo-metallic complexes (OMCs) have been shown to exhibit preferential N₂ absorption, achieved through complex formation between the OMC and a N₂ molecule. Stanford Research Institute International (SRI) and Bend Research Inc. have both reported N₂ selective solvents that display reversible chemical complexing properties, implying regenerability [22-24]. Bend Research Inc. has held patents describing such OMC-based, N₂ selective solvents for more than a decade; however, a commercial process has yet to be developed. This lack of commercialisation could be a reflection of the high cost in synthesising OMCs and may in part be because of the limitations to the absorption process as discussed. The infrequent use of existing commercialised N₂ + CH₄ absorption technologies and the lack of commercial development of N₂ selective absorbents discovered more than 40 years ago, suggest N₂ + CH₄ separations by absorption is some way off becoming competitive with other technologies.

2.6.3 Membranes

Membranes for use in gas separations are mostly thin, structured barriers between two miscible gases, which allow selective permeation of gas components from one side of the membrane to the other with the application of a trans-membrane force. For gas separations, the driving force is created by a
pressure gradient across the membrane. There are several examples of membrane separation technologies for the removal of CO₂ and H₂S in natural gas processing. The Beharra Springs gas plant in WA, for example, has been using a polymer membrane system since 1992 to reduce CO₂ and H₂S from 6 to 2.5 % and 10 to 3.2 ppmv, respectively, to meet pipeline specification [25].

The only commercialised form of a N₂ + CH₄ gas separation membrane is used in the NitroSep™ process manufactured by Membrane Technology and Research (MTR), which achieves separation of N₂ + CH₄ by exploiting a higher CH₄ membrane permeation rate [26]. The attractiveness of any membrane system is that it does not contain any moving parts (passive system), has a relatively small footprint, does not require component phase changes, and is low maintenance. The NitroSep™ membranes have a relatively low selectivity, which means multiple membrane units would be required to achieve tight product specifications. As the number of membrane units is increased, the degree of recompression required grows as the permeate stream from each stage is often recycled. In practice, the maximum number of stages is likely to be two or three, determined by the compression costs to achieve the required pressure gradients and separation efficiency. An analysis of the NitroSep™ process at 10 MMSCFD has shown that one or two stages can reduce N₂ content from a maximum 30 % to meet a 4 % pipeline specification; however, this is still well below typical LNG production flow rates and N₂ content specifications [27].

Relative to other N₂ + CH₄ gas separation technologies, membrane technology is still at an early development and commercialisation stage, as highlighted by the lack of commercial nitrogen rejection membrane processes. In a 2002 review on the future directions of membranes, Baker [28] highlights that membranes could be used for nitrogen rejection and outlines some suggested membrane
developments; however, almost a decade later only a single commercial technology has appeared. On one hand, there are indications that theoretical capabilities may not be cost effective in practice, as illustrated by the statement from MTR that the NitroSep™ process can operate to 100 MMSCFD, yet maximum installations have been around 20 MMSCFD [26, 29]. On the other hand, this could just be resistance from the industry to adopting new, relatively unproven technologies. Either way, if nitrogen rejection membranes are to gain further industry acceptance, improvements to the membranes themselves will need to be made and extensive installations and proven field testing will be required.

2.6.4 Gas adsorption

Gas adsorption is governed by interactions between gas molecules and the surface of a solid adsorbent. Adsorption occurs because the free energy of the adsorbed species on the surface of the adsorbent is lower than in the gas phase [30]. This phenomenon can be used as a basis for the selective separation of components from gas mixtures through one of three mechanisms [15]:

1. Equilibrium separations use differences in surface affinities of components at equilibrium to separate them from a gas mixture.

2. Steric separations essentially operate by restricting or sieving the adsorption of components based on molecular size. This mechanism is unique to zeolites and molecular sieves because the crystal structures of these adsorbents form uniform pore sizes, which can be used to sieve components. For design purposes, steric separations are normally treated as equilibrium separations.

3. Kinetic separations are accomplished by exploiting differences in diffusion rates of adsorbed components into the adsorbent material.
The most common adsorbent materials used in gas separations are activated carbons, zeolites, and aluminosilicates.

In a gas-solid system, circulating the solid adsorbent is difficult, so in practice the gas mixture is usually passed through a column packed with a stationary pelletised solid adsorbent. The adsorbate (adsorbed component) is separated from the gas mixture and the depleted effluent is produced at the outlet of the column. Processes based on gas adsorption are generally cyclic and have both an adsorption and desorption (regeneration) step, the latter being required once the adsorbent is saturated. This means in practice, two or more beds are required—operating asynchronously with one another—to maintain a continuous flow. The desorption process can be facilitated by a change (or swing) in temperature (thermal swing adsorption, TSA), in pressure (PSA), or sometimes a combination of both. Both TSA and PSA processes are widely used in many industrial gas separations, including applications in the natural gas industry such as the micro-scale PSA nitrogen rejection system shown in Figure 2-6. Three key properties required to design an adsorption process are:

1. Equilibrium adsorption capacity.

2. Adsorption kinetics.

3. Heats of adsorption.

A fourth property important for any separation process, selectivity, is determined for adsorption processes by point 1 and 2 above. Each of these key properties are discussed as follows.
Figure 2-6: Two bed micro-scale nitrogen rejection PSA system [31].

The equilibrium capacity determines the amount of adsorbent required to adsorb a fixed quantity of adsorbate, at a particular pressure and temperature, once equilibrium is achieved. The amount of adsorbent required for a given process effectively determines the adsorption bed size and thus is directly related to the capital cost of the system. It is therefore preferable to have adsorbents with larger capacities to minimise the column bed size and, in turn, cost.

Equilibrium adsorption data are normally presented as an isotherm. There are six types of isotherms according to the International Union of Pure and Applied Chemistry (IUPAC) classification [32]. The concave-up isotherm shown in Figure 2-7 is a Type-I isotherm, which characterises the formation of a monolayer on a microporous adsorbent and the saturation of the adsorbent pores. Only Type-I isotherms are generally suitable for cyclic separation applications [33], as it is the microporous adsorbents that generally display the highest adsorption
capacities [15, 34]. Adsorption isotherms indicate the differences in adsorption capacity that occur with changes in temperature and/or pressure, as needed to design a TSA or PSA process, for example. In a working process, the complete regeneration of the adsorbent is rarely ever achieved because of the time and energy required. Thus, adsorption isotherm data are used to determine the minimum and maximum adsorption capacities in the proposed working temperature and/or pressure range. The differences in adsorption capacity at the selected conditions are known as the adsorbent’s working capacity, and more closely represent the amount of adsorbent required to treat a fixed quantity of gas.

Figure 2-7: Type-I isotherms, illustrating changes in adsorption with both temperature for TSA and pressure for PSA.

Adsorption is a time-dependent process, and as such it is vital to study the rates of adsorption, or adsorption kinetics, for process design modelling. For most gas adsorption process design, the adsorption kinetics are modelled using lumped parameters known as mass transfer coefficients, which are more approximate and simpler than fundamental gas diffusion models [30]. Mass transfer coefficients are,
however, more suitable where average concentrations are involved and are generally preferred for gas adsorption design in packed beds.

The elution profile at the outlet of an adsorbent column illustrates the effect of mass transfer on the adsorption process; such a profile is commonly referred to as the breakthrough curve. If one considers a step change in concentration at the inlet of a packed column and monitors the outlet concentration with time, in an ideal system with completely efficient adsorption this would result in a step change at the outlet once the adsorbent was saturated; however, measured breakthrough curves do not exhibit this feature [15]. The shapes of measured breakthrough curves are determined by the gas phase dispersion and other hydrodynamic aspects of the flow through the packed bed, and by the adsorption kinetics governing mass transfer between the gas and the solid phases. Fast adsorption kinetics result in a more ideal breakthrough profile, whereas slow kinetics result in a distended breakthrough profile.

These differences in breakthrough profiles are related to the adsorbate concentration profile throughout the bed, which changes with time. The moving concentration front at the end of the profile is called the mass transfer zone (MTZ). In practice, the size of the MTZ determines the extent the adsorbent bed can be used, as illustrated in Figure 2-8. Clearly it is preferable to have a short MTZ.

![Figure 2-8: Shows the progression of the MTZ through the bed. (a) Illustrates how a small MTZ results in a small amount of unused bed; and (b) a large MTZ results in a large amount of unused bed [15].](image)
Adsorption kinetics determine the size of the MTZ, which in turn affects the bed size; thus, kinetics are important for both equilibrium and kinetic based separations. In the case of kinetic based separations, the mass transfer processes are even more important because they determine the contact time required for adsorption. This is because the kinetic selectivity is determined by the ratio of the adsorbent’s equilibrium capacities for each adsorbate as well as the ratio of their respective mass transfer coefficients. The kinetics also determine a characteristic time for adsorption to occur, and this time scale must be shorter than the residence time of the gas in the column. Since the residence time is set by the flow rate and the column dimensions, knowledge of the adsorption kinetics is also critical for the design of adsorption based processes.

Heats of adsorption provide a measure of the adsorbent-adsorbate bond strength and are required to accurately predict the performance of an adsorption process. The heats of adsorption are critical as they govern the degree of temperature change in the bed as the adsorption process occurs [35]. Such temperature changes, in turn, influence the local equilibrium adsorption and mass transfer rates; thus, they must be taken into consideration to accurately describe column bed dynamics. Heats of adsorption are also important when determining the energy required for regeneration of the adsorbent, as it is the energy required to break the adsorption bond that governs regeneration.

Dehydration of natural gas is routinely completed by TSA, which can achieve the <0.1 ppmv H₂O specification required in LNG pre-processing. The TSA process can achieve the high selectivity required to attain such a tight specification because the large heat of adsorption of H₂O compared with CH₄ (66.1 and 17.3 kJ mol⁻¹, respectively [36]) means there is a strong driving force for H₂O molecules to move from the bulk gas phase and bind to the adsorbent. The disadvantage is that the
strong bond that allowed for such effective separation needs to be broken for regeneration. The energy required is supplied by temperature swing regeneration. While the temperature input provides enough energy for regeneration, temperature cycles are slow (~40 → 120 → 40 °C), taking hours or even days to drive off the adsorbed phase. The long regeneration times mean that in a continuous flow system, the bed under adsorption must operate for at least the time required to regenerate another bed. For this to occur, the column generally needs to contain a large inventory of high capacity adsorbent, and is limited to the treatment of feed gas with a low concentration of the adsorbate so the bed does not saturate too quickly. Thus, TSA processes are only suitable for systems involving large adsorption capacity adsorbents, adsorbates with high heats of adsorption, and relatively low concentrations of adsorbate in the feed gas.

In contrast, PSA processes are generally suited to the separation of components with higher concentrations of adsorbate in the feed and low heats of adsorption. Regeneration through changes in pressure requires less energy than those through a change in temperature, which is why PSA suits lower heat of adsorption systems. The lower heats of adsorption mean the difference in the strength of adsorption between the gas phase components being separated is often smaller, which can decrease the ability to separate them; however, differences in the adsorption kinetics of each component can compensate for this. Furthermore, multiple PSA columns are often linked in stages as a way of improving product purity. The advantage of switching pressure rather than temperature is that regeneration times are much faster (in the order of seconds to minutes). More specifically, the saturated adsorbent bed can be purged quickly by a change in pressure so the adsorption phase can resume in that bed much faster than for a TSA process. This rapid regeneration capability also means fast saturation by high
adsorbate concentrations in the feed gas can be tolerated more readily than in a TSA process. In general, rapid cycling also means the inventory of adsorbent required is less for PSA processes, because for a given flow rate through a bed, the cycle time determines the mass of the adsorbent required to treat that amount of gas. This means for equal adsorbate quantities, column sizes and thus capital costs are reduced for PSA processes relative to TSA processes.

The heats of adsorption of N₂ and CH₄ on common adsorbents are between 15 and 22 kJ mol⁻¹ [37, 38], and the two molecules have very similar sizes and lack of selective reactivity, as previously stated. These similarities indicate why commercial nitrogen rejection processes based on adsorption use pressure rather than temperature swings. There are several suppliers of commercial PSA nitrogen rejection technologies: Nitrogen Sponge by IACX Energy, Nitrogen rejection unit by Tucker Gas Processing Equipment, Inc. (TGPE), and Nitrotec by CMS Energy, for example [39-41]. These technologies operate on the basis of an equilibrium separation; however, the issue with equilibrium separation of N₂ + CH₄ is CH₄ is the selectively adsorbed species on all known adsorbents [15]. The separation therefore requires the adsorption of the CH₄ fraction from the gas mixture, which means large quantities of adsorbent are required to treat small gas flows. This is the same problem faced by solvent absorption, and essentially the same solution is necessary if the adsorption process is to be applied to LNG production at the one MTPA scale, to preferentially adsorb the N₂ component.

In 1958, Habgood [14] showed that faster diffusion rates of N₂ over CH₄ could be used to separate these components. Habgood’s [14] process used a 4A zeolite adsorbent and was limited to low temperatures between -79 and 0 °C, but showed a N₂ selective separation based on the relative adsorption kinetics. Work by Frankiewicz and Donnelly [42], and a patent by Chao [43], showed various
ion-exchanged clinoptilolites can also be used to kinetically separate \( N_2 + CH_4 \).

Ackley and Yang [44] presented a PSA process in which a carbon molecular sieve could be used to separate a \( N_2 + CH_4 \) mixture on the basis of the relative adsorption kinetics. A titanosilicate called ETS-4 was synthesised and patented by Kuznicki [45], specifically designed so the adsorbent’s pore size was between the kinetic diameters of the \( N_2 \) and \( CH_4 \) molecules. In 2003, Yang [15] suggested clinoptilolite and titanosilicate adsorbents may show the most promise for a kinetic separation of \( N_2 + CH_4 \); however, the use of other zeolites and carbon molecular sieves for this purpose were also mentioned.

Although the preferential separation of \( N_2 + CH_4 \) through differences in adsorption kinetics has been shown to be possible with several different materials, only one commercial nitrogen rejection PSA technology has been established. The Molecular Gate process from Engelhard Corporation employs derivatives of the original titanosilicate ETS-4 developed by Kuznicki [46-48]. This technology is presently limited to moderate flows, but demonstrates that a kinetic \( N_2 \) selective PSA process is commercially viable.

The potential advancement of PSA processes for \( N_2 + CH_4 \) separations is likely to occur through one or both of the following pathways:

- **Novel PSA processes and optimisations**, which will require process modelling and experimental pilot plants to verify the models before commercial deployment. There are several development stages required to prove a technology to the point where it could confidently be trialled in a commercial operation. The development process of a new PSA process may take many years or even decades to reach commercial deployment. The typical development
pathway of a PSA technology, including the required laboratory and pilot-scale measurements, is shown in Figure 2-9.

- The synthesis of novel adsorbent materials.

![Figure 2-9: Development pathway of a PSA technology.](image)

Neither of these developments can take place in the absence of quality experimental data providing the necessary information about adsorption equilibrium capacities, adsorption kinetics, and heats of adsorption. For single adsorbate systems at near atmospheric temperatures and pressures, limited adsorption data do exist; however, there is a serious deficiency of multi-component gas adsorption data. This is primarily due to the difficulty of conducting multi-component adsorption experiments [49-51]. Due to the lack of multi-component adsorption data, the gas mixture adsorption equilibria, mass transfer characteristics, and heats of adsorption necessary for PSA design are often estimated from pure gas adsorption isotherms and kinetic data, used in conjunction with theoretical or empirical adsorption models [49, 52]. While simple process models can be produced by using these pure fluid parameters, economic analyses of PSA systems have shown that during the life of a facility, a 2 % increase in product recovery can yield 150 % of the cost of the PSA plant itself in generated revenue [49, 52]. Therefore, to reliably develop process models of PSA systems, multi-component adsorption data derived from experiments should be used as the
basis of the models and pilot systems. The most common traditional techniques for performing these experiments are the volumetric, gravimetric, and breakthrough methods, and there are several texts detailing these measurement techniques [34, 53-60].

2.7 Development of a low temperature PSA process for enhanced N₂ + CH₄ separations

2.7.1 Overview

The three main N₂ + CH₄ separation opportunities that have been identified in LNG processing are front-end nitrogen rejection, end-flash upgrading, and nitrogen clean-up (Figure 2-3). Each of these separation opportunities involves the availability of low temperature feed gas. As an industrial gas separation technology, PSA is a well-established process, meaning PSA columns and control hardware are readily available and can often be purchased as pre-fabricated modular skids and deployed almost immediately; however, there is still significant development occurring to advance PSA process configurations and adsorbent development. This illustrates that a substantial amount of development potential of PSA exists. In summary, PSA appears to be a very promising commercial gas separation platform with scope for further development.

A low temperature PSA adsorption process will be able to take advantage of the low feed gas temperatures available in LNG plants at each of the three locations identified in Figure 2-3, to increase adsorption capacity and therefore operational flow rate. Furthermore, it is anticipated that low temperature adsorption may improve process selectivity thereby improving the quality of the product. Breck [61, 62] described how the crystalline structure of some adsorbents may change at lower temperatures (narrowing pore openings), increasing the difference in
adsorption rates between gas components, which suggests this expectation is reasonable.

As indicated in Table 2-1, the benefit of a front-end nitrogen rejection PSA process would be the most significant of the three options proposed. This is primarily because of the reduced size of the MCHE required; thus, the plant's capital and operating costs decrease substantially. Alternatively, the prospects of developing a PSA based separation process for $N_2 + CH_4$ are better for end-flash upgrading and nitrogen clean-up applications where, although still large, the gas flow rates are generally an order of magnitude smaller than needs to be treated by front-end nitrogen rejection. For the nitrogen clean-up application a $CH_4$ selective adsorbent is required, and since the concentrations of the adsorbate in the bulk gas are small, this is likely to be an equilibrium adsorption based separation process. For the end-flash gas upgrading application, a $N_2$ selective adsorption process is required and the adsorbate concentration is larger; thus, in this case a separation based on the relative adsorption kinetics is required.

Some of the key innovation and development requirements needed to realise a low temperature PSA process in an LNG plant are:

- To increase the capability of the PSA process to treat large flow rates.
- To increase the process selectivity and hence purity of the product.
- To use readily available components for faster and cheaper commercial deployment.
- To keep PSA skid footprints as small as possible so they can be readily deployed offshore. This is particularly important for applications such as floating LNG,
where there is a need to reduce the height of cryogenic distillation columns, which could be achieved by using PSA to partially remove some of the N₂.

2.7.2 Challenges and present research

Some of the major development work for the commercial deployment of low temperature PSA processes will involve experimental adsorption measurements, process modelling, and pilot plant experimentation (Figure 2-9). To begin this development, the first step is to develop experimental apparatus capable of performing low temperature, high pressure adsorption measurements with mixtures of N₂ + CH₄. While some commercial adsorption measurement systems have entered the market, there is a limited choice of manufacturers, the systems are expensive, and the available options are generally inflexible for the specialised needs of research groups. More specifically, most commercial systems only measure pure component equilibrium capacities by dosing the adsorbent with a fixed amount of adsorbate. The uptake rates from the dosing are used to determine the adsorption kinetics, but because the technique is inherently static these results can be unreliable for designing dynamic, flowing systems. Therefore, to conduct experiments as close to process conditions as possible and reliably generate adsorption data, the design and construction of custom adsorption apparatus is required.

Research is now underway at the Centre for Energy at The University of Western Australia to develop the proposed low temperature PSA process. The authors have developed a suite of experimental adsorption tools to first test commercial adsorbents for their suitability for the proposed PSA process and generate the data for preliminary process modelling. Of particular importance to the research initiative is the dynamic column breakthrough apparatus. The
primary strength of the breakthrough technique over other experimental methods is that it provides the closest match between laboratory adsorption experiments and process-scale systems [63]. This technique provides information about adsorbent performance at process conditions, so parameters extracted from breakthrough data can be used more reliably to scale up the process to industrial size separation systems [64]. The authors have designed and constructed a low temperature, high pressure breakthrough apparatus capable of adsorption measurements of N₂ + CH₄ mixtures on commercial adsorbents. Details of the basic operation of the apparatus have been described by Hofman et al. [65].

The initial focus of the research project is to use the apparatus to examine a range of potential commercial adsorbents, then perform detailed measurements on the most suitable adsorbents, and generate fundamental adsorption data to model the proposed process and evaluate its commercial suitability. This is an ongoing research initiative.

2.8 Conclusion

In this work, the existing state of commercial N₂ + CH₄ separation technologies with respect to LNG production and discussed the opportunities for improvement was presented. The potential for furthering the use of PSA processes for such separations through the use of the low temperature conditions available in an LNG production facility was illustrated. The challenges associated with developing a low temperature PSA process have been discussed along with a snapshot of the research presently underway to address them.
2.9 Acknowledgements

The research was funded by Chevron Energy Technology Company, the Western Australian Energy Research Alliance (WA:ERA) and the Australian Research Council (Project LP0776928). One of the authors (P.S. Hofman) also received scholarships from the Australian Petroleum Production and Exploration Association (KA Richards Memorial Scholarship) and the Australia China Natural Gas Partnership Fund. The authors thank Thomas Rufford for his contribution to the literature review, and Terence Edwards for carefully reading and editing the manuscript.
Chapter 3

A dynamic column breakthrough apparatus for adsorption capacity measurements with quantitative uncertainties

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3.1 Foreword

This article is published in the journal *Adsorption* vol. 18. pp. 251-263, 2012.

The objective of the work presented in this chapter was to develop an experimental apparatus capable of performing high pressure, low temperature, adsorption measurements with mixtures of N₂ + CH₄. This work describes the constructed dynamic column breakthrough apparatus, its operation, data analysis techniques used, and results to demonstrate the capability of the system.

3.2 Abstract

A dynamic column breakthrough (DCB) apparatus was used to study the separation of N₂ + CH₄ gas mixtures using two zeolites, H⁺ mordenite and Na⁺ 13X, at temperatures of 229.2 and 301.9 K, and pressures to 792.9 kPa. The apparatus is not limited to the study of dilute adsorbates within inert carrier gases because the instrumentation allows the effluent flow rate to be measured accurately: a method for correcting apparent effluent mass flow readings for large changes in effluent composition is described. The mathematical framework used to determine equilibrium adsorption capacities from the dynamic adsorption experiments is presented and includes a method for estimating quantitatively the uncertainties of the measured capacities. Dynamic adsorption experiments were conducted with pure N₂, pure CH₄, and equimolar N₂ + CH₄ mixtures, and the results were compared with similar static adsorption experiments reported in the literature. The 13X zeolite had the greater adsorption capacity for both N₂ and CH₄. At 792 kPa, the equilibrium capacities of the 13X zeolite increased from 1.36 ± 0.10 mmol g⁻¹ for N₂ and 2.13 ± 0.14 mmol g⁻¹ for CH₄ at 301.9 K to 3.33 ± 0.12 mmol g⁻¹ for N₂ and 3.97 ± 0.19 mmol g⁻¹ for CH₄ at 229.2 K. Both zeolites preferentially adsorbed CH₄; however, the mordenite had a greater
equilibrium selectivity of $3.5 \pm 0.4$ at 301.9 K. Equilibrium selectivities inferred from pure fluid capacities using the ideal adsorbed solution theory (IAST) were limited by the accuracy of the literature pure fluid Toth models. Equilibrium capacities with quantitative uncertainties derived directly from DCB measurements, without reference to a dynamic model, should help increase the accuracy of mass transfer parameters extracted by the regression of such models to time dependent data.

3.3 Introduction

The separation and purification of gas mixtures by pressure swing adsorption (PSA) is an established industrial separation technology used, for example, in the separation of air into oxygen and nitrogen, the production of hydrogen, and the capture of volatile organic compounds from waste gas streams [4, 49, 56, 66]. The design of PSA systems requires several key input data:

- Adsorption equilibria.
- Mass transfer characteristics.
- Enthalpies of adsorption.

The three main experimental techniques used to produce such data are the volumetric, the gravimetric, and the dynamic breakthrough (or flow) methods [34, 53-60], which have been reviewed and compared with other methods by several authors, including Sircar [52, 67]. The most common type of adsorption data reported in the literature are equilibrium adsorption capacities of pure gases made by static (volumetric or gravimetric) methods, largely because these are the easiest types of measurement to make and several commercial instruments are
available to conduct them. However, while PSA systems can be based on pure fluid adsorption data measured by the static method, the design is often over-engineered to account for the critical differences between the conditions of the static experiments with pure fluids and the dynamic conditions of an industrial gas separation process. Economic analyses of PSA systems have shown that over the life of a facility, a 2 % increase in product recovery can yield 150 % of the cost of the PSA plant itself in generated revenue [49, 52]. Thus, representative dynamic adsorption data for gas mixtures are particularly valuable to the development of PSA processes with reduced design margins.

The dynamic column breakthrough (DCB) method provides a laboratory-based adsorption experiment than can more closely match the conditions in an industrial-scale gas separation process than is achievable with static adsorption experiments [63]. Consequently, the data produced with the DCB method improve the prospects for reliable scale-up of the adsorption technology [64]. However, although experiments have been made using variations of the DCB method for over 60 years [14, 68-72], it has been most commonly applied through experiments involving the pulsed injection of dilute adsorbates into an inert carrier gas passing through a column packed with the adsorbent. This may in part be due to the difficulties associated with the measurement of the flow rate of effluent from the packed column during a DCB experiment with high adsorbate concentrations in the feed gas. In such an experiment, both the flow rate and composition of the effluent from the column vary significantly and consequently can be difficult to measure accurately; for example, flow meters that use thermal sensors to determine flow are very difficult to use reliably with mixtures of arbitrary and varying composition. The most common method of extending DCB experiments beyond studies of dilute adsorbates is through the application of a dynamic
numerical model of the DCB experiment to estimate the effluent flow rate. Other key parameters such as mass and heat transfer coefficients are then generally estimated through regression of that model to the measured composition data; however, the adjustable parameters of such dynamic models are strongly correlated with each other, which makes reliable estimation of their uncertainty very difficult, and means that during a regression the models can converge to inaccurate values of those parameters if there are too many degrees of freedom. Thus, when relying on dynamic models to describe the results of DCB experiments, it is preferable to have independent information about the equilibrium adsorption capacities, which often requires an auxiliary set of measurements with a static apparatus. In this work we present an apparatus that enables adsorption capacities to be determined directly from DCB experiments at high adsorbate concentrations without reference to a dynamic model and, for the first time, a method to estimate robustly the uncertainties in the measured capacities.

