ADSORPTION BASED PORTABLE OXYGEN
CONCENTRATOR FOR PERSONAL MEDICAL
APPLICATIONS

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# Table of Contents

**Acknowledgements**

**Table of Contents**

**Summary**

**List of Figures**

**List of Tables**

**Nomenclature**

**Chapter 1: Introduction**

1.1 Overview of the Research

1.2 Chronic Obstructive Pulmonary Diseases and its Treatment

1.3 Air Separation Processes

1.3.1 Adsorption based air separation processes

1.3.2 Pressure swing adsorption (PSA) process

1.3.3 Vacuum-pressure swing adsorption (VSA and VPSA) processes

1.3.4 Rapid cycling pressure swing adsorption (RPSA) process

1.3.5 Nitrogen selective adsorbents for oxygen production

1.3.6 Zeolite adsorbents (5A, 13X and LSX zeolite)

1.3.7 Engelhard titanosilicates (ETS10)

1.3.8 Structured adsorbents for RPSA applications

1.4 Commercial Medical Oxygen Concentrators for COPD Patients

1.5 Miniaturization of Oxygen Concentrators

1.6 Objectives of the Current Research
# Table of Contents

1.7 Organization of the Thesis ................................................................. 30

Chapter 2: LITERATURE REVIEW ......................................................... 32

2.1 Overview of the Chapter .................................................................. 32
2.2 Axial Dispersion in Columns Packed with Small Particles ................. 32
2.3 Prior Studies on Pressure Drop in a PSA Column ............................... 35
2.4 Pulsed Pressure Swing Adsorption (PPSA) Processes ......................... 38
2.5 Ultra Rapid Pressure Swing Adsorption Process ............................. 45
2.6 Patents on Portable Oxygen Concentrators ..................................... 47
2.7 Chapter Conclusion ......................................................................... 50

Chapter 3: MODELING AND SIMULATION OF PULSED PRESSURE SWING ADSORPTION PROCESS ......................................................... 51

3.1 Overview of the Chapter .................................................................. 51
3.2 Process Description .......................................................................... 51
3.3 Mathematical Modeling .................................................................... 53
   3.3.1 General assumptions in PPSA process modeling ....................... 53
   3.3.2 Model equations ...................................................................... 53
   3.3.3 Equilibrium and kinetic parameters ....................................... 58
   3.3.4 Numerical simulation ............................................................... 61
3.4 Simulation Results and Discussion .................................................... 62
   3.4.1 Dynamics of adsorption and desorption ................................. 65
   3.4.2 Optimum in adsorption time and desorption time ................. 67
   3.4.3 Effect of particle diameter on process performance ............... 72
   3.4.4 Effect of pressure drop on process performance ................. 74
   3.4.5 Effect of bed length on process performance ....................... 76
3.5 Graphical Design of the Pulsed Pressure Swing Adsorption Process ... 78
# Table of Contents

3.5.1 Generalizing the simulation results ......................................................... 78
3.5.2 Correlation for the optimum adsorption and desorption times .......... 83
3.5.3 General design procedure ................................................................. 88
3.5.4 A case study in process miniaturization ......................................... 88
3.6 Chapter Conclusion ............................................................................. 89

Chapter 4: COLUMN DYNAMICS: EXPERIMENTAL DESIGN AND PROCEDURES ................................................................. 92

4.1 Overview of the Chapter .................................................................. 92
4.2 Critical Issues in Experimental Study of PPSA Process ................. 92
  4.2.1 Adsorbents ................................................................................. 94
  4.2.2 Column dimensions ............................................................... 96
  4.2.3 Selection of instruments ...................................................... 97
  4.2.4 Oxygen sensor, flow meter and pressure sensor .................... 99
  4.2.5 Optimum dead volumes and pressure drops ......................... 101
4.3 Unary Adsorption Equilibrium Experiments .................................. 103
  4.3.1 Adsorbent regeneration ....................................................... 105
  4.3.2 Experimental procedure ...................................................... 106
  4.3.3 Processing of equilibrium data ............................................ 107
4.4 Experimental Design and Procedure for Pressure Drop and
  Breakthrough Measurements .............................................................. 109
  4.4.1 Experimental set-up ............................................................. 109
  4.4.2 Pressure drop characteristics of adsorption column ............ 111
  4.4.3 Dynamic column breakthrough experiments ...................... 113
4.5 Sensor Responses ........................................................................... 119
4.6 Chapter Conclusion .......................................................................... 122
Chapter 5: COLUMN DYNAMICS: EXPERIMENTAL RESULTS,

MODELING AND SIMULATIONS

5.1 Overview of the Chapter

5.2 Unary Adsorption Equilibrium Experimental Results

5.3 Modeling of Pressure Drop along the Adsorption Column

5.3.1 Estimation of Darcy's constant

5.3.2 Effect of column to particle diameter ratio ($R_d$) on Darcy's constant

5.3.3 Pressure drop across a column packed with 75-90 µm size spherical glass beads

5.4 Modeling of Dynamic Column Breakthrough (DCB) Experiments

in an Adsorption Column Packed with 63-75 µm Size Binderless 5A Zeolite Adsorbent Particles

5.4.1 Modeling of extra column effects at the entrance of the column

5.4.2 Nonisothermal modeling of breakthrough experiments

5.4.3 Axial dispersion in a column packed with very fine zeolite particles

5.4.4 Parametric study of breakthrough modeling and simulation

5.5 Dynamic Column Breakthrough (DCB) Experiments and Simulation:

Results and Analysis

5.5.1 Single component breakthrough experiments

5.5.2 Binary breakthrough experiments

5.5.3 Equilibrium data from dynamic column breakthrough (DCB) experiments

5.6 Chapter Conclusion
Chapter 6: EXPERIMENTAL, MODELING AND SIMULATION STUDY
OF A TWO-STEP PPSA PROCESS

6.1 Overview of the Chapter
6.2 Experimental Study of Pulsed Pressure Swing Adsorption
   6.2.1 Experimental procedure
   6.2.2 Parametric study of the PPSA process
6.3 Modeling and Simulation of the Experimental PPSA Process
   6.3.1 Isothermal model
   6.3.2 Nonisothermal model
6.4 Estimation of Power Consumption in the PPSA Process
6.5 Experimental and Simulation Results of Pulsed Pressure Swing
   Adsorption Process
   6.5.1 Effect of adsorption step duration on PPSA process
   6.5.2 Effect of desorption step duration on PPSA process
   6.5.3 Effect of inlet column pressure on PPSA process performance
6.6 Limitations on Current Experimental Study of PPSA Process
6.7 A Novel Three-Step Rapid Vacuum Swing Adsorption Cycle for
   Reducing of Oxygen Concentrator Size
   6.7.1 Process description
   6.7.2 Modeling and simulation of three-step vacuum swing
       adsorption process
   6.7.3 Simulation results of three-step Rapid VSA processes
   6.7.4 Estimation of bed size factor
Table of Contents

6.8 Chapter Conclusion.................................................................................................192

Chapter 7: CONCLUSIONS AND RECOMMENDATION .................................................194

7.1 Overview of the Chapter..........................................................................................194

7.2 Conclusions.............................................................................................................194

7.3 Future Recommendations ....................................................................................197

BIBLIOGRAPHY.............................................................................................................199

APPENDIX A: DIMENSIONLESS EQUATIONS IN CHAPTER 3 .........................208

APPENDIX B: DIMENSIONLESS FORM OF NONISOTHERMAL

MODEL EQUATIONS .....................................................................................................212

APPENDIX C: EQUILIBRIUM DATA OF NITROGEN AND OXYGEN

ON BINDERLESS 5A ZEOLITE ..................................................................................216
SUMMARY

The demand for portable oxygen supply for personal use by Chronic Obstructive Pulmonary Disease (COPD) patients needing oxygen therapy has been tremendously increased in the last decade. The currently available devices for oxygen therapy have limited portability due to their size and weight that result in restricted mobility of these patients who might otherwise be more physically active. A small and light weight device, using atmospheric air as feed, can significantly improve the quality of life for those people who need oxygen therapy to overcome their lung insufficiency. The adsorption columns and the compressor are the two principal contributing factors to the size and weight of an oxygen concentrator designed based on Pressure Swing Adsorption (PSA) technology. The principal focus in this study was reduction of the adsorption column size in an oxygen concentrator for personal medical applications operated on a two-step pulsed pressure swing adsorption (PPSA) cycle. The PPSA cycle was chosen for its simplicity of operation with minimum instrumentation.

The PPSA process was first modeled to assess the extent to which the size of the oxygen concentrator might be reduced for personal medical applications. The dynamic model equations describing the process were solved using COMSOL Multiphysics software. The effects of various process parameters such as adsorption and desorption times, bed length, particle diameter and imposed pressure drop across the bed on the process performance were thoroughly investigated. The results suggested that there was a fairly wide operating window where the best possible
Summary

Oxygen purity was consistently >90% for both 5A and partially Ag exchanged Li substituted 13X zeolite adsorbents. Moreover, at a given product flow rate, the extent of size reduction was found to be limited by the (maximum) cycling frequency that was practically achievable. A graphical design methodology had also been proposed for the sizing of an oxygen concentrator for personal medical applications.

In the next step, an experimental set-up was designed with minimum dead volume and pressure drop at the entrance and exit of the column for the experimental verification of the proposed simple two-step PPSA process for reduction of adsorber size in an oxygen concentrator and also to verify the design methodology by considering the critical issues related to sizing, sensing, measurement and control. A binderless 5A zeolite was selected as adsorbent for air separation in the experimental study. The adsorption equilibrium isotherms for nitrogen and oxygen on binderless 5A zeolite adsorbent were measured at two different temperatures using a constant volume apparatus. The Langmuir adsorption isotherm model fitted the single component experimental equilibrium data very well. A 10 cm length and 0.5 in diameter jacketed adsorption column packed with 69 µm binderless 5A zeolite adsorbent particles was used for the pressure drop measurements, single component and mixture (Air-N₂ and Air-O₂) gas dynamic column breakthrough experiments, and cyclic pulsed pressure swing adsorption experiments. The pressure drop experiments were also carried out in the same column for different sized adsorbent particles in the size range 168 µm -1.6 mm to study the effect of column to particle diameter ratio on pressure drop. The novel result was that the Darcy’s law constant that fitted the experimental results was 4186.2 instead of 150 when the adsorption column was packed using 69 µm sized binderless 5A zeolite particles. The single component and two-component adsorption and desorption dynamic column breakthrough experiments
Summary

and simulations were also performed at different inlet column pressures and the other end of the column maintained at atmospheric pressure. Good agreements between the breakthrough experimental results and dynamic column breakthrough simulations were obtained. It was further concluded that the axial dispersion in the adsorption column controlled the rate of mass transfer between the gas phase and adsorbent particles and the axial dispersion was very high in the column packed with 69 µm adsorbent particles. Furthermore, a set of PPSA experiments were conducted to investigate the performance of the PPSA process for an oxygen concentrator for personal medical applications. The experimental results showed that the maximum oxygen product purity attained in a simple two-step PPSA process was limited to < 40%. The simulation results confirmed that this was due to the very high axial dispersion in the column.

Finally, a novel 3-step VSA process, using 250-600 µm adsorbent particles typically used in RPSA studies, where Darcy law constant of 150 is valid and axial dispersion is not enhanced due to particle clustering have been proposed for the size reduction of the oxygen concentrator. This study demonstrated that the 3-step VSA process using binderless 5A zeolite and superior Ag-Li-X adsorbent for air separation has a potential to significantly reduce the adsorber size and compressor size in an oxygen concentrator for personal medical applications.
LIST OF FIGURES

Figure 1.1: Comparison of respiratory system in healthy human beings and patients with COPD [NIH (2011)]...........................................................................3

Figure 1.2: Comparison of working capacity of PSA, VSA and VPSA processes for air separation on zeolite adsorbents at constant temperature. $\Delta q_1$: working capacity of PSA, $\Delta q_2$: working capacity of VPSA and $\Delta q_3$: working capacity of VSA process..........................................................7

Figure 1.3: Schematic diagram of a two bed, 4-step PSA process...........................8

Figure 1.4: Comparison of various modes of oxygen production in the Market for industrial and medical applications [UIG (2011)].....................13

Figure 1.5: Schematic diagram of a single bed, 3-step RPSA process...............16

Figure 1.6: Framework representation of 5A and 13X zeolites [Yang (2003)]. Dots indicate the cation sites on unit cell………………………………….20

Figure 1.7: Common forms of structured adsorbents (a) monoliths, (b) corrugated paper monoliths, (c) fabric adsorbents and (d) conventional bead and particulate adsorbents.................................................................22

Figure 1.8: Lightest portable oxygen concentrator available in the market [Airsep (2011)].................................................................................................................25

Figure 2.1: Effect of particle size on limiting peclet number for flow through packed columns [Ruthven (1984)].................................................................35

Figure 2.2: Plot of adsorbent weight with cyclic frequency in an ultra rapid pressure swing adsorption process [Galbraith et al., (2011)].............46
List of Figures

Figure 2.3: Effect of adsorption pressure on BSF vs total cycle time plots [Chai et al., (2011)] .................................................................47

Figure 3.1: Schematic representation of a two-step pulsed pressure-swing adsorption process..............................................................52

Figure 3.2: Comparison of bed profiles obtained from the COMSOL Multiphysics software (—adsorption and --- desorption) and an in-house simulator (o) for (a) oxygen partial pressure, (b) total bed pressure and (c) interstitial velocity in the gas phase at the end of the adsorption and desorption steps after reaching cyclic steady-state. The process parameters are \( L = 2 \text{ cm}, d_p = 0.002 \text{ cm}, \Delta P = 1.5 \text{ atm} \). Optimum adsorption and desorption times are 0.12 s and 1.2 s, respectively. ..................................................63

Figure 3.3: Profiles for (a) oxygen partial pressure, (b) nitrogen partial pressure, (c) total column pressure and (d) interstitial velocity in the gas phase plotted against dimensionless bed length showing the approach to cyclic steady-state. Starting from the 1st cycle, profiles for every 5th cycle are shown for 5A zeolite. The process parameters are \( L = 2 \text{ cm}, d_p = 0.002 \text{ cm} \) and \( \Delta P = 1.5 \text{ atm} \). Optimum adsorption and desorption times are 0.12 s and 1.2 s, respectively.................................................67

Figure 3.4: Effect of adsorption and desorption step duration on oxygen product purity and recovery from a pulsed PSA process using a 5A zeolite at two representative sets of process parameters: (a) \( L = 0.2 \text{ cm}, d_p = 0.0005 \text{ cm}, \Delta P = 1.5 \text{ atm} \); (b) \( L = 2 \text{ cm}, d_p = 0.002 \text{ cm}, \Delta P = 1.5 \text{ atm} \)........................................................................................................68

Figure 3.5: Effect of (a) desorption time and (b) adsorption time on the cyclic steady state oxygen partial pressure profile along a 5A zeolite adsorbent bed for the adsorption and desorption step durations fixed at 0.12 s and 1.2 s, respectively. Other operating parameters are \( L = 2 \text{ cm}, d_p = 0.002 \text{ cm} \) and \( \Delta P = 1.5 \text{ atm} \). See notation list for an explanation of the legends used for the cyclic steady-state oxygen partial pressure profiles.................................................................71

Figure 3.6: Effect of adsorbent particle size on (a) oxygen product purity and recovery, and (b) productivity and cycling frequency for a pulsed PSA process on 5A and Ag-Li-X zeolite. The process parameters are \( L = 2 \text{ cm}, \Delta P = 1.5 \text{ atm} \). The optimum particle diameter range is 0.002-0.008 cm..................................................................................73
Figure 3.7: Effect of imposed pressure drop on (a) oxygen product purity and recovery, and (b) productivity and cycling frequency in a pulsed PSA process for 5A and Ag-Li-X zeolite adsorbents. The process parameters are $L=2$ cm, $d_p=0.002$ cm for 5A zeolite and $L = 2$ cm and $d_p = 0.0025$ cm for Ag-Li-X. ...............................................................75

Figure 3.8: Effect of bed length on (a) oxygen product purity and recovery, and (b) productivity and cycling frequency in a pulsed PSA process for 5A and Ag-Li-X zeolites. The process parameters are $d_p = 0.002$ cm and $\Delta P = 2.5$ atm for 5A zeolite and $d_p = 0.0025$ cm and $\Delta P = 2.5$ atm for Ag-Li-X zeolite....................................................................................77

Figure 3.9: Design plots for the PPSA air separation on 5A zeolite relating the process variables to oxygen product purity and recovery. Optimum adsorption and desorption step durations were used for every combination of process variables.........................................................81

Figure 3.10: Design plots for the PPSA air separation on Ag-Li-X zeolite relating the process variables to oxygen product purity and recovery. Optimum adsorption and desorption step durations were used for every combination of process variables.........................................................82

Figure 3.11: Correlations for relating (a) the optimum adsorption step duration and (b) total cycle time to the dimensionless group $X$, which combines the PPSA process parameters. Results for both 5A and Ag-Li-X are shown.................................................................86

Figure 3.12: Correlation relating the adsorbent volume to the dimensionless group $X$ in order to deliver 5 SLPM of oxygen at a level of oxygen purity chosen in Figure 3.9 or 3.10. Correlations for 5A and Ag-Li-X zeolites are shown........................................................................................................87

Figure 3.13: Comparison of adsorbent weight used in current PPSA process........89

Figure 4.1: Scanning electron micrograph (SEM) images of ground binderless 5A zeolite adsorbent separated between 63 and 75 µm sieves are shown at two different resolutions (a) X 160 and (b) X 270.................................96

Figure 4.2: Customized column-end fittings. Arrows indicate locations where the two reducers (B, SS-100-R-2”) are soldered in appropriate holes drilled on the reducing union (A, M-810-6-2").........................................................97
Figure 4.3: (a) Schematic of column and water jacket arrangement and (b) Photograph of column with and with out jacket. The column end connections are also shown.................................................................98

Figure 4.4: Photograph of customized (a) oxygen sensor, (b) pressure sensor fittings and (c) thermocouple used in PPSA experiments. ......................99

Figure 4.5: Experimental set-up for measuring single component adsorption equilibrium isotherms of O₂ and N₂ on binderless 5A zeolite as an adsorbent.................................................................105

Figure 4.6: Experimental equilibrium adsorption isotherms of N₂ at 25°C reproduced in two different runs for the same pressure range on binderless 5A zeolite adsorbent.........................................................108

Figure 4.7: Multipurpose experimental set-up for pressure drop, column dynamics and PPSA study........................................................................110

Figure 4.8: Experimental pressure drop along a 10 cm column packed with 63-75 μ sized binderless 5A zeolite adsorbent using He gas as a flow medium. Run 1 and Run 2 show the reproducibility of experimental data.................................................................................................113

Figure 4.9: Schematic diagram used for calibration of (a) pressure sensor and (b) oxygen sensor........................................................................119

Figure 4.10: Response of pressure sensor to a step change in pressure introduced using solenoid valves.................................................................120

Figure 4.11: Response of oxygen sensor for a step change in concentration introduced using solenoid valves.................................................................121

Figure 4.12: Point by point subtraction of oxygen sensor response from cumulative breakthrough and blank responses.................................................................121

Figure 5.1: Adsorption equilibrium isotherms of nitrogen and oxygen on binderless 5A zeolite at 288.15 K and 298.15 K. The experimental data was fitted with the Langmuir isotherm model.........................................................124
List of Figures

Figure 5.2: Plot of pressure drop along the column as a function of superficial gas velocity. The column was packed with binderless 5A zeolite adsorbent particles. RMSD (Method 1) = 0.239 and RMSD (Method 2) = 0.0271. .............................................................................................130

Figure 5.3: Effect of column to particle diameter ($\frac{R_d}{d_p}$) ratio on (a) Darcy's law constant and, (b) bed voidage in a 0.5 in diameter column and packed with zeolite adsorbent particles ranging from 69 µm to 3.6mm in diameter. ........................................................................................132

Figure 5.4: Plot of pressure drop along a column of length 10 cm and packed with 75-90 µm size spherical glass beads. Bed voidage is 0.35. ............133

Figure 5.5: The schematic of (a) Tanks in series (TIS) model to estimate the dispersion in extra column volume at the entrance of the column, and (b) Tanks in series representation at the column entrance. ..........136

Figure 5.6: Fitting of corrected inlet dead volume response using TIS and DM approaches for single component breakthrough of 50% O₂ in He. For other details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results. ............138

Figure 5.7: Experimental breakthrough results compared with simulation for different values of radial dispersion factor, $\beta$. For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results. ............145

Figure 5.8: Experimentally measured pressure profiles (a) at the inlet and (b) exit of the column in adsorption and desorption steps during breakthrough measurements. Symbols represent the experimental data and lines represent the exponential model fit. Thick lines for adsorption step and thin lines for desorption step. For experimental details, see Table 5.3 and run2 in Table 5.2. .................................................................146

Figure 5.9: Effect of Darcy's constant ($k_1$) on adsorption and desorption breakthrough time compared with experimental results for a representative single component breakthrough of 50% O₂ in He. For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results. .................................................................147
List of Figures

Figure 5.10: Effect of Darcy's constant \((k_1)\) on calculated (a) inlet and (b) exit gas interstitial velocities compared with experimental results for a representative single component breakthrough of 50% O\(_2\) in He. Symbols represent the experimental data and lines represent simulation results. Thick lines represent adsorption and thin lines represent desorption respectively. For experimental details, see Table 5.3 and run 2 in Table 5.2. .................................................................148

Figure 5.11: Experimental breakthrough results compared with simulation results using Ergun equation for pressure drop for different values of the second Ergun constant \((k_2)\). For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results...............................................................149

Figure 5.12: Effect of inlet blank response on breakthrough simulation and compared with representative experimental run 2. For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results...................151

Figure 5.13: Effect of inside heat transfer coefficient \((h_{in})\) on adsorption and desorption temperature profile at the middle of the column length compared with experimental temperature measured at the centre of the column for a representative single component breakthrough of 50% O\(_2\) in He. For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results. ................................................................................................152

Figure 5.14: Experimental concentration profiles at the column exit and temperature profiles at the middle of the column are compared with simulation results for two representative single component breakthrough runs of 50% O\(_2\) in He. For experimental details, see Table 5.3 and run 2 and 4 in Table 5.2. Symbols represent experimental data and lines represent simulation results.......................156

Figure 5.15: Binary experimental concentration profiles at the column exit and temperature profiles at the middle of the column length are compared with simulation results for two representative experimental runs of N\(_2\)-Air breakthrough. For experimental details, see Table 5.3 and Table 5.2…………………………………………………………………...159

Figure 5.16: Binary experimental concentration profiles at the column exit and temperature profiles at the middle of the column length are compared
List of Figures

with simulation results for two representative experimental runs of O2-Air breakthrough. For experimental details, see Table 5.3 and Table 5.2

Figure 5.17: Comparison of adsorption equilibrium isotherm data measured using single dynamic column breakthrough (DCB) experiments and constant volume apparatus. Circles represent DCB data and triangles represent data obtained from constant volume apparatus.

Figure 6.1: Plot of oxygen mole fraction with cycle number. Cyclic steady state was attained after 30 cycles in the PPSA experiment. The process parameters for the present run were $L=10.08$ cm, $d_p=69$ µm, $P_H=2.1305$ bar, $t_a=3$ s, and $t_d=10$ s.

Figure 6.2: Effect of adsorption time ($t_a$) on (a) oxygen mole fraction and recovery, and (b) productivity and theoretical power required in PPSA process using binderless 5A zeolite adsorbent. The process parameters are $L=10.08$ cm, $d_p=63-75$ µm, $P_H=2$ bar and $t_d=10$ s.

Figure 6.3: Effect of desorption time ($t_d$) on (a) oxygen mole fraction and recovery, and (b) productivity and theoretical power of a PPSA process on binderless 5A zeolite adsorbent. The process parameters are $L=10.08$ cm, $d_p=63-75$ µm, $P_H=2$ bar and $t_a=2$ s.

Figure 6.4: Effect of inlet pressure ($P_H$) on (a) oxygen mole fraction and recovery, and (b) productivity and theoretical power of a PPSA process on binderless 5A zeolite adsorbent. The process parameters are $L=10.08$ cm, $d_p=63-75$ µm, $t_a=2$ s and $t_d=10$ s.

Figure 6.5: Effect of adsorption time on (a) oxygen mole fraction, (b) recovery and (c) productivity in PPSA process using binderless 5A zeolite adsorbent for four different combinations of Darcy's constant and axial dispersion estimation. The process parameters are $L=10.08$ cm, $d_p=63-75$ µm, $P_H=2$ bar and $t_d=10$ s.

Figure 6.6: Schematic representation of a three-step rapid vacuum swing adsorption cycle.

Figure 6.7: Effect of column length to velocity ratio ($L/V_0$) on (a) oxygen recovery and adsorption time, and (b) productivity and power consumption in a
3-step product pressurization VSA process using 5A zeolite and Ag-Li-X adsorbent. For all these runs, oxygen product purity was >94%. $L=10$ cm, $d_p=250$ µm, $P_{\text{vac}}=0.2$ bar, $t_p=6$ s and $t_d=8$ s. Thick lines for 5A zeolite and thin lines for Ag-Li-X adsorbent. ..............................188

Figure 6.8: Effect of vacuum desorption pressure ($P_{\text{vac}}$) on (a) oxygen purity and recovery, and (b) bed size factor and power consumption in a 3-step product pressurization VSA process using 5A zeolite and Ag-Li-X adsorbent. $L=10$ cm, $d_p=250$ µm, $t_p=6$ s, $t_a=3$ s and $t_d=8$ s. Thick lines for 5A zeolite and thin lines for Ag-Li-X. .........................................190

Figure 6.9: Effect of adsorbent particle size ($d_p$) on (a) oxygen purity and recovery, and (b) productivity and power consumption in a 3-step product pressurization VSA process using 5A zeolite and Ag-Li-X adsorbent. $L=10$ cm, $P_{\text{vac}}=0.2$ bar, $V_0=0.5$ m/s, $t_p=6$s, $t_a=3$s and $t_d=8$s. Thick lines for 5A zeolite and thin lines for Ag-Li-X. Solid lines for purity and productivity, and dash lines for recovery and power.........................191
LIST OF TABLES

Table 1.1: Comparison of commercially available oxygen therapy options...........4

Table 1.2: Commercially available portable oxygen concentrators......................26

Table 3.1: Equilibrium isotherm parameters for 5A and Li-Ag-X (Li94.2Na0.7Ag1.1-X-1.0) Zeolite ..........................................................60

Table 3.2: Common parameters used in the simulations ......................................60

Table 3.3: Range of values of the dimensionless groups used in the simulations .........................................................................................80

Table 3.4: Design table for a PPSA oxygen concentrator.....................................91

Table 4.1: Detailed gas flow information from PPSA process simulation for a set of preliminary process parameters..................................................95

Table 4.2: Response times of various instruments in the experimental setup (Ref: catalogs provided by the manufacturers).............................................100

Table 4.3: Comparison of gas volumes with dead volumes and estimated pressure drop in the external tubing.........................................................102

Table 4.4: Valve sequencing for breakthrough experiments. .............................116

Table 5.1: Langmuir equilibrium isotherm parameters for nitrogen and oxygen on binderless 5A zeolite adsorbent. .........................................................125

Table 5.2: Summary of the breakthrough experiments.........................................153
List of Tables

Table 5.3: Column and adsorbent specifications used in breakthrough measurements.......................... 154

Table 5.4: Optimum parameters used in isothermal and nonisothermal modeling of breakthrough experiments. ......................................................... 157

Table 6.1: Valve sequencing for 2-step, single bed PPSA process ......................... 166

Table 6.2: Summary of parameters used in modeling and simulation of PPSA processes. .................................................................................. 169

Table 6.3: Summary of parameters used in modeling and simulation of three-step VSA processes. ........................................................................ 186
NOMENCLATURE

Symbols:

\( a \)  adsorption column area \((cm^2)\)

\( a- t_a \) cyclic steady-state oxygen profile at the end of the adsorption step for an adsorption step duration indicated by the number in Figure 3.5

\( a- t_d \) cyclic steady-state oxygen profile at the end of the adsorption step for a desorption step duration indicated by the number in Figure 3.5

\( b_i \) Langmuir constants for component \( i \) \((cc/mol)\)

\( C_{ps} \) specific heat of solid adsorbent \((J/kg/K)\)

\( C_{pg} \) specific heat of gas phase \((J/kg/K)\)

\( \bar{C}_{pg} \) specific heat of gas mixture \((J/kg/K)\)

\( C_{pa} \) specific heat of adsorbed gas phase \((J/kg/K)\)

\( C_{pw} \) specific heat of wall \((J/kg/K)\)

\( c \) total gas phase molar concentration \((mol/cc)\)

\( c_i \) molar concentrations of component \( i \) in gas phase \((mol/cc)\)

\( c_{avg} \) average molar concentration of component \( A \) in feed gas at \( P_{avg} \) \((mol/cc)\)

\( c_0 \) initial molar concentration of component \( i \) in feed gas \((mol/cc)\)

\( d- t_a \) cyclic steady-state oxygen profile at the end of the desorption step for an adsorption step duration indicated by the number in Figure 3.5

\( d- t_d \) cyclic steady-state oxygen profile at the end of the desorption step for a desorption step duration indicated by the number in Figure 3.5
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_c$</td>
<td>column diameter ($cm$)</td>
</tr>
<tr>
<td>$D_L$</td>
<td>axial dispersion coefficient ($cm^2/s$)</td>
</tr>
<tr>
<td>$D_M$</td>
<td>molecular diffusivity at average column pressure ($P_{avg}$) and $25^\circ C$ ($cm^2/s$)</td>
</tr>
<tr>
<td>$D_p$</td>
<td>macropore diffusivity ($cm^2/s$)</td>
</tr>
<tr>
<td>$d_p$</td>
<td>adsorbent particle size ($cm$)</td>
</tr>
<tr>
<td>$F_{in}$</td>
<td>inlet gas volumetric flow rate ($cc/s$)</td>
</tr>
<tr>
<td>$F_{out}$</td>
<td>exit gas volumetric flow rate ($cc/s$)</td>
</tr>
<tr>
<td>$f_{cyc}$</td>
<td>cycling frequency ($1/s$)</td>
</tr>
<tr>
<td>$\Delta H_i$</td>
<td>heat of adsorption of component $i$ ($J/mol$)</td>
</tr>
<tr>
<td>$h_i$</td>
<td>inside heat transfer coefficient to the column wall ($W/m^2/K$)</td>
</tr>
<tr>
<td>$h_o$</td>
<td>outside heat transfer coefficient to the water circulating in the jacket, ($W/m^2/K$)</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Henry’s law constant for component $i$, $[(mol/cc)<em>{solid\ phase}/(mol/cc)</em>{gas\ phase}]$</td>
</tr>
<tr>
<td>$K_g$</td>
<td>thermal conductivity of gas mixture ($W/m/K$)</td>
</tr>
<tr>
<td>$K_z$</td>
<td>effective thermal conductivity of gas ($W/m/K$)</td>
</tr>
<tr>
<td>$K_w$</td>
<td>thermal conductivity of wall ($W/m/K$)</td>
</tr>
<tr>
<td>$k_1$</td>
<td>Darcy's constant in Equation (5.2)</td>
</tr>
<tr>
<td>$k_i$</td>
<td>effective mass transfer coefficients for component $i$ ($s^{-1}$)</td>
</tr>
<tr>
<td>$k_f$</td>
<td>external gas film mass transfer coefficient ($s/cm^2$)</td>
</tr>
<tr>
<td>$k_p$</td>
<td>bed permeability ($cm^2$)</td>
</tr>
<tr>
<td>$L$</td>
<td>bed length ($cm$)</td>
</tr>
<tr>
<td>$N$</td>
<td>number of tanks in Equation (5.10)</td>
</tr>
<tr>
<td>$\bar{m}$</td>
<td>average gas phase molecular weight ($kg/mol$)</td>
</tr>
<tr>
<td>$n$</td>
<td>number of cycles completed (or) data points</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>( n(j) )</td>
<td>total number of moles adsorbed in ( j^{th} ) step</td>
</tr>
<tr>
<td>( \Delta n(j) )</td>
<td>differential moles adsorbent in ( j^{th} ) step</td>
</tr>
<tr>
<td>( N_i )</td>
<td>molar flux of component ( i ) with respect to fixed coordinates (mol/cm(^2)/s)</td>
</tr>
<tr>
<td>( P )</td>
<td>total pressure (atm)</td>
</tr>
<tr>
<td>( P_a )</td>
<td>ambient pressure (atm)</td>
</tr>
<tr>
<td>( P_H )</td>
<td>total pressure at ( z = 0 ) during adsorption step (atm)</td>
</tr>
<tr>
<td>( P_L )</td>
<td>total pressure at ( z = L ) during adsorption and ( z = 0 ) during desorption (atm)</td>
</tr>
<tr>
<td>( P_v )</td>
<td>initial vacuum pressure along the column in VSA study (atm)</td>
</tr>
<tr>
<td>( P_{avg} )</td>
<td>average of inlet and outlet total pressures during adsorption (atm)</td>
</tr>
<tr>
<td>( P_d^*(j) )</td>
<td>equilibrium adsorbate pressure in ( j^{th} ) step on dose side (bar)</td>
</tr>
<tr>
<td>( P_t^*(j) )</td>
<td>equilibrium adsorbate pressure in ( j^{th} ) step on test side (bar)</td>
</tr>
<tr>
<td>( \Delta P )</td>
<td>pressure difference between the inlet and outlet of column (atm)</td>
</tr>
<tr>
<td>( p_i )</td>
<td>partial pressure of component ( I ) (atm)</td>
</tr>
<tr>
<td>( Q(t) )</td>
<td>average volumetric flow rate in Equation 5.9 (cc/s)</td>
</tr>
<tr>
<td>( q_{avg} )</td>
<td>average adsorbed phase concentration of component A at ( P_{avg} ) (mol/cc)</td>
</tr>
<tr>
<td>( \bar{q}_i )</td>
<td>average adsorbed phase concentration of component ( i ) in the particle, (mol/cc)</td>
</tr>
<tr>
<td>( q_i^e )</td>
<td>equilibrium adsorbed phase concentration of component ( i ) (mol/cc)</td>
</tr>
<tr>
<td>( q_0 )</td>
<td>equilibrium adsorbed phase concentration corresponds to ( c_0 ) (mol/cc)</td>
</tr>
<tr>
<td>( q_s )</td>
<td>saturation constant (mol/cc)</td>
</tr>
<tr>
<td>( q_p^* )</td>
<td>equilibrium adsorption capacity of particle (mol/cc)</td>
</tr>
<tr>
<td>( \Delta q_i )</td>
<td>working capacity between two operation pressures ((i=1 \text{ to } 3)) (mol/cc)</td>
</tr>
<tr>
<td>( R )</td>
<td>universal gas constant (atm·cc/mol·K)</td>
</tr>
</tbody>
</table>
**Nomenclature**

$R_d$  
column to particle diameter ratio

$r_p$  
adsorbent particle radius (cm)

$T$  
temperature (K)

$T_s$  
equilibrium isotherm temperature (K)

$T_a$  
ambient temperature (K)

$T_w$  
wall temperature (K)

$t$  
time (s)

$t_a$  
adsorption time (s)

$t_d$  
desorption time (s)

$\Delta U$  
internal change of energy (J/mol)

$u_z$  
gas phase velocity through porous media in z-direction (cm/s)

$\bar{u}_z$  
average gas velocity from Blake-Kozney equation (cm/s)

$V_{ads}$  
adsorbent volume (cm$^3$)

$V_a$  
adsorbent volume (cm$^3$)

$V_d$  
dose side volume in constant volume apparatus (cm$^3$)

$V_{dead}$  
total inlet dead volume (cm$^3$)

$V_0$  
feed gas velocity in VSA study (cm)

$V_t$  
test side volume in constant volume apparatus (cm$^3$)

$V_i$  
volume of tank $i$ in Equation (5.9) (cm$^3$)

$W$  
thoretical work done by the compressor (J)

$X$  
dimensionless function defined by Equation (3.30)

$x_{in}$  
inlet gas mole fraction defined by Equation (4.4)

$x_{out}$  
exit gas mole fraction defined by Equation (4.4)
Nomenclature

$Y$  
dimensionless function defined by Equation (3.30)

$y_i$  
mole fraction of component $i$

$y_{i0}$  
mole fraction of component $i$ in feed

$z$  
axial distance ($cm$)

$\infty$  
saturation

Greek letters

$\beta$  
radial dispersion factor in Equation (2.3)

$\epsilon$  
bed voidage

$\epsilon_p$  
particle voidage

$\gamma_1, \gamma_2$  
constants in equation for axial dispersion coefficient

$\mu$  
viscosity of gas at room temperature ($atm\cdot s$)

$\theta$  
dimensionless adsorption time, $\frac{\epsilon_p D_p}{r_p^2} \left( \frac{c_0}{q_0} \right) t_a$

$\phi$  
dimensionless mean residence time of gas

$\rho_s$  
adsorbent density ($kg/m^3$)

$\rho_g$  
average gas density ($kg/m^3$)

$\rho_w$  
wall gas density ($kg/m^3$)

$\tau$  
tortuosity factor

$\tau_i$  
residence time gas in tank $i$ ($s$)

$\omega$  
adsorption wave velocity ($cm/s$)

$\eta$  
efficiency of compressor

$\Pi_i$  
dimensionless groups $i$ (=1to11) defined by Equation (A15) – (A25) in the Appendix A
Nomenclature

$\Omega$  linear driving force model parameter

Subscripts/ superscripts/abbreviations

A  nitrogen
B  oxygen
a  adsorption step
ads  adsorbent
avg  average
B  oxygen
cur  current value
cyc  cycle
d  desorption step
e  equilibrium value
H  high pressure
i  component A or B or tank
in  inlet
out  exit
j  step
L  low pressure
p  particle
ref  reference value
s  scale factor
theo  theoretically calculated value
z  axial direction
0  feed gas
<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>dimensionless variable</td>
</tr>
<tr>
<td>Ag-Li-X</td>
<td>silver exchanged lithium substituted low silica zeolite (or AgLiLSX)</td>
</tr>
<tr>
<td>AMA</td>
<td>American Medical Association</td>
</tr>
<tr>
<td>BPR</td>
<td>back pressure regulator</td>
</tr>
<tr>
<td>BSF</td>
<td>bed size factor</td>
</tr>
<tr>
<td>BTC</td>
<td>breakthrough curve</td>
</tr>
<tr>
<td>CMS</td>
<td>carbon molecular sieves</td>
</tr>
<tr>
<td>COPD</td>
<td>chronic obstructive pulmonary disease</td>
</tr>
<tr>
<td>CSS</td>
<td>cyclic steady state</td>
</tr>
<tr>
<td>DM</td>
<td>dispersion model</td>
</tr>
<tr>
<td>DIB</td>
<td>direct input of blank experimental data in the model as feed</td>
</tr>
<tr>
<td>ETS</td>
<td>Engelhard titanosilicates</td>
</tr>
<tr>
<td>JAC</td>
<td>jacketed adsorption column</td>
</tr>
<tr>
<td>LDF</td>
<td>linear driving force model</td>
</tr>
<tr>
<td>LSX</td>
<td>low silica zeolite</td>
</tr>
<tr>
<td>LILSX</td>
<td>lithium substituted low silica zeolite</td>
</tr>
<tr>
<td>MFM</td>
<td>mass flow meter</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow meter</td>
</tr>
<tr>
<td>OA</td>
<td>oxygen analyzers</td>
</tr>
<tr>
<td>PS</td>
<td>pressure sensor</td>
</tr>
<tr>
<td>$Pe_{\infty}$</td>
<td>limiting peclet number in Equation 2.3</td>
</tr>
<tr>
<td>PSA</td>
<td>pressure swing adsorption</td>
</tr>
<tr>
<td>PPSA</td>
<td>pulsed pressure swing adsorption</td>
</tr>
<tr>
<td>PVSA</td>
<td>pressure vacuum swing adsorption (or VPSA)</td>
</tr>
<tr>
<td>RMSD</td>
<td>root mean square deviation</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>Description</td>
</tr>
<tr>
<td>--------------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>RPSA</td>
<td>rapid pressure swing adsorption</td>
</tr>
<tr>
<td>SLPM</td>
<td>standard liters per minute</td>
</tr>
<tr>
<td>SV</td>
<td>solenoid valve</td>
</tr>
<tr>
<td>TC</td>
<td>thermocouple</td>
</tr>
<tr>
<td>TIS</td>
<td>tanks in series model</td>
</tr>
<tr>
<td>TPDO₂</td>
<td>tons of oxygen per day</td>
</tr>
<tr>
<td>VSA</td>
<td>vacuum swing adsorption</td>
</tr>
<tr>
<td>VPSA</td>
<td>vacuum pressure swing adsorption (or PVSA)</td>
</tr>
<tr>
<td>URPSA</td>
<td>ultra rapid pressure swing adsorption</td>
</tr>
</tbody>
</table>
Chapter 1

INTRODUCTION

1.1 Overview of the Research

Use of oxygen-enriched streams produced from air spans from classical chemical engineering to biological and medical applications. There is a significant demand for portable oxygen supply for personal use by people needing oxygen therapy. Medical conditions in humans such as Chronic Obstructive Pulmonary Disease (COPD), limit the capacity of the lung to oxygenate blood by breathing atmospheric air. A constant supply of pure oxygen or oxygen-enriched air is essential to facilitate breathing for such patients.

As reported in world health statistics 2008, COPD is ranked as the fifth leading cause of death after HIV/AIDS and it is projected to become third leading cause of death by 2030 due to an increase in cigarette smoking rates and air pollution [WHO (2011)]. In the USA, 1 in 20 persons suffers from COPD. The demand for portable medical oxygen systems has significantly increased over the last decade because of an increasing number of COPD patients around the world.

One option for COPD patients is to use a small oxygen cylinder for breathing. The other available option is to use a device that draws in air and produces varying degrees of enriched oxygen using pressure-swing adsorption (PSA) or membrane technology, which the COPD patients can then use to facilitate their breathing. These options, due to the size and weight of the devices, have limited portability that results in restricted mobility for these patients who might otherwise be more physically
active. Therefore, an oxygen-concentrating device using atmospheric air as feed that is sufficiently small in size and lighter in weight can significantly improve the quality of life for those people who need oxygen therapy to overcome their lung insufficiency. For this reason, the main focus of current research is to study the feasibility of miniaturization of adsorption based oxygen concentrating device for personal medical applications of chronic obstructive pulmonary disease patients.

1.2 Chronic Obstructive Pulmonary Diseases and its Treatment

Chronic obstructive pulmonary disease (COPD) is the most common lung disease, which causes difficulty in breathing. It is a pair of commonly co-existing lung diseases namely, chronic bronchitis and emphysema, which become progressively worse over time. It causes the limitation of air flow to and from the lungs by narrowing the airways and hence it leads to the damage of lungs and shortness of breath in COPD patients. The respiratory systems of a healthy adult and that of a COPD affected patient are shown in Figure 1.1. The loss of surface area of air sacs for exchange of oxygen and carbon dioxide between the air and blood in COPD patients is evident from Figure 1.1. The primary causes for COPD disease are cigarette smoking, long term exposure to smoke and chemical fumes, and air pollution. There is no cure for this disease but it can be slowed down by oxygen therapy. Oxygen therapy is a treatment that provides high purity oxygen to COPD patients to overcome their lung inefficiency; therefore, the oxygen levels in blood can be maintained.

The oxygen therapy options commercially available on the market are liquid oxygen tanks, compressed oxygen tanks and oxygen concentrators, which are summarized in Table 1.1. Liquid oxygen tanks are widely used in hospitals because of their high usage requirements. Liquid oxygen and high pressure cylinders need to be
refilled after use and also require special care for storage and handling. Therefore, these options are not safe and economically viable for personal medical applications of COPD patients. In contrast, an oxygen concentrator generates oxygen using ambient air as the feed and continuously delivers oxygen to patients. Therefore, these units have a widespread use for home oxygen therapy and portable personal oxygen. Further details on commercially available air separation technologies for oxygen production from ambient air are discussed in the following section.

1.3 Air Separation Processes

The primary products of air separation, O₂, N₂ and Ar, are the key commodity chemicals in many manufacturing processes. Air separation is an energy intensive process. There are two primary technologies for air separation into oxygen and nitrogen:

(i) Cryogenic air separation processes
(ii) Non-cryogenic air separation processes

(a) Adsorption based gas separation processes

(b) Membrane based gas separation processes

(c) Chemical processes

Table 1.1: Comparison of commercially available oxygen therapy options.

<table>
<thead>
<tr>
<th>Liquid oxygen</th>
<th>High pressure compressed oxygen cylinders</th>
<th>Oxygen concentrators (Instant use)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large, small units and does not require electricity</td>
<td>Small, lightweight and does not require electricity</td>
<td>Onsite, unlimited supply of oxygen; requires electricity</td>
</tr>
<tr>
<td>Low temperature storage</td>
<td>High pressure product</td>
<td>Ambient temperature and pressure</td>
</tr>
<tr>
<td>Refilling after use</td>
<td>Replacement after use</td>
<td>Refilling not required</td>
</tr>
<tr>
<td>Expensive</td>
<td>Expensive</td>
<td>Economical</td>
</tr>
<tr>
<td>Requires special equipment and is heavy</td>
<td>Requires special cylinders</td>
<td>Portable units available but are heavy</td>
</tr>
<tr>
<td>Hard to handle</td>
<td>Very difficult to handle and not safe</td>
<td>Safest way for oxygen supply</td>
</tr>
<tr>
<td>Maintenance required</td>
<td>Requires extreme care</td>
<td>Less maintenance</td>
</tr>
</tbody>
</table>

Cryogenic air separation is the most cost effective and efficient technology currently used for production of large quantities of oxygen and nitrogen with high purity and recovery. It is based on low temperature distillation of oxygen and nitrogen due the difference in their boiling points. Cryogenic air separation plants are usually bulky in size and not suitable for onsite small scale applications such as medical oxygen delivery systems. The first two options, liquid oxygen and compressed high pressure oxygen cylinders in Table 1.1 are obtained from cryogenic distillation of air. The non-cryogenic processes separate air into oxygen and nitrogen based on
Chapter 1. Introduction

differences in the adsorption equilibrium or rate and permeation of air components on adsorbent and membrane materials respectively at room temperature and near ambient pressure. Non-cryogenic air separation processes are small in size, efficient and economical compared to cryogenic plants for the small scale production of oxygen and nitrogen. Moreover, very high product purities are not required [UIG (2011)].

Among the non-cryogenic air separation processes, membrane and chemical processes are still developing for producing high purity oxygen from air streams. Since, the invention of synthetic zeolites for air separation, the adsorption based air separation process contribute to more than 30% of the world oxygen demand in comparison to cryogenic distillation processes for small scale applications [Thorogood (1991)]. A detailed overview of adsorption based gas separation processes is presented in the following section.

1.3.1 Adsorption based air separation processes

In an adsorption based air separation process for oxygen, the air fractionation into its primary components is based on selective adsorption of N₂ over O₂ and Ar on zeolite adsorbent materials. The preferential adsorption of N₂ on zeolites is due to the quadrupole moment of N₂ molecules under the influence of a non-uniform charge distribution in the zeolite framework. O₂ and Ar have similar adsorption capacities on zeolite molecular sieves. Consequently, the maximum oxygen purity that can be attained using adsorption based air separation processes is limited to less than 95%. Nonetheless, the zeolite adsorbents are typically used for adsorption based oxygen production from air for small scale applications. However, because the zeolite adsorbents have a high capacity for the other components of ambient air, H₂O and CO₂, the regeneration of the adsorption column is also a critical issue; even a small
amount of these polar compounds present in air can significantly reduce the capacity of these zeolite adsorbents for air separation. Therefore, these compounds must be removed from air before entering the column using desiccants such as activated alumina or NaX zeolite adsorbents. When dry air is passed through a column packed with a zeolite adsorbent, the N₂ is selectively retained by the solid adsorbent and O₂-enriched product gas can be generated at the exit of the column. The adsorbed N₂ is desorbed by lowering the pressure in several ways based on which the adsorption based air separation processes are classified as follows:

(i) Pressure swing adsorption (PSA)
(ii) Vacuum- pressure swing adsorption (VSA, VPSA or PVSA)
(iii) Rapid pressure adsorption process (RPSA)

The selection of the above processes depends on the nature of the isotherms, working capacity and selectivity of nitrogen over oxygen on the chosen adsorbent. The selectivity of N₂ should be very high to produce high purity O₂ in the adsorption step. Furthermore, the desorption of nitrogen should be readily achieved by lowering the pressure to create enough capacity of the adsorbent for N₂ gas in the subsequent cycle. This will reduce the product purge gas requirement in order to remove the nitrogen from the voids of the zeolite adsorbent before starting the next cycle. The criteria for choosing the first two processes mentioned above mainly depend on the working capacity of the adsorbent, which is illustrated in Figure 1.2. If the working capacity of PSA processes \( \Delta q_1 \) is higher than the working capacity of the VPSA process \( \Delta q_2 \) and VSA process \( \Delta q_3 \), the PSA process performs better than the other two processes due to the higher difference in solid loading over the same range of adsorption and desorption pressures. Similarly, if \( \Delta q_2 > \Delta q_1 \) and \( \Delta q_3 \), the VPSA
process performance is better than the PSA and VSA processes. When the solid loading changes between the adsorption and desorption pressures is higher ($\Delta q_3 > \Delta q_1$ and $\Delta q_2$) below 1 atm, then the VSA performance is better than the VPSA and PSA processes. The rapid pressure swing adsorption process (RPSA) is characterized by the use of small-size adsorbent particles and fast cycling to improve the adsorbent productivity and decrease the bed size factor (BSF). Thus, the process miniaturization of the adsorption based air separation process is feasible with rapid cycling of the process. In all these processes, the adsorption and desorption of $N_2$ and $O_2$ is carried out in a sequential cyclic fashion using single or multiple adsorption columns. A detailed summary of all the process is presented in the following sections.

![Comparison of working capacity of PSA, VSA and VPSA processes for air separation on zeolite adsorbents at constant temperature. $\Delta q_1$: working capacity of PSA, $\Delta q_2$: working capacity of VPSA and $\Delta q_3$: working capacity of VSA process.](image)

1.3.2 Pressure swing adsorption (PSA) process

The pressure swing adsorption process separates oxygen and nitrogen from air due to the difference in adsorption of oxygen and nitrogen on zeolite adsorbents at two different pressures near and above atmospheric pressure. The high quadrupole
moment of nitrogen causes its high affinity for adsorption over oxygen and argon on zeolite materials. The PSA cycle operates at ambient temperature between super atmospheric pressure, at which the adsorption of nitrogen from air is more and gas enriched in oxygen is delivered from the other end, and atmospheric pressure, at which the bed is regenerated by lowering the pressure to 1 bar causing the adsorbed nitrogen to be released from the adsorbent. It is different from the cryogenic distillation technique for gas separation, which operates at a very low temperature below 0°C. The schematic of the basic Skarstrom cycle for the pressure swing adsorption process is shown in Figure 1.3. The cycle consists of two adsorption columns packed with zeolite adsorbent particles and has four steps: pressurization, adsorption, blowdown and purge. The valve operation sequence is shown in the table with Figure 1.3.

![Figure 1.3: Schematic diagram of a two bed, 4-step PSA process.](image)

<table>
<thead>
<tr>
<th>Step</th>
<th>V1</th>
<th>V2</th>
<th>V3</th>
<th>V4</th>
<th>V5</th>
<th>V6</th>
<th>V7</th>
<th>V8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressurization</td>
<td>√</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>√</td>
<td></td>
<td>X</td>
<td></td>
<td>√</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Blow down</td>
<td></td>
<td></td>
<td></td>
<td>√</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Purge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.3: Schematic diagram of a two bed, 4-step PSA process.
Initially both the adsorption columns are saturated with air at 1 atm. In the pressurization step, the column pressure is increased from 1 atm to super atmospheric pressure using air at high pressure from the feed end by opening solenoid valve V1. While bed 1 is in the pressurization step, bed 2 is undergoing blowdown during which the nitrogen is desorbed from the solid zeolite adsorbent by lowering the inlet column pressure to 1 atm by opening valve V4 and having the rest of the valves in the closed position. In the second step, the high pressure feed air is supplied to the inlet of bed 1 at a constant inlet gas velocity and oxygen enriched gas is delivered at the exit of the column at the column pressure. In this step, the valve V1 is opened to supply the high pressure feed air to the column at constant velocity and high purity oxygen is delivered through valve V5. During this step, bed 2 undergoes the purge step. A part of the oxygen product gas obtained from bed 1 is used to purge the second column in order to remove the desorbed nitrogen from the voids of the zeolite adsorbent by purging the column with high purity oxygen. In this step, valves V7 and V4 are opened and the other valves are closed to purge the column with an enriched oxygen stream from the first bed. In the third step, bed 1 undergoes a blowdown step in which the zeolite adsorbent is regenerated by desorbing the nitrogen adsorbed in previous step by lowering the column pressure to atmospheric pressure during which bed 2 undergoes the pressurization step. In these steps the valves V3 and V2 are opened and the other valves are in the closed position. Finally, bed 1 undergoes the purge step while bed 2 is undergoing the adsorption step. In this step, the valves V3 and V7 are opened to purge column 1 and V2 and V6 are opened to deliver the oxygen rich product at the column exit of the second bed. A part of product gas from bed 2 is used to purge the first bed. The first and second steps, pressurization and adsorption, are referred to as the first half cycle; the third and fourth steps, blow down and purge, are
referred to as the second half cycle. While bed 1 is under the first half cycle, bed 2 is under the second half cycle. One complete cycle constitutes all four steps together. Both the adsorption columns repeatedly undergo all these steps in each cycle in order to produce the enrich oxygen stream in adsorption and to desorb the nitrogen in the blowdown and purge steps. The commonly used particle size range in the conventional pressure swing adsorption process is between 0.5 to 2 mm. The process performance is usually measured in terms of oxygen purity, recovery and productivity. Several process variables, bed length, column pressure, inlet gas velocity and cycle times affect the process performance. For the conventional PSA process the effect of pressure drop along the column is not very significant in short laboratory columns packed with larger adsorbent particles. The maximum oxygen product purity obtained using the PSA process is limited to $< 95\%$; the other gas produced is Ar due to same capacity of $O_2$ and Ar on solid zeolite adsorbents.

Since the invention of Skarstrom cycle in 1964 for air drying, the cyclic adsorption based gas separation process has gone through many modifications. Several modifications to the existing Skarstrom cycle were implemented to improve the process performance, thereby lowering the capital and operating costs of the processes. The pressure equalization steps were implemented to reduce the power consumption of the processes. Instead of two beds, a multi-bed PSA process was developed for continuous operation and delivery of high flow rates of the product gases.

In case of highly nonlinear adsorption equilibrium isotherms for nitrogen on zeolite, the working capacity, $\Delta q_1$ for PSA process may not be large enough to operate the process efficiently above atmospheric pressure. In such a case, the other adsorption processes, VSA and VPSA, perform better than the PSA process.
Chapter 1. Introduction

1.3.3 Vacuum-pressure swing adsorption (VSA and VPSA) processes

Vacuum-pressure swing adsorption processes are a special class of non-cryogenic pressure swing adsorption based air separation technology in which the adsorption step is carried out at atmospheric pressure in case of VSA and just above atmospheric pressure in the VPSA or PVSA processes and desorption is under vacuum using zeolite molecular sieve adsorbent materials for selective adsorption of nitrogen. The VSA and VPSA processes separate oxygen and nitrogen from air at near ambient pressure and temperature where the working capacity \( \Delta q_2 \) of these processes is much higher than PSA processes for the same pressure range shown in Figure 1.3.

The VSA and VPSA processes have several advantages over PSA processes, which are summarized as follows.

(i) The VSA and VPSA processes operate in the low pressure range of the isotherms where the change in adsorbate loading is steepest; thus, these processes have the potential to extract the maximum adsorbent working capacity within a small pressure range. Hence, the VSA and VPSA processes are more energy efficient than PSA processes for the same product delivery rate, purity and pressure conditions. Typically the specific power of the VPSA process is less than one-third of the oxygen PSA units and is also similar to that of cryogenic oxygen plants having the same capacity.

(ii) The superior regeneration of molecular sieve zeolite adsorbents in VSA/VPSA processes under vacuum conditions in desorption step extends the life of the adsorbent material.
Chapter 1. Introduction

(iii) The fully regenerated zeolite adsorbent is more selective for nitrogen adsorption; therefore, the recovery and productivity of oxygen using VSA or VPSA processes is much higher than the conventional oxygen PSA process. Less feed air due to higher recovery which results in a smaller compressor and adsorption column.

(iv) Maintenance of the VSA and VPSA processes is greatly reduced in comparison to two-bed PSA systems because the pressure swing between the adsorption and regeneration steps is an order of magnitude lower or near ambient pressure. Therefore, VSA processes are less susceptible to sieve dusting, which avoids frequent replacement of adsorbent material after damage.

(v) The lower operating pressures in the VSA and VPSA processes also eliminate the water condensation in the feed air; thus, these processes can be operated in humid environments, whereas PSA systems require water and oil removal hardware before the adsorption unit, if oil-lubricated compressors are used.

(vi) The simplest design and efficient VSA or VPSA technology offers oxygen VPSA units that are more cost effective to produce oxygen within the flowrate range of 20-60 tons per day of oxygen (TPDO₂) at an oxygen product purity of 90-95% with an argon content between 4 to 5%. The effectiveness of VSA and VPSA processes for producing oxygen compared to conventional non-cryo genic PSA and cryogenic distillation process is shown in Figure 1.4.

PSA, VSA and VPSA processes have longer step durations that are typically more than 10s. However, the faster cycling of these processes further improves the
adsorbent productivity. Thus, it is feasible to design a lightweight and portable oxygen unit for personal medical applications. However, the faster cycling of these adsorption processes, which is feasible by increasing the rate of mass transfer between gas and solid, introduces other dynamics related flow and pressure drop. It leads to the special class of fast cycling adsorption processes known as rapid cycling pressure swing adsorption (RPSA).

![Figure 1.4: Comparison of various modes of oxygen production in the Market for industrial and medical applications [UIG (2011)].](image)

1.3.4 Rapid cycling pressure swing adsorption process

The rapid cycling pressure swing adsorption process (RPSA) is also known as the pulsed pressure swing adsorption (PPSA) process, which is an advancement in PSA technology. It has the potential to improve the adsorbent productivity and therefore, to reduce the size of the adsorber by rapid cycling of the process between the adsorption and desorption steps. RPSA processes are characterized by very fast
cycling (cycle time < 10 s) and use of small size adsorbent particles (100-500 µm) [Ruthven et al., (1993)], which results in high pressure drop along the column. The RPSA process has the following unique characteristics compared to the conventional PSA processes [Yang (1985)]:

(i) The RPSA processes are nearly isothermal due to the rapid cycling between the adsorption and desorption steps.

(ii) Use of a single column with a minimum number of valves simplifies the process design and control of RPSA processes.

(iii) To obtain better performance of these processes, the adsorption step is short to avoid product contamination with the strongly adsorbing component because of high interstitial gas velocities within the column caused by the pressure drop along the column. The desorption step is long enough to desorb the strongly adsorbed component by reducing the column inlet pressure and self purging of the front end of the column owing to desorption of the weakly adsorbing component from the product end of the column.

(iv) Fast cycling of RPSA processes yields high adsorbent productivity; hence, the miniaturization of the adsorption column size is feasible with RPSA processes compared to PSA process for comparable purity.

(v) The RPSA process has low recovery due to the high pressure drop along the column. Thus, the high energy consumption of these processes results in the use of a larger compressor compared to the conventional PSA process; also the bed utilization in the PSA process is superior to RPSA processes.

(vi) The performance of these processes is limited when the adsorbent particle size is too small or too large. The typical adsorbent particle size range used in RPSA processes is between 100-500 µm.
Chapter 1. Introduction

The first RPSA process was invented by Turnock and Kadlec (1971) for the separation of methane-nitrogen gas mixture using 5A zeolite adsorbent. They concluded that rapid cycling of the process significantly improved the nitrogen enrichment using a simple single bed, 2-step RPSA process. However, the recovery of nitrogen was very low. In order to improve the recovery and correspondingly the energy efficiency of the process, a three-step, single-bed RPSA process was proposed in the literature by Jones et al., (1980) for oxygen production from air using 5A zeolite adsorbent. The schematic of a simple RPSA process is shown in Figure 1.5, which has a single adsorption column and requires minimum instrumentation for controlling the flow and measuring the process variables. The process has 3-steps namely adsorption, delay and desorption; the valve operation in these steps is shown in the table along with the schematic in Figure 1.5. In the first adsorption step, the high pressure feed gas is supplied to the entrance of the column by opening valve V1 and the enriched gas stream depleted in strongly adsorbed component is delivered from the other end by opening valve V3. In the delay step, all three valves are closed for a short time before the desorption step. In the third step, the strongly adsorbed component is desorbed from the adsorbent by opening valve V2 thereby lowering the column inlet pressure to facilitate desorption. During the adsorption and desorption steps, the enriched weakly adsorbing component is delivered from the product end.

Since the invention of RPSA processes, several modifications have been implemented by changing the process cycle design, use of fast cycling rotary valves (novel hardware) and novel adsorption column design. Among them, the major advancements in RPSA technology are the following:

(i) The radial rapid pressure swing adsorption process (Radial RPSA)
(ii) The ultra-rapid pressure swing adsorption process (URPSA)
Chapter 1. Introduction

In the radial RPSA process the enriched product gas is delivered in the radial direction while the feed enters along the axial direction and vice-versa using small size zeolite particles as the adsorbent for separation of the gas mixture. Compared to RPSA processes, the radial RPSA process has low pressure drop and higher adsorbent utilization, which improve their productivity and recovery.