Several recent papers have reported apparatus with instrumentation that allows the effluent flow rate to be monitored and used to test the predictions of dynamic models [64, 73-76]; however, an important detail relating to the flow measurement has not been covered in these papers: the correction of the meter's reading to account for variation in the effluent composition. Several different operating principles are used by various commercially available flow meters; however, all flow meters require knowledge of one or more thermo-physical properties of the fluid being measured, such as viscosity and/or density, to convert the measured quantity (pressure drop in an orifice meter, resonance period in a coriolis meter) to a flow rate. Since such thermo-physical properties depend sensitively on fluid composition, flow meters are generally ‘calibrated’ to operate with a specific pure fluid. It is possible to use the flow meter accurately with a
different pure fluid, or even a mixture of known composition, provided the appropriate thermo-physical properties of the fluid can be calculated and also if the model relating the measured quantity to the flow rate is sufficiently well known. Of the five recent papers that incorporated an effluent flow meter, only Guntuka et al. [64] and Mulgundmath et al. [74] reported the model or type of flow meter used, and none of the papers detail how the effluent composition was used to correct the meter's raw flow reading. In this work we describe a method for obtaining accurate effluent flow measurements during DCB experiments with mixtures containing concentrated adsorbates by using an orifice-type flow meter and the measured effluent composition.

The particular motivation for this work is the development of PSA processes for separating the mixtures of $N_2 + CH_4$ present at various stages in the cryogenic plants used to produce liquefied natural gas (LNG). Adsorption based processes for separating mixtures of $N_2 + CH_4$ in natural gas processing have the potential for lower energy requirements, smaller plant footprints, and lower capital costs than the conventional cryogenic distillation technologies. Commercial PSA based separations of $N_2 + CH_4$ are already utilised within the natural gas industry using various adsorbents [40, 46, 48, 77, 78], although currently they are limited to treating feed gas flow rates of up to 15 MMSCFD ($= 5.08$ Nm$^3$ s$^{-1}$) [47]. There are several promising avenues which may lead to the further deployment of PSA processes for separating $N_2 + CH_4$, particularly in LNG plants, including:

- The ready accessibility of low temperatures and high pressures within the plant.
- The need, prior to disposal, to upgrade or purify $N_2$ or $CH_4$ dominant streams, which are a by-product of LNG production.
• The wide range of existing commercial adsorbents and/or newly developed adsorbents, which have not been adequately tested for this application.

In this work, we demonstrate how a DCB apparatus with appropriate instrumentation can be used to determine accurately equilibrium adsorption capacities for pure fluids and gas mixtures over a wide range of conditions, including those conditions relevant to the separation of N₂ and CH₄ mixtures found at various points in LNG plants. Measurements are reported for two commercially available zeolites over the range 229.2 to 301.9 K and 104.0 to 792.9 kPa using concentrated adsorbates. Importantly, we present a quantitative method to estimate the uncertainties of those adsorption capacities, which to our knowledge has not been reported elsewhere. Such equilibrium data and their uncertainty estimates are crucial to both adsorption science and engineering [49-51] yet their acquisition with static methods is generally quite challenging for gas mixtures. In subsequent work, we will apply and extend existing dynamic adsorption models to further analyse the time dependent adsorption data from this DCB apparatus, with the objectives of determining the mass and heat transfer parameters relevant to the design of PSA systems. This has been completed in Chapter 5 of this thesis.

3.4 Apparatus and materials

A schematic of the DCB apparatus is shown in Figure 3-1. The adsorption column (a 130 mm long by 22.2 mm inner diameter stainless steel tube) and an inlet cooling loop (ICL) were located inside a stirred air bath, equipped with a liquid N₂ spray cooling system. This thermally controlled zone was capable of producing temperatures between 190 and 498 K. The loop of 1/8” tubing that formed the ICL was thermally anchored to a copper spool to ensure the feed gas entering the column was in thermal equilibrium with the adsorption column. An
outlet heating loop (OHL) was installed at the column’s outlet to heat the effluent gas back to ambient temperature to ensure accurate readings at the back-pressure regulator (BPR-2), outlet mass flow meter (MFM), and mass spectrometer (MS). The BPRs (PCR-500) and MFM (M-200SCCM-D) were supplied by Alicat Scientific. The adsorbent bed temperature was monitored at three positions along the length of the column with 100 Ω platinum resistance thermometers (PRT-1 to PRT-3, at 32.7 mm, 65.4 mm, and 98.1 mm from the column entrance, respectively). These thermometers were calibrated to ITS-90 over the range 77 to 313 K with an uncertainty of 0.2 K.

![Diagram of the dynamic column breakthrough (DCB) apparatus.](image)

**Figure 3-1: Schematic diagram of the dynamic column breakthrough (DCB) apparatus.**

The flow rate and composition of gas mixtures (including pure gases) to the column was regulated by four mass flow controllers (MFC-1 to MFC-4). The full scale of each mass flow controller was $1.36 \times 10^{-4}$ mol s$^{-1}$ (200 SCCM) with an uncertainty on the flow measurement of 0.8% of the reading + 0.2% of full scale,
as stated by the manufacturer and confirmed by gravimetric flow calibrations performed in our laboratory. The MFCs (MC-200SCCM-D) were supplied by Alicat Scientific. The column outlet flow was measured by a MFM, with the same full scale and uncertainty as the MFCs. A zero-dead-volume multi-position valve (MPV-1) was used to switch the column feed gas between helium and the pure or mixed gas feed (N₂, CH₄, and He). A second zero-dead-volume multi-position valve (MPV-2) allowed the column containing the adsorbent to be bypassed.

Adsorption experiments were performed with constant column outlet pressures from 104.0 to 792.9 kPa, controlled by BPR-2. Another back-pressure regulator (BPR-1) was used at the vent of MPV-1 to prevent back-flow from the column whenever MPV-1 was actuated. The pressures at the inlet and outlet of the column were measured by independent quartz-crystal pressure transducers (QPT-1 and QPT-2), each with a full scale of 1380 kPa and a specified uncertainty over this range of 0.1 kPa.

The column effluent composition was measured using a mass spectrometer (MS, Stanford Research Systems QMS-100) through a sample capillary attached to a tee on the main flow line from the MFM. This tee configuration had two main purposes:

1. It ensured that the MFM always operated at atmospheric pressure, which decreased the need for pressure corrections of the MFM reading.

2. It controlled the sample flow to the MS within the range $1 \times 10^{-6}$ to $2 \times 10^{-6}$ mol s⁻¹ (as well as protecting the MS from overpressure) when the outlet flow from the column varied from $4 \times 10^{-6}$ to $136 \times 10^{-6}$ mol s⁻¹.

The MS had a mass range of 0 to 100 atomic mass units, a manufacturer-specified composition uncertainty of 1 mol %, and a response time
of less than 0.2 s (once gas entered the inlet of the MS). The uncertainty in the composition measurement was verified by preparing gas mixtures by varying the ratio of flows of He, N₂, and CH₄ through MFC-2, MFC-3, and MFC-4 via the column bypass direct to the MS. Further testing was performed by flowing a gravimetrically prepared mixture of 0.505N₂ + 0.495CH₄ through the MS. The gas mixture was supplied by BOC and had an estimated uncertainty of 0.2 mol %.

The volume of each section of the apparatus outside the column that contributed to the gas residence time was estimated by dimensional measurements of all components in the flow path. The BPRs and MFM were disassembled to acquire the necessary dimensional measurements of their internal volumes. The volume between MPV-1 and the column inlet was calculated to be 13.7 ± 0.4 cm³, and the volume between the column outlet and the control valve of BPR-2 was calculated to be 16.4 ± 0.4 cm³. The volume between the control valve of BPR-2 and the inlet of the MS capillary tube was determined to be 3.0 ± 0.1 cm³; this volume was at atmospheric pressure during all adsorption experiments. The volume of the 30 μm internal diameter MS capillary tube was assumed to be negligible. Thus, the total volume of the system excluding the column was estimated to be 33.1 ± 0.6 cm³.

To confirm this calculated volume, residence time measurements were made with the column removed at three different flow rates and at atmospheric pressure. The volume calculated from the residence time measurements was 36 ± 3 cm³. Although the apparatus void volume is not needed for the determined equilibrium adsorption capacities presented here, it can be used in conjunction with the packed column void volume to verify the volume of He displaced during each experiment. Verifying the amount of displaced He in each experiment establishes further confidence in the determined equilibrium adsorption capacity.
In this DCB apparatus, the effluent MFM used was of the orifice-plate type in which a pressure drop measured across a unique internal restriction, known as a laminar flow element, is used to determine the mass flow rate from an assumed gas viscosity. The flow of effluent gas mixtures can be determined with this type of meter by correcting the apparent flow rate, by the ratio of the mixture viscosity to that of the assumed gas viscosity, if the composition of the effluent gas mixture is known. The MFM used was factory calibrated for He and operated in ‘He mode’ so that the apparent flow rate corresponded to that for a gas with the viscosity of He. Then, the MS measurements of the effluent composition were used to determine the ratio of the He viscosity to that of the gas mixture's using an empirical correlation:

\[
\frac{\eta_{\text{He}}}{\eta_{\text{mix}}} = \frac{\eta_{\text{He}}}{\eta_i} = \sum_i y_i \left( a_{ij} y_j + b_{ij} y_j^2 \right)
\] (3.1)

Here, \( y_i \) is the mole fraction of component \( i \), \( \eta_i \) is the viscosity of pure component \( i \), and the \( a_{ij} \) and \( b_{ij} \) are empirical parameters determined from calibration experiments. The functional form of Equation (3.1) is based on the gas mixture viscosity correlation described by Assael et al. [79]; however, it was necessary to extend the correlation to achieve an adequate representation of viscosity ratios over a wide range of compositions. The empirical parameters \( a_{ij} \) and \( b_{ij} \) for N\(_2\), CH\(_4\), and He were determined by regression of the effluent flow rate (measured by the MFM and corrected by Equation (3.1)) to force agreement with the inlet mixture flow rate set using MFC-2, MFC-3, and MFC-4 through the column bypass loop. These flow calibration experiments with mixtures also allowed the uncertainty of composition measurements made with the MS to be checked. In
total 304 experiments with pure, binary, and ternary mixtures of N₂, CH₄, and He were conducted resulting in 12 empirical parameters determined by a least squares regression. It is important to note that Equation (3.1) was only used for the purpose of interpolating viscosity ratios as a function of composition and that the parameters $a_{ij}$ and $b_{ij}$ are not general in nature. The time delay between the MFM and the MS had a negligible effect on the efficacy of the viscosity ratio correction because of the small tube volume between these instruments (<0.3 cm³) and the fast response time of the MS. The combined uncertainties of the viscosity ratio correlation and the MS composition measurement resulted in the estimated uncertainty of the MFM reading for mixtures increasing to 1.6 % of the reading + 0.2 % of full scale.

A fully automated data acquisition and control system implemented in LabVIEW 8.2.1 [80] was used to actuate the valves, write the set points for the MFCs and BPRs, and monitor and record readings from all of the instruments. The measured mass flows and compositions were sampled once a second, while column residence times typically ranged from 10 to 1000 s. These two time scales are critical to the full analysis of the dynamic data. The thermometers monitoring the internal bed temperature along the column and the pressure transducers (QPT-1 and QPT-2) were also sampled once a second.

All gases used in this work were supplied by BOC who stated the following fractional purities: N₂ 99.999 %, CH₄ 99.995 %, and He 99.999 %. The estimated uncertainty of the adsorption measurements due to gas purity was assumed to be negligible. The adsorbents used to demonstrate the operation of this system were a synthetic H⁺ mordenite HSZ-640HOA provided by TOSOH Corporation (Japan) and a synthetic Na⁺ 13X zeolite provided by Shanghai MLC (China). Adsorbents were regenerated in a separate vessel under vacuum (10 Pa) at 573 K for 24 h and
the regeneration vessel was backfilled with \( \text{N}_2 \) before loading into the adsorption column. The mass of the regenerated mordenite and 13X samples used in the adsorption experiments were 29.036 \( \pm \) 0.005 and 26.455 \( \pm \) 0.005 g, respectively.

### 3.5 Method and analysis

The regenerated adsorbent was loaded into the column quickly to minimize the exposure of the (N\(_2\) saturated) adsorbent to the air. A 20 \( \mu \)m filter washer was fitted at the outlet end of the column, and the regenerated adsorbent was poured into the (inverted) column. The column was tapped gently to settle the pellets in the bed and around the three bed thermometers (the sensors remained in place during the loading). The packed column was then sealed with a second 20 \( \mu \)m filter washer fitted at the inlet and connected to the ICL and OHL (and pressure transducers) inside the oven. Before each adsorption experiment, the adsorbent was degassed \textit{in situ} with a \( 1.36 \times 10^{-4} \text{ mol s}^{-1} \) flow of He for a minimum of three hours at 301.7 K. Complete degassing was assumed when the effluent composition was measured to be >99.99 mol% He with the total flow reduced to \( 1.7 \times 10^{-6} \text{ mol s}^{-1} \). The reduced flow increased the fraction of any species in the effluent still desorbing and improved the ability to resolve whether the rate of desorption had reached a sufficiently low level.

Once the adsorbent was degassed, the first step in the adsorption experiment was to actuate MPV-2 to bypass the column and to set BPR-1 and BPR-2 to the required pressures. The feed gas mixture was prepared using MFC-2, MFC-3, and MFC-4. Then MPV-1 was actuated to direct the feed gas flow through the bypass to the MFM and the MS. The flow and composition readings from these downstream instruments were recorded at the conditions at which the experiment was to be performed. These values were compared to the MFM and the MS readings at the
conclusion of an adsorption experiment to verify the system had attained equilibrium. Generally a small offset was observed between the measured inlet and the effluent flow rates when the column was in the bypass mode and was evident in the raw data once the system had reached equilibrium (for example, as shown in Figure 3-2 (a)). This measurement offset was within the uncertainty of the mass flow instruments; nevertheless, the small difference was accounted for during the integration of the material balances described below by a normalisation procedure. Any offset was eliminated during data analysis by multiplying all the effluent flow meter readings acquired during the adsorption measurement by the ratio of the apparent inlet and effluent flows obtained with the column bypassed. The standard deviation of the inlet to outlet flow ratios for the measurements was 0.017. Measurements made with the MFCs operating at pressures above 110 kPa usually resulted in larger offsets of up to 5 %.

Following the initial comparisons of the inlet and effluent instrumentation using the bypass loop, MPV-1 and MPV-2 were actuated to establish a flow of He through the column and allow BPR-2 to reach its set point before the adsorption measurement commenced. Once the system had stabilised and a steady pressure gradient was observed along the column, the adsorption measurement was initiated by actuating MPV-2 to direct the feed gas mixture into the column. In a typical experiment, the feed gas took between 4 and 180 s to reach the adsorbent bed, depending on the column pressure and temperature, after MPV-2 was actuated and, once adsorption of feed gas components began, the change in effluent flow rate measured at the MFM was observed with virtually no delay. An example of the rapid change in effluent flow rate upon the feed gas reaching the column is shown in Figure 3-2 (a): the change in gas velocity due to adsorption at the start of the column propagated at the speed of sound to the MFM. As the
adsorbent approached its saturation condition the total effluent flow rate increased and then approached the inlet flow rate asymptotically. At approximately this time, the composition breakthrough would be observed with the MS and, eventually, the outlet composition measured by the MS would become equal to the feed composition determined by the MFCs, as shown in Figure 3-2 (b). Depending on the average gas velocity through the column, the composition breakthrough front was detected at the MS about 6 to 600 s after exiting the outlet of the column.

Upon completion of the adsorption step, MPV-1 was switched so that He from MFC-1 flowed into the column initiating the desorption process. Desorption data were collected from each experiment; however, only the adsorption data were used to calculate the equilibrium adsorption capacities because, as discussed by Guntuka et al. [64], the variations in effluent flow rate and composition during desorption are near or below the detection limits of the respective instruments. This observation is consistent with the results of our uncertainty analysis below, which indicates that adsorption parameters determined from dynamic desorption experiments will have much larger uncertainties than those determined from adsorption experiments.
Figure 3-2: Dynamic breakthrough profile for the adsorption of CH₄ on mordenite at 104 kPa, 301.9 K. (a) Column feed and effluent flow rates. (b) Effluent mole fraction compositions. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Equilibrium adsorption capacities and selectivities were derived from the experimental data through a material balance analysis:

\[ \text{moles in} - \text{moles out} = \text{accumulation} \]  

(3.2)

where

\[ \text{moles in} = \int_{t'=t_0}^{t} f_i \, dt' \]  

(3.3)

\[ \text{moles out} = \int_{t'=t_0}^{t} F y_i \, dt' \]  

(3.4)

\[ \text{accumulation} = \left[ n_i^{(\text{gas})} + n_i^{(\text{ads})} \right]_{t'} - \left[ n_i^{(\text{gas})} + n_i^{(\text{ads})} \right]_{t_0} = \left[ V_{\text{gas}} \rho_i \right]_{t'} - \left[ V_{\text{gas}} \rho_i \right]_{t_0} + m q_{\text{ex},i}(t) \]  

(3.5)

In Equations (3.2) to (3.4), \( f_i \) is the molar flow of component \( i \) into the column (determined by the MFCs); \( F \) is the total molar flow of effluent from the column (measured by the MFM); \( y_i \) is the mole fraction of component \( i \) at the MFM outlet (measured by the MS); and \( t_0 \) is the time at which the feed gas is directed into the column. In Equation (3.5), \( n_i^{(\text{gas})} \) is the number of moles of component \( i \) in the gas phase within the DCB apparatus void volumes, \( n_i^{(\text{ads})} \) is the number of moles of component \( i \) in the adsorbed phase, \( V_{\text{gas}} \) is the volume in the column occupied by the gas phase, \( \rho_i \) is the molar density of component \( i \) in the gas phase, \( m \) is the mass of adsorbent, and \( q_{\text{ex},i} \) is the excess adsorption capacity of component \( i \) in the adsorbed phase in moles per unit mass of adsorbent. At the start of the adsorption experiment it is assumed that the number of moles of component \( i \) adsorbed is zero \( (q_{\text{ex},i}(t_0) = 0) \). Substituting equations (3.3) to (3.5) into (3.2) gives an expression valid at any time during the adsorption experiment:
\[ \int_{t'=t_0}^{t} f_i \, dt' - \int_{t'=t_0}^{t} F_y \, dt' = (n_{i_0}^{(\text{gas})} - n_{i_0}^{(\text{gas})}) + m q_{c_{ex}}(t) = \Delta n_{i}^{(\text{gas})} + m q_{c_{ex}}(t) \quad (3.6) \]

The determination of equilibrium adsorption capacity from a breakthrough experiment requires several conditions to be met:

- The feed and effluent flow rates and compositions should be equal.
- The pressure and temperature along the adsorbent bed should be uniform and non-varying.

Adsorption is an exothermic process, and in our experiments with an undiluted gas feed, the heat released often resulted in temperature rises in the bed of more than several Kelvin. Figure 3-3 shows the measured bed temperatures during an adsorption experiment conducted near ambient conditions.

![Figure 3-3: Temperatures measured by the column thermometers PRT-1, PRT-2, and PRT-3 (see Figure 3-1) during the dynamic adsorption of CH₄ on mordenite at 104 kPa, 301.9 K, corresponding to the data shown in Figure 3-2. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.](image)
During the experiment it is apparent that the assumption that the system is isothermal is not valid, and the inclusion of an energy balance term in Equation (3.6) would be necessary to more accurately describe the thermal effects of adsorption in a time dependent model. However, the bed temperatures ultimately returned to their initial conditions by the completion of the experiment (as shown in Figure 3-3) and therefore, for the purpose of calculating equilibrium adsorption capacities, the assumption of isothermal behaviour was justified. The bed temperature measurements were also used to reject data when this thermal condition was violated on occasion because of air-bath instability during the experiment.

Under the assumptions of constant pressure and ideal gas behaviour, the component material balance in Equation (3.6) is subject to the constraint

\[ n_{tot}^{(gas)} = \text{constant}, \]

where \( n_{tot}^{(gas)} \) is the total number of moles in the gas phase. Initially the bed is filled with He and under the assumption that He does not adsorb, which is justified at the temperatures and pressures of these experiments [81]. The change in the amount of He in the gas phase once steady state is reached at \( t_{eq} \) is:

\[
\Delta n_{He}^{(gas)} = \int_{t'=t_0}^{t} f_{He} \, dt' - \int_{t'=t_0}^{t} Fy_{He} \, dt'
\]

(3.7)

The amount of gas phase He in the DCB apparatus at the initial condition includes the He in the internal pore spaces of the adsorbent pellets (pore volume or intraparticle volume), in the interparticle void volumes, and in the voids of the apparatus outside the packed column. Although the equilibrium adsorption capacities reported in this work can be calculated directly from Equations (3.6) to (3.10) using the component flow rate data without the need to calculate void volumes directly, the determination of the void volumes of the DCB apparatus
allows a consistency check to be conducted on the amount of He displaced in each experiment. Furthermore, the accounting of the void volumes in the DCB apparatus is required for the kinetic analysis of the breakthrough curves, which is discussed in Chapter 5.

The He in the gas phase is replaced with the other components in the gas phase:

\[
\sum_{j \neq \text{He}} n_j^{(\text{gas})} = \Delta n_{\text{He}}^{(\text{gas})} \rightarrow n_j^{(\text{gas})} = y_j^* \Delta n_{\text{He}}^{(\text{gas})}
\]  

(3.8)

Here \( y_j^* \) is gas phase mole fraction for component \( j \) once equilibrium has been reached, and the index \( j \) refers to any component other than He. Thus, at steady state the component material balance in Equation (3.6) becomes:

\[
mq_{\text{ex},j}^* = \int_{t'=t_0}^{t_f} f_j \, dt' - \int_{t'=t_0}^{t_f} F y_j \, dt' \quad y_j^* \int_{t'=t_0}^{t_f} f_{\text{He}} dt' - \int_{t'=t_0}^{t_f} F y_{\text{He}} dt'
\]  

(3.9)

where \( q_{\text{ex},j}^* \) is the excess adsorption capacity of component \( j \) at equilibrium. Summing Equation (3.9) over all components leads to a statement of total material balance at steady state:

\[
mq_{\text{ex,tot}}^* = \int_{t'=t_0}^{t_f} (f - F) \, dt'
\]  

(3.10)

Here \( f = \sum_i f_i \) is the total molar flow into the column and \( q_{\text{ex,tot}}^* \) is the total number of moles adsorbed per unit mass of adsorbent. For a feed gas with a single adsorbate, Equation (3.10) can be used to determine the excess adsorption capacity, without reference to the composition of the effluent flow.
To convert the excess adsorption capacity to the absolute adsorption capacity, \( q_{\text{abs},i}^* \), the density of the adsorbed phase mixture was estimated using an ideal mixing rule and predictions for the densities of the adsorbed phase for pure compounds. The densities of the pure adsorbed phases of \( \text{N}_2 \) and \( \text{CH}_4 \) were estimated to be 0.701 and 0.354 g cm\(^{-3}\), respectively, using the Ono-Kondo model [82]. The molar density of the gas mixture was determined at the measured pressure, temperature, and composition, from the GERG-2004 equation of state [83] as implemented in the software REFPROP 8.0 [16].

Equation (3.9) represents the component material balance across the column in integral form and can only be used to determine equilibrium adsorption properties from dynamic column data once the system has reached steady state. To determine \( q_{\text{ex},i}(t) \) and extract the mass transfer coefficients and heat transfer parameters, which are important inputs to process design, a full dynamic model of the DCB apparatus is needed. Such a model requires the solution of the partial differential equations describing the component material, momentum and energy balances as a function of time and position along the packed column. While such models exist in the literature [71, 84, 85], they must be adapted to the particular details of this apparatus; for example, to account for the gas residence time and effects of dispersion in the tubes and fittings external to the packed column. For this DCB apparatus, the volume of the sections between MPV-1 and BPR-2 have the most effect on the observed gas residence times because in these sections the gas pressure could be up to 1000 kPa, and thus these sections could store up to 10 times their standard volume.

The DCB apparatus provides a rapid procedure for comparing candidate adsorbents for a given gas separation application, by allowing the direct
measurement of selectivity. An adsorbent’s equilibrium selectivity, $\alpha_{ij}$ for two components in a gas mixture ($i$ is the more adsorbed component and $j$ the less adsorbed component) is defined (for example, Saha et al. [86]):

$$\alpha_{ij} \equiv \left( \frac{x_i}{x_j} \right) \left( \frac{y_j}{y_i} \right)$$  \hspace{1cm} (3.11)

Here $x_i$ is the mole fraction of component $i$ in the adsorbed phase. This quantity can be measured directly using the DCB apparatus by flowing the gas mixture across the adsorbent until equilibrium is reached, and then determining the adsorbed phase mole fractions from the measured $q_{\text{abs},i}^*/q_{\text{tot}}^*$. Such measurements are quite difficult to make using static volumetric or gravimetric adsorption systems because a capacity to both stir and sample the vapour phase is required, such as in the system described by Watson et al. [87]. As a consequence of this difficulty, estimates of an adsorbent’s selectivity are frequently made on the basis of measured pure fluid capacities. For example, Gu and Lodge [88] and Jensen et al. [89] estimated so-called ‘inferred’ or ‘ideal’ selectivities, $(\alpha_{ij})_{\text{inf}}$, as in Equation (3.12), which are computationally simple to evaluate for equimolar mixtures. These can provide an initial indication of the potential of an adsorbent for a gas separation application; however, the inferred selectivities $(\alpha_{ij})_{\text{inf}}$ computed with Equation (3.12) do not account for competition between species for adsorption sites:

$$(\alpha_{ij})_{\text{inf}} = \left( \frac{q_{\text{pure},i}^*}{q_{\text{pure},j}^*} \right)$$  \hspace{1cm} (3.12)
More rigorous predictions of mixture selectivity can be made by using, for example, the IAST developed by Myers and Prausnitz [90], although such methods can be expensive in both measurement time and computational effort. Sufficient data must be acquired to regress reliably equilibrium adsorption capacity models for the two pure fluids at the temperature of interest, and then these models must be used iteratively in the evaluation of integrals used to equate spreading pressures. In contrast, the DCB apparatus can be used to readily determine equilibrium adsorption selectivities for a gas mixture with a single measurement, which is no more difficult than a pure fluid adsorption measurement at the same condition.