Figure 1.5: Schematic diagram of a single bed, 3-step RPSA process.

<table>
<thead>
<tr>
<th>Step</th>
<th>V1</th>
<th>V2</th>
<th>V3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>✓</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>Delay</td>
<td>X</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>Desorption</td>
<td>X</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

The URPSA process is the latest development in RPSA technology that offer a promising solution to size reduction and portability issues of medical-grade oxygen concentrators for the personal use of COPD patients and in the development of advanced fuel cell powered vehicles. An URPSA process has a cycle time on the order of 1s or sub-second and the adsorbent particle size used in these processes is one order of magnitude smaller than in RPSA processes. Development of piston
driven Ultra Rapid PSA processes enhances the superior separation efficiency per unit mass of the adsorbent and has a small bed size factor at high purity and recovery. In a piston driven URPSA process, the pressurization and depressurization of the adsorbent bed are carried out by connecting the adsorption column to a cylinder where the movement of the piston at high frequency drives the adsorption and desorption steps. This process has moving parts, such as the piston, which makes them unsuitable for personal medical applications.

1.3.5 Nitrogen selective adsorbents for oxygen production

The selection of an adsorbent for any gas mixture is a critical step in order to design an effective and efficient adsorption based gas separation process. The critical factors generally considered for the selection of an adsorbent for oxygen production from air are the following:

(i) The specific nitrogen capacity of the adsorbent should be very high compared to oxygen. It determines the amount of adsorbent required for the separation and thus, the size of adsorption column.

(ii) The selectivity for N₂ over O₂ should be very high and the capacity for oxygen should be low. Therefore, the energy efficiency of the process will be higher because of high recovery of oxygen using less compressed feed air.

(iii) Air separation also depends on regenerability, which is determined by the heat of adsorption of the adsorbent. Thus, the adsorbent can be operated in sequential cycles with uniform performance, which requires that each adsorbable component must be relatively weakly adsorbed (physisorbed)
on the solid adsorbent so that the required low purge gas flow rate to clean
the bed during desorption is low.

(iv) The adsorption and desorption kinetics of N₂ and O₂ should be very fast in
an equilibrium controlled air separation process for producing oxygen in
order to run the process at high cycling frequency. Thus, the adsorbent
productivity is high and requires a small amount of adsorbent to attain the
desired product rate.

(v) Other mechanical properties that must be considered in selecting an
adsorbent for oxygen production from air are the following: high crushing
strength, low attrition, low dust and high stability against aging.

Due to these considerations, the selection of an optimum adsorbent for a given
PSA process or designing an optimum process for a given adsorbent can be fairly
complex [Sircar et al., (1998)]. The evaluation of effectiveness of an adsorbent for a
chosen PSA process includes the measurement of the equilibrium isotherms of the
feed gas components on a chosen adsorbent and implementation of detailed process
models to analyze the kinetics of adsorption [Ackley et al., (2003)]. The commonly
used nitrogen selective adsorbents for oxygen production from air using pressure
swing adsorption are reviewed in the next section.

1.3.6 Zeolite adsorbents (5A, 13X and LSX zeolite)

The most commonly used zeolite adsorbents until the invention of low silica
zeolite (LiLSX) in 1989 [Yang (2003)] for the selective adsorption of nitrogen in air
for oxygen production were 5A and 13X zeolite. The primary structural units of any
zeolite adsorbent are tetrahedral silicon (SiO₂) and tetrahedral aluminum (AlO₄).
These primary units are assembled to form secondary polyhedra building blocks such as cubes, prisms and octahedra. The secondary units are joined together by sharing an oxygen atom between the silicon and aluminum atoms located at the corners of polyhedra. The crystalline zeolite structure is formed in a regular three-dimensional crystalline framework by the assembly of secondary building units. The general formula of a zeolite is represented as follows [Yang (2003)]:

$$M_{x/n} \left[ (\text{AlO}_{2})_x (\text{SiO}_{2})_y \right] \cdot n\text{H}_2\text{O}$$

Where the $x$ and $y$ are the fractions of primary units such that $y/x \geq 1$; $n$ is the valence of the extra framework cation; $M$, balances the charge distribution in the zeolite structure; and $z$ is the number of water molecules in the structure of each unit cell. The type of cation ($M$), location and framework composition have a dominant effect on the properties of zeolite for air separation [Coe et al., (1994)] and are largely responsible for the selective adsorption of $N_2$ on zeolite adsorbents. The synthetic zeolites 5A and 13X are formed by the presence of $\text{Ca}^{2+}$ and $\text{Na}^{+}$ ions in place of $M$ in the zeolite structure. The unit cells of zeolite 5A, linked through a four-member ring, and the 13X type, linked through a six-member ring, are shown in Figure 1.6. The locations of the cations in both frameworks are also shown. The equilibrium selective adsorption of $N_2$ preferentially over $O_2$ on zeolite adsorbents is due to the interaction between the extra framework cation and the quadrupole moment of the adsorbing gases $N_2$ and $O_2$. The quadrupole moment of $N_2$ is four times higher than that of $O_2$.

Advancement in the synthesis of low silica zeolite (LSX) and exchange of extra framework cations with Li and Ag leads to the development of silver exchanged LiLSX type (AgLiLSX) zeolites. These adsorbents have a desirable combination of higher capacity, a linear isotherm for $N_2$ adsorption and a relatively low capacity for
oxygen adsorption. AgLiLSX adsorbents have a higher working capacity and selectivity for air separation by preferentially adsorbing nitrogen from feed air for oxygen production. As a result, the amount of adsorbent and power required to produce oxygen under similar process conditions are much lower compared to other adsorbents. Therefore, the synthesized AgLiLSX is currently the best adsorbent for oxygen production from air.

**Figure 1.6:** Framework representation of 5A and 13X zeolites. Dots indicate the cation sites on unit cell [Yang (2003)].

### 1.3.7 Engelhard titanosilicates (ETS 10)

Another molecular sieve that has potential for oxygen production from air by selective adsorption of nitrogen is the large-pore Engelhard titanosilicates, ETS 10. The primary structural unit in ETS 10 molecular sieves is titanium dioxide (TiO₂), instead of aluminum (AlO₄) in zeolite molecular sieves, and silicon (SiO₂). The secondary building blocks are formed by corner-sharing of tetrahedral SiO₄ and
octahedral TiO₆ bridging together with an oxygen atom [Anderson et al., (1994)]. The general chemical composition of titanosilicates is represented as:

$$M_{\text{v/e}} \left[ \left( \text{TiO}_2 \right)_x \left( \text{SiO}_2 \right)_y \right] \cdot z\text{H}_2\text{O}$$

ETS 10 is a highly crystalline and thermally stable material with large pore structures. Recent studies [Anson et al., (2008)] on determining the equilibrium isotherm using silver exchanged ETS10 showed that these materials have high selectivity for N₂ over Ar and Ar over O₂. Therefore, ETS-10 is a potential adsorbent to produce > 95% oxygen using adsorption technology in competition with the cryogenic distillation process for producing very high purity oxygen streams, which is currently limited to 95% in PSA technology using commercial zeolite molecular sieves adsorbents.

The data available on the use of this material in pressure swing adsorption experiments and simulation studies is very limited. Hence, it is difficult to assess the potential of this material for high purity oxygen production from air for small scale applications to enrich oxygen streams in medical and chemical applications.

1.3.8 Structured adsorbents for RPSA applications

Use of conventional bead or granular adsorbents, which are formed into the desired shape and size using small crystals with the help of a binder, is common in adsorption based gas separation processes. These adsorbents have a pore diffusion resistance for mass transport within the macro and micropores of the adsorbents. As a result, the fast cycling of the PSA process leads to a poor performance due to mass transfer limitations using conventional bead or granular adsorbents. The most obvious way to improve the mass transfer rate is to reduce the adsorbent particle size. On the
other hand, a decrease in adsorbent particle size markedly increases the pressure drop along a column packed with small size adsorbent particles. In addition, the significant increase in gas maldistribution, channeling and potential for fluidization of packed column further worsen the process performance. Hence, the use of adsorbents in the form of beads or granules in adsorption based gas separation implements a tradeoff between high pressure drop and mass transfer resistance. An alternative solution to reduce the pressure drop and increase the mass transfer rate while using small size adsorbent particles is the use of a structured adsorbent in RPSA processes, characterized by fast cycling between adsorption and desorption steps.

![Common forms of structured adsorbents](image)

**Figure 1.7:** Common forms of structured adsorbents (a) monoliths, (b) corrugated paper monoliths, (c) fabric adsorbents and (d) conventional bead and particulate adsorbents.

Common existing forms of structured adsorbents are the monolith and honeycomb structures, laminates, fiber and foam structures that are shown in Figure 1.7 [Rezaei and Webley (2010)]. The structured adsorbents offer low pressure drop and low mass transfer resistances compared to conventional bead or pellet form of adsorbents, whereas the adsorption capacity of structured adsorbents is inferior to the conventional particulate adsorbents for the same column volume. The fabric
structures have potential to provide very rapid mass transfer as well as high adsorbent loadings compared to the other forms of structured adsorbents. Hence the energy efficiency of rapid cycling adsorption processes can be improved by increasing the recovery of these processes using structured adsorbents with a marginal difference in adsorber size compared to the RPSA processes using conventional small size adsorbent particles or beads. However, the full potential of these adsorbents in large scale gas separation processes is still under investigation.

1.4 Commercial Medical Oxygen Concentrators for COPD Patients

Oxygen concentrators are devices to provide oxygen to COPD patients at higher concentration than available in ambient air in order to alleviate their lung inefficiency. The commercially available oxygen concentrators in the market are designed based on adsorptive gas separation of air using zeolites as adsorbents. Since their invention in the early 1970’s, tremendous advancement in adsorption technology and synthesis of superior LiX zeolite adsorbents for air separation has reduced their size and improved process performance. Therefore, these concentrators perform much better than the other two options, liquid oxygen tanks and compressed oxygen cylinders. The main features or specifications of some of the commercially available portable oxygen concentrators are summarized in Table 1.2.

An oxygen concentrator using PSA technology consists of one or more adsorption columns, a compressor and several valves to control the pressure cycling and flow sequence of atmospheric air fed to the system. The adsorption column packed with zeolite adsorbent selectively adsorbs nitrogen over oxygen in the air and delivers high purity oxygen to the patient. The captured nitrogen is desorbed from the bed by lowering the pressure. The adsorption columns and the compressor are the two
principal contributing factors to the size and weight of the device. The main issues for size and weight reduction are size reduction of the adsorption column and the compressor. A principal focus in this study is size reduction of the adsorption column.

The oxygen concentrators designed based on a conventional four-step Skarstrom PSA cycle suffer from multi-valve switching and a low production rate per unit mass of adsorbent. Therefore, they cannot be made very compact and lightweight. Although PSA units for concentrating oxygen from air have been developed for small scale medical applications, commercially available units are still not suitable for ambulatory use by an active COPD patient. Therefore, a more compact and lightweight design for an oxygen concentrator is necessary to address the problems associated with its portability and efficiency, which in turn can improve the quality of life for COPD patients.

1.5 Miniaturization of Oxygen Concentrators

The lightest portable oxygen concentrator commercially available for personal use by active people needing oxygen therapy is the free style portable oxygen concentrator from the Airsep Corporation. It weights about 2.3 kg and has the size of small desktop computer as shown in Figure 1.8. Its dimensions are summarized in Table 1.2. The currently available concentrators may not allow the free mobility of the patients for a long time and also have many disadvantages, including size, low battery life and low oxygen purity.

Improving the performance of pressure swing adsorption processes to reduce the capital and operating costs by lowering the amount of adsorbent needed for the desired separation and lowering power consumption of the process are most important for portable personal use of medical oxygen concentrators by COPD patients. Very
small size adsorbent particles to improve the rate of mass transfer and fast switching between the adsorption and desorption steps can improve the productivity of the adsorbent. The fast cycling adsorption process known as the pulsed/rapid pressure swing adsorption (PPSA or RPSA) process discussed in section 1.3.4 is characterized by a high pressure drop, and a low product recovery, but has the potential for reducing the oxygen concentrator size and weight.

Pulsed/Rapid pressure-swing adsorption (PPSA or RPSA), one of the early advancements in PSA technology, replaces a four-step Skarstrom cycle with a two-step cycle involving only adsorption and desorption steps with pressure cycling at the feed end, which induces the pressure gradient along the bed during the adsorption step. The feed flow rate is determined by the imposed pressure gradient, adsorbent particle size, bed length and the adsorption rate of the components from the feed. Thus, PPSA facilitates rapid cycling of the process and hence increases the oxygen productivity per unit mass of adsorbent, which is essential for reducing the bed size and consequently the weight of the adsorption-based oxygen concentration device.

Figure 1.8: Lightest portable oxygen concentrator available in the market [Airsep (2011)].
### Table 1.2: Commercially available portable oxygen concentrators.

<table>
<thead>
<tr>
<th>Model</th>
<th>Company</th>
<th>Size height x width x depth (cm)</th>
<th>Weight (kg)</th>
<th>Purity (%)</th>
<th>Delivery rate (SLPM)</th>
<th>Battery power (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGO</td>
<td>Devilbiss</td>
<td>49 x 31 x 18</td>
<td>8.6</td>
<td>91±3%</td>
<td>3</td>
<td>2 hr duration, 4 hr charging</td>
</tr>
<tr>
<td>Eclipse 3</td>
<td>Sequel</td>
<td>49 x 31.2 x 18</td>
<td>8.3</td>
<td>90±3%</td>
<td>0.5-3 pulse mode</td>
<td>1.3 hr duration</td>
</tr>
<tr>
<td>Evergo</td>
<td>Phillips Respironics</td>
<td>21.6 x 30.5 x 15.2</td>
<td>4.5</td>
<td>89±3%</td>
<td>1-6 pulse mode</td>
<td>3.6 hr duration</td>
</tr>
<tr>
<td>Life style</td>
<td>Airsep</td>
<td>21.8 x 15.5 x 9.1</td>
<td>4.4</td>
<td>90±3%</td>
<td>1-5 pulse mode</td>
<td>50 min duration; 2 hr 30min charging</td>
</tr>
<tr>
<td>One G₂</td>
<td>Inogene</td>
<td>27.3 x 10.1 x 24.1</td>
<td>3.3</td>
<td>87%-96%</td>
<td>1-5 pulse mode</td>
<td>4 hr duration, 4 hr charging</td>
</tr>
<tr>
<td>XPO₂</td>
<td>Invacare</td>
<td>25.4 x 17.8 x10.2</td>
<td>3.3</td>
<td>87%-96%</td>
<td>1-5 pulse mode</td>
<td>2 hr 30min duration, 3 hr charging</td>
</tr>
<tr>
<td>Free style</td>
<td>Airsep</td>
<td>21.8 x 15.5 x 9.1</td>
<td>2.3</td>
<td>90±3%</td>
<td>1-3 pulse mode</td>
<td>3 hr duration, 3 hr charging</td>
</tr>
</tbody>
</table>
The idea of rapid cycling to reduce bed size has also been applied to multi-bed and multi-step PSA processes including pressure equalization and purge steps. In the PSA literature, RPSA (rapid pressure swing adsorption) is used as a general name for PSA processes of all configurations that employ rapid cycling. Some seminal studies on miniaturization of an oxygen concentrator using the RPSA process in the open and patent literature are summarized here. Kulish and Swank (2000) studied the design of an oxygen concentrator based on the RPSA principle. They used more than three sieve beds operated sequentially so that the time for adsorption was shorter than that for the desorption of nitrogen. Ackley and Zhong (2003) patented a medical oxygen concentrator design based on a very fast cycling PSA process. The oxygen concentrator had a bed size factor of approximately 0.14 kg adsorbent/kg O₂/day. Keefer et al., (2007) used a rotor-stator assembly to implement high frequency PSA and VSA cycles in a multi-bed arrangement. They also demonstrated significant pressure drop reduction in laminated adsorbers.

In order to gain an understanding of the size reduction achieved to date via rapid cycling, it is useful to note that in two patents entitled *Miniaturized Wearable Oxygen Concentrator* [Warren (2002); Warren (2003)] two adsorbent beds were used, each of which consisted of a 0.05 m ID diameter pipe with a length of approximately 0.3 m.

The idea of ultra rapid pressure-swing adsorption (URPSA) in fact is an extension of the RPSA concept whereby a very thin bed of adsorbent particles is subjected to pressure cycling at one end at a high frequency in order to further enhance the adsorbent productivity. The only published work on URPSA is by Kopaygorodsky et al., (2004), which was a simulation study of a two-step high frequency pressure cycling between 1 and 1.5 atm pressure at the feed end of a 2 mm
thick adsorbent bed packed with a 1 micron adsorbent. The study introduces an interesting idea but did not investigate in details to understand its potentials and drawbacks.

Among the configurations proposed in RPSA studies within the available patent and publication literature, the two-step PPSA process is the simplest in terms of instrumentation required to implement the cycling. It can also be extended to a multiple bed arrangement in order to make the feeding and light product delivery continuous without introducing any additional coupling with the adsorber. These features are essential to develop an adsorption based oxygen concentrating device that is sufficiently small in size and light in weight for portable personal medical applications, such as mobile use by physically active COPD patients. In the published two- and three-step PPSA studies, the product withdrawal was continued while the bed was depressurized at the feed end. In contrast, keeping the product end closed during the desorption step led to the desorbing oxygen being partially conserved in the product end and partially used to self-purge the feed end of the adsorber. A simple, two-step and single bed PPSA process has been chosen in the present study for studying reduction of adsorber size in an oxygen concentrator.

1.6 Objectives of the Current Research

The principal objective of the present thesis is to study the possible extent of size reduction of an oxygen concentrator using a commercial adsorbent and operated on the fast cycling pulsed pressure swing adsorption (PPSA) mode such as rapid pressure swing adsorption (RPSA) and ultra rapid pressure swing adsorption (URPSA) processes for personal medical applications of active COPD patients. Rapid cycling of the adsorption process facilitates the superior separation efficiency per unit
mass adsorbent compared to a conventional PSA process.

In order to attain the primary goals of this project, the scope of the present study involved the following steps:

(i) A detailed modeling of the PPSA process was conducted and the model equations solved using COMSOL Multiphysics software with MATLAB to study the effect of various process parameters on the performance of the PPSA process for air separation using two adsorbents, 5A and silver-exchanged Lithium 13X zeolite (Ag-Li-X).

(ii) Based on an understanding of the practical constraints that limit the PPSA process operation, an experimental setup was designed and fabricated to achieve very fast cycling (cycle time < 1 s) between the adsorption and desorption steps by identifying the domain of experimental interest from the simulation study without which the experimental design would be challenging and time consuming, if not impossible.

(iii) Experiments were conducted to measure the pressure drop characteristics of the adsorption column packed with various sizes of adsorbent particles and the Darcy's law constant was calibrated.

(iv) The thermodynamic equilibrium and kinetics of adsorption were established from a set of independent equilibrium and column dynamic breakthrough experiments as well as isothermal and nonisothermal modeling and simulation of experimental results.

(v) Pulsed pressure swing adsorption experiments were conducted to study the performance of the two-step pulsed pressure swing adsorption process and the experimental results were analyzed and compared with the isothermal and nonisothermal model simulation results. The experimental results were
predicted by both isothermal and nonisothermal simulation with good accuracy.

Finally, a three-step VSA process was theoretically studied by considering the practical limitations experienced in the PPSA study using small-size adsorbent particles.

1.7 Organization of the Thesis

In chapter 2, a detailed review on fast cycling adsorption based gas separation processes such as RPSA and URPSA processes is presented. Seminal studies on the design of portable oxygen concentrators using adsorption based PSA and RPSA technologies are discussed. The pressure drop experimental and simulation results from the literature for flow through a packed adsorption column are also presented. In chapter 3, the first principle modeling and simulation of pulsed pressure swing adsorption process as well as the effect of various process parameters on performance of the PPSA process are comprehensively discussed. Based on the simulation study, a graphical design procedure is also presented for the design of the PPSA process to produce >90% oxygen at a flow rate of 5 SLPM. The detailed experimental study of adsorption isotherm measurements and experimental design of PPSA process along with the experimental procedure for pressure drop and column dynamic breakthrough experiments are discussed in chapter 4. The responses of various sensors and correction procedures to account for blank and delay are also presented in the same chapter. Chapter 5 covers the analysis of the unary equilibrium data, pressure drop experiments, and single component and mixture breakthrough results. The PPSA experiments are described and observed trends are analyzed in Chapter 6. Moreover, a detailed theoretical study of 3-step VSA process for air separation is also discussed in
Chapter 1. Introduction

this chapter. The conclusions from the experimental studies, modeling and simulation are described in chapter 7. The recommendations for further study are also presented in the same chapter.
Chapter 2

LITERATURE REVIEW

2.1 Overview of the Chapter

In chapter 1, the potential of ultra-rapid cycling processes with high productivity for reducing the size of the adsorption column in an oxygen concentrator was discussed. However, the design and development of RPSA processes requires a detailed study of adsorbent characterization, as well as flow dynamics and process characteristics of the columns packed with small-size adsorbent particles. In this chapter, therefore, a detailed overview of the literature available on axial dispersion and pressure drop in columns packed with small adsorbent particles are presented. A review of the relevant literature on adsorption based gas separation processes such as some seminal studies on rapid pressure swing adsorption (RPSA) and ultra rapid pressure swing adsorption (URPSA) process have been discussed in detail. A summary on patent literature on portable medical oxygen concentrators has also been presented.

2.2 Axial Dispersion in Columns Packed with Small Particles

The axial dispersion in packed bed reactors and adsorption processes has vital impact on process performance. In order to model these processes and to estimate the process performance, an accurate estimate of axial dispersion has been a major area of research since 1950s. A detailed review of various experimental and modeling studies on axial dispersion was summarized by Delgado (2006). Studies on axial dispersion
and pressure drop in columns packed with small size particles below 200 µm are limited in the available literature. Here a review of axial dispersion in beds packed with small size adsorbent particles is presented.

Edwards and Richards (1968) had measured the longitudinal dispersion in a bed packed with non-porous particles by introducing a pulse of argon in air flow through the bed. The particles size was varied between 0.0377-0.6 mm. They concluded that the dispersion was dominated by molecular diffusion at low flow rates (low Reynolds numbers) and convective diffusion was important at high flow rates (high Reynolds numbers). The following correlation well represented the experimentally measured axial dispersion results:

\[
D_L = 0.73D_M + \frac{0.5d_p \bar{u}_z}{1 + \frac{9.7D_M}{d_p \bar{u}_z}}; \quad 0.0377 < d_p < 0.60 cm
\]  

(2.1)

where \(D_M\) is molecular diffusivity, \(d_p\) is packing material size and \(\bar{u}_z\) is interstitial gas velocity. They concluded that the axial dispersion was very high with finer particles \((d_p = 64 \text{ to } 124 \mu m)\) and it was attributed to the formation of channels in the column.

Later Bischoff (1969) modified Equation 2.1 into a more general form shown as below:

\[
D_L = \gamma D_M + \frac{0.45d_p \bar{u}_z}{1 + \frac{7.3D_M}{d_p \bar{u}_z}}; \quad \gamma = 0.73
\]  

(2.2)

Suzuki and Smith (1971) also studied the axial dispersion in a column packed with 0.1 to 1 mm size particles over a range of Reynolds number between 0.00237 to 11.9. They also observed that the axial dispersion was a function of molecular diffusion at low flow rates and convective diffusion was significant at high flow rates,
Chapter 2. Literature Review

and Peclet number was a function of particle size.

Moulijn and Vanswaaij (1976) correlated the axial dispersion in a column with the aggregate particle diameter formed due to clustering of small size particles. They concluded that the high axial dispersion was because of channeling due to non-uniform distribution of fine particles, which was the result of large interaction forces between the non-uniform particles and it led to formation of agglomerates.

Ruthven (1984) had presented a detailed review on axial dispersion in packed columns. Langer et al., (1978) used chromatographic techniques and method of statistical moments to estimate the axial dispersion coefficients of CH$_4$ in H$_2$ in beds packed with glass beads of different sizes. They concluded that the axial dispersion coefficients were large for smaller packing size ($d_p < 0.3$ cm) and for low column length to diameter ratio. They modified the correlation (Equation 2.1) of Edwards and Richards (1968) in order to account for decrease of limiting Peclet number ($Pe_\infty$) with decrease of adsorbent particle size, as shown in Figure 2.1 for packing size $< 0.3$ cm due to the increasing number of particles agglomerated to form clusters. The limiting Peclet number($Pe_\infty$) approached to 2 for particle size $> 0.3$ cm. Significance of $\beta$ has been elaborately discussed in section 5.4.3.

\[
D_L = \gamma_1 D_M + \frac{d_p \overline{u_z}}{Pe_\infty \left(1 + \frac{B \gamma_1 D_M}{d_p \overline{u_z}}\right)}
\]  

(2.3)

\[
Pe_\infty = 2, \quad d_p \geq 0.3 \text{ cm}
\]

(2.4)

\[
Pe_\infty = 3.35 \left(\frac{d_p}{2}\right), \quad d_p \leq 0.3 \text{ cm}
\]

(2.5)

\[
\gamma_1 = 0.45 + 0.55 \varepsilon
\]

(2.6)

\[
\beta = 0.7 - 42
\]
Chapter 2. Literature Review

2.3 Prior Studies on Pressure Drop in a PSA Column

Sundaram and Wankat (1988) studied the effect of pressure drop in pressurization and blow steps of a conventional PSA process. It was shown that the effect of pressure drop along the column was very important in a rapid cycling process due to the shock wave behavior during the short durations of pressurization and adsorption steps. They also reported that the effect of pressure drop was significant even for conventional cycling schemes.

Buzanowski et al., (1989) studied the effect of pressure drop on the wave front propagation in the bed. They neglected the external film resistance and internal mass transfer resistance by choosing a large pore variety of zeolite, 13X zeolite, and small-size adsorbent pellets. They concluded that the pressure drop promoted the spreading of the concentration front in the bed due to the increase in gas velocity.

Sereno and Rodrigues (1993) numerically investigated the validity of steady state Darcy's or Ergun equation to predict the pressure drop in an adsorption column during pressurization and de-pressurization steps. They solved the full mechanical

Figure 2.1: Effect of particle size on limiting Peclet number for flow through packed columns [Ruthven (1984)].
Chapter 2. Literature Review

ergy balance equation and steady state Darcy's or Ergun equation using moving finite volume technique. From the simulation study, they observed that the steady state Darcy's or Ergun equations could be used to model the pressurization of adsorbers.

Kikkinides and Yang (1993) also carried out a theoretical and experimental study on the effect of pressure drop on the dynamics of adsorption in fixed bed under isothermal condition using 13X-PSO₂ zeolite as the adsorbent and oxygen as the adsorbate, and also they extended their theoretical study to include the industrial size adiabatic adsorber. They also considered the axial dispersion term in total pressure balance equation. They solved the model equations using Galerkin finite element method. They also observed that the presence of pressure drop caused an early breakthrough of concentration wave compared to the case with no pressure drop. It was also shown that the pressure drop could either deflate or inflate the profiles of concentration and temperature depending on certain bed parameters.

Yang et al., (1998) theoretically investigated the effect of pressure drop in a PSA process using Ergun and Darcy's law for the separation of H₂/CO using 5A zeolite material. They had considered dispersion of pressure in total pressure balance equation, which was a result of improperly representing the Fick's law. They observed that the pressure drop effect was significant during pressurization and blow down steps and it caused early breakthrough during adsorption step under nonisothermal conditions and the effect was not significant under adiabatic and isothermal conditions. It was observed that the Ergun equation showed a larger pressure drop and it took long time to reach steady state compared to Darcy's law. They also showed that the effect of pressure drop was negligible on the process performance in a multi-bed PSA process at cyclic steady state.
Ko and Moon (2000) studied the rigorous dynamic simulation and optimization of a simple two step RPSA process. They assumed equal time duration for adsorption and desorption steps. The optimum cycle time, pressure and product oxygen purity obtained by minimizing the power consumption were 14.46 s, 5.57 bar and 96.42%.

Lee et al., (2001) investigated the effect of various operating parameters on the process performance of a small-scale, two-bed, six-step pressure swing adsorption (PSA) process for air separation using 13X zeolite adsorbent. It was observed that the dominant operating factor to determine O₂ purity was changed from adsorption pressure to feed flow rate as the purge to feed ratio was increased. Later in 2005, they studied the separation of oxygen from air using carbon molecular sieves (CMS) adsorbent. They had compared the performance of different cycling sequence of a PSA process. It was observed that the performance of a cycle with pressure equalization was better than the other cycles. In both the papers, they had considered the axial dispersion term in the overall pressure balance equation.

Later, Webley and Todd (2005) studied the use of Ergun equation to represent the pressure drop under adsorbing and non-adsorbing conditions in a column packed with 1.7 mm size particles of LiLSX zeolite pellets. Using the experimentally obtained Ergun parameters to represent the pressure drop, they accurately reproduced the dynamic depressurization and breakthrough pressure profiles and the error between using full momentum balance and Ergun equation was less than 0.1%. They concluded that the Ergun equation could be used to reliably predict the experimental pressure profiles under dynamic adsorbing conditions.
Chapter 2. Literature Review

2.4 Pulsed Pressure Swing Adsorption (PPSA) Processes

The PPSA process was introduced in section 1.5. Two variants of the pulsed PSA process are rapid pressure-swing adsorption (RPSA) and ultra-rapid pressure-swing adsorption (URPSA). The earliest publication on a pulsed PSA process was by Turnock and Kadlec (1971) who studied the performance of an RPSA process for the separation of a methane-nitrogen gas mixture using 42-60 mesh size 5A zeolite molecular sieve adsorbent. An instantaneous equilibrium between the gas phase and adsorbed phase was assumed. The effect of process variables such as cycling frequency, feed gas pressure, product flow rate and temperature on the nitrogen content in the product gas was investigated experimentally and compared with theoretical simulation results. They concluded that rapid cycling of the process significantly improved the nitrogen enrichment at the expense of low recovery. Jones et al., (1980) subsequently patented the RPSA process for air separation. They found that a short bed filled with small adsorbent particles (20-120 mesh) allowed faster cycling and resulted in a substantially higher oxygen recovery. They demonstrated that rapid cycling resulted in a five-fold increase in the oxygen productivity per unit mass of adsorbent relative to the conventional Skarstrom PSA process. They also showed that the desorption time longer than the adsorption time was necessary for an efficient regeneration of the bed prior to the subsequent cycle. The patent filed by Jones and Keller in 1980 stimulated further work on RPSA.

Prichard and Simpson (1986) experimentally investigated the effect of process variables on the performance of an RPSA process for air separation using a 5A zeolite. It was shown that the product recovery and compressive efficiency was maximum with respect to the product take off rates and the change in adsorbent particle size affected the adsorption and desorption pressure swing through the bed
Chapter 2. Literature Review

due to the variation in bed resistance to the gas flow. They concluded that there was a sharp drop in pressure near the feed end during the early desorption step because the bed was far away from saturation even though the cycle gave an optimum enrichment. They were able to attain 30% oxygen purity at an oxygen flow rate of 2 SLPM using an RPSA device that weighted approximately 19 kg.

Hart and Thomas (1991) experimentally investigated the separation of a binary mixture of methane-carbon dioxide using a two-step, pulsed pressure swing adsorption process and compared with the theoretical modeling study. They conducted the breakthrough measurements of single-component and multi-component mixtures to estimate the equilibrium and kinetic parameters. It was shown that separation of the mixture was much better on 5A zeolite compared to the carbon molecular sieves. The process performance was characterized based on separability and product recovery, which were functions of various process parameters. They observed that the separation factor increased and product recovery decreased with increase in feed pressure. Compared to the experimental results, the theoretical analysis over estimated the separation factor and under estimated the product recovery due to the inherent assumptions in the model formulation.

Sircar (1991) patented an RPSA process for the separation of binary mixtures such as oxygen-nitrogen, methane-nitrogen and hydrogen-carbon dioxide that used a single adsorption column having dual adsorption layers which were alternatively operated by pressurization and depressurization. It was shown that the feed and product flow rates were continuous in a single shallow bed, dual adsorbent layer RPSA process with minimum valves and fittings and the durations of both steps were almost the same. Later in 1995, he proposed that the stacking of multiple adsorbent layers in a single adsorption column substantially increased the adsorbent productivity
using minimum number of valves to operate the process.

Alpay and Scott (1992) developed a comprehensive theoretical model for adsorption and reaction in an RPSA process and compared the computational efficiency of different numerical discretization techniques. They had considered the axial dispersion in overall continuity equation. It was mentioned that orthogonal collocation on finite element was superior to accommodate the steep pressure and concentration gradients inherent to RPSA. Later, Alpay and Kenney (1994) carried out the experimental and theoretical study on the effect of adsorbent particle size on the performance of RPSA process for air separation using 5A zeolite as an adsorbent. It was observed that the oxygen product purity was maximum at an optimum particle size but the purity was low due to the ineffective pressure swing for small particle sizes and intra-particle diffusion limitations for very large particle sizes, which were accurately predicted by model simulations using LDF approximation. They concluded that the separation capability of a pulsed RPSA process is the best for adsorption beds packed with 250 to 350 micron particles.

Baron (1993) studied the performance of a 3-step RPSA for air separation using 5A zeolite adsorbent material of particle size range 0.2-0.5 mm packed in a 1 to 2 m column. The experimental results matched well with the detailed modeling and simulation study of the process.

Lu et al., (1993) modeled a three step single bed RPSA process with complex dynamics and studied its performance under various initial and operating conditions for the separation of a binary mixture. It was mentioned that the separation performance was independent of the nature of the isotherm but it depended on the adsorption capacity of the adsorbent. They showed that the separation performance decreased with the dead volume at the feed end and slightly increased with the dead
volume at the product end. It was also observed that the attainment of cyclic steady state was much faster in an isothermal process compared to the adiabatic process due to inherent slow dynamics in heat transfer to attain the cyclic steady state temperature profiles within the bed.

Chou and Wu (1994a, b) experimentally investigated the performance of a 3 step RPSA process using 60-80 mesh 5A zeolite adsorbent particles packed in 50.8 cm column. They studied the effect of individual step durations, feed pressure and production rate on performance of the process. They observed that the process performance was maximum at an optimum combination of feed, delay and exhaust step durations and the feed time was double that of exhaust time.

Chiang and Hong (1995) proposed the radial RPSA processes in place of conventional axial RPSA processes. They experimentally studied the effect of step duration on process performance using 3 µm particles of 5A zeolite adsorbent. In this study, they concluded that very small size adsorbent particles could be used in radial RPSA process and instantaneous equilibrium was attained even for very small cycle times compared to the conventional RPSA processes. Therefore, the radial RPSA processes were shown to be more effective than axial flow RPSA process.

Zhang et al., (1998) studied the effectiveness of RPSA process over the conventional PSA processes for the separation of CO₂-N₂ mixture using silica as adsorbent. In a 3-step RPSA process, it was observed that the back flow step improved the strongly adsorbed component purity in the desorption step due to the pushing of weakly adsorbed N₂ rich gas towards the product end. They had also compared the single column and double column RPSA processes. They showed that a change in operating time increased the purity and decreased the recovery of CO₂ and also an increase in feed gas pressure improved purity, recovery and productivity of
Chapter 2. Literature Review

They concluded that the double bed RPSA delivered higher CO₂ purity, recovery and productivity.

Betlem et al., (1998) investigated the effect of relative absorbability, bed length, feed and product composition on the process performance of RPSA process involving 3 steps called pressurization, delay and depressurization. It was mentioned that the product recovery and productivity increased linearly with increase in relative adsorbability and decrease in product purity. Bed length and feed composition had no influence on product recovery whereas productivity was increased for higher feed purity and smaller bed length. They also studied the effect of recycling the raffinate and extract phases to the column inlet in RPSA process and it was observed that the recovery and adsorbent productivity increased with adsorbability by introducing extract and raffinate recycle. Finally, they concluded that the raffinate recycling was profitable for difficult separations and extract recycle was effective only for easy separations.

Kulish and Swank (2000) studied the design of an oxygen concentrator based on the RPSA principle. They used more than three beds operated sequentially so that the time for the adsorption was shorter than that for the desorption of nitrogen. The oxygen concentrators were capable of delivering 96% pure oxygen at a rate of 2-5 SLPM.

Huang and Chou (2003) theoretically compared the performance of radial and axial RPSA processes for air separation. They also studied the effect of process variables on the performance of a radial RPSA process. It was shown that the oxygen product purity was maximum at an optimum adsorbent particle size. They demonstrated that the radial RPSA process had the advantage of lower pressure drop for the same imposed pressure gradient, gas flow rate and adsorbent particle size due
to the large cross sectional area compared to an axial RPSA process.

Ackley and Zhong (2003) patented a medical oxygen concentrator design based on a very fast cycling PSA process. They used Li substituted zeolite (Oxysiv-7) as adsorbent for air separation. The oxygen concentrator had a bed size factor of approximately 0.15 kg adsorbent/kg O₂/day and was capable of delivering 15 SLPM of oxygen from air. Khiavi et al., (2007) studied the separation of hydrogen from syngas using a RPSA process. They used more than three adsorption columns, each comprised of at least one thin adsorbent sheet material with one or more adsorbents. The bed size factor was less than 4 s and a hydrogen recovery was >70% at a very high purity from a syngas feed mixture of 50% hydrogen.

Mendes et al., (2004) developed a simulator and optimization procedure to design small scale oxygen PSA/VPSA unit for air separation. Later in 2006, they implemented equalization steps to improve the oxygen recovery and lower power consumption. Among the adsorbents studied, the oxygen productivity was highest using Oxysiv 7 adsorbent. The top-top equalization step showed better performance than the other equalization configurations. They validated the simulation and optimization results with experimental oxygen concentrator data. Further, Mendes et al., (2007) developed a PSA process for producing very high purity oxygen (>95%) using AgLiLSX zeolite adsorbent within the same column.

Soo et al., (2005) theoretically studied the effect of axial dispersion on the performance of RPSA and URPSA processes using the experimental conditions of Alpay and Murray. They employed the LDF approximation to model the mass transfer within the adsorbent particle. The model was unable to predict the RPSA results of Alpay, but it was able to handle the URPSA results of Murray. They observed that the increase in axial dispersion decreased the oxygen product purity and
the effect on cycle averaged feed gas rate was insignificant.

Todd and Webley (2006) compared the results of discredited pellet gas model (DGM) and Linear driving force (LDF) model with the pilot plant experiments of RPSA process for air separation over a packed bed of LiLSX zeolite adsorbent. They observed that both models predicted the experimental results for long cycle times where the kinetics of diffusion was not important. However, for relatively short cycle times, the LDF model under predicted the experimental performance compared to the DGM model results due to over estimation of interpellant mass transfer and also showed that inter-pellet pressure drop had insignificant effect on process performance.

LaBuda et al., (2008) studied a layered RPSA process for air separation. A feed air containing moisture was treated in a column packed with two layers of adsorbents. The first layer, near to feed end, was selective for water and the second layer was selective for nitrogen adsorption. The oxygen product purity was >90% with cycle time >5 s.

Zhong et al., (2008) studied the performance of a high frequency PSA process for air separation. Considering the limitations of RPSA processes such as high pressure drop and low recovery, they proposed the criteria for the selection of adsorbent particle size, bed length and cycle time in a range such that the axial dispersion was dominating compared to the pore resistance in the adsorbent particles. For a bed length to square of particle diameter ratio between 200 to 600 mm$^{-1}$, a bed size factor of <50 lb/TPDO$_2$ was achieved at oxygen product purity of >90%, recovery between 25 to 50% and cycle time of <4 s.
2.5 Ultra Rapid Pressure Swing Adsorption Process

The idea of ultra rapid pressure-swing adsorption (URPSA), in fact, is an extension of the RPSA concept whereby a very thin bed of adsorbent particles is subjected to pressure cycling at one end at a high frequency in order to further enhance the adsorbent productivity. Some of the seminal studies on URPSA processes are summarized below:

Suzuki et al., (1996) studied a piston driven ultra rapid pressure swing adsorption process for air separation using 5A zeolite adsorbent. The process had a piston cylinder assembly packed with adsorbent particles and operated at a cycle time between 0.5 and 2 s. The effect of cycle time on process performance was experimentally investigated and matched with the simulation results. They concluded that the oxygen productivity was very high with low oxygen recovery at a maximum oxygen enrichment of 60%. Later, Singh and Jones (1997) and Arvind et al., (2002) developed a dual piston PSA process for air separation using 13X zeolite adsorbent. They studied the effect of process parameters on process performance and compared the experimental and simulation results. The dual piston PSA process was suitable for N₂ production and also was used for O₂ production. The performances of piston PSA processes were better than conventional PSA process and comparable with RPSA process.

The published work on a simple-bed, 2-step URPSA using conventional packed columns by Kopaygorodsky et al., (2004) is a simulation study of a two-step process with high frequency pressure cycling between 1 and 1.5 atm pressure at the feed end of a 2 mm thick adsorbent bed packed with a 1 micron adsorbent. The study introduced an interesting idea but did not exploit its full potential. A similar process is simulated in the present study for which its performance is maximized for oxygen
purity by optimizing the duration of both the adsorption and desorption steps for a wide range of bed lengths, adsorbent sizes and amplitude of the pressure cycling covering the domain of both RPSA and URPSA operation. Generalized design plots are developed for two promising commercial nitrogen-selective adsorbents that relate adsorbent volume to the process variables for producing at least an 80% oxygen product at a target production rate.

In very recent patent, Galbraith et al., (2011) reported the development of an ultra rapid pressure swing adsorption based oxygen concentrator using spherical alumiophosphate adsorbent particles of size 60 to 120 µm. The oxygen product purity was 85-92% at an oxygen product flow rate of 0.8 SLPM and recovery between 33-36% using an adsorbent weight of <15 g and innovative design of valves, adsorption column and choice of adsorbent. The inventors showed that the adsorbent weight decreased with increase of cycling frequency of the process as shown in Figure 2.2.

![Figure 2.2: Plot of adsorbent weight with cyclic frequency in an ultra rapid pressure swing adsorption process [Galbraith et al., (2011)].](image-url)
Chai et al., (2011) developed a Skarstrom like rapid pressure swing adsorption process for personal medical applications using LiX zeolite. They had experimentally investigated the effect of adsorbent particle size, adsorption pressure and step times on PSA process performance. Using 350 µm adsorbent particles, they attained a bed size factor was of ~25-50 lbs/TPDO₂ with an oxygen purity and recovery of 90% and ~25-35% at 3 bar pressure and cycle time of 3-5 s. The weight of adsorbent required to deliver 5 SLPM of oxygen was 230 g. They concluded that the BSF could not be indefinitely reduced by increasing the cycling frequency (lowering the cycle time) of the processes, as shown in Figure 2.3. They also proposed a snap on, light weight, highly portable medical oxygen concentrator for personal medical applications where high pressure air supply is readily available.

Figure 2.3: Effect of adsorption pressure on BSF vs. total cycle time plots [Chai et al., (2011)].

2.6 Patents on Portable Oxygen Concentrators

Krantz and Sircar (1984) patent a medical oxygen concentrator operated on a pressure swing adsorption cycle for home use of high purity medical oxygen supply to the patents. The process consisted of a single bed packed with two layers of molecular
Chapter 2. Literature Review

sieve adsorbents. The first layer, 13X or 5A zeolite, was for the removal of moisture and CO₂ from air and the second layer, Ca and Sr exchanged 13X zeolite, was for the retention of nitrogen. They concluded that the oxygen concentrator was capable of delivering more than 90% pure oxygen for the desired medical administration by the needy patients.

Dubois et al., (2003) filed a patent on portable oxygen concentrator, which was designed based on PSA technology using Lithium exchanged zeolite. They proposed that a portable oxygen concentrator was designed by combining certain technical advantages like short production cycle, small adsorbent particles, high nitrogen selective adsorbents and permitting the product oxygen flow rate as required by the patient. The portable oxygen concentrator proposed by them was capable of producing 50% to 90% oxygen from air and weighed around 10 kg.

McCombs et al., (2006) patented a compact, light-weight two-bed oxygen concentrator operated on PSA and VPSA cycles for ambulatory applications of COPD patients. The oxygen product purity was greater than 90% at product flow rate of 3 SLPM. The overall weight of the device was only about 5 lb.

A pressure/vacuum swing adsorption process (PVSA) based weight optimized portable oxygen concentrator has been patented by Occhialini et al., (2007). They also used layered adsorption beds in a five-bed process involving ten steps. The adsorbents, activated alumina in the first layer and LSX zeolite in the second layer, were packed in each adsorber for the removal of moisture, CO₂ and nitrogen from the atmospheric air. They studied the weight optimization of each component in the oxygen concentrator with respect to the process parameter such as minimum pressure during the process cycle and product flow rate. They concluded that the oxygen
concentrator designed based on above method was capable of delivering 93% pure oxygen and weighed around more than 8 lbs.

Whitley et al., (2007) has developed a dual mode medical oxygen concentrator comprising a portable oxygen generator and stationary base unit. The portable unit could be independently operated to generate oxygen at low flow rates for ambulatory use of active COPD patients. They concluded that the portable unit could deliver 0.5 to 3 SLPM of 85% pure oxygen whereas the coupled portable and stationary unit would generate 0.5 to 5 SLPM of oxygen at the same purity.

A pressure swing adsorption based portable oxygen concentrator has been patented by Atlas et al., (2007) and in which the adsorber was packed with two layers of adsorbents, Oxysiv and OxysivMDX. An oxygen conserver was used to regulate the flow of high purity oxygen to the patient. They stated that the oxygen concentrator delivered a maximum of 100% pure oxygen at a rate of 0.9 SLPM, and it had a total weight of 10 lb, a volume of 800 in³ and a battery life of around 8 hr.

Keefer et al., (2007) had used a rotor-stator assembly to implement high frequency PSA and VSA cycles in a multi-bed arrangement. They had also demonstrated significant pressure drop reduction in spiral wound laminated adsorbers. They obtained the maximum purity and recovery of >90% and 59%, respectively, using Ca-X zeolite adsorbent.

Jagger et al., (2011) designed an ambulatory oxygen concentrator for personal medical applications using VSA process and LiLSX zeolite adsorbent. The oxygen concentrator delivered oxygen product purity in the range of 85-95% at a product flow rate of 5 SLPM in the pulsed mode and recovery was 60%. The oxygen concentrator weighted around 3 lb (1.36 kg)
2.7 Chapter Conclusion

The available literature data on axial dispersion in columns packed with small size particles revealed that axial dispersion was high using small size packing due to the channeling within the column because of agglomeration of packing material and the pressure drop across the adsorption column led to the early breakthrough. Based on the literature, the rapid cyclic adsorption processes are characterized by fast cycling and high productivity compared to conventional PSA processes. Thus, the volumes of adsorbent required are smaller. Therefore, the rest of the study presented in next chapters is on pulsed pressure swing adsorption process for reduction of adsorber size in an oxygen concentrator using commercial 5A zeolite and Ag-Li-X adsorbents.
Chapter 3

MODELING AND SIMULATION OF PULSED PRESSURE SWING ADSORPTION PROCESS

3.1 Overview of the Chapter

In this chapter, the detailed mathematical model equations for pulsed pressure swing adsorption process (PPSA) are formulated from first principles and the numerical simulation of the model equations using an in-house code written in FORTRAN and COMSOL® Multiphysics software are discussed. The effects of various process parameters on PPSA process performance are also discussed in detail. A graphical procedure is presented for the design of the PPSA process from the theoretical study. Finally, the sizing of an oxygen concentrator for personal medical applications of COPD patients is described that meets the standards of the American Medical Association (AMA standards, > 90% oxygen at 5 SLPM), which is then compared with the currently available commercial oxygen concentrators and patent literature.

3.2 Process Description

The pulsed pressure-swing adsorption process (PPSA) consists of a single fixed bed packed with adsorbent particles considerably smaller in diameter than those used in conventional PSA. The PPSA cycle involves two steps: adsorption and desorption. A schematic of a single bed PPSA process is shown in Figure 3.1. During a typical adsorption step for air separation, the feed end of the column (z = 0)
is supplied with high pressure air and the product end \((z = L)\) is kept open to the atmosphere. As a result of the pressure difference across the column, high pressure air flows through the adsorbent bed from the feed to the product end. In this step nitrogen is removed by preferential adsorption and a product enriched in the less strongly adsorbed oxygen is withdrawn at atmospheric pressure from the product end of the column. During the desorption step, the product end is closed and the feed end is opened to the atmosphere. In this step the strongly adsorbed nitrogen is desorbed into the gas phase due to the rapid reduction in pressure in the bed and the desorbed gas, enriched in nitrogen, exits at the feed end of the column. The duration of both the adsorption and desorption steps affects the oxygen product purity.

![Figure 3.1: Schematic representation of a two-step pulsed pressure-swing adsorption process.](image)

**Figure 3.1:** Schematic representation of a two-step pulsed pressure-swing adsorption process.
3.3 Mathematical Modeling

3.3.1 General assumptions in PPSA process modeling

In developing a mathematical model for the PPSA process, the following assumptions are made:

1. The ideal gas law is applicable.
2. The system is assumed to be isothermal.
3. The bulk gas flow in the adsorbent bed is described by axially dispersed plug flow model and Darcy's law.
4. Adsorption equilibrium between the gas and adsorbed phase is described by a binary Langmuir isotherm model with parameters obtained from single component data.
5. A linear driving force (LDF) approximation describes the gas transport in the adsorbent.
6. The feed is approximated as a mixture of only nitrogen and oxygen in the ratio of 79:21.
7. Uniform particle size and bed voidage are assumed.
8. The molecular weight of the gas is assumed to be constant along the bed length.
9. The gas viscosity is assumed to be independent of pressure.

3.3.2 Model equations

Since a pressure difference is imposed across the adsorption column, compressible gas effects must be incorporated into the describing equations. This introduces some subtleties in developing the describing equations, in particular with
Chapter 3. Modeling and Simulation of Pulsed Pressure Swing Adsorption Process

respect to the proper formulation of the axial dispersion and boundary conditions. For this reason, the describing equations will be developed in terms of the molar fluxes and subsequently expressed in terms of the partial and total pressures.

The equations of continuity for the nitrogen (component A) and oxygen (component B) are given by

\[
\frac{\partial c_A}{\partial t} = -\frac{\partial N_A}{\partial z} - \left(\frac{1 - \varepsilon}{\varepsilon}\right) \frac{\partial \bar{q}_A}{\partial t} \tag{3.1}
\]

\[
\frac{\partial c_B}{\partial t} = -\frac{\partial N_B}{\partial z} - \left(\frac{1 - \varepsilon}{\varepsilon}\right) \frac{\partial \bar{q}_B}{\partial t} \tag{3.2}
\]

where \( N_i \), \( c_i \) and \( \bar{q}_i \) denote the molar flux with respect to a stationary reference frame, the molar concentration, and the molar adsorption per unit volume of adsorbent, respectively, of component \( i \) (A or B); the overbar denotes the average adsorbed concentration over the volume of the particles; \( \varepsilon \) denotes the voidage or void fraction in the adsorbent bed; and \( t \) and \( z \) are the temporal and spatial coordinates, respectively.

The appropriate form of Fick’s law must incorporate axial dispersion relative to the interstitial velocity, \( u_z \), through the porous media and hence is given for the two components by

\[
N_A = -c D_L \frac{\partial y_A}{\partial z} + y_A (N_A + N_B) = -c D_L \frac{\partial y_A}{\partial z} + c_A u_z \tag{3.3}
\]

\[
N_B = -c D_L \frac{\partial y_B}{\partial z} + y_B (N_A + N_B) = -c D_L \frac{\partial y_B}{\partial z} + c_B u_z \tag{3.4}
\]

where \( c = c_A + c_B \) is the molar density and \( D_L \) is the axial dispersion coefficient defined relative to the interstitial velocity. Note that Fick’s law must be defined in terms of the mole fraction driving force to ensure that \( N_A + N_B = c u_z \). Some prior studies have not properly accounted for the required compatibility between the axial
Chapter 3. Modeling and Simulation of Pulsed Pressure Swing Adsorption Process

dispersion coefficient and form of Fick’s law [Alpay et al., (1993); Lee et al., (2001); Jee et al., (2005b); Kikkinides and Yang (1993), Lee and Yang (1998)]

The molar adsorption rates are given by

\[
\frac{\partial q_A}{\partial t} = k_A(q_A^e - q_A) \\
\frac{\partial q_B}{\partial t} = k_B(q_B^e - q_B)
\]

in which \(k_i\) and \(q_i^e\) are the mass-transfer coefficient and equilibrium adsorbed molar concentration per unit adsorbent volume, respectively, for component \(i\) (A or B). The equilibrium molar adsorption is assumed to be described by the multi-component Langmuir adsorption isotherm:

\[
\frac{q_A^e}{q_s} = \frac{b_A c_A}{1 + b_A c_A + b_B c_B} \\
\frac{q_B^e}{q_s} = \frac{b_B c_B}{1 + b_A c_A + b_B c_B}
\]

in which \(q_s\) is the saturation molar adsorbed concentration per unit adsorbent volume and \(b_i\) is the Langmuir constant for component \(i\) (A or B).

The interstitial gas velocity through the porous media is related to the local pressure gradient via Darcy’s law:

\[
u_z = -\frac{k_p}{\mu} \frac{\partial P}{\partial z}
\]

in which \(\mu\) is the shear viscosity and \(k_p\) is the permeability described by the Blake-Kozeny equation as follows:

\[
k_p = \frac{d_p^2}{k_1} \left( \frac{e}{1-e} \right)^2; \quad k_1 = 150
\]
Chapter 3. Modeling and Simulation of Pulsed Pressure Swing Adsorption Process

The overall equation of continuity is obtained by adding the equations of continuity for the two species, Equations (3.1) and (3.2), while recognizing the implications of Equations (3.3) and (3.4):

\[
\frac{\partial c_A}{\partial t} = -\frac{\partial \left(c_A u_z\right)}{\partial z} - \left(\frac{1 - \varepsilon}{\varepsilon}\right) \frac{\partial}{\partial t} \left(q_A + \bar{q}_B\right)
\]  \hspace{1cm} (3.11)

It is important to note that there is no axial dispersion term in the overall continuity equation. Some prior studies of PSA [Alpay et al., (1993); Lee et al., (2001); Kikkinides and Yang (1993), Lee and Yang (1998)] have included an axial dispersion term in the overall continuity equation. This is consequence of not employing a form of Fick’s law that is consistent with the dispersion being relative to the interstitial velocity through the porous media.

Only two of the three equations given by Equations (3.1), (3.2) and (3.11) are independent. Here we will choose Equations (3.1) and (3.11), the nitrogen and overall continuity equations, respectively. When Equations (3.1) and (3.3) are combined and the ideal gas law is used to simplify the resulting equation as well as Equation (3.11), these equations assume the following form in terms of the partial and total pressures:

\[
\frac{\partial p_A}{\partial t} = D_L \frac{\partial}{\partial z} \left[ P \frac{\partial}{\partial z} \left( \frac{p_A}{P} \right) \right] - \frac{\partial}{\partial z} \left( p_A u_z - RT \left(1 - \frac{1}{\varepsilon}\right) \frac{\partial q_A}{\partial t} \right)
\]  \hspace{1cm} (3.12)

\[
\frac{\partial P}{\partial t} = -\frac{\partial}{\partial z} \left( P u_z \right) - RT \left(1 - \frac{1}{\varepsilon}\right) \frac{\partial}{\partial t} \left(q_A + \bar{q}_B\right)
\]  \hspace{1cm} (3.13)

Each of Equations (3.12) and (3.13) requires an initial and two boundary conditions and each of Equations (3.5) and (3.6) requires an initial condition. The boundary conditions are different for the adsorption (pressurization) and desorption (depressurization) steps. The initial condition for the adsorbent bed is assumed to be
equilibrium with air having a nitrogen mole fraction, \( y_{A0} \), at the prevailing pressure, \( P_L \):

\[
P_A = y_{A0} P_L
\]

\[
P = P_L
\]

\[
\bar{q}_A = q_A^a|_{P_A},
\]

\[
\bar{q}_B = q_B^a|_{P_A}
\]  

at \( t = 0, \ 0 \leq z \leq L \)  \( (3.14) \)

At each end of the column the following conditions apply for component \( i \) during both the adsorption and desorption steps:

\[
N|_{z=0^-} = \varepsilon N|_{z=0^+}, \quad \text{at} \quad z = 0
\]  \( (3.15) \)

\[
\varepsilon N|_{z=L^-} = N|_{z=L^+}, \quad \text{at} \quad z = L
\]  \( (3.16) \)

If Equations (3.15) and (3.16) are written for each component, the resulting component equations at each end of the column can be added to obtain the appropriate boundary conditions for the overall continuity equation. When Equations (3.3) and (3.4) are substituted for the molar fluxes and the ideal gas law is used to express the concentrations, molar density and mole fractions in terms of the partial and total pressures, the boundary conditions assume the following form:

\[
-PD_i \frac{\partial}{\partial z} \left( \frac{P_A}{P} \right) = u_z (y_{A0} P_H - P_A) \quad \text{at} \quad z = 0^+ \quad n(t_a + t_d) \leq t \leq (n+1)t_a + nt_d \quad (3.17)
\]

\[
\frac{\partial}{\partial z} \left( \frac{P_A}{P} \right) = 0 \quad \text{at} \quad z = 0^+ \quad (n+1)t_a + nt_d \leq t \leq (n+1)(t_a + t_d) \quad (3.18)
\]

\[
\frac{\partial}{\partial z} \left( \frac{P_A}{P} \right) = 0 \quad \text{at} \quad z = L^- \quad n(t_a + t_d) \leq t \leq (n+1)t_a + nt_d \quad (3.19)
\]
Chapter 3. Modeling and Simulation of Pulsed Pressure Swing Adsorption Process

\[ \frac{\partial}{\partial z} \left( \frac{P_a}{P} \right) = 0 \] at \( z = L \) \( (n+1)t_a + nt_d \leq t \leq (n+1)(t_a + t_d) \) (3.20)

Equations (3.17) and (3.18) give the boundary conditions for the species continuity and overall continuity equations at the end of the column defined by \( z = 0 \) during the adsorption and desorption steps, respectively. Equations (3.19) and (3.20) give the boundary conditions for the species continuity and overall continuity equations at the end of the column defined by \( z = L \) during the adsorption and desorption steps, respectively. These boundary conditions involve no approximations other than those summarized at the beginning of this model development. Some prior PSA modeling studies [Jee et al., (2005a)] involving compressible gas flow have assumed that the derivative of the partial pressure is zero at the end of the column defined by \( z = L \); Equations (3.19) and (3.20) indicate that it is the derivative of the mole fraction that is zero at \( z = L \).

3.3.3 Equilibrium and kinetic parameters

Two adsorbents, namely 5A and partially Ag-substituted Li-X zeolite (Li\(_{94.2}\)Na\(_{0.7}\)Ag\(_{1.1}\)-X-1.0 referred to as Ag-Li-X), were used to study the performance of the two-step PPSA process for oxygen enrichment from air. The equilibrium data for both adsorbents taken from published sources [Farooq et al., (1989); Hutson et al., (1999)] are summarized in Table 3.1. Other common operating parameters are given in Table 3.2.

The rate of mass transfer between the gas phase and solid is approximated using the linear driving force (LDF) model, which is an effective approximation for equilibrium-controlled processes such as air separation via a 5A zeolite. Ruthven et
al., (1993) concluded that the macro-pore resistance controls the rate of intra-particle mass transfer, which is also the controlling step in the inter-phase mass transfer, in the case of zeolite-based air separation. The LDF mass-transfer rate constants for both nitrogen and oxygen have been calculated from the following approximation:

\[
k_i = \frac{\varepsilon_p D_p}{r_p^2} \left( \frac{c_i}{q_0} \right), \quad \text{where} \ i = A \text{ or } B
\]

(3.21)

where \( D_p \) is the macro-pore diffusivity and \( \Omega \) is an empirical parameter that depends on the cycle time for faster cycling processes. The value \( \Omega = 15 \) is recommended for the macro-pore resistance for long contact times in a PSA process. A limiting value of \( \Omega = 15 \) is also found adequate for the current study based on the correlation established by Raghavan et al., (1986). The macro-pore diffusivity (\( D_p \)) was related to the molecular diffusion coefficient assuming a tortuosity factor (\( \tau \)) of 3, as suggested by Farooq et al., (1989), who also suggested a value of 0.33 for the particle porosity (\( \varepsilon_p \)). The effect of Knudsen diffusion on the macro-pore diffusivity is neglected since the pressure is always above atmospheric in the present study:

\[
D_p = \frac{D_M}{\tau}
\]

(3.22)

where \( D_M \) is the molecular diffusivity of the oxygen-nitrogen pair at the average column pressure, \( P_{\text{avg}} (= (P_H + P_L)/2) \), estimated from the Chapman-Enskog equation given in Bird et al., (2003). In the LDF approximation the external film resistance is also relatively negligible compared with the macro-pore resistance. In the limit of no flow, the Sherwood number, \( k_f d_p / D_M \), is equal to 2, which implies that the minimum value of \( k_f \) is \( D_M / r_p \). Based on an order-of-magnitude analysis, the external film resistance is about 50% of the macro-pore resistance in the limit of no-flow and it is
even less in an actual PPSA operation.