### 3.6 Quantitative estimation of uncertainty

Table 3-1 contains a list of the sources of measurement uncertainty associated with the dynamic column apparatus.

**Table 3-1: Component uncertainties associated with the dynamic breakthrough apparatus.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFM [with Equation (3.1)]</td>
<td>1.6 % of reading + 0.2 % of full scale</td>
</tr>
<tr>
<td>MFC</td>
<td>0.8 % of reading + 0.2 % of full scale</td>
</tr>
<tr>
<td>BPR</td>
<td>0.25 % of full scale</td>
</tr>
<tr>
<td>QPT</td>
<td>± 0.1 kPa</td>
</tr>
<tr>
<td>MS</td>
<td>± 1 mol%</td>
</tr>
<tr>
<td>PRT</td>
<td>± 0.2 K</td>
</tr>
<tr>
<td>Mass of adsorbent</td>
<td>± 5 mg</td>
</tr>
</tbody>
</table>

Of these uncertainty sources, the most significant is the measurement of the difference in mass flows entering and leaving the column. To estimate this quantitatively, it is convenient to define an average difference flow rate,
Then, with \( u(x) \) and \( u_r(x) \) denoting the absolute and relative uncertainties of a quantity \( x \), respectively, an error propagation analysis gives:

\[
\frac{u(q^*_{\text{ex, tot}})}{q^*_{\text{ex, tot}}} \leq \frac{u(\Delta f)}{\Delta f} \tag{3.13}
\]

because \( u_r(m) \geq u_r(\Delta f) \) and \( u_r(t_{eq} - t_0) \leq u_r(\Delta f) \). From Equation (3.10) and the definition of \( \Delta f \), its value can be calculated from difference in the inlet and effluent flow rates averaged over the time interval \( (t_{eq} - t_0) \):

\[
\Delta f = \langle f - F \rangle_{f=\text{const}} \rightarrow \Delta f = f - \langle F \rangle \tag{3.14}
\]

Here the angled brackets denote the time average. The second equality holds when the inlet flow to the column was held constant throughout the experiment, as was the case in this work. Thus:

\[
\frac{u(q^*_{\text{ex, tot}})}{q^*_{\text{ex, tot}}} \approx \frac{\sqrt{u(f)^2 + u(\langle F \rangle)^2}}{f - \langle F \rangle} \tag{3.15}
\]

It is apparent from Equation (3.15) that the uncertainty in the derived equilibrium capacity depends on the rate and magnitude of the adsorption. If \( F \) changes significantly and quickly (for example when sorption kinetics are fast), the uncertainty in the corresponding \( q^*_{\text{ex, tot}} \) determination will be much lower than if the variation in \( F \) is small and/or over a longer period (such as when sorption kinetics are slow). More importantly, the value of \( q^*_{\text{ex, tot}} \) and its uncertainty depend on the choice of \( t_{eq} \), yet a judgement is generally required because \( f \) and \( F \) approach each other asymptotically as the adsorption process approaches saturation. In
general there is a certain critical value $t^*_\text{eq}$ above which the value of $q^*_{\text{ex, tot}}$ determined from Equation (3.10) is insensitive; however, the larger the value $t_{\text{eq}}$ chosen, the greater the value of $u(q^*_{\text{ex, tot}})$. Conversely, a choice of $t_{\text{eq}}$ significantly below $t^*_\text{eq}$ will reduce the value of $u(q^*_{\text{ex, tot}})$ calculated with Equation (3.15) but lead to a systematic reduction in the estimate of $q^*_{\text{ex, tot}}$. For this reason, we evaluated $u(q^*_{\text{ex, tot}})$ using values of $t_{\text{eq}}$ such that the estimated uncertainty was about 30 to 100 % larger than the change in $q^*_{\text{ex, tot}}$ obtained with using $t^*_\text{eq}$. In practice, the return of the bed’s temperature profile to the initial condition can be used as a guide as to when $t^*_\text{eq}$ has been reached.

The uncertainty in the component equilibrium adsorption capacities determined with this DCB apparatus can be estimated in a similar way:

$$u(q^*_{\text{ex, j}}) \approx \sqrt{u(F_j)^2 + u(F^*_{\text{He}})^2 + u(y_jF^*_{\text{He}})^2}$$

$$\frac{q^*_{\text{ex, j}}}{F_j} - \frac{y_jF^*_{\text{He}}}{F_{\text{He}}}$$

(3.16)

Here, $F_j = y_jF$ is the effluent molar flow of component $j$ and $F_{\text{He}}$ is the effluent molar flow of He. The additional uncertainty associated with the measurement of the gas composition will in general mean that $u(q^*_{\text{ex, j}}) > u(q^*_{\text{ex, tot}})$; however, the $y_j$ are subject to a normalisation constraint and thus $u(q^*_{\text{ex, j}})$ will depend upon the number of species in the feed gas and in the case of a pure fluid adsorbate, the uncertainties calculated using Equations (3.15) and (3.16) are equal.

### 3.7 Results and discussion

The dynamic column breakthrough apparatus was used to test and compare two zeolite adsorbents for the separation of N$_2$ + CH$_4$ gas mixtures that have been
studied by others: mordenite and 13X. Pure fluid adsorption capacities were measured first at 301.9 K. Pure fluid measurements of the adsorbent with the largest capacities at this temperature (13X) were then conducted at 229.2 K. In addition, measurements with a gas mixture were conducted to determine whether the adsorbent’s equilibrium selectivities were comparable with those inferred from the pure fluid measurements. The measured values of \( q_{ex,N_2}^* \) and \( q_{ex,CH_4}^* \) for the pure fluids are listed in Table 3-2 for mordenite and Table 3-3 for 13X. The measured values of \( q_{ex,N_2}^* \) and \( q_{ex,CH_4}^* \) for the \( N_2 + CH_4 \) mixtures on both zeolites are listed in Table 3-4. Absolute adsorption capacities, \( q_{abs,i}^* \), for pure fluids and the \( N_2 + CH_4 \) mixtures are also listed in Table 3-2, Table 3-3, and Table 3-4. At the measurement conditions in this study the difference between absolute and excess adsorption capacities was small with \( \left( q_{abs,i}^* - q_{ex,i}^* \right) / q_{ex,i}^* \leq 0.02 \).

Dynamic data acquired during a typical pure fluid experiment are shown in Figure 3-2; analysis of the data acquired at each fixed pressure and temperature with Equation (3.10) leads to the pure fluid adsorption capacities listed in Table 3-2 and Table 3-3. The pure fluid equilibrium capacities for mordenite measured on the DCB apparatus are compared in Figure 3-4 with the volumetric adsorption measurements reported by Delgado et al. [91] and with those made in our own laboratory by Jensen et al. [89]. The latter authors measured the equilibrium adsorption capacity of the same H⁺ mordenite sample studied in this work at 303.15 K and pressures from 5 to 119.5 kPa. Delgado et al. [91] used a volumetric system to obtain equilibrium adsorption data for \( N_2 + CH_4 \) on H⁺ mordenite synthesised from ion-exchanged Na⁺ mordenite supplied by CU Chemie Uetikon AG. Their experiments were performed at 279, 293, and 308 K at pressures to 2000 kPa. From their data, Delgado et al. [91] determined parameters
for Toth models of mordenite’s N₂ + CH₄ adsorption capacities over this range of conditions. The predictions of Delgado et al.’s [91] Toth models are shown in Figure 3-4 (a) at the experimental conditions corresponding to those measured in this work. In Figure 3-4 (a) the data of Jensen et al. [89] were corrected to equivalent capacities at 301.9 K using their reported enthalpy of adsorption. The deviations of our data, and those of Jensen et al. [89] from the predictions of the Toth models developed by Delgado et al. [91], are shown in Figure 3-4 (b).

Table 3-2: Equilibrium excess (q^*_{ex,i}) and absolute (q^*_{abs,i}) adsorption capacities of N₂ + CH₄ on mordenite at 301.9 K measured on the DCB apparatus with pure fluids. The uncertainty u(q^*_{ex,i}) in the adsorption capacity measurement is also reported.

<table>
<thead>
<tr>
<th>y_i</th>
<th>P [kPa]</th>
<th>q^*_{ex,i} [mmol g⁻¹]</th>
<th>q^*_{abs,i} [mmol g⁻¹]</th>
<th>u(q^*_{ex,i}) [mmol g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>106.2</td>
<td>0.17</td>
<td>0.17</td>
<td>0.04</td>
</tr>
<tr>
<td>N₂</td>
<td>276.0</td>
<td>0.37</td>
<td>0.37</td>
<td>0.04</td>
</tr>
<tr>
<td>N₂</td>
<td>447.8</td>
<td>0.54</td>
<td>0.54</td>
<td>0.05</td>
</tr>
<tr>
<td>N₂</td>
<td>620.1</td>
<td>0.68</td>
<td>0.69</td>
<td>0.06</td>
</tr>
<tr>
<td>N₂</td>
<td>792.0</td>
<td>0.79</td>
<td>0.80</td>
<td>0.06</td>
</tr>
<tr>
<td>CH₄</td>
<td>104.0</td>
<td>0.51</td>
<td>0.51</td>
<td>0.06</td>
</tr>
<tr>
<td>CH₄</td>
<td>275.8</td>
<td>0.93</td>
<td>0.93</td>
<td>0.06</td>
</tr>
<tr>
<td>CH₄</td>
<td>447.9</td>
<td>1.18</td>
<td>1.19</td>
<td>0.07</td>
</tr>
<tr>
<td>CH₄</td>
<td>619.8</td>
<td>1.33</td>
<td>1.35</td>
<td>0.07</td>
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<tr>
<td>CH₄</td>
<td>791.7</td>
<td>1.46</td>
<td>1.48</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Table 3-3: Equilibrium excess (q^*_{ex,i}) and absolute (q^*_{abs,i}) adsorption capacities of N₂ + CH₄ on zeolite 13X at 301.9 K and 229.2 K measured on the DCB apparatus with pure fluids. The uncertainty u(q^*_{ex,i}) in the adsorption capacity measurement is also reported.
<table>
<thead>
<tr>
<th>$y_i$</th>
<th>T [K]</th>
<th>P [kPa]</th>
<th>$q_{\text{ex,i}}$ [mmol g$^{-1}$]</th>
<th>$q_{\text{abs,i}}$ [mmol g$^{-1}$]</th>
<th>$u(q_{\text{ex,i}})$ [mmol g$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>301.9</td>
<td>106.8</td>
<td>0.29</td>
<td>0.29</td>
<td>0.05</td>
</tr>
<tr>
<td>N$_2$</td>
<td>301.9</td>
<td>792.9</td>
<td>1.34</td>
<td>1.36</td>
<td>0.10</td>
</tr>
<tr>
<td>N$_2$</td>
<td>229.2</td>
<td>792.6</td>
<td>3.28</td>
<td>3.33</td>
<td>0.12</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>301.9</td>
<td>104.8</td>
<td>0.50</td>
<td>0.50</td>
<td>0.06</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>301.9</td>
<td>792.5</td>
<td>2.09</td>
<td>2.13</td>
<td>0.14</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>229.2</td>
<td>792.3</td>
<td>3.89</td>
<td>3.97</td>
<td>0.19</td>
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Table 3-4: Excess ($q^*_{\text{ex}}$) and absolute ($q^*_{\text{abs}}$) adsorption capacities determined from the DCB measurements with $N_2 + CH_4$ mixtures and predicted with the Ideal Adsorbed Solution Theory ($q^*_{\text{IAST}}$) using pure fluid Toth model parameters for mordenite and 13X reported by Delgado et al. [91] and Cavenati et al. [37], respectively. Also listed are the adsorption selectivities ($\alpha_{CH_4,N_2}$) of CH$_4$ over $N_2$ on mordenite and 13X measured with $N_2 + CH_4$ mixtures on the DCB ($\alpha_{CH_4,N_2,\text{meas}}$) and predicted with the IAST models ($\alpha_{CH_4,N_2,\text{IAST}}$). The average uncertainties in ($\alpha_{CH_4,N_2,\text{meas}}$) for mordenite and 13X are ± 0.4 and ± 0.2, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T</th>
<th>P</th>
<th>$q^*_{\text{ex},N_2}$</th>
<th>$q^*_{\text{ex},CH_4}$</th>
<th>$u(q^*_{\text{ex,tot}})$</th>
<th>$q^*_{\text{abs},N_2}$</th>
<th>$q^*_{\text{abs},CH_4}$</th>
<th>$q_{\text{IAST},N_2}$</th>
<th>$q_{\text{IAST},CH_4}$</th>
<th>($\alpha_{CH_4,N_2,\text{meas}}$)</th>
<th>($\alpha_{CH_4,N_2,\text{IAST}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mordenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>301.9</td>
<td>105.1</td>
<td>0.09</td>
<td>0.26</td>
<td>0.06</td>
<td>0.09</td>
<td>0.26</td>
<td>0.08</td>
<td>0.30</td>
<td>3.43</td>
<td>3.88</td>
</tr>
<tr>
<td></td>
<td>301.9</td>
<td>275.8</td>
<td>0.15</td>
<td>0.57</td>
<td>0.06</td>
<td>0.15</td>
<td>0.57</td>
<td>0.16</td>
<td>0.61</td>
<td>3.65</td>
<td>3.93</td>
</tr>
<tr>
<td></td>
<td>301.9</td>
<td>447.9</td>
<td>0.21</td>
<td>0.75</td>
<td>0.08</td>
<td>0.21</td>
<td>0.76</td>
<td>0.21</td>
<td>0.81</td>
<td>3.55</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>301.9</td>
<td>620.0</td>
<td>0.26</td>
<td>0.87</td>
<td>0.08</td>
<td>0.26</td>
<td>0.88</td>
<td>0.24</td>
<td>0.96</td>
<td>3.46</td>
<td>3.98</td>
</tr>
<tr>
<td></td>
<td>301.9</td>
<td>791.8</td>
<td>0.31</td>
<td>0.92</td>
<td>0.08</td>
<td>0.32</td>
<td>0.93</td>
<td>0.27</td>
<td>1.06</td>
<td>3.30</td>
<td>3.98</td>
</tr>
<tr>
<td>13X</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>301.9</td>
<td>106.0</td>
<td>0.14</td>
<td>0.25</td>
<td>0.06</td>
<td>0.14</td>
<td>0.25</td>
<td>0.13</td>
<td>0.30</td>
<td>1.75</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>301.9</td>
<td>792.9</td>
<td>0.59</td>
<td>1.18</td>
<td>0.15</td>
<td>0.60</td>
<td>1.20</td>
<td>0.60</td>
<td>1.40</td>
<td>2.03</td>
<td>2.28</td>
</tr>
<tr>
<td></td>
<td>229.2</td>
<td>792.8</td>
<td>1.12</td>
<td>2.56</td>
<td>0.29</td>
<td>1.15</td>
<td>2.61</td>
<td>1.65</td>
<td>3.35</td>
<td>2.31</td>
<td>2.03</td>
</tr>
</tbody>
</table>
Figure 3-4: Adsorption capacity of $N_2 + CH_4$ on mordenite at 302 K measured with pure fluids using the DCB apparatus. (a) Equilibrium capacities measured in this work and by Jensen et al. [89] are shown together with capacities calculated using the Toth isotherm parameters reported by Delgado et al. [91]. (b) Deviations between the measured capacities and those calculated using the Toth isotherm models.
The $N_2$ equilibrium capacities measured with the DCB apparatus are in excellent agreement with those predicted using the Toth model from Delgado et al. [91], with all the deviations being within the estimated experimental uncertainty of the dynamic measurements. The deviations of the measured $CH_4$ equilibrium capacities from the model are slightly larger, and are about twice the estimated uncertainty of our data. Unfortunately, Delgado et al. [91] did not report their actual data or associated uncertainties, and only reported the parameters of the Toth models fit to their data. Thus it is not possible to determine whether the deviations from the Toth model are smaller than the combined uncertainties of the data and the model. The consistency of the DCB data with those of Jensen et al. [89] for both the $N_2 + CH_4$ equilibrium capacities of mordenite is within the experimental uncertainty of this work.

In Figure 3-5 we compare the equilibrium $N_2 + CH_4$ capacities of 13X measured for pure fluids on the DCB apparatus to the adsorption capacities calculated from the Toth model parameters published by Cavenati et al. [37]. Cavenati et al. [37] measured the adsorption capacities of $N_2 + CH_4$ on a 13X sample from CECA (France) at 298, 308, and 323 K and pressures to 5000 kPa using a static volumetric adsorption apparatus. At 301.9 K, the capacities measured with the DCB apparatus at pressures near 105 kPa are consistent with the results of Cavenati et al. [37] within the experimental uncertainty. At 793 kPa, the $N_2 + CH_4$ capacities measured with the DCB apparatus deviate from the Toth model predictions by 1.2 and 2.7 times the experimental uncertainty, respectively. Again, it is difficult to assess the magnitude of these deviations because Cavenati et al. [37] did not estimate the uncertainty of their data or report the average deviation of their data from the best-fit models. Nevertheless, the level of agreement observed between data sets is generally as good as can be expected for
experimental measurements of adsorption using different instruments, techniques and adsorbent samples. Furthermore, it is likely that some of these differences are due to the precise nature of the adsorbent samples and their history prior to measurement.

Figure 3-5: Adsorption capacity of N$_2$ + CH$_4$ on 13X at 302 K and 229 K measured with pure fluids using the DCB apparatus. The data points were measured in this work. Toth parameters from Cavenati et al. [37] were used to calculate the model curves: the dashed curves correspond to an extrapolation of the models, which were regressed to data measured in the range 298 K to 323 K.

The pure fluid DCB measurements at 301.9 K indicated that 13X has a larger equilibrium capacity for both N$_2$ + CH$_4$ than mordenite. Extrapolating the Toth adsorption capacity models of Cavenati et al. [37] for 13X to 229.2 K suggests that the N$_2$ + CH$_4$ capacities would increase from their values at 301.9 K by a factor of 2.9 and 2.2, respectively at a pressure of 793 kPa. Such increases could be helpful in reducing the necessary size of a 13X PSA tower used in a gas separation process.
To test this prediction, dynamic adsorption measurements were conducted with the 13X zeolite at 229.2 K and 793 kPa. In Figure 3-5, the results of these low temperature pure fluid measurements are shown together with the capacities predicted using the extrapolated Toth models. The ratios of the measured values of $q_{CH_4}^*$ and $q_{N_2}^*$ at the two temperatures were 1.9 and 2.4, respectively. For both fluids the actual increases in capacity are 20% below the increases predicted with the extrapolated models, while the fractional differences between the measured and predicted capacities were -30% for N$_2$ and -40% for CH$_4$. This example demonstrates the dangers of extrapolating adsorption capacity models down in temperature, in this case about 70 K below the lowest temperature measurements of Cavenati et al. [37]. As a corollary, it demonstrates the importance of low temperature adsorption capacity measurements if the potential advantages of operating a PSA process at temperatures accessible in cryogenic gas plants are to be assessed reliably.

Selectivity is the other key adsorbent property that needs to be quantified for gas separation applications and, while estimates from pure fluid measurements are possible, measurements with mixtures are crucial if selectivity is to be determined accurately. Figure 3-6 shows characteristic dynamic data for the effluent gas flow and composition for the adsorption of a 0.53N$_2$ + 0.47CH$_4$ gas mixture on mordenite at 792 kPa and 301.9 K. The slightly increased noise apparent in the effluent flow rate in comparison with that shown in Figure 3-2 is due to the action of the BPR, which maintained the column at the higher pressure (the time series for the pressures at each end of the column are also shown plotted on the right axis of Figure 3-6 (a)). Analysis of the dynamic mixture data such as those shown in Figure 3-6 using Equation (3.9) enable component and total equilibrium adsorption capacities to be determined. Figure 3-7 shows these
capacities for the set of $yN_2 + (1-y)CH_4$ mixtures, with $y = 0.51 \pm 0.02$, in equilibrium with mordenite at 301.9 K as a function of mixture pressure.

Figure 3-6: Dynamic adsorption of 0.53N$_2$ + 0.47CH$_4$ on mordenite at 792 kPa, 301.9 K. (a) Column effluent flow rate (left axis) and pressures at each end of column (right axis). (b) Effluent mole fraction compositions. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
The total and component adsorption capacities for N₂ and CH₄ from these gas mixtures are listed in Table 3-4. Also shown are the predicted adsorbed capacities for each component calculated using the IAST, which was implemented using the algorithm of Valenzuela and Myers [51] together with the pure fluid Toth isotherm parameters of Delgado et al. [91] for mordenite and Cavenati et al. [37] for 13X. No parameters were adjusted within the IAST models. In most cases, the predictions of the adsorbed N₂ and CH₄ capacities are consistent with the values measured by the DCB apparatus within the experimental uncertainties. The largest difference between the measured adsorption capacity and the predictions of the IAST model was in the adsorption of N₂ + CH₄ on 13X at 229.2 K; however, the discrepancy of about 26 % in $q_{\text{ex, tot}}^*$ in this case is due principally to the low temperature extrapolation of the models used for pure fluid capacities (see Figure 3-5) rather than of the IAST itself. This emphasises how the predictions of the IAST model are sensitive to the uncertainties of the pure fluid adsorption isotherms, which increase significantly when models are extrapolated beyond the data to which they were regressed.

The selectivities, $\alpha_{\text{CH}_4, \text{N}_2}$, calculated using Equation (3.11) for mordenite and 13X are presented in Table 3-4, along with the selectivities predicted from the IAST models. The measured values of $\alpha_{\text{CH}_4, \text{N}_2}$ were approximately constant with pressure and temperature for both zeolites; the observed variations were comparable with the estimated uncertainty in the measured mixture selectivity. For mordenite at 301.9 K, $\alpha_{\text{CH}_4, \text{N}_2}$ had an average value of 3.5 ± 0.1, while for 13X the average was 2.0 ± 0.3. In a 2012 review by Rufford et al. [92], the equilibrium capacities and selectivities of 26 adsorbents were compared and tabulated. The largest equilibrium selectivity at 298 K and 100 kPa was 4.25 for MSC-3K-161, which is
greater than for both zeolite samples measured at these conditions in this study. Furthermore, the CH₄ capacity was 1.01 mmol g⁻¹, which is significantly greater than for both samples. This benchmark indicates that for both the 13X and mordenite zeolites, the equilibrium capacities and selectivities are unlikely to be sufficient for a large scale industrial gas separation process. The selectivities estimated using the IAST models based on the pure fluid isotherms were 7 to 20 % larger for the mordenite and up to 32 % larger for the 13X. These deviations again reflect the propagation of pure fluid adsorption isotherm uncertainties in the calculation of predicted selectivities and underscore the importance of conducting mixture measurements when screening and assessing adsorbents for gas separation applications.

Figure 3-7: Adsorption capacities for \( yN_2 + (1-y)CH_4 \) gas mixtures, with \( y = 0.51 \pm 0.02 \), in equilibrium with mordenite at 301.9 K.
3.8 Conclusion

In this work, a column breakthrough apparatus capable of multi-component adsorption measurements over a wide range of pressure and temperature was described. We also presented a detailed description of the experimental procedure and the methods of analysing the data to determine equilibrium capacities with quantitative uncertainties. Adsorption capacity data for the mordenite and 13X zeolites were presented to demonstrate the apparatus can be used to:

- Generate equilibrium isotherms for pure gases and mixtures.
- Rapidly compare adsorbents for a gas separation application based on capacity and selectivity.
- Test adsorbents with mixtures at low temperatures and high pressures. We also demonstrated that a reliance on pure fluid measurements to estimate equilibrium selectivities can result in significant errors.

The mordenite and 13X zeolites both showed preferential adsorption of CH$_4$ over N$_2$. At low temperatures the equilibrium capacity and selectivity of the 13X increased significantly; however, for both the 13X and mordenite zeolites the equilibrium capacities and selectivities are unlikely to be sufficient for a large scale industrial gas separation process.

3.9 Acknowledgements

The research was funded by Chevron Energy Technology Company, the Western Australian Energy Research Alliance and the Australian Research Council (Project LP0776928). One of us (PSH) also received scholarships from the Australia-China Natural Gas Technology Partnership Fund and the Australian
Petroleum Production and Exploration Association. We thank Craig Grimm for helping to construct the apparatus, as well as, Guillaume Watson, Brendan Graham, and Thomas Saleman for their contributions to the research, and Mike Johns and Brent Young for carefully reading the manuscript. We are grateful to TOSOH Corporation and Shanghai MLC for supplying the zeolites studied in this work.
Chapter 4

Screening adsorbents for $N_2 + CH_4$ separations
4.1 Overview

This chapter outlines principles, procedures, and outcomes from experiments designed to identify adsorbents that could be used to complete a preliminary evaluation of the proposed low temperature pressure swing adsorption (PSA) process. This investigation was targeted at identifying both a CH₄ equilibrium selective adsorbent and a N₂ kinetically selective adsorbent. In Chapter 2, an overview of the published data revealed that zeolites and activated carbons were the most common types of adsorbents used for the equilibrium separation of N₂ + CH₄, and that 4A zeolite, clinoptilolites, carbon molecular sieves, and titanosilicates displayed kinetic selectivity for N₂ over CH₄ [15, 42-45]. Seven commercially available, non-proprietary adsorbents, which were representative of the types of adsorbents identified in Chapter 2, were selected for experimental screening. Adsorption experiments were then performed on the selection of adsorbents at conditions conducive to the identification of adsorbents for use in a potential low temperature PSA process. The cohort of adsorbents tested was then compared based on equilibrium adsorption capacity, equilibrium selectivity, and kinetic behaviour, to identify the most promising CH₄ equilibrium selective and N₂ kinetically selective adsorbents.