Table 3.1: Equilibrium isotherm parameters for 5A<sup>a</sup> and Li-Ag-X (Li<sub>94.2</sub>Na<sub>0.7</sub>Ag<sub>1.1</sub>-X-1.0)<sup>b</sup> Zeolite.

<table>
<thead>
<tr>
<th>Parameter*</th>
<th>5A</th>
<th>Ag-Li-X</th>
</tr>
</thead>
<tbody>
<tr>
<td>q&lt;sub&gt;a&lt;/sub&gt; (mol/cc)</td>
<td>5.23 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>3.162 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>b&lt;sub&gt;A&lt;/sub&gt; (cc/mol)</td>
<td>2813.7</td>
<td>28613</td>
</tr>
<tr>
<td>b&lt;sub&gt;B&lt;/sub&gt; (cc/mol)</td>
<td>893.5</td>
<td>2204.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Farooq et al., (1989);
<sup>b</sup> Hutson et al., (1999);
* A is nitrogen and B is oxygen.

Table 3.2: Common parameters used in the simulations.

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Air (N&lt;sub&gt;2&lt;/sub&gt;:O&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>79:21</td>
</tr>
<tr>
<td>Bed voidage (ε)</td>
<td>0.33</td>
</tr>
<tr>
<td>Particle voidage (ε&lt;sub&gt;p&lt;/sub&gt;)</td>
<td>0.35</td>
</tr>
<tr>
<td>Gas constant (R), atm·cc/mol·K</td>
<td>82.05</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>298.15</td>
</tr>
<tr>
<td>Product pressure (P&lt;sub&gt;L&lt;/sub&gt;), atm</td>
<td>1</td>
</tr>
<tr>
<td>Reference pressure (P&lt;sub&gt;R&lt;/sub&gt;), atm</td>
<td>1</td>
</tr>
<tr>
<td>Feed pressure (P&lt;sub&gt;H&lt;/sub&gt;), atm</td>
<td>1.5–10.5</td>
</tr>
<tr>
<td>Adsorbent size (d&lt;sub&gt;p&lt;/sub&gt;), cm</td>
<td>0.0005–0.01</td>
</tr>
<tr>
<td>Bed length (L), cm</td>
<td>0.2–30</td>
</tr>
<tr>
<td>Molecular diffusivity (D&lt;sub&gt;M&lt;/sub&gt;), cm&lt;sup&gt;2&lt;/sup&gt;/s</td>
<td>0.204</td>
</tr>
<tr>
<td>Viscosity of air (μ), atm·s</td>
<td>1.8x10&lt;sup&gt;-10&lt;/sup&gt;</td>
</tr>
<tr>
<td>Adsorbent particle density, g/cc</td>
<td>1.20</td>
</tr>
</tbody>
</table>

The effective axial dispersion coefficient has been estimated from the correlation given by Ruthven:

\[
D_L = \gamma_1 D_M + \gamma_2 d_p \bar{u}_z \tag{3.23}
\]

In the above equation, \( \gamma_1 \) and \( \gamma_2 \) are constants whose typical values are 0.7 and 0.5, respectively. The average interstitial velocity \( \bar{u}_z \) is obtained from the following form of Darcy's law where \( k_p \) is given by Equation (3.10):
Chapter 3. Modeling and Simulation of Pulsed Pressure Swing Adsorption Process

\[ \bar{u}_z = \frac{k_r \Delta p}{\mu L} \]  

(3.24)

3.3.4 Numerical simulation

Equations (3.12) and (3.13), the species and overall continuity equations, respectively, expressed in terms of the partial and total pressures in the gas phase are coupled with the solid phase loading through Equations (3.5) and (3.6), and with the interstitial gas velocity through Equation (3.9). Equations (3.7) and (3.8) are the adsorption equilibrium isotherm relationships for nitrogen and oxygen.

The set of coupled partial differential equations (PDEs) was solved using the COMSOL\textsuperscript{®} Multiphysics (formerly FEMLAB\textsuperscript{®}) software package. This software is a dynamic tool that uses the finite element method to solve partial differential equations encountered in real world engineering and scientific problems. It has several basic application modes related to various fields of engineering and science. It uses the integral approach to conservation, which does not suffer from Gibbs instability. The integral approach to conservation makes the code stable against any abrupt change/shock. To solve the above set of equations for the adsorption and desorption steps, the coefficient form of the PDE under COMSOL\textsuperscript{®} Multiphysics in application modes was used. The number of mesh elements was increased until the bed profiles and process performance indicators showed no further change. A grid of 960 mesh elements was used in the axial direction. The outputs from COMSOL\textsuperscript{®} Multiphysics were exported to MATLAB\textsuperscript{®} at the end of each step. The switch between adsorption and desorption steps was coded in MATLAB\textsuperscript{®}, which controlled the cycling and plotted the profiles at the end of each step for every cycle. Starting from the initial condition of an adsorbent bed saturated with respect to feed air at atmospheric pressure, the partial and total pressures, and velocity profiles in the fluid phase, and
adsorbate loading profiles in the adsorbent phase evolved in time until reaching a cyclic steady-state. Cyclic steady state implies that the instantaneous partial and total pressure profiles are identical during each successive cycle. A change in oxygen purity by $\leq 0.1\%$ in 5 cycles was used as the criterion to confirm cyclic steady-state. Depending on the parameter values, it required simulating 50-220 cycles to reach cyclic steady-state according to the aforementioned criterion.

To assess the accuracy of COMSOL® Multiphysics, the results were compared with an in-house simulator coded in FORTRAN® wherein orthogonal collocation was applied in the special dimension to convert the system of PDEs to a system of ordinary differential equations (ODEs) in time. The oxygen partial pressure, total pressure, and velocity profiles for the cyclic operation shown in Figure 3.2 confirm quantitative agreement between the predictions of the two simulators. For the same conditions the time required in COMSOL® was on the order of 0.6-0.7 min/cycle as opposed to 7-8 min/cycle using the in-house simulator.

### 3.4 Simulation Results and Discussion

Performance of the PPSA process was analyzed based on the product purity, recovery and productivity. Purity is the average oxygen mole fraction in the product stream delivered during the adsorption step. Recovery is defined as the ratio of the moles of oxygen in the product stream to the moles of oxygen fed to the column during the adsorption step. Productivity is defined as the volume of oxygen product delivered in the adsorption step per unit volume of adsorbent per unit time.

It should be noted that the oxygen and argon adsorption isotherms are indistinguishable for the two nitrogen selective adsorbents used in this study. Hence, all the simulation results for oxygen purity have been scaled down by a factor of
21/22 in order to account for the presence of argon when atmospheric air is used as the feed. Atmospheric air also contains water vapor and CO\textsubscript{2} in trace amounts, which have been neglected in the simulations. Since zeolites have a very strong affinity for water vapor and CO\textsubscript{2}, the recommendation is to remove these trace components separately using a periodically replaceable filter before the PPSA unit. Therefore, neglecting water vapor and CO\textsubscript{2} in the simulation is justifiable.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure32.png}
\caption{Comparison of bed profiles obtained from the COMSOL Multiphysics software (—adsorption and --- desorption) and an in-house simulator (o) for (a) oxygen partial pressure, (b) total bed pressure and (c) interstitial velocity in the gas phase at the end of the adsorption and desorption steps after reaching cyclic steady-state. The process parameters are \( L = 2 \text{ cm}, \, d_p = 0.002 \text{ cm}, \, \Delta P = 1.5 \text{ atm} \). Optimum adsorption and desorption times are 0.12s and 1.2s, respectively.}
\end{figure}
Before presenting the findings from this simulation study, it is also important to discuss the impact of the assumptions related to adsorption heat effect, binary equilibrium calculation and intra-adsorbent gas transport. The heat effect should be assessed for a PPSA process being developed for mobile use by physically active patients who need oxygen therapy. For such applications, typically small-diameter adsorbers (1-2 cm in diameter) will be used where a high ratio of heat transfer area to packed volume will allow fast dissipation of the heat of adsorption and keep the temperature rise to a minimum. Hence, the isothermal assumption is reasonable.

The extended Langmuir isotherm model based on single component parameters has been used in the simulation. Oxygen and nitrogen molecules are very similar in size and their saturation capacities are close enough to force an average saturation capacity without affecting the fit of the single component data in the range of interest. This makes the extended Langmuir isotherm thermodynamically consistent. There is no evidence to suggest that interaction between two non-polar gases such as oxygen and nitrogen can give rise to any significant non-ideality to compromise the predictions from this simulation study.

Although the pore diffusion model is a more realistic representation of the intra-adsorbent gas transport, several studies [Ruthven et al., (1993)] have shown that the difference between the pore diffusion model and LDF approximation in a cyclic process simulation can be minimized by adjusting $\Omega$ (see Equation (3.21)). A number of correlations for adjusting $\Omega$ as a function of the dimensionless cycle time, $\theta$, have been proposed in the literature. The ones that are based on analytically comparing the particle uptake have used linear isotherms. Correlations based on a direct comparison of PSA simulation results have used different degrees of isotherm non-linearity. It is generally agreed that a constant value $\Omega = 15$ works well when $\theta \geq 1.0$ for both linear
and non-linear isotherms. More recently, Todd and Webley (2006) have shown excellent agreement between the LDF model with $\Omega = 15$ and pore diffusion model predictions for RPSA air separation on LiLSX in the range $\theta \geq 1.0$. These authors came to the same conclusion based on a particle uptake study in an earlier publication [Todd and Webley (2002)]. The $\theta$ values are well above 1 for most of the other operating conditions simulated in this study. For one or two exceptional cases, the values for oxygen are still $> 1$ and the nitrogen values lie between 0.1 and 1. Hence, the use of Equation (3.21) with $\Omega = 15$ in the present study is a quantitatively reliable representation of the macro-pore controlled intra-particle diffusional transport of oxygen and nitrogen in the two adsorbents.

The PPSA performance depends on several process parameters such as the duration of the adsorption and desorption steps, adsorbent particle diameter, pressure drop across the column and bed length. The influence of these parameters is discussed in the following sections.

### 3.4.1 Dynamics of adsorption and desorption

The oxygen and nitrogen partial pressure, total pressure, and interstitial velocity profiles within the adsorption bed plotted at the end of the first step and every fifth step thereafter until reaching cyclic steady-state operation are shown in Figure 3.3. COMSOL® Multiphysics in conjunction with MATLAB® also allows tracking the evolution of various bed profiles within the duration of each step. Such visualization capability helps to physically understand and gain insight into the process. The sharp drop in partial pressure of nitrogen in Figure 3.3(b) was due to the rapid (selective) nitrogen adsorption at the feed end of the bed, which resulted in the
sharp rise in oxygen partial pressure ahead of the nitrogen front observed in Figure 3.3(a). The increase in velocity near the feed end of the bed, shown in Figure 3.3(d), was due to the total pressure gradient near the bed entrance where the adsorbed phase was in equilibrium with feed air. The subsequent decrease in velocity was due to nitrogen adsorption exceeding the opposing effect of pressure gradient. During the desorption step the feed end was opened to the atmosphere and the product end was closed. By tracking the total pressure profile within the duration of the desorption step, it was observed that a pressure maximum occurred inside the bed whereby a pressure wave travelled in both directions before near atmospheric pressure was attained throughout the bed. Since the product end was closed during this step, this wave caused the pressure at the product end to rise above atmospheric, which explains the pressure gradient from outlet to inlet seen in Figure 3.3 (c) at the end of the desorption step. The residual (reverse) gradient of pressure at the end of the desorption step depended on the duration of this step. It is evident from Figures 3.3(a) and 3.3(b) that during the desorption step, both nitrogen and oxygen were released from the adsorbed phase. Gas desorbed from the region behind the penetration of the adsorption front was rich in nitrogen and quickly exited through the bed inlet. In the region ahead of the penetration of the adsorption front, the desorbing gas was rich in oxygen and was conserved in the gas phase by preventing its excessive release through the inlet, which contributed to the product purity in the subsequent cycle. It is also evident from the profiles in Figure 3.3 that while the dynamics of the total column pressure were very fast and reached cyclic operation within a few cycles, the partial pressure profiles of both the gases required a large number of cycles to converge to cyclic steady-state operation. Lu et al., (1993) have reported similar behavior for a three-step RPSA process where a hold step was
introduced between the adsorption and desorption steps. The specific criterion used to confirm cyclic steady-state in this study is detailed in section 3.3.3.

3.4.2 Optimum in adsorption time and desorption time

Oxygen product purity from a pulsed PSA process using 5A zeolite and Ag-Li-X zeolite as the adsorbents was maximized by optimizing the duration of the adsorption and desorption steps for every set of operating parameters. Oxygen product purity using 5A zeolite as the adsorbent is plotted as a function of the duration of the

Figure 3.3: Profiles for (a) oxygen partial pressure, (b) nitrogen partial pressure, (c) total column pressure and (d) interstitial velocity in the gas phase plotted against dimensionless bed length showing the approach to cyclic steady-state. Starting from the 1st cycle, profiles for every 5th cycle are shown for 5A zeolite. The process parameters are $L = 2$ cm, $d_p=0.002$ cm and $\Delta P = 1.5$ atm. Optimum adsorption and desorption times are 0.12 s and 1.2 s, respectively.

3.4.2 Optimum in adsorption time and desorption time

Oxygen product purity from a pulsed PSA process using 5A zeolite and Ag-Li-X zeolite as the adsorbents was maximized by optimizing the duration of the adsorption and desorption steps for every set of operating parameters. Oxygen product purity using 5A zeolite as the adsorbent is plotted as a function of the duration of the
desorption step for three adsorption times for two different sets of operating parameters in Figure 3.4.

![Figure 3.4: Effect of adsorption and desorption step duration on oxygen product purity and recovery from a pulsed PSA process using a 5A zeolite at two representative sets of process parameters: (a) $L = 0.2$ cm, $d_p = 0.0005$ cm, $\Delta P = 1.5$ atm; (b) $L = 2$ cm, $d_p = 0.002$ cm, $\Delta P = 1.5$ atm.](image)

It is interesting to note that there was an optimum combination of the adsorption and desorption step durations at which the oxygen product purity became maximum for each set of operating parameters. In order to understand this phenomenon, the oxygen and nitrogen partial pressure profiles in the bed at the end of the adsorption and desorption steps after reaching cyclic steady-state operation were...
studied by varying either the desorption or the adsorption step duration while keeping the other constant; the results are shown in Figure 3.5. The purpose of the adsorption step was to preferentially remove as much nitrogen from the incoming feed air as possible near the feed end of the adsorption bed and push enriched oxygen towards the product end. But the purity of the oxygen product obtained in the adsorption step was also dependent on the state of the gas phase composition at the end of the desorption step in the previous cycle. In a conventional four-step PSA cycle, an external purge using raffinate product sweeps the bed voids clean of the preferentially extracted component of the feed that is desorbed from the adsorbent due to pressure reduction and at the same time promotes further desorption of the extract. It was discussed in relation to the results shown in Figure 3.3 that during desorption in the two-step PPSA process, oxygen-rich gas desorbed from the product end flowed towards the open feed end thus creating a self-purge effect. For a given adsorption time, a very short desorption step meant that desorbed oxygen did not have enough time to sufficiently sweep the bed and a large amount of nitrogen was left behind in the voids of the bed near the feed end. The residual nitrogen reduced the purity of the oxygen product in the subsequent adsorption step. A very long desorption time, on the other hand, resulted in an excessive loss of desorbed oxygen that outweighed the additional nitrogen capacity created at the feed end of the bed as a result of the longer self-purge. The consequence was also a drop in oxygen product purity. These observations are evident from Figure 3.5(a). Therefore, it appears that there is an optimum desorption time that maximizes the conservation of enriched oxygen desorbed from the product end without compromising nitrogen purging. The results in Figure 3.5(b) show the effect of changing the adsorption time for a fixed desorption time. The volume of gas fed to the adsorber was controlled by the duration of the
Chapter 3. Modeling and Simulation of Pulsed Pressure Swing Adsorption Process

adsorption step when all other operating conditions were held constant. Increasing the adsorption time increased the penetration of the adsorption wave front deeper into the bed as can be clearly seen in Figure 3.5(b). Since a pressure drop was imposed along the bed length during the adsorption step, an advancing adsorption front also meant a decreasing driving force for mass transfer. As such, a very long adsorption step pushed un-adsorbed nitrogen toward the product end and reduced the oxygen product purity. In contrast, a very short adsorption time limited the penetration of the adsorption front. Although there was a sharp rise in the oxygen concentration ahead of the adsorption front, the zone of high purity oxygen remained confined to the middle of the bed since the allowed adsorption time was insufficient for it to reach the product end. Therefore, the optimum adsorption step duration maximized the oxygen product purity by regulating the penetration of the mass-transfer front. A balance was struck such that the oxygen-rich zone reached the product end, but limited nitrogen contamination resulting from a reduced driving force at the leading edge of the advancing mass-transfer front. Trends similar to those in Figure 3.5 were also observed in case of the Ag-Li-X zeolite.

All the process performance results presented in the subsequent sections are for the optimum combination of the adsorption and desorption step times for the corresponding set of process variables. A thorough manual search using small time step increments was conducted in order to determine the optimum adsorption and desorption step durations \([t_a, t_d]\) for a set of (base case) process variables. In order to determine the optimum adsorption time for another combination of process variables, Equation (3.25) was used to calculate a good first approximation \(t_a\) based on the assumption that the optimum adsorption time is proportional to the average residence time of the feed gas in the adsorption column under non-adsorbing...
conditions:

\[
\frac{L}{\bar{u}_z} \text{ current} = \frac{(t_d)_{\text{current}}}{(t_d)_{\text{ref}}}
\]  

(3.25)

where \( \bar{u}_z \) is the average interstitial gas velocity calculated using Darcy's law in combination with the Blake-Kozeny equation given by Equations (3.9) and (3.10), respectively. Use of the Blake-Kozeny equation to calculate the average interstitial velocity under non-adsorbing conditions permitted calculating a first approximation

Figure 3.5: Effect of (a) desorption time and (b) adsorption time on the cyclic steady state oxygen partial pressure profile along a 5A zeolite adsorbent bed for the adsorption and desorption step durations fixed at 0.12 s and 1.2 s, respectively. Other operating parameters are \( L = 2 \) cm, \( d_p = 0.002 \) cm and \( \Delta P = 1.5 \) atm. See notation list for an explanation of the legends used for the cyclic steady-state oxygen partial pressure profiles.
of the new optimum adsorption time for a change in any one or more of the process parameters, namely the imposed pressure drop, adsorbent particle size, and bed length. The Blake-Kozeny equation assumes a linear pressure gradient in the bed, which is a good approximation for the computed total pressure profiles under the adsorption conditions shown in Figure 3.3. The first approximation of the new optimum desorption time was obtained by equating \( \frac{t_a}{t_d} \) to \( \frac{t_a}{t_d} \) \_ref. Starting from the first approximation, the adsorption and desorption times were varied further to obtain the optimum combination that maximized the oxygen product purity for the chosen new combination of operating parameters.

### 3.4.3 Effect of particle diameter on process performance

For a specific bed length and imposed pressure drop, the effect of adsorbent particle diameter on oxygen product purity, recovery and productivity was investigated by optimizing the adsorption and desorption times with respect to particle diameter for 5A and Ag-Li-X zeolite adsorbents; the results are plotted in Figure 3.6. For both adsorbents the oxygen product purity went through a broad maximum when plotted as a function of adsorbent particle diameter. However, the recovery decreased and productivity increased monotonically with increasing particle diameter. Since the bed resistance to gas flow increased with decreasing particle size, the pressure drop during the adsorption step was confined near the feed end of the bed, therefore leaving most of the bed underutilized for separation. This explains the sharp drop in oxygen purity in the limit of extremely small particles. On the other hand, increasing particle size reduces the bed resistance and increased the gas flow under a constant (imposed) pressure gradient. Increasing the particle size increased the intra-particle
mass transfer resistance and hence the spread of the mass transfer front. Increasing gas flow added to this spread by contributing additional axial dispersion. Therefore, increasing the adsorbent particle size eventually led to a drop in oxygen product purity. Alpay and Kenney (1994) also observed an optimum in oxygen product purity extending over a range of particle diameters for an RPSA process. The optimum cycling frequency for a given set of operating parameters is the inverse of the cycle time, which is the sum of the optimum adsorption and desorption times. The cycling frequency increased with increasing particle diameter as shown in Figure 3.6 (b).

Figure 3.6: Effect of adsorbent particle size on (a) oxygen product purity and recovery, and (b) productivity and cycling frequency for a pulsed PSA process on 5A and Ag-Li-X zeolite. The process parameters are $L = 2$ cm, $\Delta P = 1.5$ atm. the optimum particle diameter range is 0.002-0.008 cm.
The increase in oxygen productivity with increasing adsorbent particle size was a direct consequence of an increase in the cycling frequency. The decrease in oxygen recovery with increasing particle size was also a result of the decreased duration of the adsorption step that limited the penetration of the mass transfer front and hence the amount of (enriched) oxygen collected in the product. Although the selectivity of nitrogen relative to oxygen is much higher for the Ag-Li-X than for the 5A zeolite, this did not give any significant performance advantage for an RPSA cycle operated slightly above atmospheric pressure.

3.4.4 Effect of pressure drop on process performance

The process performance indicators such as oxygen product purity, recovery, and productivity have been plotted as a function of imposed pressure drop in Figure 3.7 for a specific bed length and an adsorbent particle diameter chosen from the optimum particle size range shown in Figure 3.6; results for both the 5A and Ag-Li-X zeolites are shown. The adsorption and desorption times were optimized for every change in the pressure drop. For a pulsed PSA process, the pressure gradient within the adsorption bed and the bed permeability govern the gas flow through the adsorber. The bed permeability mainly depends on the adsorbent particle diameter and bed porosity. The oxygen product purity was low when the imposed pressure drop was very low, but quickly increases with increasing pressure drop and approached a nearly constant high purity level as can be seen from Figure 3.7 (a). The increase in oxygen product purity with increasing pressure drop resulted from the increased driving force for mass transfer associated with higher pressures. This allowed more nitrogen to be adsorbed upstream of the adsorption front, thereby increasing the oxygen enrichment downstream. For a fixed bed length and particle size, the feed velocity also increased
with increasing pressure drop, which in turn increased the axial dispersion in the bed. The oxygen purity profile levelled off due to the opposing effects of increased mass-transfer driving force and increased axial dispersion. For both adsorbents the oxygen recovery and cycling frequency displayed a minimum with increasing pressure drop imposed on a fixed length of the adsorbent bed. Whereas the minimum in cycling frequency occurred at approximately the same pressure drop for both adsorbents, the
minimum in the recovery occurred at a lower pressure in the 5A zeolite. Since the increase in oxygen purity was a result of the increased preferential adsorption of nitrogen, there was also some accompanying loss of oxygen to the solid phase that led to the drop in oxygen recovery observed in Figure 3.7(a). Intuitively, one would expect a drop in oxygen purity along with a rise in recovery when axial dispersion becomes important. The constant oxygen product purity observed at higher pressure drops has already been explained; in addition, this may also be attributed to the fact that the adsorption and desorption times have been individually optimized for every combination of process parameters investigated in this study. A net rise in the oxygen productivity with increasing feed pressure (and hence pressure drop across the adsorber) was the combined effect of changing oxygen product flow rate and optimum cycling frequency.

### 3.4.5 Effect of bed length on process performance

The effect of bed length on oxygen product purity, recovery, productivity, and optimum cycling frequency is shown in Figure 3.8 for a fixed adsorbent particle size and pressure drop; both 5A and Ag-Li-X zeolites were investigated. For every change in bed length, the adsorption and desorption times were optimized to maximize the oxygen product purity. For a fixed adsorbent size and imposed inlet pressure, the feed flow rate decreased with increasing bed length. Axial dispersion, which becomes important due to the high flow rate for very small bed lengths, caused a decrease in the oxygen product purity. The importance of axial dispersion decreased with increasing adsorber length leading to an increase in oxygen purity, which ultimately levelled off at a constant (high) value as shown in Figure 3.8(a). The oxygen recovery passed through a shallow maximum for both 5A zeolite and Ag-Li-X adsorbents. The
simultaneous increase in oxygen product purity and recovery with increasing bed length implies a sharpening of the mass-transfer front owing to the increase in residence time.

Figure 3.8: Effect of bed length on (a) oxygen product purity and recovery, and (b) productivity and cycling frequency in a pulsed PSA process for 5A and Ag-Li-X zeolites. The process parameters are $d_p = 0.002$ cm and $\Delta P = 2.5$ atm for 5A zeolite and $d_p = 0.0025$ cm and $\Delta P = 2.5$ atm for Ag-Li-X zeolite.

However, it is clear from Figure 3.8(b) that the cycling frequency decreased markedly with increasing bed length in order to maintain high product purity for a PPSA process in a long bed. A drop in the oxygen product recovery beyond a certain
bed length resulted from the drop in product gas velocity with increasing bed length for a constant imposed pressure drop. A marked drop in productivity with increasing bed length was the compound effect of decreasing product rate and cycling frequency, the former being a consequence of the decreasing feed rate.

3.5 Graphical Design of the Pulsed Pressure Swing Adsorption Process

3.5.1 Generalizing the simulation results

In order to generalize the results from the numerical simulations, the possibility of correlating the process performance indicators in terms of dimensionless groups consisting of the process parameters was investigated. The set of Equations (3.5) through (3.9) and Equations (3.12) through (3.23) were made dimensionless by using appropriate scale factors [Krantz (2007)] in order to obtain the minimum parametric representation in terms of eleven dimensionless groups as shown in Appendix A. Hence, the oxygen product purity, recovery and productivity are functions of the eleven dimensionless groups identified in Equation (A26) and defined in Appendix A. Note that the groups, $\Pi_2$, $\Pi_3$, $\Pi_5$, $\Pi_6$, $\Pi_8$, $\Pi_{11}$, are dependent only on adsorbent properties, composition and physical properties of the feed gas, product delivery pressure, and temperature. Therefore, for air separation using a specified adsorbent, product delivery pressure and temperature, the oxygen product purity, recovery and productivity will be functions of only the five dimensionless groups $\Pi_1$, $\Pi_4$, $\Pi_7$, $\Pi_9$ and $\Pi_{10}$. The particle diameter, ratio of particle diameter to bed length and maximum pressure have been isolated into the dimensionless groups $\Pi_1$, $\Pi_4$, and $\Pi_7$, respectively, whereas the adsorption and desorption times have been isolated into the dimensionless groups $\Pi_9$ and $\Pi_{10}$, respectively. In section 3.4.2, it was observed that
the oxygen product purity was a maximum for an optimum combination of adsorption and desorption step durations for a specified bed length, adsorbent particle size and pressure drop. Once the oxygen product purity is maximized with respect to the durations of the adsorption and desorption steps for a given set of process parameters, the process performance becomes independent of dimensionless groups $\Pi_9$ and $\Pi_{10}$; this follows from the fact that the maximization introduces two additional independent equations that can be used to eliminate $\Pi_9$ and $\Pi_{10}$. Hence, for a fixed adsorbent delivering an oxygen-enriched product at atmospheric pressure the maximum oxygen purity depends only on the three dimensionless groups $\Pi_1$, $\Pi_4$ and $\Pi_7$. Hence, the PPSA process performance was computed in terms of the three dimensionless groups $\Pi_1$, $\Pi_4$ and $\Pi_7$ over an extensive range of values summarized in Table 3.3 that cover the full domain of the PPSA process operation including URPSA. Correlating the process performance indicators, oxygen product purity, recovery and productivity, with the aforementioned dimensionless groups will guide the designer in selecting a proper set of process parameters for a specific application. The oxygen product recovery and productivity determine the feed pump size and adsorbent volume for a specified production rate.

Presentation of the simulation results requires further consideration from the point of user convenience. In the present study, since $P_L$ has been fixed at 1 atm, varying $\Pi_7$ effectively means only is varying $P_H$. Similarly, varying $\Pi_1$ means only varying $d_p$ since the other parameters in this dimensionless group are fixed by the adsorbent (5A or Ag-Li-X) and gas mixture (oxygen and nitrogen) chosen in the simulations. Hence, instead of making the users calculate the dimensionless groups using the values of the constituent dimensional parameters fixed in the simulations, it is more user-friendly to plot the PPSA process performance indicators as a function of
Chapter 3. Modeling and Simulation of Pulsed Pressure Swing Adsorption Process

d_p/L (=\Pi_4) for different d_p values for a fixed value of P_H. Such plots for three representative P_H values are given in Figure 3.9 for 5A zeolite. Similarly, the results for the Ag-Li-X zeolite are shown in Figure 3.10. Only the purity and recovery plots are given in Figures 3.9 and 3.10. Although not evident from the dimensional analysis presented in the Appendix A, it was found that productivities correlate very well with another dimensionless group that contains all three process parameters. This advantage has been exploited in the next section to package the productivity data in a way that allows direct determination of required adsorbent volume for a specified production rate.

Table 3.3: Range of values of the dimensionless groups used in the simulations.

<table>
<thead>
<tr>
<th>Dimensionless group</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>\Pi_1</td>
<td>1.42 x 10^{-5} - 2.27 x 10^{-2}</td>
</tr>
<tr>
<td>\Pi_2</td>
<td>2.03</td>
</tr>
<tr>
<td>\Pi_3</td>
<td>127.95 (5A zeolite); 773.95 (Ag-Li-X)</td>
</tr>
<tr>
<td>\Pi_4</td>
<td>6.67 x 10^{-5} - 5 x 10^{-3}</td>
</tr>
<tr>
<td>\Pi_5</td>
<td>0.115 (5A zeolite); 1.17 (Ag-Li-X)</td>
</tr>
<tr>
<td>\Pi_6</td>
<td>0.0365 (5A zeolite); 0.09 (Ag-Li-X)</td>
</tr>
<tr>
<td>\Pi_7</td>
<td>2.5-5.5</td>
</tr>
<tr>
<td>\Pi_8</td>
<td>0.79</td>
</tr>
<tr>
<td>\Pi_{11}</td>
<td>6.6</td>
</tr>
</tbody>
</table>

In Figures 3.9 and 3.10, for a chosen P_H and d_p, a change in d_p/L quantifies the effect of a change in bed length on oxygen purity and the corresponding recovery. Similarly, for a chosen P_H and d_p/L, the figures show the effect of a change in d_p on oxygen purity and recovery. It is clear that for some d_p values covered in this investigation there is a critical bed length below which the oxygen purity drops drastically. An optimum in oxygen purity with respect to d_p is also evident from the
Figure 3.9: Design plots for the PPSA air separation on 5A zeolite relating the process variables to oxygen product purity and recovery. Optimum adsorption and desorption step durations were used for every combination of process variables.
Figure 3.10: Design plots for the PPSA air separation on Ag-Li-X zeolite relating the process variables to oxygen product purity and recovery. Optimum adsorption and desorption step durations were used for every combination of process variables.
figures. For the PPSA cycle investigated in this study, the oxygen product purity in Ag-Li-X zeolite was lower compared to that in the 5A zeolite for the same set of process parameters. In the domain of investigation oxygen recovery was in the range 10-25% in 5A and in Ag-Li-X zeolite the recovery varied from 10 to 55%.