4.2 Adsorbent selection

Table 4-1 lists the seven adsorbents selected for experimental screening. These were selected from the types of adsorbents previously found to be useful for the separation of N₂ + CH₄, on the basis that these would be the most likely to have adsorption properties that improve at low temperatures. The selection was limited by sample availability and constrained to commercially available, non-proprietary, samples.
Table 4-1: Adsorbents selected for screening measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Supplier</th>
<th>BET Surface Area [m² g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13X</td>
<td>Synthetic Zeolite (Na⁺)</td>
<td>Shanghai Mole Sieve Co.</td>
<td>600 [81]</td>
</tr>
<tr>
<td>Linde 4A</td>
<td>Synthetic Zeolite (Na⁺)</td>
<td>Sigma-Aldrich (Australia)</td>
<td>400 [81]</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Natural Zeolite</td>
<td>Zeolite Australia Pty. Ltd.</td>
<td>450# [93]</td>
</tr>
<tr>
<td>Chabazite</td>
<td>Natural Zeolite</td>
<td>Zeox Corporation (USA)</td>
<td>415 [89]</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Synthetic Zeolite (H⁺)</td>
<td>TOSOH Corporation (Japan)</td>
<td>343 [89]</td>
</tr>
<tr>
<td>Norit RB3</td>
<td>Activated Carbon</td>
<td>Norit (Singapore)</td>
<td>1100-1220 [94, 95]</td>
</tr>
<tr>
<td>MSC-3K-161</td>
<td>Carbon Molecular Sieve</td>
<td>Shirasagi (Japan)</td>
<td>523 [96]</td>
</tr>
</tbody>
</table>

# - unspecified measurement technique.

A key property common to all of the selected adsorbents is the presence of micropores. The IUPAC classification defines micropores as pores with widths <20 Å, mesopores with widths between 20 and 500 Å, and macropores as pores with widths >500 Å [97]. It is the presence of micropores in an adsorbent that generally facilitates the largest surface area adsorbents. Large surface areas are important as they generally result in more capacity to adsorb gas within the adsorbent. All other properties being equal, it is the microporous, high surface area adsorbents that exhibit the highest adsorption capacities [15, 34].

For the separation of N₂ + CH₄, adsorbents with pores bigger than the largest adsorbate molecule, CH₄ (3.8 Å), would be equilibrium controlled, adsorbing both N₂ + CH₄; these adsorbents would therefore be CH₄ selective. Rodríguez-Pérez et al. [98] found that most pores in Norit RB3 range between 5 and 20 Å, which means that this adsorbent is likely to be equilibrium selective. This pore range is consistent with most commercial activated carbons, which have high surface areas, high adsorption capacities, and which predominantly have pore sizes <25 Å [99, 100]. General 13X, chabazite, and H⁺ mordenite samples have effective pore sizes of around 10, 4.9, and 7.4 Å, respectively [101, 102]. Similarly to Norit RB3, these
Adsorbents are also likely to display equilibrium selectivity because their pore sizes are larger than that of CH₄. The effective pore size generally refers to the limiting size of the pore opening, or the smallest dimension between opposite walls that an adsorbate molecule can pass through [34]. The molecular diameter of the adsorbate molecule, used to compare against the adsorbent’s effective pore size, is generally described by an effective molecular diameter. The nature of effective descriptions of molecule and pore sizes means that predictions of access or exclusion of the adsorbate into the adsorbent pores are not always definitive.

As pore sizes within an adsorbent approach the molecular size of CH₄, diffusion of CH₄ through the adsorbent pores becomes impeded, resulting in N₂ (with a smaller molecular diameter, 3.6 Å) reaching the adsorption sites first, before ultimately being displaced by CH₄; this property is further enhanced in adsorbents with uniform pore size distributions [14, 15]. This behaviour describes kinetic separation, sometimes called partial molecular sieving, which is likely to be displayed in the 4A, clinoptilolite, and MSC-3K-161 adsorbents because their effective pore sizes are around 4, 3.5, and 3 to 4 Å, respectively [101, 103]. It is possible that the effective pore size of clinoptilolite may block both molecules completely; however, the published pore diameter is an effective value and is close enough to the molecular diameter of N₂ that it warrants testing. Carbon molecular sieves are materials that have a controlled distribution of pore sizes, primarily a narrow distribution of micropores <10 Å [104]. Rutherford and Do [103] found that Takeda 3A carbon molecular sieve, which is a different pellet size but has the same average micropore distribution as MSC-3K-161 [105], has micropores predominantly between 3 and 4 Å.

If an adsorbent’s pore sizes are between 3.6 and 3.8 Å, true molecular sieving of CH₄ can occur through complete steric hindrance of the CH₄ molecule. This may
be displayed in the MSC-3K-161 sample. Although 4A has an effective pore size above this range, it has been shown to display kinetic selectivity at low temperatures, which has been suggested to be the result of a contraction of the crystal structure, causing narrowing of the pore openings (discussed in Chapter 2) [14, 61, 62]. The 4A, clinoptilolite, and MSC-3K-161 samples have potential for partial or full molecular sieving at reduced temperatures.

This selection of adsorbents covers a range of the types of adsorbents likely to highlight the following adsorption behaviours at reduced temperatures:

- Increased adsorption capacity.
- Improved equilibrium selectivity.
- Induction of kinetic selectivity or even complete molecular sieving.
- Improved kinetic selectivity.

### 4.3 Experimental adsorbent screening program

#### 4.3.1 Selection of experimental conditions

The experimental conditions were selected to provide sufficient data to compare and identify potential adsorbent materials with confidence, while keeping the experiments to be performed to a reasonable number and timeframe. The adjustable experimental parameters that needed to be selected were temperature, pressure, composition, and feed flow rate. Two key requirements determined the selection of these experimental parameters:

- To be able to make comparisons against the bulk of the literature data, commonly published at pressures around 100 kPa and temperatures around 303 K.
• To investigate adsorbent behaviour and performance at conditions close to those of the proposed low temperature PSA process.

Two temperatures were selected for the adsorbent screening: 303 and 233 K. The lower of the temperatures identified in Chapter 2 as being optimal for integration to an LNG production facility (between -30 and -40 °C) was selected to investigate the maximum effect on adsorption at low temperatures.

Low and high pressures were selected to compare adsorption, with a change in pressure likely to correspond to the ‘pressure swing’ conditions in a PSA process; however, this was limited to the pressure range of the apparatus. Two pressures were sufficient to evaluate adsorption changes with pressure, thus intermediate pressures were not measured during the adsorbent screening. The minimum pressure was selected by opening the back-pressure regulator completely, which resulted in measurements close to atmospheric pressure (~101.3 kPa).

The three compositions, pure N₂, pure CH₄, and an equimolar binary mixture of N₂ + CH₄, were measured at each combination of pressure and temperature. The binary measurements were required to evaluate the separation performance of adsorbents, which could not be sufficiently achieved with only pure fluid measurements. Dynamic binary breakthrough data would be used to provide evidence of kinetic separations or molecular sieving; a particularly important function of the screening experiments.

The flow rates for the experimental runs were chosen to optimise the experiment run time, while maintaining signal resolution. The mass flow rate for the high pressure experiments was chosen to be higher than the low pressure experiments to decrease the run time required. The disadvantage of increasing
flow rate, and therefore gas velocity, is that with a fixed sampling rate of once per second, the number of time steps available to resolve the flow rate and composition breakthrough profiles is reduced. At higher pressures, the volumetric flow rate is decreased, which inherently lowers the gas velocity. Therefore, the feed mass flow rate was increased for the high pressure experiments without concern of detriment to the sampling resolution. Table 4-2 shows the resultant experimental screening program for each of the seven adsorbent samples. Each adsorbent required a total of 12 experimental measurements. To maintain an experimental timeline, adsorption measurements were not repeated during material screening; however, a consistency check could be made between pure fluid and mixture measurements for each adsorbent.

Table 4-2: Screening experiment conditions used for each adsorbent.

<table>
<thead>
<tr>
<th>T</th>
<th>Feed flow rate</th>
<th>P</th>
<th>y.N₂</th>
<th>y.CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>[mol s⁻¹]</td>
<td>[kPa]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>----------------</td>
<td>----</td>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>302</td>
<td>5.11 × 10⁻⁵</td>
<td>101.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>302</td>
<td>6.81 × 10⁻⁵</td>
<td>790.8</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>302</td>
<td>5.11 × 10⁻⁵</td>
<td>101.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>302</td>
<td>6.81 × 10⁻⁵</td>
<td>790.8</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>302</td>
<td>5.11 × 10⁻⁵</td>
<td>101.3</td>
<td>0.5</td>
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</tr>
<tr>
<td>302</td>
<td>6.81 × 10⁻⁵</td>
<td>790.8</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>233</td>
<td>5.11 × 10⁻⁵</td>
<td>101.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>233</td>
<td>6.81 × 10⁻⁵</td>
<td>790.8</td>
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<td>233</td>
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<td>101.3</td>
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</tr>
<tr>
<td>233</td>
<td>6.81 × 10⁻⁵</td>
<td>790.8</td>
<td>1</td>
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<tr>
<td>233</td>
<td>5.11 × 10⁻⁵</td>
<td>101.3</td>
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<td>0.5</td>
</tr>
<tr>
<td>233</td>
<td>6.81 × 10⁻⁵</td>
<td>790.8</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
4.3.2 Experimental measurements

Adsorption experiments were conducted with the DCB apparatus at the conditions listed in Table 4-2. Towards the end of the screening measurements, the stirred air-bath failed and was beyond repair. The stirred air bath was replaced with a thermally controlled and stirred liquid glycol bath, capable of maintaining temperatures between 243 and 373 K, with a temperature stability of ± 0.01 K. The inlet cooling loop and column were submerged into the glycol bath without any changes to the configuration of the apparatus flow path. Although the lower temperature limit achievable with the DCB apparatus was reduced through this change, the glycol bath greatly improved the thermal stability and accuracy of the temperature of the system. Furthermore, the bath control was integrated into the existing LabVIEW control software, which allowed remote control of the bath temperature, resulting in the capability of automated temperature cycling. The low temperature mordenite experiments and all MSC-3K-161 experiments were performed with the glycol bath configuration.

4.4 Adsorbent screening results and discussion

4.4.1 Experimental measurement observations

It was expected that for each experiment, the pressure, temperature, and binary compositions recorded would differ slightly from the specified set points. The pressure recorded for an experimental run was the average column pressure, which would vary between experiments even with identical back-pressure regulator set-points. This variation was because the pressure drop along the column, and therefore the average pressure, changed primarily due to differences in column adsorbent packing and gas velocities. Pressure fluctuations of ± 2 kPa were expected. Equimolar binary mixture measurements requiring gas, delivered
by two mass flow controllers, were expected to lead to composition differences of up to ±2 mol %. Differences between the internal temperature bed sensors and set point temperature were expected because the air bath control thermometer was located externally to the column, at the top of the air bath. At lower temperatures, imperfect stirring of the liquid N₂ spray within the air bath was estimated to lead to temperature fluctuations of ±2 K.

The magnitude of difference between temperatures of the low temperature experiments was found to be greater than expected. After examining the temperature profiles of the low temperature experiments, most experiments were found to be offset from the set point but stable enough throughout the adsorption phase of the experiment for analysis; however, a small number of experiments were unstable during the adsorption phase and were not analysed further. These observed differences were caused by small amounts of ice forming on the liquid N₂ spray delivery nozzle. This likely caused temperature gradients within the air bath despite the constant stirring. As the ice formed it appeared to result in step-changes in the temperature, in the order of minutes, rather than a slow gradual change over tens of minutes or hours, as might be expected. It was thought that this may have been the result of individual holes in the nozzle becoming blocked fairly rapidly. The step-change-like behaviour was fortunate, as it meant that the data from most of the adsorption runs could be used; provided the step-change did not occur mid-experiment. As the temperature during the experiments was generally stable, it was decided to proceed with the experimental schedule. Once the stirred air bath was replaced with the glycol bath, the problem with the low temperature offset did not occur again.

Adsorption equilibrium was not reached for some of the measurements on MSC-3K-161 and 4A. The adsorption of CH₄ on MSC-3K-161 produced the usual
reduction in flow rate from adsorption; however, the return of the flow rate to match the inlet flow rate was extremely slow for all measurements with CH$_4$. Figure 4-1 shows an example of the slow return of the flow rate of CH$_4$ at 105.9 kPa and 302.9 K, which still had not reached the inlet flow rate even after 8000 s; other experiments at these conditions usually took around 1000 s to reach equilibrium. The low temperature pure CH$_4$ runs were not attempted on MSC-3K-161 because of the slow adsorption rates already observed at higher temperatures; the binary measurements were completed although these did not reach an equilibrium state. These binary experiments were only run long enough to provide information regarding the kinetically separative behaviour.

![Figure 4-1: Difference between inlet flow rate and outlet flow rate CH$_4$ adsorption on MSC-3K-161 at 105.9 kPa and 302.9 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.](image)

The same slow adsorption was observed on 4A for both N$_2$ + CH$_4$; however, this was only observed at high pressure and low temperature. Very little change in overall flow rate was observed for 4A at low pressure and low temperature; the
return of the flow rate to match the inlet flow indicated equilibrium had been reached (Figure 4-2). However, it is possible that adsorption may have still been occurring slowly but the change in flow rate was beyond the resolution of the DCB apparatus.

![Figure 4-2: Difference between inlet flow rate and outlet flow rate for CH₄ adsorption on Linde 4A at 104.6 kPa and 213.5 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.](image)

The slow adsorption in these cases presented two problems. First, in selected cases the attainment of equilibrium was not obvious; and second, there was uncertainty associated with the calculated capacity, even if equilibrium was reached. The adsorption capacity values were calculated where possible using the incomplete data sets, to provide estimates of the equilibrium capacities and the associated uncertainties. For MSC-3K-161 at 105.9 kPa and 302.9 K, and 4A at 792.4 kPa and 232.9 K, even though equilibrium had not been reached, the adsorption capacity and uncertainty for MSC-3K-161 and 4A at these conditions were estimated to be 0.1 ± 0.5 and 0.4 ± 0.3 mmol g⁻¹, respectively. This result
shows that in cases where the magnitude of flow rate change due to adsorption is small and the time period is large, the uncertainty in the measurement can be larger than the value of the measurement itself.

Considering that 4A and MSC-3K-161 were candidate adsorbents to display kinetically separative behaviour, as discussed in section 4.2, the slow adsorption observed for CH₄ on MSC-3K-161, and both N₂ + CH₄ on 4A, is likely to be a result of the slower diffusion of these gases. Comparing these two adsorbents, it is only the adsorption rate of CH₄ that was observed to be significantly slower for MSC-3K-161, whereas on 4A at low temperatures, both the adsorption of N₂ + CH₄ slowed. Therefore, based on these observations alone, MSC-3K-161 is likely to have a larger difference between the rates of adsorption for N₂ + CH₄; all experimental parameters being equal, larger differences in adsorption rates increase kinetic selectivity.

### 4.4.2 Adsorbent equilibrium capacities

Table 4-3, Table 4-4, and Table 4-5 contain the ranked adsorption equilibrium capacities for the pure N₂, pure CH₄, and binary N₂ + CH₄ measurements, respectively. Rankings were made based on the maximum adsorption capacities measured, which was generally the high pressure, low temperature, measurement for each adsorbent. In the cases where these experiments were excluded because of experimental failure, the rankings were made based on the highest capacities measured at similar conditions between adsorbents. The three adsorbents expected to exhibit kinetically separative behaviour—4A, clinoptilolite, and MSC-3K-161—generally displayed lower adsorption capacities compared with the other four adsorbents.
Table 4.3: Adsorbents ranked in order of N₂ equilibrium adsorption capacity from highest to lowest.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T [K]</th>
<th>Feed flow rate [mol s⁻¹]</th>
<th>P [kPa]</th>
<th>q* . N₂ [mmol g⁻¹]</th>
<th>u(q*) . N₂ [mmol g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13X</td>
<td>228.4</td>
<td>6.95 × 10⁻⁵</td>
<td>792.6</td>
<td>3.28</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>220.3</td>
<td>5.04 × 10⁻⁵</td>
<td>106.2</td>
<td>1.90</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>302.0</td>
<td>6.96 × 10⁻⁵</td>
<td>792.9</td>
<td>1.34</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>302.0</td>
<td>5.09 × 10⁻⁵</td>
<td>106.5</td>
<td>0.29</td>
<td>0.05</td>
</tr>
<tr>
<td>Chabazite</td>
<td>238.7</td>
<td>6.68 × 10⁻⁵</td>
<td>107.3</td>
<td>1.45</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>301.6</td>
<td>7.04 × 10⁻⁵</td>
<td>792.8</td>
<td>1.35</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>301.6</td>
<td>5.41 × 10⁻⁵</td>
<td>107.4</td>
<td>0.46</td>
<td>0.04</td>
</tr>
<tr>
<td>Norit RB3</td>
<td>233.9</td>
<td>6.97 × 10⁻⁵</td>
<td>792.4</td>
<td>2.96</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>219.6</td>
<td>5.01 × 10⁻⁵</td>
<td>105.9</td>
<td>1.21</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>301.9</td>
<td>6.88 × 10⁻⁵</td>
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<td>0.08</td>
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<td></td>
<td>301.8</td>
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<td>0.04</td>
</tr>
<tr>
<td>MSC-3K-161</td>
<td>244.1</td>
<td>6.85 × 10⁻⁵</td>
<td>902.4</td>
<td>2.08</td>
<td>0.14</td>
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<tr>
<td></td>
<td>302.9</td>
<td>7.02 × 10⁻⁵</td>
<td>901.4</td>
<td>1.21</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>244.2</td>
<td>6.77 × 10⁻⁵</td>
<td>108.7</td>
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</tr>
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<td>106.2</td>
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</tr>
<tr>
<td>Linde 4A</td>
<td>227.2</td>
<td>6.74 × 10⁻⁵</td>
<td>792.3</td>
<td>0.74*</td>
<td>0.16*</td>
</tr>
<tr>
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<td>301.8</td>
<td>7.00 × 10⁻⁵</td>
<td>792.5</td>
<td>0.68</td>
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<tr>
<td></td>
<td>225.9</td>
<td>5.07 × 10⁻⁵</td>
<td>105.8</td>
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</tr>
<tr>
<td></td>
<td>301.8</td>
<td>5.07 × 10⁻⁵</td>
<td>106.2</td>
<td>0.14</td>
<td>0.05</td>
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<tr>
<td>Clinoptilolite</td>
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<tr>
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</tr>
<tr>
<td></td>
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<td>5.04 × 10⁻⁵</td>
<td>106.2</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* - Adsorption experiments did not reach equilibrium.
Table 4-4: Adsorbents ranked in order of CH₄ equilibrium adsorption capacity from highest to lowest.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T [K]</th>
<th>Feed flow rate [mol s⁻¹]</th>
<th>P [kPa]</th>
<th>q⁺.CH₄ [mmol g⁻¹]</th>
<th>u(q⁺).CH₄ [mmol g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit RB3</td>
<td>235.1</td>
<td>6.74 × 10⁻⁵</td>
<td>792.4</td>
<td>5.16</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>229.7</td>
<td>5.16 × 10⁻⁵</td>
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</table>

* - Adsorption experiments did not reach equilibrium.
Table 4-5: Adsorbents ranked in order of total equilibrium adsorption capacities for the binary mixture of $N_2 + CH_4$ from highest to lowest.

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<tr>
<th>Sample</th>
<th>T</th>
<th>Feed flow rate</th>
<th>P</th>
<th>y.N$_2$</th>
<th>y.CH$_4$</th>
<th>q*.N$_2$</th>
<th>q*.CH$_4$</th>
<th>q*.Total</th>
<th>u(q*).Total</th>
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<tr>
<td>Norit RB3</td>
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<td>792.6</td>
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<td>3.77</td>
<td>4.50</td>
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<td>2.03</td>
<td>0.19</td>
</tr>
<tr>
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<td>0.51</td>
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<td>0.10</td>
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<td>3.48</td>
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<tr>
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<td>1.07</td>
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<td>0.55</td>
<td>0.74</td>
<td>0.07</td>
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<td>Linde 4A</td>
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<td>792.5</td>
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<td>0.50</td>
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<td>0.17*</td>
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<td>0.17*</td>
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<td>0.52</td>
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</table>

# - Adsorption experiments did not reach equilibrium.
The capacities measured for Clinoptilolite were far lower than all other adsorbents measured. Jayaraman et al. [106, 107] studied multiple ion-exchanged forms of clinoptilolite for N₂ + CH₄ separations at low pressures (<100 kPa) and 295 K. Of the samples they tested, the Na⁺ exchanged form displayed the highest adsorption capacity and displayed a higher N₂ equilibrium capacity, which was proposed to be the result of molecular sieving. The N₂ + CH₄ capacities measured by Jayaraman et al. [106, 107] at 100 kPa and 295 K, were 0.62 and 0.27 mmol g⁻¹, respectively, compared to 0.03 and 0.01 mmol g⁻¹, respectively, measured in this study at similar conditions. The lower adsorption values measured in this study were most likely because the sample used was raw and not purified, containing a mixture of Ca²⁺, Mg²⁺, and K⁺ cations, according to supplier information [93]. It is of interest that the clinoptilolite measurements at 302.9 K in this study also show a higher N₂ pure gas capacity, which is consistent with the N₂ equilibrium selectivity found by Jayaraman et al. [106, 107]. The low temperature results from this work show that the adsorption capacity of clinoptilolite decreases at lower temperatures, which is likely to be the result of molecular exclusion from pore size reductions at reduced temperatures. Therefore, while the purified Na⁺ form of clinoptilolite exhibits much higher adsorption capacity than the sample measured in this work, these results suggest that the adsorption capacity of a Na⁺ clinoptilolite sample is unlikely to improve at low temperatures.

Toth model parameters for Linde 4A published by Jensen et al. [89] were used to generate isotherms at 301.8 K to compare with the results in this work (Figure 4-3).
The equation for the Toth isotherm model with temperature dependence is:

\[
q_{\text{abs}}^{\text{calc}} = q_{\text{max}} \frac{KP}{\left(1 + (KP)^n\right)^{1/n}} \tag{4.1}
\]

\[
K = K_0 \exp\left(\frac{-\Delta H}{RT}\right) \tag{4.2}
\]

Here \(q_{\text{abs}}^{\text{calc}}\) is the absolute adsorption, \(R\) is the molar gas constant, \(\Delta H\) is the enthalpy of adsorption, \(P\) is pressure, and \(q_{\text{max}}, K, K_0, \) and \(n\), are adjustable parameters.

The equilibrium capacities measured with the DCB apparatus are lower than those predicted using the Toth model from Jensen et al. [89], with all the deviations greater than the estimated experimental uncertainty of the dynamic measurements. Possible explanations for this discrepancy are that adsorption rates on 4A are slower than can be resolved by the DCB apparatus, or that differences in sample regeneration removed more contaminants, increasing the capacity for adsorption. Jensen et al. [89] regenerated their sample at 623 K, whereas 573 K was used in this study. The 4A adsorbent is highly hydrophilic, so the increased temperature used by Jensen et al. [89] may have driven off excess water, increasing the adsorbent capacity. The model used by Jensen et al. [89] was only fitted to measurements below 120 kPa, so comparisons above this pressure were completed by model extrapolation. The uncertainty in the model used by Jensen et al. [89] is not included in this comparison; however, this would also account for part of the deviation observed.
Figure 4-3: Adsorption capacity of N$_2$ and CH$_4$ on 4A at 301.8 K. The N$_2$ and CH$_4$ data points were measured in this work. Toth parameters from Jensen et al. [89] were used to calculate the model curves, which are extrapolated at pressures above 120 kPa.

Toth model parameters published by Watson et al. [38] for the same MSC-3K-161 adsorbent used in this study, were used to generate N$_2$ isotherms at 244.1 and 302.9 K to compare with the results of this work (Figure 4-4). All capacities measured in this work were lower than those predicted by the Toth model. The capacities measured at 244.1 K were consistent with the model of Watson et al. [38] almost within the experimental uncertainty. At 302.9 K, the N$_2$ capacities measured deviated from the Toth model predictions by 1.1 and 2.6 times the experimental uncertainty at 106.2 and 901.4 kPa, respectively.

Again, the differences in adsorption capacity may be the result of differences in regeneration. Watson et al. [38] regenerated their sample at 673 K, whereas 573 K was used in this study. Despite these differences, the agreement between the N$_2$ adsorption on MSC-3K-161 measured in the two studies is satisfactory. This suggests that the CH$_4$ equilibrium capacities measured by Watson et al. [38] could
be used for estimating adsorption capacities at conditions that could not be measured adequately with the DCB apparatus.

Figure 4-4: Adsorption capacity of N$_2$ on MSC-3K-161 at 244.1 and 302.9 K using Toth parameters from Watson et al. [38]. The N$_2$ data points at 244.1 and 302.9 K were measured in this work.

Higher adsorption capacities were exhibited by the four adsorbents likely to be equilibrium selective: mordenite, 13X, chabazite, and Norit RB3. Mordenite and 13X were compared to published data in Chapter 3 and the results were generally consistent with the published values. Toth model parameters, published by Jensen et al. [89] for the same chabazite adsorbent in this study, were used to generate isotherms for N$_2$ + CH$_4$ to compare with the results of this work. These are shown in Figure 4-5.
Figure 4-5: Adsorption capacity of (a) N\textsubscript{2} and (b) CH\textsubscript{4} on chabazite at 301.6 and 238.6 K. The 301.6 and 238.6 K data points were measured in this work. Toth parameters from Jensen et al. [89] were used to calculate the model curves, which are extrapolated at pressures above 120 kPa.
The N\textsubscript{2} measurements are in close agreement with the model curves, within a single standard uncertainty at 301.6 K and 1.7 times the standard uncertainty at 238.6 K. The CH\textsubscript{4} measurements deviate further, with the 301.6 K measurements under predicted by 1.6 and 0.7 times the standard uncertainty at 107.4 and 792.8 kPa, respectively. The CH\textsubscript{4} measurement at 238.6 K displayed the greatest deviation and was under-predicted by 4.4 times the standard uncertainty of the measurement in this work. Again, the model used by Jensen et al. [89] was only fitted to measurements below 120 kPa, so comparisons above this pressure were completed by model extrapolation.

Of the four equilibrium selective adsorbents tested, Norit RB3 displayed the highest CH\textsubscript{4} capacity of the pure CH\textsubscript{4} and equimolar binary measurements. Dual-site Langmuir (4.3) parameters published by Dreisbach et al. [108] for Norit R1 Extra were used to generate N\textsubscript{2} + CH\textsubscript{4} isotherms at 298 K to compare with the results in this work at ~302 K (Figure 4-6). The dual site Langmuir model is:

\[ q_{\text{abs}}^{\text{calc}} = m^{(b)} \frac{bP}{1+bP} + m^{(d)} \frac{dP}{1+dP} \]  

(4.3)

Here \(m^{(b)}\) and \(b\) are the saturation capacity and affinity parameter on the first set of adsorption sites, and \(m^{(d)}\) and \(d\), are the parameters on the second set of sites.