### 3.5.2 Correlation for the optimum adsorption and desorption times

It has been discussed in section 3.4.2 that for every combination of operating parameters there is an optimum combination of adsorption and desorption step durations at which the oxygen purity is maximum. How the duration of the adsorption and desorption steps has been optimized for several parameter combinations subsequently simulated to study the PPSA process performance is also detailed in section 3.4.2. The semi-empirical approach described below gives a dimensionless correlation that relates the optimum adsorption and desorption step durations to the operating process variables ($P_H$, $d_p$, and $L$).

For equilibrium-controlled adsorption the optimum adsorption time ($t_{a,\text{theo}}$) can be estimated from the residence time of the adsorption wave in the adsorber:

$$t_{a,\text{theo}} = \frac{L}{\omega}$$

(3.26)

where $L$ is the adsorber length and $\omega$ is the adsorption wave velocity. For a trace-component system that follows a linear adsorption isotherm, the adsorption wave velocity in an initially clean bed is given by

$$\omega = \frac{\bar{u}_z}{1 + \frac{(1 - \varepsilon)}{\varepsilon} K}$$

(3.27)

where $\bar{u}_z$ is the interstitial gas velocity and $K$ is the dimensionless Henry’s law constant. A trace-component system implies a very small amount of adsorbate in the
feed such that the equilibrium relationship is linear and the change in velocity due to adsorption is negligible. For such a system Darcy's law in combination with the Blake-Kozeny equation [Equations (3.9) and (3.10)] relates the interstitial velocity to the adsorber length, adsorbent particle diameter, bed voidage, and imposed pressure drop. When Equations (3.9), (3.10) and (3.27) are substituted into Equation (3.26), the following equation is obtained:

\[
\frac{(t_a)_{theo}}{1 + \left(1 - \frac{\epsilon}{\epsilon}\right) K} = \frac{150}{\frac{\Delta P d_p^2}{\mu L^2} \left(\frac{\epsilon}{1 - \epsilon}\right)^2}
\]  

(3.28)

which can be further rearranged to the following form:

\[
\frac{P}{\mu} \left(\frac{(t_a)_{theo}}{1 + \left(1 - \frac{\epsilon}{\epsilon}\right) K}\right) = \frac{150}{\left\{ \frac{P_L P_{\mu}}{P_L - 1} \right\} d_p^2 \left(\frac{\epsilon}{1 - \epsilon}\right)^2}
\]

(3.29)

Equation (3.29) has the general form

\[
Y = \frac{150}{X}
\]

(3.30)

where

\[
Y = \frac{\frac{P}{\mu} (t_a)_{theo}}{1 + \left(1 - \frac{\epsilon}{\epsilon}\right) K} \equiv \Pi_9 \quad \text{and} \quad X = \left(\frac{P_L P_{\mu}}{P_L - 1}\right) \frac{d_p^2}{L^2} \left(\frac{\epsilon}{1 - \epsilon}\right)^2 = \left(\Pi_7 - 1\right) \left(\frac{\Pi_4}{\Pi_2}\right)^2
\]

\(\Pi_2, \Pi_4, \Pi_7\) and \(\Pi_9\) are the same dimensionless groups defined in the Appendix A.

In order to examine if the optimum adsorption time normalized with respect to bed capacity in a PPSA system involving a nonlinear adsorption isotherm and bulk separation can be similarly correlated to the process parameters, \(Y\) was modified according to the following equation to account for a binary feed mixture following an extended Langmuir isotherm and plotted against \(X\):
In the above equations, \( \frac{q_{\text{avg}}}{c_{\text{avg}}} \) can be written in terms of the dimensionless groups as follows:

\[
\frac{q_{\text{avg}}}{c_{\text{avg}}} = \frac{K_A}{1 + 0.5\Pi_5\Pi_8(\Pi_7 + 1) + 0.5\Pi_6(1-\Pi_8)(\Pi_7 + 1)}
\]

In the above equation, \( A \) denotes the more strongly adsorbed component, nitrogen; \( q_{\text{avg}} \) is the equilibrium concentration of nitrogen at the average pressure \( P_{\text{avg}} \), in the bed corresponding to the nitrogen concentration in the feed. The plots are shown in Figure 3.11(a). It is interesting to note that the optimized adsorption times obtained from the simulation for air separation by PPSA on 5A and Ag-Li-X indeed are correlated by an equation similar to Equation (3.30) that was derived for a trace-component system obeying a linear adsorption isotherm. The correlations are

\[
Y = 9.41/X \quad \text{for the 5A zeolite and} \quad Y = 7.72/X \quad \text{for the Ag-Li-X zeolite.}
\]

The constants 9.41 and 7.72 can be viewed as empirical compensations for the isotherm non-linearity, change in velocity due to adsorption, and the effect of residual bed loading on the wave velocity. The cycling frequency obtained from the optimized adsorption and desorption times was also plotted against \( X \) and the results along with the correlations are shown in Figure 3.11 (b). Since the equilibrium capacities of oxygen and nitrogen in the two adsorbents are significantly different, the closeness of the correlations in Figures 3.11(a) suggests the possibility of an adsorbent-independent approximate correlation between \( Y \) and \( X \).

By evaluating the appropriate dimensionless groups constituting the variables \( X \) and \( Y \), the optimum adsorption time and cycling frequency can be obtained directly
either from Figures 3.11(a) and 3.11(b) or from the correlations included in these figures for both adsorbents. The optimum desorption time can then be easily calculated from the known optimum adsorption time and cycling frequency. Proper selection of the adsorption and desorption times based on the availability of commercially available cycling valves and pumps is an important consideration for the miniaturization of an oxygen concentrator to meet the needs of active COPD patients.

Figure 3.11: Correlations for relating (a) the optimum adsorption step duration and (b) total cycle time to the dimensionless group $X$, which combines the PPSA process parameters. Results for both 5A and Ag-Li-X are shown.
Chapter 3. Modeling and Simulation of Pulsed Pressure Swing Adsorption Process

In order to complete the sizing of a PPSA process, the necessary amount of adsorbent must be determined, which is related to the productivity by the following equation:

$$\text{Adsorbent volume (cc)} = \frac{\text{Oxygen delivery rate (cc of oxygen/h)}}{\text{Oxygen productivity (cc of oxygen/cc of adsorbent/h)}}$$

(3.33)

The calculated adsorbent volume for an oxygen delivery rate of 5 SLPM plotted as a function of X in Figure 3.12 gives excellent correlations for both adsorbents. Oxygen concentration in the product stream is dependent on the chosen process parameters according to the correlations in Figure 3.9 and 3.10. It is useful to recall that the AMA requires $\geq 90\%$ oxygen at a rate of 5 SLPM for personal medical applications.

Since the cycling frequency increases with increasing X, it is now clear that within the range of process parameters required to ensure high ($\geq 90\%$) product purity, the reduction in size of a pulsed pressure-swing adsorber depends on how fast the process can be cycled.

Figure 3.12: Correlation relating the adsorbent volume to the dimensionless group X in order to deliver 5 SLPM of oxygen at a level of oxygen purity chosen in Figure 3.9 or 3.10. Correlations for 5A and Ag-Li-X zeolites are shown.
3.5.3 General design procedure

Based on the results in Figures 3.9–3.12, a generalized design procedure can be proposed for the production of an enriched oxygen stream from air at an oxygen flow rate of 5 SLPM:

1. Set the design specification for oxygen purity in the product stream.
2. Select appropriate values of $P_H$, $d_p$, and $d_p/L$ from Figure 3.9 or 3.10 to ensure the specification set in step 1.
3. Calculate the value of the dimensionless group $X$ corresponding to the process parameters chosen in step 2.
4. Obtain the optimum adsorption time and cycling frequency from Figures 3.11(a) and 3.11(b), respectively, for the value of $X$ obtained in step 3. If the adsorption step duration is achievable, then proceed to the next design step; otherwise change the dimensionless groups to achieve an implementable adsorption step duration. Since the desorption step duration is longer than the adsorption step duration, the latter is the deciding factor.
5. Calculate the optimum desorption time from the optimum adsorption time and cycling frequency determined in step 4.
6. Obtain the volume of adsorbent required to produce 5 SLPM of oxygen at the desired purity from Figure 3.12 using the $X$ value calculated from step 3.

3.5.4 A case study in process miniaturization

The design specification is set as > 90% oxygen purity in the product stream delivered at a rate of 5 liters of oxygen per minute to remain well within the AMA standard. High pressure oxygen concentrators are not suitable for ambulatory use by
an active COPD patient due to the potential hazards associated with a high pressure system. Therefore, the maximum pressure that can be used in the design of an oxygen concentrator is limited to few atmospheres above the ambient pressure. Similarly, the (high) frequency of the available valves limits the choice of adsorbent particle size. Based on these considerations, an adsorbent particle diameter of 0.002 cm and a pressure drop of 2.5 atm were chosen; possible combinations of bed length and cycling frequency were then explored for both 5A and Ag-Li-X adsorbents. Selected results are summarized in Table 3.4, which illustrate the role of cycling frequency in PPSA process miniaturization. The adsorbent weight used in the PPSA process was compared with the commercially available and patented oxygen concentrators and is shown in Figure 3.13. It is evident from this figure that the PPSA process has the potential to miniaturize the size of adsorber in an oxygen concentrator provided the fast cycling valves and sensors are available.

![Figure 3.13: Comparison of adsorbent weight used in current PPSA process.](image)

### 3.6 Chapter Conclusion

A mathematical model for a two-step pulsed pressure swing adsorption (PPSA) process was developed from first principles and the process performance was
analyzed successfully by solving the dynamic model equations using COMSOL Multiphysics® software. COMSOL Multiphysics® together with MATLAB® facilitate observing the transient profiles within a single cycle, which are useful for understanding the PPSA process behavior.

PPSA air separation on 5A and Ag-Li-X zeolites has been thoroughly investigated. For both adsorbents the oxygen product purity is a maximum for any combination of operating parameters at unique optimum adsorption and desorption times. The optimum desorption time is longer than the optimum adsorption time to ensure proper regeneration of the bed. These optima arise owing to the self-purging of the bed with the low velocity and high purity desorbed oxygen from the region ahead of adsorption front.

The results from extensive simulations covering a wide range of operating conditions have been consolidated in three design plots (Figures 3.9 or 3.10, 3.11 and 3.12) for PPSA air separation on 5A and Ag-Li-X zeolites that allow direct determination of the required process parameters (while considering the practical limitations on each of them) and adsorbent volume in order to achieve desired oxygen purity at an oxygen delivery rate of 5 SLPM. For the same combination of process parameters the 5A zeolite gives higher oxygen product purity but lower recovery (and hence higher adsorbent volume) compared to the Ag-Li-X zeolite.

The extent of miniaturization of an oxygen concentrator operated on a PPSA cycle is constrained by the upper limit of rapid cycling that is practically achievable. A significant reduction in size is feasible using commercially available nitrogen-selective adsorbents while keeping the cycling within implementable operating conditions and satisfying AMA specification of $\geq 90\%$ pure oxygen at a rate of 5 SLPM.
Table 3.4: Design table for a PPSA oxygen concentrator.

<table>
<thead>
<tr>
<th>Oxygen purity* (mol. fraction)</th>
<th>Bed length (cm)</th>
<th>Adsorption time (s)</th>
<th>Cycling frequency (Hz)</th>
<th>Adsorbent Volume (cc)</th>
<th>Weight of adsorbent (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5A Ag-Li-X</td>
<td>0.92</td>
<td>0.7</td>
<td>0.009</td>
<td>7.48</td>
<td>55.2</td>
</tr>
<tr>
<td>5A Ag-Li-X</td>
<td>0.93</td>
<td>0.8</td>
<td>0.011</td>
<td>5.82</td>
<td>36.6</td>
</tr>
<tr>
<td>5A Ag-Li-X</td>
<td>0.93</td>
<td>0.9</td>
<td>0.014</td>
<td>4.67</td>
<td>44.1</td>
</tr>
<tr>
<td>5A Ag-Li-X</td>
<td>0.94</td>
<td>1</td>
<td>0.018</td>
<td>3.8</td>
<td>52.1</td>
</tr>
<tr>
<td>5A Ag-Li-X</td>
<td>0.95</td>
<td>2</td>
<td>0.071</td>
<td>1.05</td>
<td>155.9</td>
</tr>
<tr>
<td>5A Ag-Li-X</td>
<td>0.95</td>
<td>3</td>
<td>0.160</td>
<td>0.49</td>
<td>295.9</td>
</tr>
<tr>
<td>5A Ag-Li-X</td>
<td>0.95</td>
<td>4</td>
<td>0.284</td>
<td>0.29</td>
<td>466.3</td>
</tr>
<tr>
<td>5A Ag-Li-X</td>
<td>0.95</td>
<td>5</td>
<td>0.444</td>
<td>0.19</td>
<td>663.6</td>
</tr>
<tr>
<td>5A Ag-Li-X</td>
<td>0.95</td>
<td>10</td>
<td>1.777</td>
<td>0.05</td>
<td>1984.9</td>
</tr>
</tbody>
</table>

* rounded to two decimal places.

$P_H = 3.5 \text{ atm}; \ d_p = 0.002 \text{ cm}; \text{ Oxygen delivery rate} = 5 \text{ SLPM}.$
Chapter 4

COULMN DYNAMICS: EXPERIMENTAL DESIGN AND PROCEDURES

4.1 Overview of the Chapter

Having identified the domain of experimental interest from the simulation study detailed in chapter 3, an experimental setup was designed to validate the simulation model and the proposed graphical design methodology. In this chapter, the experimental process design is detailed including the critical issues related to sizing, sensing, measurement and control. The experimental procedure for pressure drop, and adsorption equilibrium and kinetics measurements are also discussed in details.

4.2 Critical Issues in Experimental Study of PPSA Process

The results from the theoretical simulation study presented in chapter 3 have led to the following process design considerations:

(i) To achieve the high purity and better performance, the PPSA process had to be cycled at a fast rate and in most of the cases the cycle times were in fractional seconds, which were very small compared to a conventional PSA process. It was observed that the optimum desorption step duration was nearly ten times of adsorption step duration, where the PPSA process performance was maximum. The adsorption step durations, which were in milliseconds (ms), dictated the necessary response time while selecting various instruments used for analysis, detection and control of the experimental process.
(ii) From the simulation results, the optimum adsorbent particle size was in the micron range, which was much smaller compared to the commercial grade materials available in the market. For a fixed bed length and pressure drop, the individual step duration was inversely related to the square of adsorbent particle size, which meant the process had to be cycled four times faster for every doubling of the adsorbent size. Thus, the response time of available sensors and control devices guided the choice of adsorbent particle size.

(iii) On the other hand, although the cycling frequency was directly proportional to the square of bed length, the portability issue limited how much the bed length could be increased.

(iv) Similarly, the cycling frequency was directly proportional to pressure drop along the bed length, but the maximum pressure of the device was limited by the safety issue for personal use.

(v) From the simulation results, it was observed that the required adsorber diameter was much bigger than the adsorber length to deliver 5 SLPM of high purity oxygen. If the adsorber diameter was bigger than the adsorber length, the flow distribution within the bed would not be uniform. The practical solution to this problem is to use several smaller diameter columns in parallel. Since all the parallel columns could be uncoupled and identical, it was concluded that using one small diameter column was sufficient for experimental validation.

(vi) In the experimental design of a PPSA process with a small column, minimizing the dead volumes at the entrance and exit of the column were very critical. Otherwise, feed and product contamination from mixing with residual gas in the dead space could severely compromise the process performance.
In order to have a good estimate of the expected gas volume and flow rate in and out of the column during the two steps of a PPSA process, detailed simulations were carried out for a set of preliminary operating parameters chosen on the basis of design considerations discussed above. The results are tabulated in Table 4.1. Although, the adsorbent particle size range covered in Table 4.1 could not be achieved in the experiments, the results, nevertheless, were very useful to specify the flow rate range of the flow controllers and meters, and appropriately size the fittings, valves and piping to keep the dead volumes at the minimum level while also keeping the pressure drop in the feed line as low as possible. Selection of adsorbent material, adsorber dimensions, fittings, valves, sensors and controllers is discussed next.

4.2.1 Adsorbents

5A zeolite was used in the experimental study due to ease of availability. Extruded binderless 1.6 mm particles were procured from a local supplier. The particles were ground and sieved to different size ranges necessary for pressure drop characterization experiments. The binderless extruded 5A material was chosen over 5A zeolite with binder to avoid any uneven distribution of the core material and binder after grinding and sieving. It was observed that the zeolite particles formed clusters upon size reduction below 100 µm, most likely due to static charges developed on the surface. The clusters clogged the screens and thus the sieving of charged zeolite particles was difficult. The minimum particle size range obtained after grinding and sieving of 1.6 mm size binderless 5A zeolite material was in the range 63-75 µm, which was chosen for breakthrough and PPSA experimental study. SEM images of the ground particles obtained between 63 and 75 µm sieves are shown in Figure 4.1 at two different resolutions.
Table 4.1: Detailed gas flow information from PPSA process simulation for a set of preliminary process parameters.

<table>
<thead>
<tr>
<th>L (cm)</th>
<th>( t_s/t_d ) (s)</th>
<th>( d_p ) (cm)</th>
<th>( \Delta P ) (atm)</th>
<th>Volume in (cc)</th>
<th>Volume in (L/m)</th>
<th>Volume out (adsorption) (cc)</th>
<th>Volume out (adsorption) (L/m)</th>
<th>Volume out (blow down) (cc)</th>
<th>Volume out (blow down) (L/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.072/0.7</td>
<td>0.002</td>
<td>2.5</td>
<td>12.18</td>
<td>10.15</td>
<td>0.57</td>
<td>0.48</td>
<td>11.33</td>
<td>0.97</td>
</tr>
<tr>
<td>3</td>
<td>0.162/1.5</td>
<td>0.002</td>
<td>2.5</td>
<td>17.86</td>
<td>6.61</td>
<td>0.88</td>
<td>0.33</td>
<td>16.82</td>
<td>0.67</td>
</tr>
<tr>
<td>4</td>
<td>0.29/2.5</td>
<td>0.002</td>
<td>2.5</td>
<td>22.95</td>
<td>4.75</td>
<td>1.25</td>
<td>0.26</td>
<td>21.42</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>0.5/5</td>
<td>0.002</td>
<td>2.5</td>
<td>33.36</td>
<td>4.00</td>
<td>1.50</td>
<td>0.18</td>
<td>31.81</td>
<td>0.38</td>
</tr>
<tr>
<td>10</td>
<td>1.8/17</td>
<td>0.002</td>
<td>2.5</td>
<td>77.98</td>
<td>2.60</td>
<td>3.56</td>
<td>0.12</td>
<td>63.67</td>
<td>0.23</td>
</tr>
<tr>
<td>2</td>
<td>0.05/0.65</td>
<td>0.002</td>
<td>4</td>
<td>21.44</td>
<td>25.73</td>
<td>0.76</td>
<td>0.92</td>
<td>19.36</td>
<td>1.79</td>
</tr>
<tr>
<td>3</td>
<td>0.11/1.5</td>
<td>0.002</td>
<td>4</td>
<td>26.47</td>
<td>14.44</td>
<td>0.89</td>
<td>0.49</td>
<td>25.31</td>
<td>1.01</td>
</tr>
<tr>
<td>4</td>
<td>0.2/2.5</td>
<td>0.002</td>
<td>4</td>
<td>44.51</td>
<td>13.35</td>
<td>1.62</td>
<td>0.48</td>
<td>38.69</td>
<td>0.93</td>
</tr>
<tr>
<td>10</td>
<td>1.1/13</td>
<td>0.002</td>
<td>4</td>
<td>108.8</td>
<td>5.93</td>
<td>4.72</td>
<td>0.26</td>
<td>88.32</td>
<td>0.41</td>
</tr>
<tr>
<td>2</td>
<td>0.015/0.21</td>
<td>0.0045</td>
<td>2.5</td>
<td>12.93</td>
<td>51.05</td>
<td>0.33</td>
<td>1.31</td>
<td>12.55</td>
<td>3.62</td>
</tr>
<tr>
<td>4</td>
<td>0.061/0.75</td>
<td>0.0045</td>
<td>2.5</td>
<td>24.64</td>
<td>24.23</td>
<td>0.74</td>
<td>0.73</td>
<td>23.77</td>
<td>1.90</td>
</tr>
<tr>
<td>5</td>
<td>0.095/1.134</td>
<td>0.0045</td>
<td>2.5</td>
<td>35.86</td>
<td>22.65</td>
<td>1.12</td>
<td>0.71</td>
<td>29.72</td>
<td>1.57</td>
</tr>
<tr>
<td>10</td>
<td>0.381/4.11</td>
<td>0.0045</td>
<td>2.5</td>
<td>67.58</td>
<td>10.64</td>
<td>2.49</td>
<td>0.39</td>
<td>58.77</td>
<td>0.86</td>
</tr>
<tr>
<td>15</td>
<td>0.856/8.73</td>
<td>0.0045</td>
<td>2.5</td>
<td>109.99</td>
<td>7.70</td>
<td>4.45</td>
<td>0.31</td>
<td>104.70</td>
<td>0.72</td>
</tr>
</tbody>
</table>
4.2.2 Column dimensions

The idea of using several small diameter identical columns operating in parallel to avoid undesirable length to column diameter ratio has already been discussed. This, of course, may give rise to excessive weight and make the unit unportable if stainless steel is used. Alternative light weight material can potentially solve the problem, but that is another research topic. Going along the idea of using a collection of identical, small-diameter columns operating in parallel, it was also discussed that conducting PPSA experiments with just one column would be

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Figure 4.1: Scanning electron micrograph (SEM) images of ground binderless 5A zeolite adsorbent separated between 63 and 75 µm sieves are shown at two different resolutions (a) X 160 and (b) X 270.
sufficient to validate the model. The diameter was chosen such that the L/D ratio was sufficiently high to neglect the entrance effect. The column was constructed from standard stainless steel seamless tubing with dimensions: 1.27 cm OD, 1.08 cm ID and a length of 10.08 cm.

Standard fittings were customized in the departmental workshop to connect column ends with the feed and product lines. The customization allowed connecting the pressure and oxygen sensors exactly at two ends of the column, as shown in Figure 4.2. A water jacket was welded over the body of the column to maintain a constant temperature in the column by circulating water at a controlled temperature. The schematic diagram of the jacketed column and the pictures of the jacketed and unjacketed columns are shown in the Figure 4.3.

![Customized column-end fittings](image)

Figure 4.2: Customized column-end fittings. Arrows indicate locations where the two reducers (B, SS-100-R-2) are soldered in appropriate holes drilled on the reducing union (A, M-810-6-2). *Swagelok catalog reference number.*

### 4.2.3 Selection of instruments

In selecting suitable instruments for sensing and control, the response time of the device was critical to ensure compatibility with cycling frequency. The smallest
adsorption step duration in Table 4.1 was 381 ms for a 10 cm column in the range of feed pressure and particle size investigated. All devices were selected in such a way that the response times were much less than 381 ms. Various instruments used in experimental study and their response times, as specified by the respective manufacturers, are summarized in Table 4.2. Evidences of these devices performing satisfactorily in the PPSA experiments have been presented in a later section. Photographs of oxygen sensor probe, pressure sensor and thermocouple are shown in Figure 4.4.

Figure 4.3: (a) Schematic of column and water jacket arrangement and (b) Photograph of column with and with out jacket. The column end connections are also shown.
4.2.4 Oxygen sensor, flow meter and pressure sensor

In order to verify the PPSA process simulations discussed in chapter 3, reliable measurements of oxygen concentration entering and leaving the column were very important in the experimental study. In the simulation, oxygen product purity was calculated by volume–averaging the concentration of oxygen in the gas stream leaving the product end during the adsorption step. To match the experimental measurements with the theoretical simulation, it was essential to measure the oxygen purity exactly at the exit of the product end along with the flow rate of the gas leaving the column. In view of this consideration, a very thin oxygen sensor probe, working based on fluorescence technology, was selected for point measurement of oxygen concentration right at the exit of the bed. The point measurement was attained by selecting a very thin (1/16") diameter probe which avoided the estimation of back mixed product composition around the probe. Based on the partial pressure of oxygen in the surrounding gas, the optical property (fluorescence) of the die (Ruthenium

Figure 4.4: Photograph of customized (a) oxygen sensor, (b) pressure sensor fittings and (c) thermocouple used in PPSA experiments.
compound trapped in sol-gel matrix) attached at the tip of the probe changed that was detected and analyzed by a spectrometer (model number USB 4000).

### Table 4.2: Response times of various instruments in the experimental setup (Ref: catalogs provided by the manufacturers).

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Manufacturer</th>
<th>Model No</th>
<th>Response time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solenoid Valves</td>
<td>Asco Joucomatic solenoid valves</td>
<td>100600243</td>
<td>5-10</td>
</tr>
<tr>
<td>Mass flow meters and controller</td>
<td>Alicat mass flow meter and controller</td>
<td>M-SLPM-D/5M</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Piezo-resistive pressure sensor</td>
<td>Honey well</td>
<td>40PC150G3A</td>
<td>1</td>
</tr>
<tr>
<td>Thermocouple</td>
<td>Alpha</td>
<td>CHAL-001</td>
<td>1000</td>
</tr>
<tr>
<td>Optical oxygen sensor</td>
<td>Ocean optics</td>
<td>FOXY-R</td>
<td>0.2</td>
</tr>
<tr>
<td>Digital output module (for controlling solenoid valves)</td>
<td>National Instruments</td>
<td>NI9472</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Thermocouple differential analog input module</td>
<td>National Instruments</td>
<td>NI9211</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>Analog input module (Data acquisition from sensors)</td>
<td>National Instruments</td>
<td>NI9215</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Alicat mass flow meters and controller with a response time of <10 ms were chosen to measure the feed and product gas flow rates. These meters operated based on the principle of poiseuille flow equation in which the pressure drop along a small restriction was linearly related to the gas velocity passing through the restriction under laminar flow conditions. The laminar flow conditions were attained using a specially designed Laminar Flow Element (LFE) within the device.

The readily available Honeywell pressure sensor (40PC 150G3A) was chosen and was custom-fitted as per design requirements for absolute pressure measurements.
exactly at the two end of the column. The response time of these sensors was 1 ms, which was fastest among all the sensor. A pressure sensor attached to the customized fitting is shown in Figure 4.4 (b).

4.2.5 Optimum dead volumes and pressure drops

As highlighted earlier, feed and product contamination from mixing with the residual gas in the dead space can severely compromise the process performance. For example, in the breakthrough experiments, both the residence time and spread of breakthrough curve are affected. In case of a PPSA experiment, if the dead volume at the feed end was higher than the volume of feed coming in during the adsorption step, it could be significantly diluted with the high purity nitrogen gas left over in the dead volume from the previous desorption step. Similarly, the product gas volume should be much higher than the dead volume at the product end in order to measure the true composition of the new product gas as closely as possible without the influence of the left over gas from the previous step. While this is not an issue after cyclic steady state has been reached, the mixing in a relatively large dead volume affects the measured transient product concentration. The dead volumes and pressure drop at both ends due to different sizes of tubings corresponding to the minimum lengths necessary to connect the fittings and valves have been summarized in Table 4.3. The total gas volume over the duration of an adsorption/desorption step must be several times higher than that of the dead volume. In the present experimental design, the target was to keep it 10 times higher.

The pressure drop in the tubing attached at feed and product ends of the bed affect the pressure boundary conditions at the respective ends. This pressure drop should be as minimum as possible to attain the atmospheric pressure boundary
conditions at the product end during the high pressure adsorption step and at the feed end during the desorption step. Similarly, by minimizing the pressure drop in the feed line, the pressure at the feed end during adsorption step will be very close to the pressure set at the gas supply source.

Table 4.3: Comparison of gas volumes with dead volumes and estimated pressure drop in the external tubing.

<table>
<thead>
<tr>
<th>Tubing type</th>
<th>Dead volume (cc)</th>
<th>Gas Volume (cc)</th>
<th>Maximum Pressure drop (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adsorption</td>
<td>Desorption</td>
<td>Adsorption</td>
</tr>
<tr>
<td>Feed side</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/4&quot; (with 1/16&quot; thermocouple)</td>
<td>2.570</td>
<td>Max. =110 Min. =12.19</td>
<td>213 x 10^-5</td>
</tr>
<tr>
<td>1/8&quot; (with 1/32&quot; thermocouple)</td>
<td>0.440</td>
<td>Max. =104.7 Min. =11.33</td>
<td>1.3</td>
</tr>
<tr>
<td>1/8&quot; (with out thermocouple)</td>
<td>0.470</td>
<td>Max. =4.45 Min. =0.57</td>
<td>145 x 10^-4</td>
</tr>
<tr>
<td>Product side</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/8&quot;</td>
<td>0.096</td>
<td></td>
<td>141 x 10^-6</td>
</tr>
<tr>
<td>1/4&quot;</td>
<td>0.543</td>
<td></td>
<td>137 x 10^-2</td>
</tr>
</tbody>
</table>

In the current study, several design alternatives were compared by changing the tubing size and by changing the location of various measuring and controlling devices. The results in Table 4.3 represent the important alternatives. At the product end, the optimum dead volume and pressure drop could be attained by using 1/8" tubing to connect the column end to the solenoid valves to control the flow. The other measuring devices such as oxygen and pressure sensors were attached to the column end fittings through a customized port connection shown in Figure 4.2. At the feed end, dead volume was high relative to the minimum gas volume during adsorption and desorption steps for 1/4" tubing with 1/16" thermocouple and pressure drop was very high for 1/8" tubing with 1/32" thermocouple. Both the dead volume and
pressure drop were optimized by choosing 1/8" tubing without thermocouple. The thermocouple was placed at the middle of the column through a side tapping, as shown in Figure 4.3.

Having discussed the critical issues governing the choice of sensors, adsorbent size and column dimensions for the experimental studies in the last several sections, the set-up design and procedures for equilibrium, pressure drop and breakthrough experiments are discussed next.

4.3 Unary Adsorption Equilibrium Experiments

The single component adsorption isotherms of N\textsubscript{2} and O\textsubscript{2} were measured at two different temperatures using a constant volume apparatus for both oxygen and nitrogen on a binderless 5A zeolite adsorbent sample. Sample preparation has been detailed in section 4.2.1.

The constant volume apparatus used in this study is schematically shown in Figure 4.5. It required 1 g of adsorbent and was constructed in an earlier study on equilibrium isotherm measurements on new materials. The apparatus basically consisted of two sections, namely test and dose sides, which were connected by a manual valve, V\textsubscript{2}. The dose side was connected to the feed line through the manual valve, V\textsubscript{1}, and the test side was connected to discharge and vacuum lines through two manual valves, V\textsubscript{3} and V\textsubscript{4}, respectively. The discharge line was used to relieve the pressure and discharge the gas to the fume hood after completing the isotherm measurements. The vacuum line was connected to a vacuum pump (ABM, Model No: 4EKG63CX-4), which facilitated adsorbent regeneration and allowed measurements in the sub-atmospheric pressure range. The adsorbent was placed in the test chamber using very fine nets placed at the entrance and exit of the test chamber to retain the
adsorbent particles. An absolute pressure transducer (MKS, Model PMP131-A2201R4S, range: 0-1000 psi) was connected to the dose side to measure the initial and final system pressures, which were essential to carry out the mass balance and estimate the equilibrium adsorbed amount. A temperature sensor (thermocouple) was connected to the test chamber to measure the temperature inside the test chamber during isotherm measurement and regeneration. The quick connectors were useful to attach or detach the test chamber from the apparatus while adsorbent loading and regeneration. A digital pressure calibrator (Fluke, Model 700P07) was used to periodically calibrate the pressure transmitters in order to ensure accuracy of the measured pressure signals. A multimeter (Hewlett Packard, Model 34401A) that could read up to 0.1 mV accurately read the voltage signal from the absolute pressure transducer. During the experimental runs, the dose and test chambers were completely immersed in a constant temperature water bath, which was maintained at the desired temperature by using a heavy duty thermostat (Lauda RK8 KS). The leak checking of the device was performed by pressurizing the entire system to the highest desirable pressure. In order to ensure that there was no leak in the system, the system pressure was monitored for 24 hours and a constant pressure reading over this period confirmed that the system was perfectly leak-proof.

The volumes of the dose and test sections including the associated tubings were carefully measured and these were be 32.18 ± 0.01 cc and 8.37 ± 0.01 cc, respectively. This was established by taking average of 5 repeat measurements, which was important because the calculation of equilibrium data from constant volume experiments depended on the measured system volume. About 0.6 g of the binderless 5A zeolite pellets was used in the adsorption experiments. The adsorbent weight was taken after regeneration. The density of the adsorbent materials was measured using
the specific gravity bottle method and carbon tetrachloride (CCl₄) as the solvent, which has bigger molecular diameter (6.65 Å) and could not enter in the 5 Å pores of the adsorbent crystals. The solvent, however, entered the inter-crystalline macrospores. The obtained density gave the crystal density, not the pellet density.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>V 1 to 4</td>
<td>Manual valves</td>
</tr>
<tr>
<td>PT</td>
<td>Pressure transducer</td>
</tr>
<tr>
<td>PG</td>
<td>Pressure gauge</td>
</tr>
<tr>
<td>TS</td>
<td>Temperature sensor</td>
</tr>
<tr>
<td>QC</td>
<td>Quick connectors</td>
</tr>
<tr>
<td>DC</td>
<td>Dose chamber</td>
</tr>
<tr>
<td>TC</td>
<td>Test chamber</td>
</tr>
</tbody>
</table>

Figure 4.5: Experimental set-up for measuring single component adsorption equilibrium isotherms of O₂ and N₂ on binderless 5Å zeolite as an adsorbent.

4.3.1 Adsorbent regeneration

The adsorbent placed inside the test chamber was regenerated in-situ using a local heater attached to the body of the chamber. The temperature was gradually increased at a rate of 20°C/15 min using a temperature controller attached to the
heater until it reached the desired set point of 350 °C. The gradual increase of temperature was important to prevent the damage of adsorbent and device from a sudden thermal shock to the system. The regeneration was carried out over a period of 24 h. During regeneration, vacuum was continuously pulled with intermediate flushing of the system with helium gas for 5 min after every 4 h to increase the effectiveness of regeneration.

4.3.2 Experimental procedure

The system was cooled down to room temperature after regeneration and the vacuum line was disconnected by closing the valve V4. It was brought to the desired constant experimental temperature by allowing it to attain thermal equilibrium with the constant temperature water bath, which also gave a steady voltage output signal from the absolute pressure transducer (PT). The pressure and temperature of the system were noted and the valve V2 was closed to isolate the test side from the dose side. Let this system pressure and temperature be denoted by 

\[ \left( \begin{array}{c} P_d^n(j-1) \\ T_s \end{array} \right) \]

and \( T_s \), respectively. The subscripts \( d \) and \( t \) represent dose side and test side, respectively, and the superscript \( \infty \) denotes complete equilibrium. \( j \) in the argument is the pressure step indicator and is introduced to develop a general data processing algorithm which is discussed in the next section.

A known amount of adsorbate gas was then added to the dose side through the manual valve V1 and then it was allowed some time to attain the system temperature. Now, let this new pressure of the dose side be denoted by \( P_d^n(j) \) when the temperature stabilized to \( T_s \). The valve V2 was opened to introduce a step change in pressure on the test side by allowing the gas in the dose side to flow into the test side. The system
was allowed to reach a new equilibrium pressure. Let the new equilibrium system pressure be $P^e \left[ P^e_0 (j) = P^e_t (j) \right]$. The temperature inside the test chamber was noted to be constant, as read from the thermocouple, $T_s$. The valve $V_2$ was then closed again after recording the new equilibrium system pressure to prepare for introducing the next step change in pressure on the test side, and the entire procedure described above was repeated. This was continued until equilibrium system pressure reached the target upper level, which was about 10 bar in the present study. Depending on the particular adsorbent-adsorbate under consideration and the experimental system temperature used, the time required to approach towards equilibrium varied. Therefore, sufficiently long time was allowed to ensure equilibrium. For these measurements, the step size was limited by the desired number of data points in the experimental pressure range of the isotherm. It was decided to limit the step size to ~0.5 bar.

### 4.3.3 Processing of equilibrium data

The amount adsorbed in each step was estimated by performing a mass balance between the test and dose sides. Assuming the ideal gas law was valid in the pressure range of interest for the adsorbate gases, the following mass balance was applicable for the $j^{th}$ equilibrium step:

$$
\frac{P_0^d (j) - P^e (j)}{R_g T_s} \cdot V_d = \left\{ P^e (j) - P^e (j-1) \right\} \cdot \frac{V_t - V_a}{R_g T_s} + \Delta n (j) \quad (4.1)
$$

$$
\Delta n (j) = n (j) - n (j-1); \quad \text{where } j = 1, 2, 3, \ldots \quad (4.2)
$$

$V_d$, $V_t$ and $V_a$ were volumes of the dose side, test side and adsorbent particles, respectively. $\Delta n (j)$ was the number of moles adsorbed by the adsorbent particles as a
result of pressure perturbation in step \( j \). \( n(j) \) was the total number of moles adsorbed up to the \( j^{th} \) step and was in equilibrium with the adsorbate at pressure \( P_d^e(j) = P_i^e(j) \). The adsorbent volume \( V_a \) calculated from the measured mass and calculated density was, in fact, the external contour volume of the particles (i.e., pore volume was included). \( q_p \) represents the capacity of the adsorbent particles in the solid phase corresponding to the gas pressure at equilibrium and it was calculated from the following equation: \( q_p^* = n(j) / V_a \). Representative N\(_2\) adsorption isotherm measured at 25°C on binderless 5A zeolite, plotted as \( q_p \) vs. \( p \), is shown in Figure 4.6. This was repeated twice under similar conditions. The results from the repeat measurements are also included in the figure, which confirm the reproducibility of the experimental results. Complete measured equilibrium data have been presented in chapter 5.

![Graph of solid loading vs. pressure for two runs](image.png)

**Figure 4.6:** Experimental equilibrium adsorption isotherms of N\(_2\) at 25°C reproduced in two different runs for the same pressure range on binderless 5A zeolite adsorbent.
4.4 Experimental Design and Procedure for Pressure Drop and Breakthrough Measurements

4.4.1 Experimental set-up

The schematic of the experimental set-up is shown in Figure 4.7. It consisted of a jacketed adsorption column (JAC) packed with binderless 5A zeolite particles of the chosen size range. The controllers, sensors and valves at the two ends of the adsorption column were mounted on two panels. The experimental set-up had the flexibility to change the adsorber lengths in between these mounting panels. The dimensions of the column used are given in section 4.2.2. The feed flow to the adsorber was guided by a solenoid valve (SV2, SV1 or SV5, Asco, model no: 10600243) and the flow rate was measured using a mass flow meter (MFC/MFM1, Alicat, model: M-100SLPM-D/10M). MFC/MFM indicates that it was actually a mass flow controller which performed the function of a mass flow meter when operated on fully open mode. The feed and product end pressures were measured using the pressure sensors (PS1 and PS2, Honeywell, model no: 40PC 150G3A) connected directly to the column ends through a customized arrangement discussed earlier and shown in Figure 4.2. Similarly, the product flow was regulated and measured by using a solenoid valve (SV3) and a mass flow meter (MFC/MFM3), respectively. The oxygen concentration was measured using oxygen analyzer probes (OA1 and OA2, Ocean optics, Spectrometer model: USB4000) placed at the two ends of the column. In case of PPSA experiments, the desorbing gas flow was guided by using a solenoid valve (SV4) and measured on a mass flow meter (MFM2). A 1/16" thermocouple was used to measure the temperature at the middle of the column through a side probe.
Instruments hardware and a dedicated personal computer. NI 9215 module was used to directly read the signals from the flow meters and pressure sensors, and another module (NI9211) was used to measure the thermocouple signals. The solenoid valves...
Chapter 4. Column Dynamic: Experimental Design and Procedures

were controlled using a National Instruments digital output module (NI 9417, see Table 4.2). The entire data-acquisition/control system was implemented in Lab-View software. All the mass flow meters used in the experimental set-up directly displayed the local gas pressure and temperature along with the flow rate on the body of the meter, which was helpful for adjusting the inlet pressure in BTC experiments. As shown in the schematic diagram, the experimental set-up had additional provisions for the feed to by-pass the column by opening the solenoid valve SV6. The column pressure was regulated using the back pressure regulator (BPR) in the product line. All the mass flow meters and controller were calibrated before conducting the experiments.

4.4.2 Pressure drop characteristics of adsorption column

The use of small-size adsorbent particles in a PPSA process improves the mass transfer rate. However, the pressure drop along the column also increases with decreasing adsorbent particle size. In spite of the wide applications of porous media flow (analogous to flow through the voids in a packed bed) in chemical engineering, civil engineering and hydrology, the literature available on pressure drop along a column packed with very small (micron) size particles is very limited. Therefore, pressure drop experiments were conducted to study the pressure drop characteristics of the adsorption column and examine the validity of Darcy and Ergun equations for flow through packed beds in the particle size of interest in this study.

The pressure drop experiments were conducted in the experimental setup described in section 4.4.1 and schematically shown in Figure 4.7. The jacketed column used in this study and described in section 4.2.2 was carefully packed with the adsorbent particles of the desired size range. The column was periodically tapped
while filling to ensure uniform distribution of adsorbent particles in the column. Two very fine nets (500 openings per sq. in) were placed at the two ends of the adsorber in order to retain fine adsorbent particles in the adsorption column. The oxygen sensor ports were blocked using blind nuts during pressure drop measurements. To collect the voltage signals from the sensors, all of them were connected to a multimeter (Hewlett Packard, Model 34401A) which could read up to 0.1 mV accurately, in addition to the data acquisition system discussed in section 4.4.1. The solenoid valves SV1, SV2 and SV3 were opened to allow the gas to flow through the column and the remaining solenoid valves were kept closed throughout the pressure drop measurements. A constant flow rate of helium, a non-adsorbing gas, was set on the inlet mass flow controller, MFC/MFM1. It took some time for the pressure profile to fully develop and reach steady state along the column when the exit mass flow meter (MFM) read the same flow rate set on inlet mass flow controller (MFC/MFM1). Another indication was stable output voltage readings from the inlet and exit pressure sensors located at the column ends. The steady state inlet and exit pressures gave the pressure drop along the column at a given feed flow rate. The above mentioned procedure was repeated to measure the pressure drop at several other flow rates. The same experimental procedure was repeated for four more different adsorbent particle sizes in the same adsorption column to study the effect of column \( D_c \) to adsorbent particle \( d_p \) diameter ratio on pressure drop per unit length. The pressure drop measurements were also carried out with 75-90 µm spherical glass beads. In all these experiments, the exit column pressure was atmospheric. Representative results from the pressure drop experiments are shown in Figure 4.8 together with repeat runs confirming reproducibility. The results from the pressure drop experiments have been analyzed in chapter 5.
4.4.3 Dynamic column breakthrough experiments

Dynamic column breakthrough experiments are useful for verifying equilibrium data obtained from volumetric experiments conducted with a few particles. They are also useful for establishing the transport mechanism. Its similarity with the real cyclic adsorption process experiments further provides preliminary data for testing the basic assumptions of the process model. In this study, the single component and binary breakthrough experiments were conducted at different inlet pressures by introducing a step change in mole fraction of the adsorbable component (or one of the two adsorbable components in case of binary) in the feed to the column inlet.

The same experimental set-up detailed in section 4.4.1 and also used for pressure drop measurements discussed in section 4.4.2 was used in breakthrough experiments. The column described in section 4.2.2 was packed with 65-73 µm
binderless 5A zeolite adsorbent particles. In these experiments, the inlet mass flow controller (MFC/MFM1) was used as a mass flow meter by fixing the set point to the maximum value. The wall temperature was maintained at $23 \pm 2^\circ C$ by circulating water in the jacket at a constant flow rate of 200 ml/min. There was a thermocouple at the middle of the column to monitor the change in bed temperature due to adsorption/desorption during experiments. A point oxygen sensor with zero dead volume was chosen to continuously monitor the entrance and exit oxygen concentrations during both adsorption and desorption breakthrough experiments. The oxygen sensor was calibrated using 5 different known samples of oxygen and nitrogen mixture. Although the dead volumes were kept as small as possible in the experimental design, the mixing of fresh gas with residual gas in the inlet dead volume during breakthrough measurements still led to some dispersion of feed gas composition entering the adsorption column. Therefore, the effect of dead volume at the entrance of the column had to be properly accounted without which it was very difficult to analyze the measured breakthrough responses which were measured at the column exit. The dead volume at the exit of the column was very small since the point oxygen sensor probe was located exactly at the exit of the column. Therefore, the effect of mixing in the dead volume at the exit of the column was not significant on breakthrough measurements. The detailed characterization of the inlet dead volume and other experimental details are discussed in the following subsections.

4.4.3.1 Experimental procedure

The adsorbent packed jacketed column was regenerated at 350°C for 24 h in an oven with continuous application of vacuum to the column. All the ports for the sensors were blocked with blind nuts. During regeneration, the column was flushed
with helium gas after every 4 h for about 10 min to increase the effectiveness of regeneration. After regeneration, the adsorption column was isolated using blind nuts at the column ends to prevent moisture adsorption from the surroundings and it was cooled to room temperature. The column was then connected to the experimental rig. All the sensor probes were put in place and water circulation through the jacket was commenced. The sequence of opening /closing of solenoid valves for different steps during breakthrough experiments are shown in Table 4.4. For the single component breakthrough experimental runs, a 50:50 mixture of O₂-He was used as feed gas while pure He was used to initialize the bed or desorb O₂. For the binary runs, air was used alternately with pure O₂ or N₂ to investigate interaction. All breakthrough experiments had three steps: initialization, adsorption and desorption. In first step, the solenoid valves SV1, SV2 and SV3 were opened to a constant pressure pure helium gas supply source. The inlet pressure was maintained by a pressure regulator on the gas cylinder and the exit was open to the atmosphere. Before opening the exit to the atmosphere, the device was thoroughly examined for any leak. After establishing a uniform clean bed initial condition with helium, a step change in feed gas composition was introduced at the inlet of the column by closing SV1 and opening SV5 connected to the gas cylinder containing a 50:50 mixture of O₂ and He. The pressure on both pure He and O₂-He mixture gas cylinders were adjusted to minimize pressure fluctuation at the inlet of column after introducing step change. Otherwise, the difference in pressure at the inlet introduced additional dynamics in the breakthrough curve, resulting in deviation from the constant inlet pressure assumption in the model. After O₂ breakthrough was complete, the adsorbed O₂ in the bed was desorbed by purging with pure helium gas, which was implemented by closing SV5 and opening SV1. Complete equilibrium of the column with the feed gas in each step was confirmed
from the readings of exit oxygen sensor and mass flow meter, which showed same readings as that at the inlet. During the experiments, the voltage output signals from the inlet and outlet pressure and flow sensors, thermocouple at the middle of the column and exit oxygen detector were continuously recorded in the data logging system described earlier.

For binary experiments, the column was initially equilibrated with pure nitrogen or oxygen at a desired inlet column pressure in the first step. The column thus saturated with either pure nitrogen or oxygen was then purged with air until readings of oxygen analyzer and exit mass flow rate became constant indicating complete saturation with air by displacing excess oxygen or nitrogen depending on the initialization. Finally in the third step, the column saturated with air was flushed with either pure O₂ or N₂ until breakthrough of the pure feed was complete.

<table>
<thead>
<tr>
<th>Solenoid valve</th>
<th>Saturation</th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>SV1</td>
<td>√</td>
<td>X</td>
<td>√</td>
</tr>
<tr>
<td>SV2</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>SV3</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>SV4</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SV5</td>
<td>X</td>
<td>√</td>
<td>X</td>
</tr>
<tr>
<td>SV6</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

√: indicates open position  
X: indicates closed position

In both single component and mixture breakthrough experiments, the concentration breakthrough at the end of the column was much faster compared to the time needed for the temperature at the middle of the column to return to the baseline, even for a small temperature rise. Although ideally the concentration breakthrough
should not be completed until the entire bed temperature return to the baseline, the
detectability of a small concentration change in the tailing part of the breakthrough
curve depends on the detector sensitivity. To be doubly sure, on an average each step
in breakthrough experiment was conduct for 180 s to complete heat dissipation and
equilibrium.

In breakthrough experiments, the inlet column pressure varied for a very short
time during the early part after introducing a step change at the column entrance
because of the difference in adsorption properties of gases in feed mixture on 5A
zeolite, even though the delivery pressures on gas cylinder were adjusted as much as
possible to attain the same inlet column pressure. Furthermore, it also led to some
oscillation of inlet feed gas velocity.

4.4.3.2 Experimental data analysis

Estimation of single component equilibrium data from breakthrough
experiments has been discussed in detail by Malek and Farooq (1996). In case of
single component measurements, the equilibrium data obtained from breakthrough
experiments was compared with the data from independent equilibrium measurements
conducted using constant volume apparatus. The equilibrium amount adsorbed was
calculated from breakthrough experiments from the following mass balance across the
adsorption column.

Mass balance in case of adsorption breakthrough measurement

\[
\int_{0}^{t_{\text{ads}}} \left( F_{\text{in}}(t) - F_{\text{out}}(t) \frac{x_{\text{out}}(t)}{x_{\text{in}}} \right) dt = \frac{aL\varepsilon RT_{\text{a}}}{P_{\text{a}}x_{\text{in}}} \left[ \frac{P_{\text{avg}}(t) x_{\text{in}}}{RT_{c}} + \left( \frac{1 - \varepsilon}{\varepsilon} \right) q \right]
\]  

(4.3)

Mass balance in case of desorption breakthrough measurement

\[
\int_{0}^{t_{\text{des}}} \left( F_{\text{in}}(t) - F_{\text{out}}(t) \frac{x_{\text{out}}(t)}{x_{\text{in}}} \right) dt = \frac{aL\varepsilon RT_{\text{a}}}{P_{\text{a}}x_{\text{in}}} \left[ \frac{P_{\text{avg}}(t) x_{\text{in}}}{RT_{c}} + \left( \frac{1 - \varepsilon}{\varepsilon} \right) q \right]
\]
\( \int_{0}^{t_{\text{des}}} F_{\text{out}}(t) \left( \frac{x_{\text{out}}(t)}{x_{\text{in}}} \right) \, dt = \frac{a L \varepsilon R T_{a}}{P_{a} x_{\text{in}}} \left[ P_{\text{avg}}(t) x_{\text{in}} + \left( \frac{1 - \varepsilon}{\varepsilon} \right) q \right] \)  

(4.4)

Here \( P_{\text{avg}}(t) = \left( \frac{P_{\text{in}}(t) + P_{\text{out}}}{2} \right) \), \( F_{\text{in}}(t) \) and \( F_{\text{out}}(t) \) are the inlet and out gas mass flow rates in cc/s. Here a linear pressure profile was assumed in the bed while calculating \( P_{\text{avg}}(t) \). \( P_{\text{in}}(t) \) and \( P_{\text{out}} \) are the inlet and exit pressure of the column. \( x_{\text{in}} \) and \( x_{\text{out}}(t) \) represent the inlet and exit oxygen mole fractions measured during the breakthrough runs; \( P_{a} \) (bar) and \( T_{a} \) (K) are the ambient pressure and temperature; \( a \) (cm\(^2\)) is adsorption column area, \( L \) (cm) is length of the column, \( \varepsilon \) is the bed voidage and \( R \) (bar cc mol\(^{-1}\)K\(^{-1}\)) is gas constant. In the above equations (4.3) and (4.4), the only unknown was \( q \) (mol/cc), which was calculated for each run.

### 4.4.3.3 Blank experiments for dead volume characterization

To obtain the true response of the column for a step change in feed gas composition, the experimental breakthrough curves must be corrected with blank experiments to account for the mixing in the inlet dead volume. Otherwise, it will not be possible to accurately estimate the kinetics and equilibrium information from the breakthrough results.

Even though the dead volume was minimum, the dispersion of feed gas entering the column due to mixing in inlet dead volume affected the residence time and dispersion of the column breakthrough response.

In this study, the dispersion due to mixing in the inlet dead volume was captured by measuring the feed gas mole fraction entering the column during breakthrough measurements using the oxygen sensor (OA1) shown in Figure 4.7,
which was exactly located at the entrance of the column i.e., just at the end of the dead volume. The blank response was modeled by adopting two different methods namely, tanks in series model (TIS) and dispersion model (DM). Inlet blank experimental data was also directly used, which was referred in short as DIB. These three approaches to account for the dead volume in breakthrough experiments are compared in details in chapter 5.

4.5 Sensor Responses

Response time is the time required for the sensor to attain 100% of the step change introduced to the signal being measured. The response times of pressure and oxygen sensors complied in Table 4.2 based on manufacturers' brochure were experimentally verified using arrangements shown in Figure 4.9. The solenoid valves, interfaced with data acquisition system and Labview, were used to introduce a step change in pressure and concentration. The measured responses included the delay, if any, in opening/closing of the solenoid valves.

![Figure 4.9: Schematic diagram used for calibration of (a) pressure sensor and (b) oxygen sensor.](image)

The pressure sensor response was measured by introducing a step change in pressure from a low pressure \( P_L \) to a high pressure \( P_H \) by closing the solenoid valves.
valve connected after the sensor as shown in Figure 4.9 (a). The normalized sensor response is plotted as a function of time in Figure 4.10. The response time of pressure sensor along with solenoid valve for a step change in pressure was approximately 130 ms, as may be seen from Figure 4.10. In order to study the oxygen sensor response, the sensor was connected after the solenoid valves, as shown in Figure 4.9 (b). A step change in oxygen concentration was introduced by simultaneously closing the solenoid valve, SV1, connected to the helium gas line and opening the solenoid valve, SV2, connected to 50% O₂-He gas mixture line. The responses of the oxygen sensor for a step change from pure He to 50:50 O₂-He mixture and the reverse are shown in Figure 4.11. The response time is ~1 s to reach 90% and 3 s to reach 100% of the step change in concentration. Since the oxygen sensor response had a spread as shown Figure 4.11, the combined response of the column and inlet blank response had the cumulative spread due to sluggishness in oxygen sensor response together with the actual spread due to adsorption column and/or inlet dead volume. In order to obtain the true response of column and blank, the sensor response must be subtracted from cumulative response of column and blank response, respectively.

Figure 4.10: Response of pressure sensor to a step change in pressure introduced using solenoid valves.
Since, the oxygen sensor response is the same for different flow rates and concentrations, a systematic point by point correction procedure was implemented in MATLAB to obtain the corrected response of column and/or blank. For example, the point by point correction of the sensor response from the cumulative BTC experimental data is shown in Figure 4.12 for breakthrough of 50% O₂-He mixture in a column initial saturated with He at 30 psi.

Figure 4.11: Response of oxygen sensor for a step change in concentration introduced using solenoid valves.

Figure 4.12: Point by point subtraction of oxygen sensor response from cumulative breakthrough and blank responses.
4.6 Chapter Conclusion

Column design and selection of sensors and controlling devices for measuring the process performance were guided by the detailed process simulation results and critical issues in minimizing the dead volume and pressure drop at the entrance and exit of the column. The unary adsorption isotherms of O₂ and N₂ on 5A zeolite measured using a constant volume apparatus available in the laboratory were reproducible. A multipurpose experimental set-up with minimum unavoidable dead volume and pressure drop in the piping at the entrance and exit of the column was designed and fabricated for pressure drop, breakthrough and PPSA experiments as part of this study. A detailed point by point correction procedure for subtracting the sensor response from blank response at the column inlet and breakthrough response at the exit of column is presented. The experimental results are analyzed in the next chapter.
Chapter 5

COLUMN DYNAMICS: EXPERIMENTAL RESULTS, MODELING AND SIMULATIONS

5.1 Overview of the Chapter

The experimental design and procedures for measuring equilibrium, pressure drop in a packed column and dynamic column breakthrough response of O\textsubscript{2}, N\textsubscript{2} and their mixture in 5A zeolite were presented in chapter 4. In this chapter, the experimental results are analyzed and modeled to explain the observed trends of the equilibrium data, pressure drop characteristics in the particle size range smaller than the range studied in the open literature, and corresponding dynamic column breakthrough behavior.

5.2 Unary Adsorption Equilibrium Experimental Results

Single component adsorption isotherm data is very useful for process modeling and simulation of any adsorption based gas separation process. Reliable prediction of multi-component equilibrium behavior using single component isotherm information is important for process simulation and design. This reduces the burden of tediousness and time-consuming multi-component adsorption measurements. Single component adsorption isotherms of nitrogen and oxygen on binderless 5A zeolite measured at different temperatures in this study are shown in Figure 5.1. The Langmuir isotherm model predictions are also shown in the same figure.
Chapter 5. Column Dynamics: Experimental Results, Modeling and Simulation

The Langmuir isotherm is the simplest and most frequently used form of theoretical adsorption equilibrium isotherm model and its multi-component extension is very easy to implement in process modeling and simulation. The assumptions behind the Langmuir isotherm are as follows:

1. Each adsorption site can accommodate only one adsorbate molecule.
2. All the adsorption sites are energetically homogeneous.
3. There is no interaction between the molecules adsorbed on adjacent sites

Considering the above assumptions, the general form of Langmuir model is:

\[
\frac{q}{q_s} = \frac{bc}{1 + bc}; \quad b = b_o e^{-\Delta U/RT}
\]  

(5.1)

In the above equation, \(q_s\) is the saturation capacity, \(q\) is solid loading in equilibrium with gas phase concentration \(c\) and \(b\) is the Langmuir constant, which is a function of temperature \(T\) and internal change of energy \(\Delta U\) due to adsorption.

![Graph showing adsorption equilibrium isotherms of nitrogen and oxygen on binderless 5A zeolite at 288.15 K and 298.15 K. The experimental data was fitted with the Langmuir isotherm model.](image)

**Figure 5.1:** Adsorption equilibrium isotherms of nitrogen and oxygen on binderless 5A zeolite at 288.15 K and 298.15 K. The experimental data was fitted with the Langmuir isotherm model.
To predict the mixture adsorption equilibrium isotherms from single component data, the primary thermodynamic requirement [Sircar and Rao (1999)] for an extended Langmuir isotherm is that the both adsorbate molecules must have the same saturation capacity. This requirement is a reasonable approximation in case of molecules like oxygen and nitrogen that are very close in size. Therefore, the model parameters for both gases were simultaneously fitted by forcing to a common saturation capacity \(q_s\) and the results are summarized in Table 5.1. Equations 3.7 and 3.8 in chapter 3 are the extended Langmuir isotherms for a binary mixture.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>(q_s) (mol/cc)</th>
<th>(b_o) (cc/mol)</th>
<th>(\Delta U) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N(_2))</td>
<td>8.03 x10(^{-3})</td>
<td>0.52</td>
<td>4.88</td>
</tr>
<tr>
<td>Oxygen (O(_2))</td>
<td>13.47</td>
<td></td>
<td>2.21</td>
</tr>
</tbody>
</table>

### Table 5.1: Langmuir equilibrium isotherm parameters for nitrogen and oxygen on binderless 5A zeolite adsorbent.

#### 5.3 Modeling of Pressure Drop along the Adsorption Column

Since the pressure drop along the column affects the gas flow through the column, an appropriate model to predict the pressure drop characteristics is important for accurate estimate of the PPSA process performance. The experiments described in section 4.4.2 were carried out to examine the validity of Darcy's law and Ergun equation for modeling the pressure drop characteristic of the adsorption column.

Darcy's law and Ergun equation have been widely used in many areas, namely chemical engineering, civil engineering, geology and hydrology, to predict the flow through porous media. The underlying assumptions behind the Darcy's law and Ergun equation are as follows:
(i) Bed porosity is uniform along the bed length and cross sectional area.

(ii) Bed permeability is constant throughout the bed.

(iii) Column packed with uniform sized spherical particles.

(iv) No channeling or bypass of flowing fluid through the packed column.

(v) Pressure drop along the column is linear.

The general form of Darcy's law is as follows, which was presented in terms of interstitial velocity ($u_z$) in Chapter 3.

\[
\frac{\Delta P}{L} = \frac{\mu}{k_p} u_z; \quad k_p = \frac{d_p^2}{k_1 \left(1 - \frac{\varepsilon^2}{150}\right)}; \quad k_1 = 150
\]  

(5.2)

where $\Delta P / L$ is pressure drop along the adsorption column of length, $L$, $u_z (= \varepsilon u_z)$ is superficial gas velocity, $\mu$ is gas viscosity and $k_p$ is bed permeability, which is a function of adsorbent particle size ($d_p$), bed voidage ($\varepsilon$) and Darcy's constant ($k_1$).

Darcy's law relates the pressure drop along the column with flow rate and bed permeability. Since many of the above assumptions may not be valid for flow through porous media under all experimental conditions, some publications [Raichura (1999), Macdonald et al., (1979)] suggest that the empirical Darcy's constant ($k_1 = 150$), which depends on column diameter to particle diameter ratio ($R_u = D_c / d_p$), must be calibrated with pressure drop experiments conducted under actual conditions. Darcy’s law is valid only for laminar flow conditions, whereas the Ergun equation also considers the transition and turbulent flow conditions. Hence, the Ergun equation is useful to predict the flow through porous media under high flow rates.