All capacities measured for Norit RB3 in this work were lower than those predicted by the dual site Langmuir model. A likely explanation for this difference is that Norit R1 Extra has a larger surface area (1450 m\textsuperscript{2} g\textsuperscript{-1}, BET measured by Himeno et al. [109]), which is likely to lead to the increased capacities observed. In future work, the increased capacity displayed by Norit R1 Extra would make this adsorbent a target candidate for low temperature screening.
Figure 4-6: Adsorption capacity of $\text{N}_2 + \text{CH}_4$ on Norit R1 Extra using dual-site Langmuir parameters from Dreisbach et al. [108] at 298 K. The $\text{N}_2 + \text{CH}_4$ data points were measured in this work on Norit RB3 at ~302 K.

The adsorption capacity measurements in this work display consistently lower values than those of the same adsorbent samples published in the literature. Although this may be attributed to differences in regeneration temperatures, as previously discussed, the differences may also be attributed to the measurement techniques used. Jensen et al. [89] and Watson et al. [38] measured the same type of adsorbent samples using a static equilibrium type apparatus. An interesting study for future work would be to conduct identical measurements on the same samples, regenerated under identical conditions to investigate the degree of differences between determined capacities as a direct result of the measurement techniques themselves.

4.4.3 Comparison of selectivities

Pure fluid data from the four equilibrium selective adsorbents were fitted to the Sips isotherm model with temperature dependence [110]. The pure fluid
parameters were then used with the extended Sips isotherm model to predict binary isotherm data, which was subsequently used to calculate equilibrium selectivities (outlined in Chapter 3). The Sips model symbols are defined as for the Toth model:

\[
q_{abs}^{calc} = q_{max} \frac{(KP)^n}{1 + (KP)^n} \quad (4.4)
\]

\[
K_i = K_{0i} \exp \left( \frac{-\Delta H_i}{RT} \right) \quad (4.5)
\]

\[
q_{abs,i}^{calc} = q_{max,i} \frac{(K_i P_i)^{n_i}}{1 + \sum_{j=1}^{n}(K_j P_j)^{n_j}} \quad (4.6)
\]

The Sips equation is a combination of the Langmuir and Freundlich isotherm model equations, reducing to the Freundlich equation at low adsorbate concentrations and predicting a monolayer adsorption capacity at high concentrations, typical of the Langmuir equation [111]. The Sips model was used because the characteristics described above, mathematical simplicity, and easy extension to multicomponent adsorption are desirable for describing the wide range of adsorption capacities encountered when screening a variety of adsorbents [56].

At most, four data points were used for fitting each Sips model to the pure gas data. The fitted Sips parameters are shown in Table 4-6. Since the number of data points was about equal to the number of parameters, the fit statistics are not meaningful and are not reported here.
Table 4-6: Pure gas Sips parameters calculated for each selected adsorbent.

<table>
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<tr>
<th>Sample</th>
<th>Gas</th>
<th>$q_{max}$ [mmol g$^{-1}$]</th>
<th>$\Delta$H [kJ mol$^{-1}$]</th>
<th>$K_0 \times 10^6$ [kPa$^{-1}$]</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
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<td>20.89</td>
<td>0.457</td>
<td>0.856</td>
</tr>
<tr>
<td>Chabazite</td>
<td>N$_2$</td>
<td>2.224</td>
<td>22.26</td>
<td>0.264</td>
<td>0.843</td>
</tr>
<tr>
<td></td>
<td>CH$_4$</td>
<td>8.450</td>
<td>8.465</td>
<td>1.237</td>
<td>0.388</td>
</tr>
</tbody>
</table>

While it is generally not ideal to perform a fit with such a small dataset, it is important to note that in this case the purpose of the isotherm modelling was to compare predicted mixture data with experimental mixture measurements. This did mean that there was less physical meaning for each fitted parameter—the use of these model parameters to generate isotherms over a range of conditions is not recommended.

The selected adsorbents were ranked on the basis of measured mixture selectivities. Table 4-7 shows the selectivities predicted using pure fluid Sips parameters with the extended Sips model, and the measured mixture selectivities. The highest selectivity observed was for mordenite at 233 K and 100 kPa; however, the high pressure data is of more relevance for comparison of adsorbents, as this is where the adsorption phase of the PSA process would occur. In this case, the selectivity of Norit RB3 at 233 K and 790 kPa is higher than for mordenite. Furthermore, the adsorption capacity of Norit RB3 at these conditions is almost double compared with the capacity at 303 K and 790 kPa. The selectivity and capacity for Norit RB3 at 233 K and 790 kPa makes this the best choice for an
equilibrium selective adsorbent. One of the most important observations is that, for both of these adsorbents, the selectivity improves at reduced temperatures.

Another important observation was that the predicted selectivities of mordenite and 13X at 790 kPa and 233 K were identical; however, the experimental binary measurements show that at these same conditions, the selectivity of mordenite increased by 85 %, whereas 13X reduced by almost 10 %. This was further illustrated by the Norit RB3 results, which showed almost an identical under-prediction of equilibrium selectivity. These results again highlight the value of the binary experimental adsorption measurements and show that equilibrium selectivity can increase significantly at reduced adsorption temperatures. Another similar demonstration of the value of binary experimental measurements can be seen in the chabazite results. In this case, the extended Sips model predicts that chabazite will have equilibrium N₂ selectivity, while the binary experimental measurements show CH₄ equilibrium selectivity.
Table 4-7: Measured capacities and selectivities for binary mixtures of $0.5N_2 + 0.5CH_4$ together with values predicted using the extended Sips models.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T [K]</th>
<th>P [kPa]</th>
<th>$q^{*}_{\text{Sips N}_2}$ [mmol g$^{-1}$]</th>
<th>$q^{*}_{\text{Sips CH}_4}$ [mmol g$^{-1}$]</th>
<th>$\alpha_{\text{Sips}}$</th>
<th>$q^{*}_{\text{expt N}_2}$ [mmol g$^{-1}$]</th>
<th>$q^{*}_{\text{expt CH}_4}$ [mmol g$^{-1}$]</th>
<th>$\alpha_{\text{expt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mordenite</td>
<td>233</td>
<td>100</td>
<td>0.33</td>
<td>1.08</td>
<td>3.3</td>
<td>0.23</td>
<td>1.30</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>790</td>
<td>0.60</td>
<td>1.60</td>
<td>2.7</td>
<td>0.39</td>
<td>1.91</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>100</td>
<td>0.07</td>
<td>0.26</td>
<td>3.5</td>
<td>0.08</td>
<td>0.23</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>790</td>
<td>0.31</td>
<td>0.90</td>
<td>2.9</td>
<td>0.32</td>
<td>0.84</td>
<td>2.6</td>
</tr>
<tr>
<td>Norit RB3</td>
<td>233</td>
<td>100</td>
<td>0.38</td>
<td>1.33</td>
<td>3.5</td>
<td>0.28</td>
<td>1.52</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>790</td>
<td>1.16</td>
<td>3.28</td>
<td>2.8</td>
<td>0.72</td>
<td>3.76</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>100</td>
<td>0.11</td>
<td>0.36</td>
<td>3.2</td>
<td>0.10</td>
<td>0.40</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>790</td>
<td>0.53</td>
<td>1.37</td>
<td>2.6</td>
<td>0.40</td>
<td>1.54</td>
<td>3.8</td>
</tr>
<tr>
<td>Chabazite</td>
<td>303</td>
<td>790</td>
<td>0.84</td>
<td>0.59</td>
<td>0.7</td>
<td>0.38</td>
<td>1.27</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>0.22</td>
<td>0.40</td>
<td>1.8</td>
<td>0.18</td>
<td>0.54</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>233</td>
<td>790</td>
<td>1.87</td>
<td>0.21</td>
<td>0.1</td>
<td>0.69</td>
<td>0.75</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>1.13</td>
<td>0.32</td>
<td>0.3</td>
<td>0.52</td>
<td>0.52</td>
<td>1.0</td>
</tr>
<tr>
<td>13X</td>
<td>233</td>
<td>790</td>
<td>0.97</td>
<td>2.64</td>
<td>2.7</td>
<td>1.02</td>
<td>2.50</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>0.56</td>
<td>1.33</td>
<td>2.4</td>
<td>0.52</td>
<td>1.13</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>790</td>
<td>0.57</td>
<td>1.18</td>
<td>2.1</td>
<td>0.59</td>
<td>1.18</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>0.13</td>
<td>0.24</td>
<td>1.8</td>
<td>0.13</td>
<td>0.23</td>
<td>1.8</td>
</tr>
</tbody>
</table>
4.4.4 Examination of binary breakthrough curves

Binary experimental breakthrough curves were examined to identify equilibrium selective and kinetically separative behaviour. An equimolar N₂ + CH₄ feed was used for this purpose. For an equimolar equilibrium-controlled adsorption N₂ + CH₄ experiment, as CH₄ is preferentially adsorbed over N₂, the resulting breakthrough curve will show a N₂ maximum; however, for N₂ kinetically controlled adsorption, as the N₂ was first adsorbed, the resulting breakthrough curve would initially display a CH₄ maximum. While the magnitude of the maximum will depend on the selectivity, uptake rate, and gas velocity, a visual inspection of the breakthrough curve can be used to rapidly identify kinetic selectivity.

Figure 4-7 and Figure 4-8 show two typical breakthrough separations observed for equilibrium selective adsorbents: Norit RB3, 13X, mordenite, and chabazite. While the amplitude of the N₂ composition maximum and timescale varied between experimental runs and adsorbents, the shape of this general breakthrough profile was the same for these four adsorbents. The breakthrough of N₂ over CH₄ confirmed that these adsorbents were all CH₄ selective and equilibrium controlled.
Figure 4-7: Breakthrough Curve for $0.5\text{N}_2 + 0.5\text{CH}_4$ feed on 13X at 106.0 kPa and 302.1 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-8: Breakthrough Curve for $0.5\text{N}_2 + 0.5\text{CH}_4$ feed on Norit RB3 at 105.3 kPa and 230.1 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 4-9 shows a breakthrough profile observed for clinoptilolite at 792.7 kPa and 302.1 K, which displays a CH₄ maximum. This finding suggests that CH₄ is excluded from being adsorbed, consistent with Jayaraman et al. [106, 107]. At lower temperatures, the measurements on clinoptilolite showed almost no difference between the N₂ and CH₄ breakthrough curves, indicating that neither component was selectively adsorbed.

Figure 4-9: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on Clinoptilolite at 792.7 kPa and 302.1 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 4-10 shows the breakthrough profile observed for 4A at 792.5 kPa and 301.8 K, which shows that there is a very slight CH₄ breakthrough before N₂, indicating a small amount of initial N₂ adsorption over CH₄. Figure 4-11 shows the breakthrough profile at a similar pressure, but at low temperature. In this case, CH₄ clearly breaks through first, meaning N₂ is preferentially adsorbed during the initial adsorption period. From the results of Habgood [14] and Jensen et al. [89], the adsorbent is known to be CH₄ equilibrium selective at this temperature. Thus, this result confirms the predictions of increased kinetic separation at reduced temperatures.

![Figure 4-10: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on 4A at 792.5 kPa and 301.8 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.](image-url)
Figure 4-11: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on 4A at 792.1 kPa and 237.6 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-12 is the breakthrough profile collected for MSC-3K-161 at 107.2 kPa and 302.8 K. This profile shows a CH₄ maximum, which indicates that initially there is preferential N₂ adsorption in the column. After a period of time, the measured effluent N₂ + CH₄ compositions cross over, indicating that the adsorbed N₂ is being displaced by CH₄. This result indicates that MSC-3K-161 also displays kinetic selectivity for N₂. At 901.5 kPa and 302.9 K (Figure 4-13), this demonstration of kinetic selectivity is emphasised as the breakthrough profile is extended over a longer time period due to the higher pressure and therefore lower gas velocity. Figure 4-14 shows an increase in the CH₄ maximum of the composition breakthrough curve at low temperature and high pressure. Without a quantitative comparison of the uptake rates, which would require a full dynamic model (discussed in Section 3.5), a definitive improvement in kinetic selectivity cannot be established; however, this screening result suggests a potential improvement to the separation at low temperature that is greater than that observed for the 4A adsorbent.
Figure 4-12: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on MSC-3K-161 at 107.2 kPa and 302.8 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 4-13: Breakthrough Curve for 0.5N₂ + 0.5CH₄ feed on MSC-3K-161 at 901.5 kPa and 302.9 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 4-14: Breakthrough Curve for 0.5N$_2$ + 0.5CH$_4$ feed on MSC-3K-161 at 901.6 kPa and 243.7 K. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

4.5 Conclusions

Based on a comparison of equilibrium capacity, equilibrium selectivity, and kinetic behaviour (inferred from binary breakthrough curves) among the selected adsorbent materials, Norit RB3 shows the most potential as an adsorbent for a CH$_4$ equilibrium selective process and MSC-3K-161 as an adsorbent for a N$_2$ kinetically separative process. Encouragingly, not only did the equilibrium capacity of Norit RB3 increase at low temperatures, but the selectivity also increased. The results for MSC-3K-161 were also promising as they showed increased capacity for N$_2$ at reduced temperatures, and the qualitative analysis of the binary breakthrough curves suggested that the kinetic separation of N$_2$ + CH$_4$ improved at low temperatures.
Chapter 5

Detailed adsorption studies of Norit RB3 activated carbon and MSC-3K-161 carbon molecular sieve
5.1 Overview

This chapter discusses the collection, analysis, and validation of the adsorption capacities, mass transfer coefficients, and heats of adsorption for Norit RB3 activated carbon and MSC-3K-161 carbon molecular sieve, which were selected for further investigation on the basis of their equilibrium capacity, equilibrium selectivity, and kinetic behaviour (Chapter 4). Dynamic experiments were conducted over a range of conditions to produce data to generate adsorption isotherms and heats of adsorption. A model of the breakthrough process was developed to extract the mass transfer coefficients (MTCs). These MTCs and generated isotherm data were then used in the model to predict the results of binary experiments. No further parameter adjustments were found necessary, thereby establishing a level of confidence in the use of these models for future designs of low temperature pressure swing adsorption (PSA) processes based on these adsorbents.

5.2 Development of a process model of the dynamic column breakthrough apparatus

5.2.1 Description of the apparatus section to be modelled

To mathematically describe breakthrough curves generated with the dynamic column breakthrough (DCB) apparatus used in this study, the adsorption column itself had to be considered, as did the extra-column components, such as the tubing and conical sections (Figure 5-1). The extra-column components contribute to the retention time and broadening of the experimental breakthrough curve, and therefore must be accounted for to accurately compare experimental results with the theoretical model. This is especially true for experiments with
concentrated adsorbate feeds, variable pressures and temperatures, and significant extra-column volumes, such as those conducted in this study. Figure 5-1 shows the main components that comprise the flow path of the DCB apparatus, which contribute to the experimental breakthrough curve.

![Flow path components](image)

**Figure 5-1: Flow path components that contribute to the experimental breakthrough curve for the DCB apparatus, with the sections under different pressures highlighted.**

The first element is the multi-position valve 1 (MPV-1) where the feed flow starts at the beginning of an experiment, and the last element is the mass spectrometer (MS) where the compositional breakthrough curve is measured. All components between these elements contribute to the breakthrough profile and must be considered because of:

- Gas velocity variations in extra-column components that are caused by adsorption in the packed column and also from the pressure step across back-pressure regulator 1 (BPR-1).

- Broadening of the breakthrough curve, resulting from gas dispersion and gas mixing in extra-column volumes.

### 5.2.2 Modelling software used for the process model

The model used to describe the DCB apparatus in this work was produced using Aspen Adsorption V7.1 by Aspen Technology, Inc. [112], which is a comprehensive industrial flow-sheet simulator designed specifically to model adsorption processes. Aspen Adsorption is capable of modelling packed bed
adsorption processes, including additional structures, such as valves, pipes, and voids that are required to fully describe a process; thus, it is suitable to describe the DCB apparatus in this work. A useful aspect of this software is that elements in the flow-sheet simulator used to model industrial scale systems are identical to those used to model small-scale experimental systems.

5.2.3 Implemented model

While Aspen Adsorption is capable of describing different size tubes, connectors, valves, and pressure controllers, some simplifications and assumptions were made as the model was implemented. The DCB apparatus was represented in the model as an inlet tube, inlet cone to the column, adsorption column, outlet cone from the column, and outlet tube. The Aspen Adsorption flow sheet of this representation is shown in Figure 5-2.

![Figure 5-2: Flow sheet of DCB apparatus implemented into Aspen Adsorption.](image)

The inlet and outlet tubes were each modelled as an isothermal plug flow tube reactor (PFTR). That is, they were modelled as simplified empty adsorption columns to account for velocity and compositional changes within the tubes. The isothermal assumption was justified, as more than 90 % of the tubing was thermally anchored, as discussed in Section 3.4. One of the main simplifications made to the outlet tube model was to combine the sections before and after BPR-1 into a single tube. The pressure ratio between each side of BPR-1 could be as high as 10 during an experiment, so the effective volume was multiplied by the pressure
ratio to account for the section of tube that remained at atmospheric pressure during an experiment.

The inlet and outlet cones to the column were treated separately from the inlet and outlet tubing because their length to average radius ratio was large (~4). These sections were more like two separate void tanks at either end of the adsorption column, rather than tubing. Each of the conical sections were implemented into the process model as constantly stirred tank reactors (CSTR). A limitation of this assumption was that the residence time hold-up in the conical sections was not accurately accounted for by the CSTR models.

The packed adsorption column was rigorously modelled with consideration of material, momentum, and energy balance. The governing equations used by the Aspen Adsorption software to describe the packed column are discussed in the following sections [112]. Although they are non-trivial and generally require numerical solution, these equations are themselves derived from the more fundamental, three-dimensional continuity equations that govern the hydrodynamics of porous media flow using the method of volume averaging [113, 114].

**Material balance**

The gas phase material balance on each adsorbing component $i$ is given by:

$$
\varepsilon_b \frac{\partial C_i}{\partial t} = \varepsilon_l D_{l,i} \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial (\varepsilon_g C_i)}{\partial z} - \left( \frac{1 - \varepsilon_b}{\varepsilon_b} \right) \rho \frac{\partial q_i}{\partial t}
$$

(5.1)

where

- $\varepsilon_b$ is the total bed voidage
- $C$ is the gas phase concentration (mol m$^{-3}$)
- $t$ is the time (s)
εᵢ is the interparticle voidage

\( D_L \) is the axial dispersion coefficient (m² s⁻¹)

\( z \) is the axial coordinate (m)

\( v_g \) is the gas phase superficial velocity (m s⁻¹)

\( \rho_s \) is the adsorbent bulk density (kg m⁻³)

\( q \) is the adsorbent loading (mol g⁻¹)

This includes terms from left to right for gas phase accumulation, axial dispersion, convection, and rate of flux to the solid surface.

**Transfer model**

In this investigation, the linear driving force (LDF) model (5.2) proposed by Glueckauf and Coates [115] was used to describe the mass transfer. The LDF model, with a lumped MTC, is often used for practical analysis of dynamic adsorption data and adsorptive process design [116]:

\[
\frac{\partial q}{\partial t} = MTC_{LDF} (q^* - q)
\]  

(5.2)

where \( q^* \) is the adsorbent loading at equilibrium (mol kg⁻¹)

\( MTC_{LDF} \) is the linear driving force mass transfer coefficient (s⁻¹)

Mass transfer coefficients derived from the LDF model are generally sufficient for engineers to research and design preliminary systems because they are simple, analytical, and physically consistent [116]. They are determined experimentally and often correlated to empirical equations using dimensionless numbers such as the Sherwood, Schmidt, and Reynolds numbers, allowing the MTCs to be predicted over a set of conditions [30, 117]. More simply, MTCs can be treated as a basic experimental property for a system and correlated as functions
of operating variables such as superficial gas velocity, temperature, and pressure.

One example of an empirical equation used to correlate experimentally determined
MTCs is [112]:

\[
MTC = \frac{k_{0,IP}}{P} \exp\left(\frac{-E_{act,IP}}{RT}\right)
\]

(5.3)

where \( k_{0,IP} \) is the inverse pressure dependent pre-exponential factor (Pa m s\(^{-1}\))

\( P \) is pressure (Pa)

\( E_{act,IP} \) is the activation energy of the inverse pressure dependent
Arrhenius relationship (J mol\(^{-1}\))

\( R \) is the universal gas constant (8.314, J K\(^{-1}\)mol\(^{-1}\))

\( T \) is the temperature (K)

In this example the MTC has an inverse pressure relationship, which is
applicable where adsorption is controlled primarily by molecular diffusion, since
the molecular diffusivity varies inversely with total pressure. This type of
empirical expression can be used to minimise the complexity of the correlation and
allow predictions of MTCs suitable for preliminary design.

The MTC is a composite parameter related to the three primary transport
resistances, by an extension to the Glueckauf approximation [55, 118]:

\[
\frac{1}{MTC_{LDF}K} = \frac{r_p}{3k_f} + \frac{r_p^2}{15c_pD_p} + \frac{r_c^2}{15KD_c}
\]

(5.4)

where \( K \) is Henry’s law equilibrium constant

\( r_p \) is the particle radius (m) – the cylindrical pellets used in this work
were treated as spherical particles using a shape factor
approximation of 0.91 [55].
\( k_f \) is the external fluid film mass transfer coefficient (m s\(^{-1}\))

\( \varepsilon_p \) is the intraparticle voidage

\( D_p \) is the pore diffusivity (m\(^2\) s\(^{-1}\))

\( r_c \) is the crystal or microparticle radius (m)

\( D_c \) is the intracrystalline diffusivity (m\(^2\) s\(^{-1}\))

The terms in this equation from left to right include external film resistance, macropore resistance, and micropore resistance. Although lumped MTCs were used in this research, this extended expression highlights the individual mass transfer resistances that contribute to the value of the MTCs.

**Hydrodynamic behaviour**

The hydrodynamic behaviour in the adsorption column was treated as a one (spatial) dimensional problem, only considering concentration, velocity, and temperature gradients in the axial direction. The non-uniformity of adsorbent particle packing causing channelling has been investigated by LeVan and Vermeulen [119] who found that bed diameter to particle diameter should be greater than 20 to avoid channelling; however, Carberry [120] suggests bed to particle diameters should be 6 to avoid radial temperature gradients [121]. The bed to particle diameters for Norit RB3 and MSC-3K-161 used in this work are 7.4 and 12.3, respectively, representing a good compromise between these two recommendations. Concentrated adsorbate feeds were used for all experiments in this work, which cause significant flow effects, including changes in axial dispersion, gas velocity, and pressure drop in the bed. Axial dispersion occurs through two main mechanisms [55]:
1. Molecular diffusion.

2. Convective mixing.

The effects from molecular diffusion and convective mixing are generally treated as additive; thus, most predictive equations for dispersion include a molecular diffusion and convective mixing term. Gaseous axial dispersion has been reviewed by Langer et al. [122] who compared experimental data with correlations at different conditions. The equation proposed by Edwards and Richardson [123] was selected and used to calculate the axial dispersion coefficient in this study. The constants derived from the experiments performed by Edwards and Richardson [123] were used, as they most closely matched the experimental conditions in this research [122]. The general form of the equation is:

\[
D_L = \gamma_1 D_m + \frac{v_g r_p}{P_e \left(1 + \beta \gamma_1 \frac{D_m}{v_g r_p}\right)}
\]  

(5.5)

where \(D_m\) is the molecular diffusivity \((m^2 s^{-1})\), which was calculated using the Chapman-Enskog equation. Cussler discussed this to be accurate on average to 8% [26].

\(P_e\) is the limiting value of the Peclet number

\(\gamma_1\) is inverse tortuosity \((\tau^{-1})\)

\(\beta\) is the radial dispersion factor

The parameters used by Edwards and Richardson [123] were \(\gamma_1 = 0.73\), \(\beta = 13\), and \(P_e = 2\), experimentally determined for packed spheres to be suitable for \((0.008 < \text{Reynolds} < 50), (0.0377 < r_p < 0.60 \text{ cm})\), and bed length to diameter ratio \(\approx 10\) [122].
 Isotherm model

The Sips isotherm model discussed in Chapter 4 was used to represent measured experimental data. Ideal adsorbed solution theory (IAST) was used to derive mixture isotherms to compare with experimental mixture data, and to generate isotherms where mixtures were not measured. The IAST, developed by Myers and Prausnitz [90], has a sounder thermodynamic basis than the extended Sips model and has been shown in many cases to better predict adsorption in multicomponent systems, including binary gas mixtures on carbon adsorbents [124]. The IAST predicts multicomponent adsorption systems based on the adsorbed phase being treated as an ideal solution of the adsorbed components and requires only the input of single component isotherm parameters. The main drawback of IAST is that the increased accuracy comes at a computational cost associated with iterative integration to determine the solution.

Momentum balance

A momentum balance was included in the form of the Ergun equation [125] to describe the pressure drop for a given column velocity. The Ergun equation is useful as it is a general pressure drop correlation and can be used in laminar and turbulent flow regimes. The equation used by Aspen Adsorption was:

\[
\frac{\partial P}{\partial z} = -\left(1.5 \times 10^{-3} \left(1 - \varepsilon_i\right)^2 \frac{\mu \rho}{\left(2r_p \Psi\right)^2 \varepsilon_i^3} + 1.75 \times 10^{-5} M \rho_g \frac{(1 - \varepsilon_i)}{2r_p \Psi \varepsilon_i^3 \nu_g} \right)
\]

where

\[\Psi\] is the sphericity factor

\[\mu\] is the dynamic viscosity (N s m\(^{-2}\))

\[M\] is the molecular weight of the gas (g mol\(^{-1}\))
\( \rho_g \) is the density of the gas (kg m\(^{-3}\))

**Gas phase energy balance**

The gas phase energy equation used by Aspen Adsorption was:

\[
-k_g \frac{\partial^2 T_g}{\partial z^2} + C_{vg} \rho_g \frac{\partial T_g}{\partial z} + \varepsilon_g C_{vg} \rho_g \frac{\partial T_g}{\partial t} + P \frac{\partial Q}{\partial z} + HTCa_p (T_g - T_s) + \frac{AH_w}{D_g} (T_g - T_w) = 0 \tag{5.7}
\]

where \( k_g \) is the gas phase thermal conductivity (W m\(^{-1}\) K\(^{-1}\))

\( T_g \) is the gas phase temperature (K)

\( C_{vg} \) is the specific gas phase heat capacity at constant volume (J mol\(^{-1}\) K\(^{-1}\))

\( HTC \) is the gas-solid heat transfer coefficient (W m\(^{-2}\) K\(^{-1}\))

\( a_p \) is the specific particle surface area per bed unit volume (m)

\( T_s \) is the solid phase temperature (K)

\( H_w \) is the gas-wall heat transfer coefficient (W m\(^{-2}\) K\(^{-1}\))

\( D_g \) is the bed diameter (m)

\( T_w \) is the wall temperature (K)

The terms in this equation from left to right are axial gas thermal conduction, gas convection, gas phase enthalpy accumulation, compression effect, gas-solid heat transfer, and gas to internal wall heat transfer.

**Solid phase energy balance**

The solid phase energy equation used by Aspen Adsorption was:

\[
-k_s \frac{\partial^2 T_s}{\partial z^2} + \rho_s C_{ps} \frac{\partial T_s}{\partial t} + \rho_s \sum_{i=1}^{n} (C_{ps_i} \rho_s \frac{\partial q}{\partial t}) + \rho_s \sum_{i=1}^{n} \left( \Delta H_i \frac{\partial q}{\partial t} \right) - HTCa_p (T_g - T_s) = 0 \tag{5.8}
\]

where \( k_s \) is the solid phase thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
\( C_{ps} \) is the adsorbent specific heat (J mol\(^{-1}\) K\(^{-1}\))

\( C_{paw} \) is the adsorbed phase specific heat (J mol\(^{-1}\) K\(^{-1}\))

\( H_i \) is the heat of adsorbed phase rate (J m\(^{-3}\) s\(^{-1}\))

The terms in this equation from left to right are axial solid thermal conduction, solid phase enthalpy accumulation, heat of adsorbed phase, heat of adsorption, and gas-solid heat transfer.

**Wall phase energy balance**

The wall phase energy equation used by Aspen Adsorption was:

\[
-k_w \frac{\partial^2 T_w}{\partial z^2} + \rho_w C_{pw} \frac{\partial T_w}{\partial t} - H_w \frac{4D_g}{(D_g + W_r)^2} (T_g - T_w) + H_{amb} \frac{4(D_g + W_r)^2}{(D_g + W_r)^2 - D_g^2} (T_w - T_{amb}) = 0 \quad (5.9)
\]

where

- \( k_w \) is the wall thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
- \( \rho_w \) is the density of the wall (kg m\(^{-3}\))
- \( C_{pw} \) is the wall specific heat (J mol\(^{-1}\) K\(^{-1}\))
- \( W_r \) is the column wall thickness (m)
- \( H_{amb} \) is the wall to ambient heat transfer coefficient (W m\(^{-2}\) K\(^{-1}\))
- \( T_{amb} \) is the ambient temperature (K)

The terms in this equation from left to right are axial wall thermal conduction, heat of column wall, gas-wall heat transfer, and wall to ambient heat transfer.

**Implemented model parameters**

The variable parameters implemented into Aspen Adsorption and their respective sources are shown in Table 5-1. Adsorbent specific heat and thermal conductivity were assumed to be the same for both Norit RB3 and MSC-3K-161, taken from published values for similar carbon based adsorbents. The adsorbed
phase specific heat \( (C_{pa}) \) was assumed to be equal to the heat capacity of the pure gas, which has been reported previously by Kapoor and Yang [126]. Liu and Ritter [127] assumed \( C_{pa} \) to be equal to that of the saturated liquid, and in subsequent work [128] discussed that obtaining an accurate value of \( C_{pa} \) was not a trivial exercise. Walton and LeVan [129] found the value of \( C_{pa} \) was likely to lie between the heat capacity of the pure gas and the saturated liquid. The properties for a 316 stainless steel wall are well known; however, the wall-ambient heat transfer \( (H_{amb}) \) was assumed to be the same as a published coefficient for a 316 stainless steel column in air. The assumptions made for \( C_{pa} \) and \( H_{amb} \) should be considered to be an area of improvement for future work.

| Table 5-1: Parameters implemented into Aspen Adsorption model for each adsorbent. |
|---------------------------------|--------|--------|
| Parameter                       | Norit RB3 | MSC-3K-161 |
| Mass of loaded adsorbent        | g       | 20.735 ± 0.005 | 30.973 ± 0.005 |
| Adsorbent bulk density \( (\rho_s) \) | kg m\(^{-3}\) | 405.9 | 606.3 |
| Adsorbent specific heat \( (C_{ps}) \) [130, 131] | MJ kg\(^{-1}\) K\(^{-1}\) | 0.00105 | 0.00105 |
| Adsorbent thermal conductivity \( (k_s) \) [130, 132] | MW m\(^{-1}\) K\(^{-1}\) | \(5 \times 10^{-7}\) | \(5 \times 10^{-7}\) |
| Interparticle voidage \( (\varepsilon_i) \) [133] | - | 0.397 | 0.397 |
| Pellet radius \( (r_p) \) | mm | 1.5 ± 0.1 | 0.9 ± 0.1 |
| Adsorbed phase specific heat \( (C_{pa,CH_4}) \) [17] | MJ kmol\(^{-1}\) K\(^{-1}\) | 0.03569 | 0.03569 |
| Adsorbed phase specific heat \( (C_{pa,N_2}) \) [17] | MJ kmol\(^{-1}\) K\(^{-1}\) | 0.02912 | 0.02912 |
| Wall thickness \( (W_r) \) | mm | 2.4 ± 0.1 | 2.4 ± 0.1 |
| Wall bulk density \( (\rho_w) \) [134] | kg m\(^{-3}\) | 8000 | 8000 |
| Wall specific heat \( (C_{pw}) \) [131, 134, 135] | MJ kg\(^{-1}\) K\(^{-1}\) | \(5 \times 10^{-4}\) | \(5 \times 10^{-4}\) |
| Wall thermal conductivity \( (k_w) \) [136] | MW m\(^{-1}\) K\(^{-1}\) | \(1.6 \times 10^{-5}\) | \(1.6 \times 10^{-5}\) |
| Wall-ambient heat transfer \( (H_{amb}) \) [135] | MW m\(^{-2}\) K\(^{-1}\) | \(1.2 \times 10^{-7}\) | \(1.2 \times 10^{-7}\) |
5.2.4 Solution of the implemented model

Aspen Adsorption uses combinations of partial differential equations (PDEs), ordinary differential equations (ODEs), and algebraic equations to describe model elements. Spatial derivative terms within the PDEs are discretised with several choices of differencing schemes available. The standard and most simple upwind differencing scheme (UDS) was chosen for this work as it is unconditionally stable and non-oscillatory [112]. The UDS is suggested for initial investigations as it performs well in most cases; however, this scheme may introduce numerical dispersion to the result. The time integrator used was the standard implicit Euler with variable step size. This scheme remains stable in most cases, but decreases in accuracy, as the step size is increased. This numerical dispersion can be minimised and accuracy maintained, by increasing the number of spatial nodes and decreasing the time step used in the simulation. The disadvantage with these actions is the increased simulation time required; however, for single breakthrough experiment modelling the increase in simulation time can be tolerated. Nevertheless, this could become prohibitive simulating cyclic multi-bed processes. The time required to achieve a solution for the simulations in this work ranged from 10 to 3600 s on a Core 2 Duo T7300 CPU running at 2.0 GHz. The implemented solver and parameters are shown in Table 5-2.
Table 5-2: Solver and parameters implemented into Aspen Adsorption.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integration method</td>
<td>Implicit Euler</td>
</tr>
<tr>
<td>Linear solver</td>
<td>MA48</td>
</tr>
<tr>
<td>Non-linear solver</td>
<td>Mixed Newton</td>
</tr>
<tr>
<td>Absolute tolerance</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Relative tolerance</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Initial step size (s)</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Minimum step size (s)</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>Space discretisation</td>
<td>1st order upwind differencing scheme</td>
</tr>
<tr>
<td>Number of adsorption column nodes</td>
<td>100</td>
</tr>
<tr>
<td>Number of tube nodes</td>
<td>50</td>
</tr>
</tbody>
</table>

5.3 Extra-column void volume

The total extra-column volume (Figure 5-1) of the DCB apparatus was measured using three different methods: gravimetric, blank breakthrough, and dimensional measurements. The result of each of these measurements is shown in Table 5-3.

Table 5-3: Measured extra-column void volumes.

<table>
<thead>
<tr>
<th>Measurement method</th>
<th>Measured section</th>
<th>Measured volume [cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric</td>
<td>Total</td>
<td>38.3 ± 2.9</td>
</tr>
<tr>
<td>Blank breakthrough</td>
<td>Total</td>
<td>36.0 ± 3.0</td>
</tr>
<tr>
<td>Dimensional</td>
<td>Inlet tube</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>Inlet cone</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>Outlet cone</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>High pressure outlet tube</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>Low pressure outlet tube</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>33.1 ± 0.6</td>
</tr>
</tbody>
</table>

The gravimetric and blank breakthrough measurements were performed with the column removed and the inlet and outlet cones connected together. The
Gravimetric measurement was completed by filling the extra-column volume with pressurised gas from a small sample cylinder. The cylinder was connected to the outlet of the mass flow meter (MFM), with MPV-1 plugged to isolate the flow path volume. The difference in mass from the depressurisation of the sample cylinder was used to calculate the extra-column volume. The advantage to making gravimetric measurements in this way is that the change in mass, and therefore the gas introduced into the void volume, can be determined accurately. However, additional measured volume that does not contribute to the flow path is also introduced and occurs as internal ‘dead-end voids’ that are connected to the flow path. For example, it measures the voids to sensors in the MFM and BPR-2, the tubing to quartz-crystal pressure transducer 1 and 2 (QPT-1 and QPT-2) and any other fittings, which are essentially dead-ends to gas flow. For this reason, it is likely that the extra-column volume determined by gravimetric measurement is an overestimation in the context of a dynamic model.

Blank breakthrough measurements were performed by displacing gas in the extra-column volume with an alternate gas. The extra-column volume was then calculated from the amount of gas displaced from the system. This type of blank measurement is probably the most reliable way of determining the extra-column void volume as it directly measures the gas that would be evolved during an experiment [63, 70]. While blank measurements are a valuable tool for determining the overall extra-column volume, it is difficult to determine the volumes of the individual system components with this technique.

A dimensional analysis was also conducted by manually measuring each of the system components. A duplicate BPR and MFM were disassembled to acquire the necessary internal dimensional measurements; some sections of the instruments were sealed and had to be estimated. This introduced uncertainty to
the volume determined at the outlet of the column, particularly the low pressure section. One of the key assumptions made in calculating the tube volumes was that the tube cross-sections were uniform along the length of the tubes. The total extra-column volume determined by dimensional measurement was the lowest of the three methods, potentially because of an underestimation of sealed components or irregularities along tube lengths. Importantly, all three methods determined volumes that were consistent within their combined statistical uncertainties.

The total system volume was taken to be 36.0 cm$^3$, as determined by blank breakthrough measurements. The dimensional measurements were used to determine the distribution of void volumes in the inlet tube, inlet cone, outlet cone, high pressure outlet tube, and low pressure outlet tube. As there was a discrepancy of 2.9 cm$^3$ between the two methods, the difference in volume was added to the low pressure outlet tube because the sealed sections of the BPR, MFM, and connection to the MS were thought to be the most likely sources of uncertainty in the dimensional measurements.

The determined volumes were implemented into the Aspen Adsorption model and blank breakthroughs were modelled with the adsorption column removed. Figure 5-3 shows the comparison between experimentally measured blank breakthroughs at 108.6 and 793.0 kPa, at 302.0 K, and blank breakthroughs modelled with Aspen Adsorption. This result displays excellent agreement between the measured and modelled blank breakthroughs, showing that the total volume was closely estimated to the correct value and that the combination of PFTRs and CSTRs work well to predict the blank breakthrough profiles. Furthermore, this result shows that the limitation of not modelling the residence time hold up in the CSTRs appears to be insignificant.
Figure 5-3: Comparison of experimental blank measurements at 108.6 and 793.0 kPa, at 302.0 K, with blank profiles modelled in Aspen Adsorption. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

5.4 Norit RB3 activated carbon

5.4.1 Adsorption equilibria and heats of adsorption

The adsorption isotherms of pure N\textsubscript{2} and CH\textsubscript{4} were measured at three temperatures to a maximum pressure of 902.9 kPa with the DCB apparatus and were then fitted to the Sips isotherm model (Figure 5-4 and Figure 5-5, respectively). For each regression, 11 data points were used (included in Appendix A). The deviations between the measured adsorption capacities and fitted Sips model for N\textsubscript{2} and CH\textsubscript{4} are also shown. All calculated pure gas capacities were within the experimental uncertainty of the measured data.

The adsorption isotherms of equimolar binary N\textsubscript{2} and CH\textsubscript{4} were measured at three temperatures to a maximum pressure of 903.2 kPa with the DCB apparatus. Equimolar binary isotherms were predicted using IAST with the pure gas Sips
parameters. The measured isotherm data and predicted IAST Sips model at each temperature, with the deviations of the models from the data, are shown in Figure 5-6, Figure 5-7, and Figure 5-8. The measured adsorption capacities and those predicted by the IAST Sips model are in excellent agreement, with only 8 of 42 points deviating by more than the experimental uncertainty, and none by more than two standard deviations. This result suggests that IAST could be used to reliably predict mixture data for the Norit RB3 adsorbent, reducing the need for additional binary gas equilibrium adsorption measurements.

At reduced adsorption temperatures, the favourability of the measured isotherms increased [30]; that is, the Henry's law region of the isotherm steepened over the same pressure range as temperature decreased. This was more evident for CH₄, which is advantageous, as Norit RB3 would be used for a CH₄ equilibrium selective process. Having a favourable isotherm is important because it means a smaller change in pressure will induce a larger adsorbent working capacity (discussed in Chapter 2). Another benefit of a favourable isotherm is that they generally reduce problems caused by axial-diffusion, dispersion, and slow mass transfer [30]. As adsorbate moves through a column, adsorption occurs at the particle surface; however, adsorbate further from the surface is swept ahead and blurs the adsorption front. Flow near the column wall moves faster because of the decreased adsorption in this area, also increasing blurring of the adsorption front. For a favourable isotherm, there is a stronger driving force for the adsorbate swept ahead of the front to be adsorbed, retarding the front end of the mass transfer zone (MTZ), whereas adsorbate at the end of the MTZ is in contact with a nearly saturated adsorbent and is therefore carried forward at a faster rate. Overall, a favourable isotherm creates a balance between blurring effects and self-sharpening. Generally, as the isotherm becomes more favourable, the size of
the MTZ decreases, which is beneficial for PSA processes because the MTZ limits the extent to which the adsorbent bed can be utilised.

Figure 5-4: (a) Equilibrium adsorption capacity of N₂ on Norit RB3 measured using the DCB apparatus with fitted Sips model. (b) Deviations between the measured capacities and those calculated using the Sips isotherm model.
Figure 5-5: (a) Equilibrium adsorption capacity of CH₄ on Norit RB3 measured using the DCB apparatus with fitted Sips model. (b) Deviations between the measured capacities and those calculated using the Sips isotherm model.
The fitted model parameters for pure N$_2$ and CH$_4$ are shown in Table 5-4. To compare the experimental and modelled curves, the normalised root mean square error (NRMSE) was calculated for each component and reported as an average of the components. The calculation was performed using:

\[
RMSE = \sqrt{\frac{\sum_{i=1}^{N}(X_{\text{experiment},i} - X_{\text{model},i})^2}{N}} \tag{5.10}
\]

\[
NRMSE = \frac{RMSE}{X_{\text{experiment,max}} - X_{\text{experiment,min}}} \tag{5.11}
\]

where \(RMSE\) is the root mean square error

\(N\) is the number of data points

\(X_{\text{experiment}}\) is the value of the experimental point

\(X_{\text{model}}\) is the value of the modelled point

**Table 5-4:** Parameters of the Sips model fitted to pure gas adsorption capacities on Norit RB3.

<table>
<thead>
<tr>
<th>Sips model</th>
<th>N$_2$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{\text{max}}$ [mmol g$^{-1}$]</td>
<td>4.78 ± 1.60</td>
<td>7.26 ± 1.10</td>
</tr>
<tr>
<td>$K_0 \times 10^6$ [kPa$^{-1}$]</td>
<td>1.21 ± 0.79</td>
<td>0.67 ± 0.28</td>
</tr>
<tr>
<td>-$\Delta$H [kJ mol$^{-1}$]</td>
<td>14.31 ± 1.60</td>
<td>16.88 ± 0.96</td>
</tr>
<tr>
<td>$n$</td>
<td>0.90 ± 0.10</td>
<td>0.76 ± 0.09</td>
</tr>
<tr>
<td>NRMSE</td>
<td>2.9 %</td>
<td>1.4 %</td>
</tr>
</tbody>
</table>
Figure 5-6: (a) Equilibrium adsorption capacities of N$_2$ and CH$_4$ on Norit RB3 at 302.4 K with a $0.5N_2 + 0.5CH_4$ feed measured using the DCB apparatus, and predicted isotherms using IAST with Sips isotherms. (b) Deviations between the measured capacities and those predicted using IAST with Sips isotherms.
Figure 5-7: (a) Equilibrium adsorption capacities of N₂ and CH₄ on Norit RB3 at 273.3 K with a 0.5N₂ + 0.5CH₄ feed measured using the DCB apparatus, and predicted isotherms using IAST with Sips isotherms. (b) Deviations between the measured capacities and those predicted using IAST with Sips isotherms.
Figure 5-8: (a) Equilibrium adsorption capacities of $N_2$ and $CH_4$ on Norit RB3 at 243.7 K with a $0.5N_2 + 0.5CH_4$ feed measured using the DCB apparatus, and predicted isotherms using IAST with Sips isotherms. (b) Deviations between the measured capacities and those predicted using IAST with Sips isotherms.
5.4.2 Extraction of mass transfer coefficients

The MTCs were determined by fitting the component flow rates simulated with Aspen Adsorption to the experimental data. The extracted MTCs for pure N\textsubscript{2} and CH\textsubscript{4} on Norit RB3 and the fitting error are shown in Table 5-5 and Table 5-6, respectively. Norit RB3 has larger pore sizes than CH\textsubscript{4} and is therefore equilibrium selective, as discussed in Section 4.2, which is shown by the similar magnitude of the extracted N\textsubscript{2} and CH\textsubscript{4} MTCs. The NRMSE between the experimental component flow rate breakthrough curves and those of the fitted models ranged from 0.02 to 0.64 % for N\textsubscript{2} and 0.07 to 0.47 % for CH\textsubscript{4}.

Table 5-5: Extracted N\textsubscript{2} MTCs on Norit RB3.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>P [kPa]</th>
<th>Feed flow rate [mol s\textsuperscript{-1}]</th>
<th>MTC\textsubscript{experiment} [s\textsuperscript{-1}]</th>
<th>NRMSE of fit %</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.0</td>
<td>105.0</td>
<td>3.380 × 10\textsuperscript{-5}</td>
<td>0.0308</td>
<td>0.04</td>
</tr>
<tr>
<td>302.3</td>
<td>105.4</td>
<td>3.385 × 10\textsuperscript{-5}</td>
<td>0.0317</td>
<td>0.04</td>
</tr>
<tr>
<td>302.3</td>
<td>106.7</td>
<td>5.072 × 10\textsuperscript{-5}</td>
<td>0.0550</td>
<td>0.02</td>
</tr>
<tr>
<td>302.2</td>
<td>108.2</td>
<td>6.771 × 10\textsuperscript{-5}</td>
<td>0.0805</td>
<td>0.03</td>
</tr>
<tr>
<td>302.4</td>
<td>108.7</td>
<td>6.772 × 10\textsuperscript{-5}</td>
<td>0.0801</td>
<td>0.03</td>
</tr>
<tr>
<td>302.3</td>
<td>304.6</td>
<td>6.781 × 10\textsuperscript{-5}</td>
<td>0.0439</td>
<td>0.02</td>
</tr>
<tr>
<td>302.3</td>
<td>504.1</td>
<td>6.806 × 10\textsuperscript{-5}</td>
<td>0.0177</td>
<td>0.09</td>
</tr>
<tr>
<td>302.4</td>
<td>702.8</td>
<td>6.778 × 10\textsuperscript{-5}</td>
<td>0.0096</td>
<td>0.18</td>
</tr>
<tr>
<td>302.1</td>
<td>902.9</td>
<td>3.561 × 10\textsuperscript{-5}</td>
<td>0.0066</td>
<td>0.32</td>
</tr>
<tr>
<td>302.3</td>
<td>902.4</td>
<td>6.824 × 10\textsuperscript{-5}</td>
<td>0.0027</td>
<td>0.34</td>
</tr>
<tr>
<td>273.6</td>
<td>108.7</td>
<td>6.764 × 10\textsuperscript{-5}</td>
<td>0.0631</td>
<td>0.05</td>
</tr>
<tr>
<td>273.8</td>
<td>504.8</td>
<td>6.788 × 10\textsuperscript{-5}</td>
<td>0.0112</td>
<td>0.11</td>
</tr>
<tr>
<td>274.3</td>
<td>902.9</td>
<td>6.793 × 10\textsuperscript{-5}</td>
<td>0.0047</td>
<td>0.48</td>
</tr>
<tr>
<td>245.1</td>
<td>106.6</td>
<td>6.780 × 10\textsuperscript{-5}</td>
<td>0.0391</td>
<td>0.05</td>
</tr>
<tr>
<td>241.9</td>
<td>502.7</td>
<td>6.764 × 10\textsuperscript{-5}</td>
<td>0.0063</td>
<td>0.21</td>
</tr>
<tr>
<td>245.0</td>
<td>901.0</td>
<td>6.949 × 10\textsuperscript{-5}</td>
<td>0.0040</td>
<td>0.64</td>
</tr>
</tbody>
</table>
Table 5-6: Extracted CH₄ MTCs on Norit RB3.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>P [kPa]</th>
<th>Feed flow rate [mol s⁻¹]</th>
<th>MTC&lt;sub&gt;experiment&lt;/sub&gt; [s⁻¹]</th>
<th>NRMSE of fit %</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.4</td>
<td>104.7</td>
<td>3.433 × 10⁻⁵</td>
<td>0.0132</td>
<td>0.18</td>
</tr>
<tr>
<td>302.4</td>
<td>103.7</td>
<td>5.131 × 10⁻⁵</td>
<td>0.0228</td>
<td>0.10</td>
</tr>
<tr>
<td>302.5</td>
<td>106.4</td>
<td>6.812 × 10⁻⁵</td>
<td>0.0301</td>
<td>0.08</td>
</tr>
<tr>
<td>302.7</td>
<td>304.4</td>
<td>6.814 × 10⁻⁵</td>
<td>0.0177</td>
<td>0.08</td>
</tr>
<tr>
<td>302.6</td>
<td>503.9</td>
<td>6.831 × 10⁻⁵</td>
<td>0.0116</td>
<td>0.07</td>
</tr>
<tr>
<td>302.6</td>
<td>703.0</td>
<td>6.863 × 10⁻⁵</td>
<td>0.0071</td>
<td>0.12</td>
</tr>
<tr>
<td>302.2</td>
<td>902.4</td>
<td>3.393 × 10⁻⁵</td>
<td>0.0018</td>
<td>0.46</td>
</tr>
<tr>
<td>302.2</td>
<td>902.4</td>
<td>3.384 × 10⁻⁵</td>
<td>0.0017</td>
<td>0.47</td>
</tr>
<tr>
<td>302.4</td>
<td>902.2</td>
<td>6.725 × 10⁻⁵</td>
<td>0.0047</td>
<td>0.26</td>
</tr>
<tr>
<td>302.4</td>
<td>902.6</td>
<td>6.728 × 10⁻⁵</td>
<td>0.0048</td>
<td>0.27</td>
</tr>
<tr>
<td>273.8</td>
<td>106.5</td>
<td>6.822 × 10⁻⁵</td>
<td>0.0336</td>
<td>0.12</td>
</tr>
<tr>
<td>274.2</td>
<td>504.7</td>
<td>6.792 × 10⁻⁵</td>
<td>0.0067</td>
<td>0.13</td>
</tr>
<tr>
<td>273.7</td>
<td>902.8</td>
<td>6.731 × 10⁻⁵</td>
<td>0.0038</td>
<td>0.37</td>
</tr>
<tr>
<td>244.9</td>
<td>104.7</td>
<td>6.798 × 10⁻⁵</td>
<td>0.0163</td>
<td>0.22</td>
</tr>
<tr>
<td>244.3</td>
<td>503.1</td>
<td>6.733 × 10⁻⁵</td>
<td>0.0050</td>
<td>0.23</td>
</tr>
<tr>
<td>244.5</td>
<td>900.8</td>
<td>6.710 × 10⁻⁵</td>
<td>0.0029</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Although relatively small, the uncertainty between the experimental data and model increased as pressure increased and temperature decreased. One possible reason for this was that a portion of the experimental system (outlet heating loop) remained at atmospheric temperature during low temperature measurements, whereas the external temperature of the entire system was considered constant in the model (held at the initial bed temperature). The gas in the section held at atmospheric temperature during an experiment would have a lower density than predicted by the model, which would increase the volumetric flow rate in that section. The difference between the experimental and predicted volumetric flow rate would widen at decreased temperatures and increased pressures, possibly explaining the deviations observed. To account for different external system component temperatures would require an energy balance on each of the extra-
column components at different external temperatures; however, this would significantly increase modelling time with only a relatively small improvement to be made.

Component flow rate breakthrough curves and bed temperature profiles with fitted model predictions were selected to show the quality and general nature of the fits. Figure 5-9 shows the breakthrough profile of N₂ at the lowest pressure and highest flow rate measured on Norit RB3, which corresponds to the fastest breakthrough time with the least amount of adsorption. For this case, the model predicts the experimental breakthrough curve well; the main deviation is the early breakthrough roll-up of the He component flow before N₂ breakthrough. The breakthrough roll-up is the result of an increase in gas velocity, from the outlet of the adsorption column, as the adsorption bed reaches saturation. The He component flow rate increases during roll-up and reaches a maximum when the He remaining in the outlet cone and tubing is replaced with a larger fraction of the adsorbate. At this point the He component flow rate decreases until it is completely driven from the system; however, the total component flow rate will continue to increase to the flow rate of the inlet adsorbate/s. Figure 5-10 and Figure 5-11 represent the middle of the range of experimental measurements for pressure and temperature for N₂ and CH₄, respectively. Figure 5-12 shows the breakthrough profile of CH₄ at the highest pressure and lowest flow rate of those measured on Norit RB3, which corresponds to the longest breakthrough time and largest adsorption capacity. Under these conditions, the preliminary decrease in the experimental He flow displays a slightly larger initial trough and smaller breakthrough roll-up than predicted by the model. A feature common to all of the presented curves is that the measured change in the He flow rates closely matches the model, which indicates that velocity changes in the column are well accounted
The small differences observed are likely to be explained primarily by the contributions of instrumental errors in the experimental measurements and the simplifying assumptions of the model.

Figure 5-9: Dynamic adsorption of N₂ on Norit RB3 at 108.2 kPa, 302.2 K. (a) Column effluent flow rate of He and N₂ with fitted model to 300 seconds. (b) Bed temperature profiles with fitted model to 600 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-10: Dynamic adsorption of N₂ on Norit RB3 at 504.8 kPa, 273.8 K. (a) Column effluent flow rate of He and N₂ with fitted model. (b) Bed temperature profiles with fitted model. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-11: Dynamic adsorption of CH$_4$ on Norit RB3 at 504.7 kPa, 274.2 K. (a) Column effluent flow rate of He and CH$_4$ with fitted model. (b) Bed temperature profiles with fitted model. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-12: Dynamic adsorption of CH₄ on Norit RB3 at 900.8 kPa, 244.5 K. (a) Column effluent flow rate of He and CH₄ with fitted model. (b) Bed temperature profiles with fitted model. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Larger deviations can be seen between the experimental and modelled temperature profiles shown in Figure 5-9 through Figure 5-12, between about 0.5 to 1 K difference at each of the curve peaks. The temperature predicted by the model is an average across the cross-section of the adsorption column; however, the temperature sensor mounted in the column (Figure 5-13) is a very local temperature measurement. Furthermore, measurements from the temperature sensor in the column are a combination of contact with adsorbent particles and the surrounding gas. The complex hydrodynamics of the flow surrounding the sensor arising from the randomly packed particles, and the locally released heat of adsorption will cause fluctuations in the measured temperatures. In essence, it is difficult to assign a definite temperature to a region of space that is heterogeneous and stochastic. Figure 5-13 also highlights an important assumption of the model, which is the energy transfer to the column wall. This would be affected by the ratio of the column wall area in contact with gas, to the area in contact with the adsorbent particle.

![Diagram of packed column cross-section showing random packing of adsorbent in contact with a temperature sensor and the column wall.](image)

**Figure 5-13:** Packed column cross-section showing random packing of adsorbent in contact with a temperature sensor and the column wall.
Some of the inaccuracies with the bed sensors could be overcome by obtaining bed temperatures with alternative techniques such as thermal imaging, which does not suffer from variability introduced by the local measurement environment.

Nevertheless, within the constraints caused by experimental temperature measurements and the assumptions made for the parameters used in the model energy balance, the model predictions are useful to identify the general temperature-time profiles along the adsorption column and generated peak temperatures within 1 K.

5.4.3 Correlation of mass transfer coefficients

The measured MTCs were correlated against the superficial gas velocity, $v_{gp}$, which is a key parameter often used in empirical correlations to predict MTCs [30, 117]. Figure 5-14 shows a linear relationship between the $N_2$ and $CH_4$ MTCs and $v_{gp}$. Since the intraparticle diffusion (macropore and micropore) cannot be affected by gas velocity, this strong dependence is likely to be reconciled by external film resistance [55]. These results suggest that the external film resistance (the first term on the right hand side of Equation (5.4)) is the dominant resistance under the conditions measured. This trend is typical of an external film resistance, which should decrease as the increased gas velocity dissipates the film at the pellet surface.
From the observed dependence in Figure 5-14, the extracted MTCs were regressed to the following empirical equation, which was chosen based on the observed behaviour of the MTCs and \( v_g \):

\[
MTC = k_a v_g
\]  

(5.12)

where \( k_a \) is an empirical fitting parameter (m^{-1}).

The adjustable parameters determined for each of the fits were:

- \( N_2 \): \( k_a = 17.72 \) m^{-1}.
- \( CH_4 \): \( k_a = 7.43 \) m^{-1}.

The MTC values calculated with Equation (5.12) at each experimental \( v_g \) for \( N_2 \) and \( CH_4 \) are shown in Table 5-7 and Table 5-8, respectively, and are compared with the corresponding experimentally measured MTCs. A significant limitation of the relationship in Equation 5.12 is that the MTCs are unbounded with increasing...
\( v_g \) whereas in practice once the velocity reaches the point where the film resistance is completely dissipated, the pore resistance will become the dominant term, as per Equation (5.4). Unfortunately, the data measured here do not clearly show such a resistance transition. For this reason, Equation (5.12) should not be extrapolated beyond the velocity range measured in this work. Furthermore, it should not be used to estimate MTCs at conditions of pressure and temperature beyond the range of the data reported here. This second constraint is needed because it is possible that particular combinations of pressure, temperature, and molar flow rate could result in a \( v_g \) within the velocity range of regressed data, even if the pressure and temperature are far removed from the conditions examined here. In such cases it is very likely that the MTCs predicted by the model would be inaccurate.

The deviations between the measured and predicted MTCs for N\(_2\) and CH\(_4\) are shown in Figure 5-15 and Figure 5-16, respectively. The uncertainties shown in these plots are 50 % of the measured values. At this uncertainty level, four of the N\(_2\) MTCs lie outside this range; however, three of these values are within one additional standard uncertainty. All of the CH\(_4\) MTCs predicted by the model lie within the 50 % uncertainty range. This suggests that the regressed models can predict the measured MTCs within about 50 % of the measured values at the conditions of temperature, pressure, and velocity studied in this research.
### Table 5-7: Modelled Norit RB3 N₂ MTCs.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>P [kPa]</th>
<th>(v_g) [m s(^{-1})]</th>
<th>MTC(_{\text{model}}) [s(^{-1})]</th>
<th>(\Delta\text{MTC}_{\text{expt-model}}) [s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.0</td>
<td>105.0</td>
<td>(2.070 \times 10^{-3})</td>
<td>0.0367</td>
<td>-0.0059</td>
</tr>
<tr>
<td>302.3</td>
<td>105.4</td>
<td>(2.067 \times 10^{-3})</td>
<td>0.0366</td>
<td>-0.0050</td>
</tr>
<tr>
<td>302.3</td>
<td>106.7</td>
<td>(3.059 \times 10^{-3})</td>
<td>0.0542</td>
<td>0.0008</td>
</tr>
<tr>
<td>302.2</td>
<td>108.2</td>
<td>(4.026 \times 10^{-3})</td>
<td>0.0713</td>
<td>0.0092</td>
</tr>
<tr>
<td>302.4</td>
<td>108.7</td>
<td>(4.011 \times 10^{-3})</td>
<td>0.0711</td>
<td>0.0090</td>
</tr>
<tr>
<td>302.3</td>
<td>304.6</td>
<td>(1.433 \times 10^{-3})</td>
<td>0.0254</td>
<td>0.0185</td>
</tr>
<tr>
<td>302.3</td>
<td>504.1</td>
<td>8.689 \times 10^{-4}</td>
<td>0.0154</td>
<td>0.0023</td>
</tr>
<tr>
<td>302.4</td>
<td>702.8</td>
<td>6.207 \times 10^{-4}</td>
<td>0.0110</td>
<td>-0.0014</td>
</tr>
<tr>
<td>302.1</td>
<td>902.9</td>
<td>2.537 \times 10^{-4}</td>
<td>0.0045</td>
<td>0.0021</td>
</tr>
<tr>
<td>302.3</td>
<td>902.4</td>
<td>4.866 \times 10^{-4}</td>
<td>0.0086</td>
<td>-0.0059</td>
</tr>
<tr>
<td>273.6</td>
<td>108.7</td>
<td>(3.626 \times 10^{-3})</td>
<td>0.0643</td>
<td>-0.0012</td>
</tr>
<tr>
<td>273.8</td>
<td>504.8</td>
<td>(7.840 \times 10^{-4})</td>
<td>0.0139</td>
<td>-0.0027</td>
</tr>
<tr>
<td>274.3</td>
<td>902.9</td>
<td>(4.392 \times 10^{-4})</td>
<td>0.0078</td>
<td>-0.0031</td>
</tr>
<tr>
<td>245.1</td>
<td>106.6</td>
<td>(3.317 \times 10^{-3})</td>
<td>0.0588</td>
<td>-0.0197</td>
</tr>
<tr>
<td>241.9</td>
<td>502.7</td>
<td>(6.929 \times 10^{-4})</td>
<td>0.0123</td>
<td>-0.0059</td>
</tr>
<tr>
<td>245.0</td>
<td>901.0</td>
<td>(4.022 \times 10^{-4})</td>
<td>0.0071</td>
<td>-0.0032</td>
</tr>
</tbody>
</table>

### Table 5-8: Modelled Norit RB3 CH₄ MTCs.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>P [kPa]</th>
<th>(v_g) [m s(^{-1})]</th>
<th>MTC(_{\text{model}}) [s(^{-1})]</th>
<th>(\Delta\text{MTC}_{\text{expt-model}}) [s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.4</td>
<td>104.7</td>
<td>(2.111 \times 10^{-3})</td>
<td>0.0157</td>
<td>-0.0025</td>
</tr>
<tr>
<td>302.4</td>
<td>103.7</td>
<td>(3.185 \times 10^{-3})</td>
<td>0.0237</td>
<td>-0.0008</td>
</tr>
<tr>
<td>302.5</td>
<td>106.4</td>
<td>(4.121 \times 10^{-3})</td>
<td>0.0306</td>
<td>-0.0005</td>
</tr>
<tr>
<td>302.7</td>
<td>304.4</td>
<td>(1.442 \times 10^{-3})</td>
<td>0.0107</td>
<td>0.0070</td>
</tr>
<tr>
<td>302.6</td>
<td>503.9</td>
<td>(8.735 \times 10^{-4})</td>
<td>0.0065</td>
<td>0.0051</td>
</tr>
<tr>
<td>302.6</td>
<td>703.0</td>
<td>(6.288 \times 10^{-4})</td>
<td>0.0047</td>
<td>0.0024</td>
</tr>
<tr>
<td>302.2</td>
<td>902.4</td>
<td>(2.419 \times 10^{-4})</td>
<td>0.0018</td>
<td>0.0000</td>
</tr>
<tr>
<td>302.2</td>
<td>902.4</td>
<td>(2.413 \times 10^{-4})</td>
<td>0.0018</td>
<td>-0.0001</td>
</tr>
<tr>
<td>302.4</td>
<td>902.2</td>
<td>(4.798 \times 10^{-4})</td>
<td>0.0036</td>
<td>0.0012</td>
</tr>
<tr>
<td>302.4</td>
<td>902.6</td>
<td>(4.798 \times 10^{-4})</td>
<td>0.0036</td>
<td>0.0012</td>
</tr>
<tr>
<td>273.8</td>
<td>106.5</td>
<td>(3.734 \times 10^{-3})</td>
<td>0.0277</td>
<td>0.0058</td>
</tr>
<tr>
<td>274.2</td>
<td>504.7</td>
<td>(7.856 \times 10^{-4})</td>
<td>0.0058</td>
<td>0.0009</td>
</tr>
<tr>
<td>273.7</td>
<td>902.8</td>
<td>(4.345 \times 10^{-4})</td>
<td>0.0032</td>
<td>0.0006</td>
</tr>
<tr>
<td>244.9</td>
<td>104.7</td>
<td>(3.385 \times 10^{-3})</td>
<td>0.0252</td>
<td>-0.0088</td>
</tr>
<tr>
<td>244.3</td>
<td>503.1</td>
<td>(6.961 \times 10^{-4})</td>
<td>0.0052</td>
<td>-0.0001</td>
</tr>
<tr>
<td>244.5</td>
<td>900.8</td>
<td>(3.877 \times 10^{-4})</td>
<td>0.0029</td>
<td>0.00001</td>
</tr>
</tbody>
</table>
Figure 5-15: Deviations between the measured $N_2$ MTCs and those calculated using Equation (5.12).

Figure 5-16: Deviations between the measured $CH_4$ MTCs and those calculated using Equation (5.12).
Mass transfer data for Norit RB3 for \( \text{N}_2 \) and \( \text{CH}_4 \) could not be found in the literature; however, Shen et al. [137] performed \( \text{N}_2 \) measurements on a coal tar pitch activated carbon, with a similar surface area (845.9 m\(^2\) g\(^{-1}\)), and Malek and Farooq [138] performed \( \text{CH}_4 \) measurements on an unidentified activated carbon, with a surface area of 970 m\(^2\) g\(^{-1}\).

Shen et al. [137] performed breakthrough experiments at a constant \( \text{N}_2 \) pressure of 50 kPa, temperatures between 303 and 423 K, with \( \nu_g \) between \( 7.71 \times 10^{-3} \) and \( 1.00 \times 10^{-2} \) m s\(^{-1}\). The overall MTCs measured for these conditions ranged between 1.07 and 4.27 s\(^{-1}\), which is consistent with the higher measurement temperatures and that the \( \nu_g \) in their work was 4 to 10 times larger than in this study. Furthermore, Shen et al. [137] used activated carbon beads with a smaller \( r_p \) (0.545 mm) than those used in this work, which would also increase the measured MTCs. The observed differences in the MTCs are reasonable considering the measurements made by Shen et al. [137] were outside the conditions studied in this work, and the samples used for the two studies were different.

Malek and Farooq [138] performed breakthrough experiments with \( \text{CH}_4 \) at pressures between 199 and 651 kPa, temperatures between 299 and 338 K, with a \( \nu_g \) between \( 5.92 \times 10^{-3} \) and \( 1.69 \times 10^{-2} \) m s\(^{-1}\). The overall MTCs measured for these conditions ranged between 0.14 and 0.65 s\(^{-1}\), which are again higher than those measured in this work. One possible reason for the smaller observed difference is because the particle size (\( r_p = 1.3 \) mm) is quite close to that in this study. It is difficult to determine to what extent other physical adsorbent properties are responsible for the observed differences without knowing the exact type of adsorbent Malek and Farooq [138] studied.
5.4.4 Parameter testing with binary adsorbate experiments

Experimentally measured binary breakthrough curves were compared with modelled breakthrough curves at identical conditions to test the parameters derived for Norit RB3. For this test, the pure N₂ and CH₄ isotherm parameters with IAST were used, and the component N₂ and CH₄ MTCs were predicted using the regressed MTC model for the pure fluids. The interaction of the pure fluid MTCs in binary mixtures was considered negligible in this study, based on previous studies by Mohr et al. [139] and Ackley and Yang [44]. Mohr et al. [139] studied the pure and binary kinetics of N₂ and CH₄ on 4A zeolite and found little difference between the pure component and mixture kinetics. Ackley and Yang [44] studied a PSA process for N₂ + CH₄ separations and concluded that the only physical data required for estimates of PSA performance were independently measured pure gas isotherms and diffusivities. Four comparisons were made to encompass the extremities of the pressure and temperature range measured. Table 5-9 shows the experiments that were modelled for comparison, the calculated MTCs used in the model, and the NRMSE of each of the fits.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>P [kPa]</th>
<th>v_g [m s⁻¹]</th>
<th>y_N₂</th>
<th>y_CH₄</th>
<th>N₂ MTC_{model} [s⁻¹]</th>
<th>CH₄ MTC_{model} [s⁻¹]</th>
<th>NRMSE of fit %</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.3</td>
<td>107.6</td>
<td>4.084 × 10⁻³</td>
<td>0.51</td>
<td>0.49</td>
<td>7.24 × 10⁻²</td>
<td>3.03 × 10⁻²</td>
<td>3.37</td>
</tr>
<tr>
<td>302.2</td>
<td>902.9</td>
<td>5.061 × 10⁻⁴</td>
<td>0.51</td>
<td>0.49</td>
<td>8.97 × 10⁻³</td>
<td>3.76 × 10⁻³</td>
<td>3.72</td>
</tr>
<tr>
<td>244.8</td>
<td>106.3</td>
<td>3.338 × 10⁻³</td>
<td>0.51</td>
<td>0.49</td>
<td>5.91 × 10⁻²</td>
<td>2.48 × 10⁻²</td>
<td>4.07</td>
</tr>
<tr>
<td>241.9</td>
<td>902.8</td>
<td>4.081 × 10⁻⁴</td>
<td>0.51</td>
<td>0.49</td>
<td>7.23 × 10⁻³</td>
<td>3.03 × 10⁻³</td>
<td>5.11</td>
</tr>
</tbody>
</table>

Figure 5-17 and Figure 5-18 show excellent agreement between the modelled component flow rates and experimental data. Figure 5-19 and Figure 5-20 show
slightly more deviation between the modelled component flow rates and experimental data indicated by the higher NRMSE. Considering that the comparison of the IAST Sips binary isotherm data with the experimental data was excellent, the small discrepancy observed is more likely from inaccuracy of the MTCs. This may be in part because of the simple model used to generate the MTC values for each component. It also might indicate that the assumption of negligible interaction between the MTCs begins to break down at lower temperatures. Although the focus of this comparison was the component flow rates, the agreement between the modelled and experimental bed temperature profile peaks was found to be comparable to those achieved with the pure component temperature profiles (agreement within 1 K).

This result shows that the parameters generated for Norit RB3 and the model used to predict pure component N₂ and CH₄ MTCs could be used to design a preliminary process with an uncertainty between 3 and 5 %, within the range of temperatures and pressures measured.
Figure 5-17: Comparison between $0.51N_2 + 0.49CH_4$ experiment on Norit RB3, at 107.6 kPa, 302.3 K, and modelled component flow rates of He, $N_2$, and $CH_4$, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 5-18: Comparison between $0.51N_2 + 0.49CH_4$ experiment on Norit RB3, at 902.9 kPa, 302.2 K, and modelled component flow rates of He, $N_2$, and $CH_4$, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-19: Comparison between 0.51N₂ + 0.49CH₄ experiment on Norit RB3, at 106.3 kPa, 244.8 K, and modelled component flow rates of He, N₂, and CH₄, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 5-20: Comparison between 0.51N₂ + 0.49CH₄ experiment on Norit RB3, at 902.8 kPa, 241.9 K, and modelled component flow rates of He, N₂, and CH₄, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
5.5 MSC-3K-161

5.5.1 Adsorption equilibria and heats of adsorption

The adsorption isotherms of pure N\textsubscript{2} were measured at three temperatures to a maximum pressure of 903.0 kPa with the DCB apparatus (11 data points) and fitted to the Sips isotherm model (Figure 5-21). The data used for fitting are included in Appendix A. The deviations between the measured adsorption capacities and those predicted by the Sips model are in excellent agreement; all within the experimental uncertainty. Similarly to Norit RB3, the N\textsubscript{2} isotherms tend to become more favourable with reduced adsorption temperature, which is a promising result considering that MSC-3K-161 is intended for use in a N\textsubscript{2} capture process; thus, maximising N\textsubscript{2} adsorption is desirable.

The fitted model parameters for pure N\textsubscript{2} and CH\textsubscript{4} are shown in Table 5-10. The NRMSE was calculated for each component and reported as an average of the components, as discussed in Section 5.4.1. The CH\textsubscript{4} Sips parameters were determined by fitting the model to the data published by Watson et al. [38] at temperatures closest to those in this work. The explanation for using CH\textsubscript{4} data published by Watson et al. [38] is given in Section 4.4.2. The data used for the fitting are included in Appendix A.

Table 5-10: Pure gas Sips parameters calculated for MSC-3K-161.

<table>
<thead>
<tr>
<th>Sips model</th>
<th>N\textsubscript{2}</th>
<th>CH\textsubscript{4}#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q\textsubscript{max} [mmol g\textsuperscript{-1}]</td>
<td>2.76 ± 0.60</td>
<td>4.50 ± 0.04</td>
</tr>
<tr>
<td>K\textsubscript{0} × 10\textsuperscript{6} [kPa\textsuperscript{-1}]</td>
<td>1.04 ± 1.10</td>
<td>0.96 ± 0.20</td>
</tr>
<tr>
<td>-ΔH [kJ mol\textsuperscript{-1}]</td>
<td>16.79 ± 3.10</td>
<td>18.01 ± 0.48</td>
</tr>
<tr>
<td>n</td>
<td>0.83 ± 0.16</td>
<td>0.58 ± 0.06</td>
</tr>
<tr>
<td>NRMSE</td>
<td>1.0 %</td>
<td>3.7 %</td>
</tr>
</tbody>
</table>

# - Calculated from the data of Watson et al. [38].
Figure 5-21: (a) Equilibrium adsorption capacity of N$_2$ on MSC-3K-161 measured using the DCB apparatus with fitted Sips model. (b) Deviations between the measured capacities and those calculated using the Sips isotherm model.
5.5.2 Extracted mass transfer coefficients

The MTCs were determined by fitting the simulated component flow rates to the experimental data. The extracted MTCs and fitting error for pure \( \text{N}_2 \) and \( \text{CH}_4 \) on MSC-3K-161 are shown in Table 5-11 and Table 5-12, respectively. The narrow distribution of micropores in MSC-3K-161, discussed in Section 4.2, gives rise to kinetic selectivity, which is shown by the large differences in magnitude between the extracted \( \text{N}_2 \) and \( \text{CH}_4 \) MTCs.

Table 5-11: Extracted \( \text{N}_2 \) MTCs on MSC-3K-161.

<table>
<thead>
<tr>
<th>( T ) [K]</th>
<th>( P ) [kPa]</th>
<th>Feed flow rate ([\text{mol s}^{-1}])</th>
<th>( \text{MTC}_{\text{experiment}} ) ([\text{s}^{-1}])</th>
<th>NRMSE of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.9</td>
<td>104.1</td>
<td>(3.396 \times 10^{-5})</td>
<td>0.00568</td>
<td>0.04</td>
</tr>
<tr>
<td>302.9</td>
<td>106.9</td>
<td>(6.771 \times 10^{-5})</td>
<td>0.00815</td>
<td>0.02</td>
</tr>
<tr>
<td>302.9</td>
<td>303.7</td>
<td>(6.799 \times 10^{-5})</td>
<td>0.0105</td>
<td>0.03</td>
</tr>
<tr>
<td>302.8</td>
<td>502.9</td>
<td>(6.842 \times 10^{-5})</td>
<td>0.0111</td>
<td>0.06</td>
</tr>
<tr>
<td>302.9</td>
<td>702.7</td>
<td>(6.930 \times 10^{-5})</td>
<td>0.00973</td>
<td>0.06</td>
</tr>
<tr>
<td>302.9</td>
<td>900.8</td>
<td>(3.579 \times 10^{-5})</td>
<td>0.00327</td>
<td>0.17</td>
</tr>
<tr>
<td>302.9</td>
<td>901.4</td>
<td>(7.017 \times 10^{-5})</td>
<td>0.00802</td>
<td>0.08</td>
</tr>
<tr>
<td>273.0</td>
<td>107.9</td>
<td>(6.764 \times 10^{-5})</td>
<td>0.00326</td>
<td>0.03</td>
</tr>
<tr>
<td>273.2</td>
<td>504.4</td>
<td>(6.797 \times 10^{-5})</td>
<td>0.00529</td>
<td>0.09</td>
</tr>
<tr>
<td>273.5</td>
<td>903.0</td>
<td>(6.843 \times 10^{-5})</td>
<td>0.00477</td>
<td>0.20</td>
</tr>
<tr>
<td>244.2</td>
<td>108.7</td>
<td>(6.771 \times 10^{-5})</td>
<td>0.00114</td>
<td>0.01</td>
</tr>
<tr>
<td>244.1</td>
<td>504.0</td>
<td>(6.794 \times 10^{-5})</td>
<td>0.00243</td>
<td>0.20</td>
</tr>
<tr>
<td>244.1</td>
<td>902.4</td>
<td>(6.850 \times 10^{-5})</td>
<td>0.00286</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 5-12: Extracted \( \text{CH}_4 \) MTCs on MSC-3K-161.

<table>
<thead>
<tr>
<th>( T ) [K]</th>
<th>( P ) [kPa]</th>
<th>Feed flow rate ([\text{mol s}^{-1}])</th>
<th>( \text{MTC}_{\text{experiment}} ) ([\text{s}^{-1}])</th>
<th>NRMSE of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.9</td>
<td>104.8</td>
<td>(3.366 \times 10^{-5})</td>
<td>0.0000215</td>
<td>0.03</td>
</tr>
<tr>
<td>302.9</td>
<td>105.9</td>
<td>(6.759 \times 10^{-5})</td>
<td>0.0000220</td>
<td>0.07</td>
</tr>
<tr>
<td>302.9</td>
<td>902.4</td>
<td>(3.407 \times 10^{-5})</td>
<td>0.000223</td>
<td>0.62</td>
</tr>
<tr>
<td>302.9</td>
<td>902.5</td>
<td>(6.750 \times 10^{-5})</td>
<td>0.000267</td>
<td>0.31</td>
</tr>
<tr>
<td>273.6</td>
<td>503.5</td>
<td>(6.520 \times 10^{-5})</td>
<td>0.00000866</td>
<td>0.05</td>
</tr>
<tr>
<td>244.1</td>
<td>901.3</td>
<td>(3.310 \times 10^{-5})</td>
<td>0.00000263</td>
<td>0.42</td>
</tr>
</tbody>
</table>
The NRMSE between the experimental component flow rate breakthrough curves and those predicted by the dynamic model ranged from 0.01 to 0.46 % for N\textsubscript{2} and 0.07 to 0.62 % for CH\textsubscript{4}, showing excellent agreement between the models and the experimental measurements. For N\textsubscript{2}, the difference between the experimental data and model again increased at lower temperatures. This is likely to have occurred for the same reasons as those discussed for Norit RB3 in Section 5.4.2. It is difficult to draw strong conclusions for trends in deviations for the CH\textsubscript{4} measurements with this limited data; however, it does appear that they increase with pressure.

Component flow rate breakthrough curves and bed temperature profiles with fitted model predictions were again selected to show the quality and general nature of the fits. Figure 5-22 shows the breakthrough profile of N\textsubscript{2} at the lowest pressure and highest flow rate of those measured on MSC-3K-161, which corresponds to the fastest breakthrough time with the least amount of equilibrium adsorption. The model predicts the experimental breakthrough curve well, including the temperature bed profile peaks and general shape. A similar result was also seen at low pressure and low temperature (Figure 5-23).

Figure 5-24 and Figure 5-25 show the experimental measurements of N\textsubscript{2} at high pressure with varying temperature. In both cases, the model deviates further from experimental results than at the low pressure measurements; however, the most noticeable difference is that the bed temperature profile peaks no longer accurately match and are over-predicted by about 1 to 1.5 K. The broadening of the temperature peaks is predicted well by the model.

Figure 5-26 and Figure 5-27 show typical profiles of CH\textsubscript{4} on MSC-3K-161. These results show that during the CH\textsubscript{4} measurements, there was very little temperature generated in the adsorption bed. In Figure 5-26, the fluctuations
observed are the temperature control of the apparatus, which indicates there is no measurable heat generated by adsorption.

Figure 5-22: Dynamic adsorption of N₂ on MSC-3K-161 at 106.9 kPa, 302.9 K. (a) Column effluent flow rate of He and N₂ with fitted model and (b) bed temperature profiles with fitted model; both to 800 seconds. The number of data points shown here has been reduced for clarity; however, the experimental sampling rate was 1 Hz.
Figure 5-23: Dynamic adsorption of N$_2$ on MSC-3K-161 at 108.7 kPa, 244.2 K. (a) Column effluent flow rate of He and N$_2$ with fitted model to 1500 seconds and (b) bed temperature profiles with fitted model to 4000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-24: Dynamic adsorption of N\textsubscript{2} on MSC-3K-161 at 900.8 kPa, 302.9 K. (a) Column effluent flow rate of He and N\textsubscript{2} with fitted model and (b) bed temperature profiles with fitted model; both to 3000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-25: Dynamic adsorption of N₂ on MSC-3K-161 at 902.4 kPa, 244.1 K. (a) Column effluent flow rate of He and N₂ with fitted model and (b) bed temperature profiles with fitted model; both to 3000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-26: Dynamic adsorption of CH₄ on MSC-3K-161 at 105.9 kPa, 302.9 K. (a) Column effluent flow rate of He and CH₄ with fitted model to 500 seconds and (b) bed temperature profiles with fitted model to 2000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-27: Dynamic adsorption of CH₄ on MSC-3K-161 at 901.3 kPa, 244.1 K. (a) Column effluent flow rate of He and CH₄ with fitted model and (b) bed temperature profiles with fitted model; both to 8000 seconds. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
5.5.3 Correlation of mass transfer coefficients

Similarly to Norit RB3, the MTCs measured for MSC-3K-161 were compared against the superficial gas velocity, $v_g$, shown in Figure 5-28. Unlike with Norit RB3, there is no obvious dependence with $v_g$ for either N$_2$ or CH$_4$, suggesting that the transfer resistance is not controlled by an external film in this case. This result suggests that the MTCs could be correlated with pressure and temperature using a model incorporating an Arrhenius relationship, such as Equation (5.3).

![Figure 5-28: Comparison of N$_2$ and CH$_4$ MTCs on MSC-3K-161 with $v_g$, not showing any obvious dependence.](image)

Figure 5-28 shows the MTC dependence with pressure for both N$_2$ and CH$_4$ at the three temperatures measured. For N$_2$ at 302.9 K, the MTCs reach a maximum at about 500 kPa with increasing pressure, and then decrease with further increase in pressure. This is because at low pressures (and correspondingly low loadings) transport will almost certainly be controlled by diffusion in the micropores, which varies strongly with loading. The maximum is likely to arise from a transition from
micropore diffusion control, where \( D_c \) is small and \( D_p \) is large, to macropore diffusion at higher pressures. In this regime, the inverse pressure dependence of \( D_p \) and the strong increase in \( D_c \) at higher loadings means that the mass transfer rate becomes limited by \( D_p \).

![Graph: MTC vs Pressure for N\(_2\) and CH\(_4\) at three temperatures](image)

**Figure 5-29:** The MTC pressure dependence of \( \text{N}_2 \) (left axis) and \( \text{CH}_4 \) (right axis) at three temperatures for MSC-3K-161.

For \( \text{CH}_4 \), the limited number of data points makes it more difficult to deduce the exact nature of any trend with pressure; however, at 302.9 K there was an order of magnitude increase in the MTC when the pressure increased from 105 to 902 kPa, which suggests that micropore diffusion was still dominant given the low loadings. At lower temperatures, the MTC values for \( \text{CH}_4 \) were so small that it is difficult to resolve any trends with pressure.

Figure 5-29 also shows that both the \( \text{N}_2 \) and \( \text{CH}_4 \) MTCs decrease with decreasing temperature, which is consistent with the Arrhenius temperature dependence in Equation (5.3). For \( \text{N}_2 \), the decrease with temperature is quite pronounced, significantly more so than the observed pressure dependence at
constant temperature. Since the N\(_2\) data exhibited no consistent trend with pressure (the quadratic for N\(_2\) was only apparent at 303 K) and since the total variation in the N\(_2\) MTCs with pressure was small, the pressure term in Equation (5.3) was dropped and the resulting equation used for fitting the N\(_2\) MTCs was:

\[
MTC_{N_2} = k_0 \exp \left( \frac{-E_{\text{act}}}{RT} \right) \tag{5.13}
\]

where \(k_0\) is the pre-exponential factor (s\(^{-1}\))
\(E_{\text{act}}\) is the activation energy of the Arrhenius relationship (J mol\(^{-1}\))

For CH\(_4\), at 303 K it was important to capture the observed increase in pressure because without accounting for this order of magnitude increase, the ratio between the N\(_2\) and CH\(_4\) MTCs would not be adequately described. To account for the positive trend of the CH\(_4\) MTC with increasing pressure, Equation (5.3) was modified to:

\[
MTC_{CH_4} = k_{0,p} \exp \left( \frac{-E_{\text{act},p}}{RT} \right) \tag{5.14}
\]

where \(k_{0,p}\) is the pressure dependent pre-exponential factor (Pa\(^{-1}\) s\(^{-1}\))
\(E_{\text{act},p}\) is the activation energy of the Arrhenius relationship (J mol\(^{-1}\))

The measured N\(_2\) and CH\(_4\) MTCs were regressed to Equations (5.13) and (5.14), respectively, which resulted in the best fit values of the adjustable parameters:

- N\(_2\): \(k_0 = 1.994\) (s\(^{-1}\)) and \(E_{\text{act}} = 13.88 \times 10^3\) (J mol\(^{-1}\)).

- CH\(_4\): \(k_{0,p} = 31.68\) (Pa\(^{-1}\) s\(^{-1}\)) and \(E_{\text{act},p} = 64.07 \times 10^3\) (J mol\(^{-1}\)).
The MTC values calculated with Equations (5.13) and (5.14) at each of the measured experimental conditions for N₂ and CH₄ are shown in Table 5-13 and Table 5-14, respectively. The deviations between the measured and predicted MTCs for N₂ and CH₄ are shown in Figure 5-30 and Figure 5-31, respectively. The uncertainties shown in these plots are 50 % of the measured values. For N₂, one point lies within two additional standard uncertainties and one additional point just outside the 50 % range, and for CH₄, only one point lies just outside this range. This suggests that the fitted models can predict the measured MTCs within about 50 % of the measured values at the measured conditions of temperature and pressure in this research.

**Table 5-13: Modelled N₂ MTCs on MSC-3K-161.**

<table>
<thead>
<tr>
<th>T [K]</th>
<th>P [kPa]</th>
<th>( v_g ) [m s(^{-1})]</th>
<th>MTC(_{\text{model}}) [s(^{-1})]</th>
<th>( \Delta \text{MTC}_{\text{expt-model}} ) [s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.9</td>
<td>104.1</td>
<td>( 2.103 \times 10^{-3} )</td>
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<td>-0.00239</td>
</tr>
<tr>
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<td>106.9</td>
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</tr>
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<td>303.7</td>
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<td>0.00243</td>
</tr>
<tr>
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<td>502.9</td>
<td>( 8.770 \times 10^{-4} )</td>
<td>0.00806</td>
<td>0.00308</td>
</tr>
<tr>
<td>302.9</td>
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<td>( 6.359 \times 10^{-4} )</td>
<td>0.00807</td>
<td>0.00166</td>
</tr>
<tr>
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<td>900.8</td>
<td>( 2.562 \times 10^{-4} )</td>
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<td>-0.00480</td>
</tr>
<tr>
<td>302.9</td>
<td>901.4</td>
<td>( 5.021 \times 10^{-4} )</td>
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<td>-0.00006</td>
</tr>
<tr>
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<td>-0.00115</td>
</tr>
<tr>
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<td>504.4</td>
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</tr>
<tr>
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<td>903.0</td>
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</tr>
<tr>
<td>244.2</td>
<td>108.7</td>
<td>( 3.236 \times 10^{-3} )</td>
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<td>-0.00101</td>
</tr>
<tr>
<td>244.1</td>
<td>504.0</td>
<td>( 7.007 \times 10^{-4} )</td>
<td>0.00214</td>
<td>0.00029</td>
</tr>
<tr>
<td>244.1</td>
<td>902.4</td>
<td>( 3.944 \times 10^{-4} )</td>
<td>0.00214</td>
<td>0.00071</td>
</tr>
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</table>
Table 5-14: Modelled CH₄ MTCs on MSC-3K-161.

<table>
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<th>T</th>
<th>P</th>
<th>$v_g$</th>
<th>MTC&lt;sub&gt;model&lt;/sub&gt;</th>
<th>ΔMTC&lt;sub&gt;expt-model&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>[K]</td>
<td>[kPa]</td>
<td>[m s&lt;sup&gt;−1&lt;/sup&gt;]</td>
<td>[s&lt;sup&gt;−1&lt;/sup&gt;]</td>
<td>[s&lt;sup&gt;−1&lt;/sup&gt;]</td>
</tr>
<tr>
<td>302.9</td>
<td>104.8</td>
<td>3.366 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
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<td>-8.163 × 10&lt;sup&gt;−6&lt;/sup&gt;</td>
</tr>
<tr>
<td>302.9</td>
<td>105.9</td>
<td>6.759 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>2.999 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>-8.008 × 10&lt;sup&gt;−6&lt;/sup&gt;</td>
</tr>
<tr>
<td>302.9</td>
<td>902.4</td>
<td>3.407 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>2.559 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td>-3.355 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
</tr>
<tr>
<td>302.9</td>
<td>902.5</td>
<td>6.750 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>2.556 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td>1.177 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
</tr>
<tr>
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<td>503.5</td>
<td>6.520 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>9.384 × 10&lt;sup&gt;−6&lt;/sup&gt;</td>
<td>-7.262 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
</tr>
<tr>
<td>244.1</td>
<td>901.3</td>
<td>3.310 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>5.569 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>2.077 × 10&lt;sup&gt;−6&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Figure 5-30: Deviations between the MTCs measured for N₂ and those calculated using the Arrhenius MTC model; Equation (5.13).
Mass transfer coefficients for MSC-3K-161 for N\textsubscript{2} and CH\textsubscript{4} measured in a flowing system at the conditions of temperature and pressure in this work were unavailable in the literature. Measurements of N\textsubscript{2} and CH\textsubscript{4} kinetics on the same type of adsorbent, but at low pressures, were made by Cavenati et al. [140]. Furthermore, two other studies on similar carbon molecular sieves were used for comparison [96, 141]. The main finding reported by Cavenati et al. [140] was a ratio of 133 for the determined linear driving force constants between N\textsubscript{2} to CH\textsubscript{4} at 308 K at pressures lower than 10 kPa. In this study, the same ratio was 264 at the closest temperature (303 K) and lowest pressure measured (104.1 kPa), which is the same order of magnitude difference between the two components.

Bae and Lee [96] reported apparent time constants (D r\textsuperscript{-2}) for N\textsubscript{2} and CH\textsubscript{4} on Takeda CMS-T3A, between 100 and 1600 kPa, at 303 K [96]. Although the raw data points were not published, it is clear from their results that at around 100 kPa, the ratio of N\textsubscript{2} to CH\textsubscript{4} was two orders of magnitude, and at around 900 kPa the ratio

![Figure 5-31: Deviations between the MTCs measured for CH\textsubscript{4} and those calculated using the pressure dependent Arrhenius MTC model; Equation (5.14).](image-url)
reduces to just over an order of magnitude. These results are similar to those observed in this research.

Srinivasan et al. [141] report Langmuir kinetic coefficients for $N_2$ on an unidentified CMS adsorbent and connect them with mass transfer coefficients. They report values between 100 and 1200 kPa at 293 K, which span $1.75 \times 10^{-3}$ to $4.5 \times 10^{-3}$ s$^{-1}$. This was consistent with work published by Rutherford and Coons [104], who report $N_2$ rate constants on Takeda 3A carbon molecular sieve between 27 and 227 kPa at 293 K, which span $4.5 \times 10^{-3}$ to $9.0 \times 10^{-3}$ s$^{-1}$. These values are the same order of magnitude of those measured in this study at similar temperatures and pressures. All of these comparisons with the literature increase confidence in the reliability of the measurements made here.

The most promising aspect of the MTC results on MSC-3K-161, is the difference in magnitude between the $N_2$ and $CH_4$ MTCs as temperature is decreased. Examining a potential adsorption pressure of ~900 kPa, the 303 K $CH_4$ MTC is an order of magnitude smaller than $N_2$ at about the same pressure and temperature; however, at 243 K the $CH_4$ MTC is lower by three orders of magnitude than the $N_2$ MTC (Figure 5-32).
Figure 5-32: The modelled MTCs of N₂ and CH₄ with temperature at a pressure of 900 kPa. The difference between the N₂ and CH₄ MTCs significantly increases with reduced temperature.

This result shows that the difference in adsorption rate between N₂ and CH₄ is significantly increased at lower temperatures; strongly suggesting a low temperature kinetically selective process would be an improvement over an equivalent process at atmospheric temperature.

5.5.4 Parameter testing with binary adsorbate experiments

Experimentally measured binary adsorbate breakthrough curves were compared with modelled breakthrough curves at identical conditions to test the parameters derived for MSC-3K-161. The N₂ isotherm parameters measured in this study and CH₄ isotherm parameters derived from the data published by Watson et al. [38] were used with the IAST Sips model. The N₂ and CH₄ MTCs were predicted using the regressed MTC models for each component, with the same assumption of no binary mixture interactions as was made for Norit RB3. Four comparisons were again made to encompass the extremities of the pressure and
temperature range measured. Table 5-15 shows the experiments that were modeled for comparison, the calculated MTCs used in the model, and the NRMSE of each of the fits.

**Table 5-15: MSC-3K-161 binary experimental measurement compared with model, including the calculated MTCs used in the model and the NRMSE of each of the fits.**

<table>
<thead>
<tr>
<th>T [K]</th>
<th>P [kPa]</th>
<th>y,N₂</th>
<th>y,CH₄</th>
<th>N₂ MTC&lt;sub&gt;model&lt;/sub&gt; [s&lt;sup&gt;⁻¹&lt;/sup&gt;]</th>
<th>CH₄ MTC&lt;sub&gt;model&lt;/sub&gt; [s&lt;sup&gt;⁻¹&lt;/sup&gt;]</th>
<th>NRMSE of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>302.8</td>
<td>107.2</td>
<td>0.51</td>
<td>0.49</td>
<td>8.06 × 10⁻³</td>
<td>3.01 × 10⁻⁵</td>
<td>4.50</td>
</tr>
<tr>
<td>302.9</td>
<td>901.5</td>
<td>0.51</td>
<td>0.49</td>
<td>8.07 × 10⁻³</td>
<td>2.56 × 10⁻⁴</td>
<td>3.63</td>
</tr>
<tr>
<td>243.8</td>
<td>106.7</td>
<td>0.51</td>
<td>0.49</td>
<td>2.12 × 10⁻³</td>
<td>6.34 × 10⁻⁸</td>
<td>4.15</td>
</tr>
<tr>
<td>243.4</td>
<td>901.6</td>
<td>0.52</td>
<td>0.48</td>
<td>2.10 × 10⁻³</td>
<td>5.09 × 10⁻⁷</td>
<td>4.31</td>
</tr>
</tbody>
</table>

Figure 5-33 and Figure 5-34 show good agreement between the model and experimental data for the component flow rates. An important aspect of the comparison of Figure 5-33 and Figure 5-34 is that the time scales are vastly different between the two experiments, yet in both cases the model predicts the experimental data well. This also provides additional confidence in the determined MTCs. Figure 5-35 and Figure 5-36 also shows the model predicts the component flows well at low temperature conditions. The main deviation observed is between the modelled CH₄ component flow rates and the experimental data for both the low pressure comparisons. The most likely cause for this difference is from the uncertainty in the predictions of the MTCs used in the model; however, there may be some uncertainty introduced from the isotherms predicted from using IAST.

The differences in the binary experimental data for MSC-3K-161 and the modelled breakthrough could be improved by using a better mass transfer model. This would improve the description of the observed transitions of the pure fluid MTCs between macropore, micropore, and film dominated resistances, which were not well captured by the model used in this study. For MSC-3K-161, data from
another published source [38] was used to generate isotherm parameters for one of the components, and IAST was used to predict binary behaviour. Although no parameter adjustments were needed to match the experimental mixture data within the specified uncertainty, measuring binary isotherms to confirm the IAST predictions should be considered for future work.

Overall, the results for MSC-3K-161 are sufficient to design a preliminary process with an uncertainty between 3 and 5 %, within the range of temperatures and pressures measured.

![Graph](image)

Figure 5-33: Comparison between 0.51N₂ + 0.49CH₄ experiment on MSC-3K-161, at 107.2 kPa, 302.8 K, and modelled component flow rates of He, N₂, and CH₄, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-34: Comparison between 0.51\(\text{N}_2\) + 0.49\(\text{CH}_4\) experiment on MSC-3K-161, at 901.5 kPa, 302.9 K, and modelled component flow rates of \(\text{He}, \text{N}_2,\) and \(\text{CH}_4,\) with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

Figure 5-35: Comparison between 0.51\(\text{N}_2\) + 0.49\(\text{CH}_4\) experiment on MSC-3K-161, at 106.7 kPa, 243.8 K, and modelled component flow rates of \(\text{He}, \text{N}_2,\) and \(\text{CH}_4,\) with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.
Figure 5-36: Comparison between $0.51\text{N}_2 + 0.49\text{CH}_4$ experiment on MSC-3K-161, at 901.6 kPa, 243.4 K, and modelled component flow rates of He, N$_2$, and CH$_4$, with fitted model using derived isotherm and MTC parameters. The number of data points shown here has been reduced for clarity; the experimental sampling rate was 1 Hz.

5.6 Conclusions

The isotherms for Norit RB3 and MSC-3K-161 showed not only increased capacities, but they also became more favourable (increased Henry’s constants) at lower temperatures. For both adsorbents, this shows that a low temperature adsorption process will result in increased bed adsorption capacity and is likely to increase bed usage from a shorter MTZ, which is particularly important for the equilibrium controlled Norit RB3. A rigorous model describing the breakthrough apparatus and column dynamics was successfully used to extract mass transfer coefficients over a range of conditions. The model predicted the component flow rates and bed temperature profiles very well over a range of conditions for both adsorbents. Mass transfer coefficients were regressed to simple models, which
were shown to predict MTC adequately enough to describe binary adsorption experiments with no further parameter adjustment. The ratio of N₂ to CH₄ MTCs for MSC-3K-161 increased from 30 at 903 kPa, 303 K, to 1087 at 902 kPa 244 K, which showed that the difference in uptake rates, giving rise to kinetic selectivity, increased significantly at lower temperatures. The fundamental adsorption data for the two adsorbents measured showed that equilibrium capacity, equilibrium selectivity, isotherm favourability, and ratio of the rate constants all improved at lower adsorption temperatures, providing evidence that improvements to N₂ + CH₄ separations could be made by adopting low temperature adsorption. Furthermore, these data provide a basis for the development of improved N₂ + CH₄ separations based on low temperature PSA processes.
Chapter 6

Conclusions and recommendations for future research
6.1 Conclusions

This research represents the first steps towards the goal of developing low temperature PSA processes for $\text{N}_2 + \text{CH}_4$ separations to improve LNG production efficiency. The research in this thesis has made a number of contributions towards the attainment of this goal, which are summarised below.

- A review of the current state of commercial $\text{N}_2 + \text{CH}_4$ separation technologies with respect to LNG production identified the strengths and limitations of each technology. This contribution is important not only for the development of low temperature PSA in this research, but could provide important insights for other areas of separations research, such as the use of membranes at low temperatures.

- This work examined a typical LNG production facility and identified key opportunities for improvement, including front-end nitrogen rejection, end-flash upgrading and nitrogen clean-up. The exact locations where new technologies could be placed in an LNG production facility were identified.

- The research in this thesis illustrated the potential to use a PSA process utilising the low temperature conditions available in an LNG production facility; the challenges associated with the development of this process were identified.

- A dynamic column breakthrough apparatus was designed, constructed, and commissioned. This apparatus was capable of concentrated adsorbate, multi-component, adsorption measurements over a range of pressures and temperatures representative of an LNG facility. A mathematical framework was presented that determines equilibrium adsorption capacities from the dynamic
adsorption experiments. A method for quantitatively estimating the uncertainties of the measured capacities was also presented.

- A screening investigation identified two adsorbents for further study. One of the most important outcomes of this investigation was that the developed DCB apparatus was shown to be able to quickly and simply identify kinetically separative behaviour through analysis of equimolar binary mixture breakthrough experiments.

- Fundamental adsorption data for Norit RB3 and MSC-3K-161 were generated and tested for use in preliminary process modelling of equilibrium selective and kinetically selective low temperature PSA processes. The fundamental adsorption data for the two adsorbents measured showed that equilibrium capacity, equilibrium selectivity, isotherm favourability, and kinetic selectivity all improved by adopting low temperature adsorption conditions. This provided evidence that improvements to N$_2$ + CH$_4$ separations can be made by using a low temperature adsorption process.

In Chapter 2, a flow diagram was introduced (Figure 2-9) that showed a proposed development pathway of a low temperature PSA process from conceptualisation to commercialisation. The work in this thesis has made significant contributions to the first and second stages of the development pathway and has brought low temperature PSA for improved LNG production efficiency through N$_2$ + CH$_4$ separations a step closer to realisation. The next key steps to achieve commercial realisation would be process modelling of the PSA process, construction and operation of a pilot plant, then field deployment and testing.
6.2 Recommendations for future research

The preliminary nature of this research meant that a number of different areas were investigated. A diverse approach was required to establish a foundation for the development of a low temperature PSA process. A consequence of the breadth of this work is that several areas could be expanded on by researchers investigating \( \text{N}_2 + \text{CH}_4 \) separations in LNG production, low temperature PSA processes, and/or DCB adsorption experiments.

Although the DCB apparatus has been refined and can operate at pressures to 1000 kPa, a suggested improvement to the capability of the apparatus is to expand the pressure range to expected operating pressures of a PSA process; this range would likely be >3000 kPa. This improvement would enable higher pressure adsorption measurements, increasing the reliability of the generated isotherms over a wider range of pressures, and also allow the investigation of equilibrium and kinetic selectivity at conditions closer to those encountered in an LNG plant. The results in this work show that the kinetic selectivity of MSC-3K-161 did not change significantly at higher pressure; however, the adsorption capacity continued to increase. This suggests that higher pressure measurements would be valuable to investigate whether this type of behaviour extends to the pressures encountered in LNG plants. The connections, tubing, multi-position valves, and column are rated to over 7000 kPa; however, the current limiting elements are the flow controllers, back-pressure regulator, and pressure gauges. To physically replace these elements is a straightforward process and would require very little modification to the apparatus. The primary reason these were not installed on the current system is that there are very few options for mass flow controllers and
back-pressure regulators rated above 1000 kPa, and the few that are available are significantly more expensive than those on the current apparatus.

Replacing the stirred air-bath with a thermally controlled and stirred liquid glycol bath provided improvements to the DCB apparatus as discussed in Chapter 4; however, the low temperature capability was increased to a minimum of 243 K, which limited measurements later in this work. Several earlier screening measurements performed at around 233 K showed increased adsorption capacity and selectivity, which could improve further at even lower temperatures. A suggested improvement to the system would be to replace the liquid glycol bath with a model capable of lower temperatures. The implementation would likely be easy; the cost of such a unit would be the expected limiting factor. If this improvement were to be made, lower temperature adsorption measurements are suggested for future work.

Future screening of adsorbent materials should include a range of activated carbons for a CH₄ equilibrium selective process. The Norit R1 Extra sample identified in Chapter 4 would be a suggested adsorbent to target. For a N₂ kinetically separative process other available carbon molecular sieves should be investigated further.

The single parameter MTC used in this study was shown to have limitations describing the different mass transport resistances over changing conditions. It is suggested that the kinetic model used to model future breakthrough curves should at the very least be a bi-LDF model, including separate macropore and micropore resistances. This would allow a more complete description of the multiple mass transport resistances in play and allow more accurate correlations to be produced.

The DCB apparatus in this work was designed and constructed specifically for the research described in this thesis; however, the apparatus can be used to
study other separations important to gas processing with little to no modification. For example, helium recovery in natural gas processing is sometimes completed by PSA [4] and could potentially be improved through low temperature adsorption. Low temperature He + CH₄ adsorption measurements could be conducted immediately with the developed apparatus. Other well established PSA separations, such as oxygen or nitrogen generation, could also potentially benefit from low temperature adsorption, which could be investigated using this apparatus. There are many PSA separations that vary in their developmental maturity; however, throughout the course of this research, it appears that low temperature adsorption processes are generally all in their infancy. Therefore, the low temperature measurement component of this work appears to have great potential for application to a broad range of PSA separation processes.
References


## Appendix A

### Table A-1: Norit pure N₂ experimental measurements.

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Table A-2: Norit pure CH₄ experimental measurements.

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Table A-3: Norit binary experimental measurements.

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Table A-4: MSC-3K-161 pure N$_2$ experimental measurements.

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<th>P</th>
<th>q*.N$_2$</th>
<th>u(q*)N$_2$</th>
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<td>[mmol g$^{-1}$]</td>
<td>[mmol g$^{-1}$]</td>
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Table A-5: MSC-3K-161 pure CH\textsubscript{4} data from Watson et al. [38] used for fitting.

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