The general form of Ergun equation is as follows:

\[
\frac{\Delta P}{L} = \frac{\mu}{k_p} u + \phi u^2; \quad \phi = \frac{1.75 \rho}{d_p} \left(\frac{1 - \varepsilon}{\varepsilon^3}\right)
\]  

(5.3)
where $\rho$ is gas density. The first term on right hand side represents the Darcy's law and is significant under laminar flow conditions and second term accounts for the pressure drop under turbulent flow conditions. Both terms are important under the transition flow conditions. Since, the average adsorbent particle size used in breakthrough experiments and PPSA experiments was 69 µm (size range: 65-73 µm) and also the pressure drops along the column in all the experiments were less than 4 bar, the first term, which is a function of particle size, is more significant than the second term. After a detailed comparison of Darcy's law and Ergun equation against experimental pressure drop results, the simple Darcy's law was found adequate and chosen for modeling pressure drop characteristic of the adsorption column and used to predict the flow behavior in breakthrough and PPSA process simulations. The results for only Darcy's law are discussed below.

### 5.3.1 Estimation of Darcy's constant

$k_1$ in Darcy's law was obtained by minimizing the error between the experimentally measured pressure drop along the column and estimated pressure drop from Darcy's model (Equation 5.2) in two different ways. The root mean square deviation (RMSD) was defined by the following equation:

$$
RMSD = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^{n} \left( \frac{\Delta P}{L} \right)_{\text{exp}} - \left( \frac{\Delta P}{L} \right)_{\text{model}}^2}
$$

In the above equation, $\left( \frac{\Delta P}{L} \right)_{\text{exp}}$ was the experimentally measured pressure drop along the column, $\left( \frac{\Delta P}{L} \right)_{\text{model}}$ was the estimated pressure drop along the column.
using Darcy's law and ‘n’ was number of data points. The estimation of Darcy's constant using Method 1 and Method 2 detailed below.

**Method 1:** In this method, the empirical Darcy's constant, $k_1$, was obtained by minimizing the RMSD between the experimental pressure drop measured as function of superficial inlet velocity and model estimate according to Equation 5.2. In this approach, the change in interstitial velocity along the column length was not taken into account in the pressure drop calculation. The main assumption was that the pressure drop along the column was linear from entrance to exit of the column. This may not be valid in a very long column or a column packed with small-size packing material and having high pressure drop.

**Method 2:** To precisely estimate the Darcy's constant for flow through a column packed with very small-size zeolite adsorbent particles, a detailed pressure drop model was developed from differential total mass and momentum balance across the porous packed bed, together with the differential form of the Darcy's law applied locally along the column length.

The assumptions made to develop the pressure drop model are as follows.

1. The adsorbent particles are spherical, smooth and inert.
2. No adsorption of the flow media on the packing material.

The total mass balance across the column after attaining a steady state pressure drop along the column takes the following form:

$$\frac{\partial (cu_z)}{\partial z} = c \frac{\partial u_z}{\partial z} + u_z \frac{\partial c}{\partial z} = 0 \quad (5.5)$$

where $c$ is the total concentration of gas entering and leaving the column and $u_z (= u/\varepsilon)$ is interstitial gas velocity. The above equation is reduced to the following form upon substitution of ideal gas law.
The momentum balance equation for flow through packed column is given by the differential form of Darcy's law:

\[ \frac{\partial P}{\partial z} + u_x \frac{\partial P}{\partial z} = 0 \]  

(5.6)

In order to solve Equations 5.6 and 5.7, two boundary conditions are necessary, which were chosen as follows according to the experimental conditions:

Boundary conditions

\[ u_z = u_0 \quad \text{at} \quad z = 0 \]
\[ P = p_a \quad \text{at} \quad z = L \]  

(5.8)

The equations were solved in COMSOL Multiphysics together the optimization routine, Fminsearch, from MATLAB to find the Darcy's constant \( k_1 \) that minimized the RMSD between the experimentally measured and calculated pressure drops.

The best fit of the two methods to the experimental results obtained from a 10 cm long column packed with 63-75 µm binderless 5A zeolite adsorbent particles are shown in Figure 5.2, together with the corresponding optimum \( k_1 \) values. The two \( k_1 \) values were somewhat different and Method 2 gave a lower RMSD. Therefore, Method 2 was adopted for estimation of Darcy's constant in the rest of the study.

### 5.3.2 Effect of column to particle diameter ratio \( (R_d) \) on Darcy's constant

It should be noted that the optimum \( k_1 \) value from either method reported in the previous section is much higher than 150. In order to further understand these results, the experiments were performed by varying the column to particle diameter.
Chapter 5. Column Dynamics: Experimental Results, Modeling and Simulation

ratio \( (R_d) \).

![Plot of pressure drop along the column as a function of superficial gas velocity. The column was packed with binderless 5A zeolite adsorbent particles. RMSD (Method 1) = 0.239 and RMSD (Method 2) = 0.0271.](image)

**Figure 5.2:** Plot of pressure drop along the column as a function of superficial gas velocity. The column was packed with binderless 5A zeolite adsorbent particles. RMSD (Method 1) = 0.239 and RMSD (Method 2) = 0.0271.

The optimum Darcy's constant \( (k_f) \) values obtained in these experiments along with the data available in the literature are plotted as a function of \( R_d \) in Figure 5.3(a). It should be noted that the literature data are for non-adsorbing particles. The Darcy's constant was approximately 150 at \( R_d \approx 24 \) and further increase or decrease of \( R_d \) resulted in an increase of the Darcy's constant in case of the adsorbent particles. The wall effect becomes significant as the column to particle diameter decreases below 24 and it results in increase of bed voidage near the column wall. As a consequence, it causes channeling towards the column wall, which leads to an increase in pressure drop due to longer flow path from entry to exit thus increasing Darcy's constant above 150. The Darcy's constants obtained from experiments in this study in the region \( R_d < 24 \) were close to the data available in the literature, as shown
in Figure 5.4 (a). The data for $R_d > 24$, for crushed zeolite particles <500 µm in size, also showed an increase in $k_i$. In this region, there is no available information in the literature. In the literature, it has been predicted that the Darcy's constant will remain at 150 if column to particle diameter ratio is increased beyond 24. However, the Darcy's constant increased up to 4136.2 for further increase of column to particle diameter ratio in the present study. As already mentioned, the data for $R_d > 24$ represents decreasing particle size without changing the column diameter. The reason for increase in Darcy's constant is most likely due to the very small charged zeolite adsorbent particles that led to clustering and therefore the formation of zones with different bed voidage and permeability within the column. This resulted in variation of bed resistance to gas flow across the column, thus increasing the length of the flow path from inlet to exit. Furthermore, the surface roughness of ground zeolite particles (see Figure 4.1) may also have contributed to increased pressure drop. In Figure 5.3(b), it is shown that a minimum was observed in bed voidage ($\varepsilon$) with particle size. The bed voidage increased significantly for very small particles which indirectly support the possibility of clustering.

5.3.3 Pressure drop across a column packed with 75-90 µm size spherical glass beads

To further verify if the surface roughness of the crushed zeolite particles and their charged nature leading to clustering might have caused the significant increase in pressure drop along the column for $R_d > 24$, pressure drop experiments were performed with a column of same diameter and length, but packed with inert spherical glass beads in the size range 75-90 µm, which was close to the smallest size of
crushed 5A zeolite particles (63-75 µm). The bed voidage for glass beads was 0.346 compared to 0.556 for the zeolite particles. The best-fit Darcy's constant, as may be seen from Figure 5.4, was 124.77, which is close to 150.

Figure 5.3: Effect of column to particle diameter \(R_{dp}=D_c/d_p\) ratio on (a) Darcy’s law constant and, (b) bed voidage in a 0.5 in diameter column and packed with zeolite adsorbent particles ranging from 69 µm to 3.6mm in diameter.

Therefore, the indirect evidence seem to suggest that the surface roughness and clustering of small zeolite adsorbent particles obtained by crushing bigger
binderless particles led to the increase of Darcy's constant beyond 150 for size <500 μm.

![Figure 5.4: Plot of pressure drop along a column of length 10 cm and packed with 75-90 μm size spherical glass beads. Bed voidage is 0.35.](image)

5.4 Modeling of Dynamic Column Breakthrough (DCB) Experiments in an Adsorption Column Packed with 63-75 μm Size Binderless 5A Zeolite Adsorbent Particles

Breakthrough experiments are important to validate the models for simulation of any adsorptive gas separation process. A detailed mathematical model for breakthrough curves is also necessary to analyze the equilibrium and kinetics of gas transport in 5A zeolite adsorbent. The model equations and boundary conditions for the adsorption step discussed in section 3.2 have been used for isothermal modeling of the dynamic column breakthrough experiments. It was assumed that the molecular diffusion in the macropores controlled the rate of mass transfer, which was approximated using the linear driving force model (LDF). The additional equations to investigate the importance of heat effect are presented in section 5.4.2. The
breakthrough experiments, primarily divided into 3 steps, initialization, adsorption and desorption, have been detailed in section 4.4.3. The column inlet pressure was maintained at the desired level by saturating the column with one of the feed gases (initialization) used in the breakthrough experiments before introducing a step change in feed gas composition at the entrance of the column. The boundary conditions discussed in section 3.1 were adjusted, as appropriate, to closely capture what could be achieved experimentally. For example, in the breakthrough measurements, the experimentally measured concentration profiles at the inlet of the column after subtracting the sensor response still included the dispersion due to the mixing of residual gas with fresh gas in the remaining unavoidable dead volume at the entrance of the column. In order to predict the experimental breakthrough response at the column exit, it is important to consider the dispersion in the extra-column dead volume at the inlet in the simulation. The detailed procedure for correcting the blank response and cumulative response of the column from oxygen sensor response has been discussed in section 4.5.

5.4.1 Modeling of extra column effects at the entrance of the column

In the experimental design, the oxygen sensor probes, which were point sensors with zero internal dead volume, were located exactly at the entrance and exit of the column during measurements. Since the dead volume at the column exit was located after the point oxygen sensor, the dispersion in the exit dead volume did not affect the exit gas composition analysis. In contrast, the mixing in dead volume at the column entrance changed the feed gas composition entering the adsorber. Therefore, modeling of inlet blank experiments to estimate the dispersion in inlet dead volume was necessary. It was performed in the following three different ways:
(i) Tanks in series model (TIS)

(ii) Dispersion model (DM)

(iii) Direct use of inlet blank experimental data (DIB)

5.4.1.1 Tanks in series model (TIS)

Tank in series (TIS) model has been used in the literature to characterize the axial dispersion in flow systems [Levenspiel (2004)]; Rajendran et al., (2008) used this approach to model the experimental blank response at the exit of an adsorption column. It was a single parameter model where the number of tanks, equal in volume and connected in series, was obtained by matching the response of the TIS model with the experimental blank response. In this study, the tank volume was allowed to vary to better represent the blank response. This, of course, increased the number of fitting parameters. The schematic representation of the tanks in series model is shown in Figure 5.5. The number of tanks, optimum volume of each tank and sequence of tanks were obtained by minimizing the error between the response of TIS model and experimental blank response. The optimization routine, Fmincon, in MATLAB was used to obtain the optimum parameters to represent the experimental blank data.

The mass balance around tank 'i' is written as follows [Rajendran et al., (2008)].

\[
\frac{dC_i}{dt} = \frac{Q(t)}{V_i}(C_{i-1} - C_i)
\]

\[
= \frac{1}{\tau_i(t)}(C_{i-1} - C_i); \quad \tau_i(t) = \frac{Q(t)}{V_i}; \quad i = 1, 2, 3, \ldots \ldots \ldots \ldots \ldots \ldots N
\]

\[
V_{\text{dead}} = \sum_{i=1}^{N} V_i
\]

where \(V_{\text{dead}}\) is the total inlet dead volume, \(\tau_i\) is the residence time of tank \(i\) and \(Q(t)\)
is the average flow rate at the inlet pressure observed in blank experiments. In the above equation, the fitting parameters $V_i (i=1toN)$ and $N$ were obtained by matching the TIS model response with the blank experiments. The TIS model, with the best fit tank volumes ($V_i$) and number of tanks ($N$), was then used in breakthrough simulations to calculate the response from the dead volume that actually entered the column.

Figure 5.5: The schematic of (a) Tanks in series (TIS) model to estimate the dispersion in extra column volume at the entrance of the column, and (b) Tanks in series representation at the column entrance.

5.4.1.2 Dispersion model (DM)

Levenspiel (1998) has proposed the following analytical solution for a linear equilibrium controlled, dispersed plug flow adsorption system subjected to simplified boundary conditions:

$$
\frac{c}{c_0} = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{tu_{\phi}}{4\phi D_l} \right)^{1/2} - L \left( \frac{\phi}{4tD_l} \right)^{1/2} \right] + \exp \left( \frac{uL}{D_l} \right) \text{erfc} \left[ \left( \frac{tu_{\phi}}{4\phi D_l} \right)^{1/2} + L \left( \frac{\phi}{4tD_l} \right)^{1/2} \right]
$$

(5.11)

$$
\phi = 1 + \left( \frac{1-\varepsilon}{\varepsilon} \right) K
$$

(5.12)
where $D_λ$ is the dispersion parameter, $u_z$ is interstitial gas velocity, $t$ is time, $ϕ$ is dimensionless mean residence time of gas in the adsorber, $K$ is Henry’s constant and $L$ is the length of the adsorber. For a non adsorbing system ($ϕ=1$), the above equation reduces to the following form in terms of Peclet number $P_e = \frac{u_z L}{D_λ}$:

\[
\frac{c}{c_0} = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{tP_e u_z}{L} \right)^{1/2} - \left( \frac{Pe}{4tL} \right)^{1/2} \right] + \exp(Pe) \text{erfc} \left( \frac{tP_e u_z}{L} \right) + \left( \frac{Pe}{4tL} \right)^{1/2}
\]

(5.13)

In the above equation, the parameters, $P_e$ and $u_z / L$ have been estimated using the SOLVER in Microsoft Excel by minimizing the error between $c / c_0$ calculated from Equation 5.13 and experimental blank response. After estimating these two parameters, the above model was used to calculate the concentration at the column inlet in the breakthrough simulation.

### 5.4.1.3 Direct use of inlet blank experimental data (DIB)

In this method, the measured inlet gas composition at the entrance of the column (after the inlet blank volume), corrected for the spread in detector response, was directly used as an input boundary condition in adsorption column breakthrough simulation. This approach required interpolation of experimental inlet blank response data, which was also implemented in COMSOL® Multiphysics within the breakthrough simulation environment.

As seen from the representative results shown in Figure 5.6, the TIS and DM models were practically indistinguishable from each other. Both these models fitted the early part of the inlet dead volume responses very well, but deviated somewhat in
the later part. Therefore, inlet blank response corrected for the detector spread was
directly used to represent the dead volume response at the column inlet in the
breakthrough simulation study.

5.4.2 Nonisothermal modeling of breakthrough experiments

Except the second assumption, all other assumptions in section 3.3.1 made in
the isothermal simulation model also applied for the nonisothermal model. In
addition, the following assumptions were made.

1. The radial concentration and temperature gradients were negligible.
2. The column wall was in equilibrium with the cooling water circulated in the
   water jacket.
3. Thermal equilibrium between solid and gas phase was assumed.

The component mass balances in terms of molar fluxes have been given by
Equations 3.1 and 3.2. The energy balance equation for the adsorber bed, subjected to
the aforementioned additional assumptions, is:
Chapter 5. Column Dynamics: Experimental Results, Modeling and Simulation

\[
\left(1 - \frac{\varepsilon}{\rho_s}C_{ps} \frac{\partial T}{\partial t} + \bar{m}c_{ps} \frac{\partial \left(q_i T \right)}{\partial t}\right) + \bar{m}C_{pg} \frac{\partial (cT)}{\partial t} = \frac{K}{\varepsilon} \frac{\partial^2 T}{\partial z^2} - \bar{m}C_{pg} \frac{\partial (cu_z T)}{\partial z} \\
+ \frac{1 - \varepsilon}{\varepsilon} \sum_{i=1}^{N} (-\Delta H_i) \frac{\partial q_i}{\partial t} - \frac{2h}{\varepsilon r_i} (T - T_w)
\]

(5.14)

where, \(T\) and \(T_w\) are gas phase temperature in the column (K) and wall temperature (K), respectively. \(C_{ps} (J/kg/K)\), \(C_{ps} (J/kg/K)\) and \(C_{pg} (J/kg/K)\) denote the specific heat of solid adsorbent, adsorbed gas phase and gas phase in the void space. \(\rho_s\) is adsorbent density (kg/m\(^3\)), \(\rho_g \left(= M_{avg}c\right)\) is average gas density (kg/m\(^3\)), \(c\) is gas phase concentration (mol/m\(^3\)), \(u_z\) is interstitial gas velocity (m/s), \(q_i\) is moles of component \(i\) adsorbed on the solid (mol/m\(^3\)), \(\bar{m}\) is average gas phase molecular weight (kg/mol), \(K_z\) is the effective thermal conductivity of gas (W/m/K), \(\Delta H_i\) is the heat of adsorption of component \(i\) (J/mol) and \(h_i\) is inside heat transfer coefficient to the column wall (W/m\(^2\)/K).

The energy balance equation for the column wall is:

\[
\rho_w C_{pw} \frac{\partial T_w}{\partial t} = K_w \frac{\partial^2 T_w}{\partial z^2} + \frac{2r_i h_i}{r_i^2 - r_o^2} (T - T_w) - \frac{2r_o h_o}{r_o^2 - r_i^2} (T_w - T_u)
\]

(5.15)

where \(\rho_w\) is wall density (kg/m\(^3\)), \(C_{pw}\) is specific heat of wall(J/kg/K), \(K_w\), \(h_0\) denote the thermal conductivity of wall (W/m/K) and outside heat transfer coefficient (W/m\(^2\)/K) to the water circulating in the jacket and \(T_u\) is circulating water temperature (K). In view of the assumption 2 above, which is valid in case of small diameter laboratory adsorption columns, the energy balance for the column wall given by Equation 5.15 was neglected.

Further simplification of Equation (5.14) results in the following equation.
\[ \frac{\partial T}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \bar{m}C_{pa}T \sum_{i=1}^{n} \frac{\partial q_i}{\partial t} = \frac{K_s}{\varepsilon} \frac{\partial^2 T}{\partial z^2} - \bar{m}C_{pa}T \left( \frac{\partial c}{\partial t} + \frac{\partial (cu)}{\partial z} \right) - \rho_s C_{pa} u_z \frac{\partial T}{\partial z} \]

\[ + \frac{1 - \varepsilon}{\varepsilon} \sum_{i=1}^{n} (-\Delta H_i) \frac{\partial q_i}{\partial t} \frac{2h}{\varepsilon \varepsilon_i} (T - T_u) \]  

(5.16)

where \( \lambda = \left( \rho_s \bar{C}_{pa} + \frac{1 - \varepsilon}{\varepsilon} \rho_s C_{pa} + \frac{1 - \varepsilon}{\varepsilon} \bar{m}C_{pa} \sum_{i=1}^{n} q_i \right) \)

Equation (5.16) can be further simplified using the overall equation of continuity (Equation (3.11)) given in chapter 3. Therefore the final form of energy balance equation is as follows

\[ \frac{\partial T}{\partial t} = \frac{K_s}{\varepsilon} \frac{\partial^2 T}{\partial z^2} - \rho_s \bar{C}_{pa} u_z \frac{\partial T}{\partial z} + \frac{1 - \varepsilon}{\varepsilon} \sum_{i=1}^{n} \left( (-\Delta H_i) + \bar{m}C_{pa}T - \bar{m}C_{pa}T \right) \frac{\partial q_i}{\partial t} \frac{2h}{\varepsilon \varepsilon_i} (T - T_u) \]  

(5.17)

In this study, it is assumed that \( \bar{C}_{pa} = C_{pa} \). The equations for flow through porous media, mass transfer rate and adsorption equilibrium have been discussed in chapter 3 [Equations. (3.5) and (3.9)].

The component and over all continuity equations, Equations (3.1) and (3.11), expanded using ideal law, takes the following form when \( T \) is not constant:

\[ \frac{\partial y_A}{\partial t} + \frac{y_A \partial P}{\partial t} - \frac{y_A \partial T}{T \partial t} = D_A \left( \frac{\partial^2 y_A}{\partial z^2} + \frac{1}{P} \frac{\partial y_A}{\partial z} - \frac{1}{T \partial z} \frac{\partial y_A}{\partial z} \right) \]

\[ - \left( y_A \frac{\partial u_z}{\partial z} + u_z \frac{\partial y_A}{\partial z} - \frac{u_z y_A}{T \partial z} \right) \frac{RT}{P} \left( 1 - \varepsilon \right) \frac{\partial q_A}{\partial t} \]  

(5.18)

\[ \frac{\partial P}{\partial t} - \frac{P \partial T}{T \partial t} = \left( -P \frac{\partial u_z}{\partial z} - u_z \frac{\partial P}{\partial z} + u_z P \frac{\partial T}{T \partial z} \right) - RT \left( 1 - \varepsilon \right) \frac{\partial (\bar{q}_A + \bar{q}_b)}{\partial t} \]  

(5.19)

The initial and boundary conditions required to solve the above Equations (5.18) and (5.19) are given in chapter 3 and they are not affected by the heat effect. The boundary conditions for the energy balance equations follow from analogy of mass and heat transfer for the fluid phase and from the operating conditions for the column wall. The following initial and boundary conditions apply for the energy balance
Equation (5.17):

Initial conditions

\[
\begin{align*}
T &= T_0 \\
T_w &= T_0
\end{align*}
\] at \( t = 0, \ 0 \leq z \leq L \) \quad (5.20)

Boundary conditions

\[
\begin{align*}
-K_z \frac{\partial T}{\partial z} &= \rho g \bar{c}_{pg} \mu (T_0 - T) \\
T_w &= T_a
\end{align*}
\] at \( z = 0^+ \) \quad (5.21)

\[
\begin{align*}
\frac{\partial T}{\partial z} &= 0 \\
T_w &= T_a
\end{align*}
\] at \( z = L \) \quad (5.22)

5.4.3 Axial dispersion in a column packed with very fine zeolite particles

The following equation discussed in section 3.3.2 is a general correlation for estimating the effective axial dispersion coefficient:

\[
D_L = \gamma_1 D_m + \gamma_2 d_p \bar{u}_z
\] (5.23)

where \( \gamma_1 = \frac{1}{\sqrt{2}} = 0.707 \) and \( \gamma_2 = 0.5 \). \( D_m \) is molecular diffusivity, \( d_p \) is adsorbent particle size and \( \bar{u}_z \) is interstitial gas velocity. The first term represents the contribution from molecular diffusion and the second term represents the dispersion due to turbulent mixing caused by splitting and recombination of flowing gas around the adsorbent particles [Ruthven (1984)]. But the above equation is valid under turbulent flow conditions and large particles, \( R_p > 0.15 \text{cm} \). Langer et al., (1978) proposed the following modified equation for estimating the effective axial dispersion coefficient for a wide range of flow rates and particle sizes:
where, $Pe_{\infty}$ is the limiting value of Peclet number which is a function of adsorbent particle size according to Equation (5.26), and $\beta$ is the radial dispersion factor. A better estimate of axial tortuosity factor, $\gamma_1$, can be obtained from the following correlation, which is a function of bed voidage [Ruthven (1984)].

$$\gamma_1 = 0.45 + 0.55 \varepsilon$$

(5.25)

The term $\beta \gamma_1 D_M$ accounts for the effect of radial concentration and velocity gradients on axial dispersion. At low flow rates, $\beta \gamma_1 D_M \gg d_p \bar{u}_z$, the molecular diffusion term (first term) in Equation (5.24) dominates the axial dispersion and therefore, it is independent of gas velocity. At high flow rates, $\beta \gamma_1 D_M \ll d_p \bar{u}_z$, the turbulent contribution (second term) dominates axial dispersion and, therefore, axial dispersion increases and the increase is directly proportional the gas velocity. In the transition regime where $\beta \gamma_1 D_M \approx d_p \bar{u}_z$, both the mechanisms are important. The theoretical value of $\beta$ is estimated as 8 from a highly turbulent random walk model. Many authors proposed a range of values for $\beta$ between 0.7 and 45. For small size particles, Hsu and Haynes (1981) proposed a value of 0.7 for $\beta$ in a column packed with 340 µm NaY zeolite catalyst particles. In another study, Langer et al., (1978) proposed a value of 1 for $\beta$ in a column packed with 560 µm spherical glass beads.

In general, the value of limiting Peclet number ($Pe_{\infty}$) depends on particle size [Ruthven (1984)]:

$$D_L = \gamma_1 D_M + \frac{d_p \bar{u}_z}{Pe_{\infty} \left(1 + \frac{\beta \gamma_1 D_M}{d_p \bar{u}_z}\right)}$$

(5.24)
The limiting Peclet number approaches a theoretically expected value of 2 for $d_p \geq 0.3 \text{ cm}$ and it is directly proportional to the particle size for $d_p \leq 0.3 \text{ cm}$. Therefore, limiting Peclet number increases with increase in particle size for small particles and approaches a constant value of 2 for $d_p \geq 0.3 \text{ cm}$. In case of small particles, $Pe_\infty$ is low and axial dispersion is high because of the tendency of small particles to stick together to form clusters and the cluster acts as a single particle in the flow regime. The clustering of small particles might be a consequence of large interaction forces between the particles compared to gravity force. It causes non-uniform distribution of fine particles and leads to the channeling in the column. In conclusion, the parameter $\beta$ characterizes the effect of local radial concentration and velocity gradients on axial dispersion and the parameter $Pe_\infty$ characterizes the effect of channeling on axial dispersion in a column packed with fine particles. Hence, the above equation for axial dispersion coefficient, with a fitting parameter $\beta$ and the limiting peclet number ($Pe_\infty$) estimated from Equation (5.26), has been used to characterize the dispersion in the present study.

### 5.4.4 Parametric study of breakthrough modeling and simulation

#### 5.4.4.1 Assessment of Langer correlation for estimating axial dispersion

The Langer correlation [Equation (5.24)] for axial dispersion in a packed column suggests that very small size adsorbent particles can significantly increase axial dispersion due to clustering and consequent channeling in the column. As
discussed in section 5.4.3, the radial dispersion factor ($\beta$) captures the effect of radial concentration and velocity gradients on axial dispersion and the limiting value of Peclet number ($Pe_\infty$) captures the clustering effect. In the literature, discussed in the previous section, the limiting value of Peclet number ($Pe_\infty$) has been very well correlated with adsorbent particle size for $d_p < 0.3\,\text{cm}$ and is equal to 2 for $d_p > 0.3\,\text{cm}$.

However, there is no available correlation for radial dispersion factor ($\beta$) with any of the process parameters in the literature. Estimation of these parameters from dispersion experiments in a short column with low bed permeability is prone to high error because of very short residence time when the pressure drop is in the desirable high range. Therefore, the effect of varying the radial dispersion factor ($\beta$) on the spread of breakthrough profile was studied. The results are compared in Figure 5.7 with a representative experimental run. It is important to note that Darcy's constant ($k_i$) was fixed from an independent experimental study. Hence, for the results in Figure 5.7, $\beta$ was the only fitting parameter. $\beta$ equal to 0.2 gave the best fit and this value was used to analyze the remaining experimental breakthrough results.

### 5.4.4.2 Effect of Darcy and Ergun parameters on breakthrough curve

To analyze the effect of Darcy's constant on breakthrough simulations, the isothermal model equations were solved using COMSOL® Multiphysics with MATLAB. Based on the experimental observation that the temperature change was $\pm 4^\circ\text{C}$, it was decided to try out the isothermal model first. In these simulations, the experimentally measured inlet and exit pressures were applied as pressure boundary conditions in the model. The inlet concentration boundary condition was applied as
discussed in section 5.4.1. The outputs from the simulation were inlet and exit velocities and concentration breakthrough at the column exit. Experimentally measured inlet and exit pressure profiles were suitably fitted with exponential equations, and used as the pressure boundary conditions in the simulations. Representative fit of pressure profiles are shown in Figure 5.8. The breakthrough simulation results for three different Darcy's constant ($k_i$) values have been compared with the representative experimental results in Figure 5.9 and 5.10.

![Figure 5.7: Experimental breakthrough results compared with simulation for different values of radial dispersion factor, $\beta$. For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results.](image)

The mean residence time of adsorption column breakthrough is very sensitive to the Darcy's constant ($k_i$), as may be seen from Figure 5.9. According to Darcy's law Equation (5.2), the bed permeability ($k_p$), which is a measure of bed resistance ($\mu/k_p$) to gas flow, is inversely proportional to Darcy's constant. Since the bed permeability ($k_p$) decreases with increase of Darcy's constant, the bed resistance
increases decreasing the interstitial gas velocity for the same pressure drop along the column. The trends in Figure 5.10 are consistent with these expectations. It is clear that using a Darcy's constant ($k_i$) of 4136.2, which was obtained independently from the pressure drop experiments conducted in the same column under non-adsorption conditions and detailed in section 5.2, the predicted breakthrough from simulation

Figure 5.8: Experimentally measured pressure profiles (a) at the inlet and (b) exit of the column in adsorption and desorption steps during breakthrough measurements. Symbols represent the experimental data and lines represent the exponential model fit. Thick lines for adsorption step and thin lines for desorption step. For experimental details, see Table 5.3 and run2 in Table 5.2.
matched very well with the experimental results. These results confirm adequacy of the methodology adopted in this study to calibrate increased bed resistance for $R_d > 24$ observed for crushed 5A zeolite adsorbent.

![Graph showing adsorption and desorption breakthrough time compared with experimental results for a representative single component breakthrough of 50% O₂ in He. For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results.](image)

In order to confirm that the Darcy's constant corresponding to the best fit of the oxygen breakthrough at the column exit also satisfies overall mass balance, the experimental and predicted velocity profiles at the inlet and exit of the column are also compared in Figure 5.10 for the same representative run (run 2 given Table 5.3). Even through, the source (cylinder) pressure was held constant; the column inlet pressure dropped for a very short time in the early part of the adsorption step due to the adsorption of oxygen. Similarly, a rise in inlet pressure was observed in the desorption step because of oxygen desorption. For $k_i = 4136.2$, the simulated exit...
velocity in adsorption step matched very well with experimental results, but deviated somewhat from the experimental results in the desorption step. However, at the inlet, the model prediction was closer to the experimental data during desorption than during adsorption.

Figure 5.10: Effect of Darcy's constant ($k_i$) on calculated (a) inlet and (b) exit gas interstitial velocities compared with experimental results for a representative single component breakthrough of 50% O$_2$ in He. Symbols represent the experimental data and lines represent simulation results. Thick lines represent adsorption and thin lines represent desorption respectively. For experimental details, see Table 5.3 and run 2 in Table 5.2.
In order to assess if the Ergun equation is more appropriate than Darcy's law for simulation of breakthrough with large pressure drop, the second Ergun constant \(k_2\) was varied while keeping the first Ergun constant \(k_1\) equal to optimized Darcy's constant, i.e. \(k_1 = 4136.2\). As shown in the Figure 5.11, irrespective of \(k_2\), the simulated breakthrough profiles for all three cases match very well with the experimental breakthrough results of 50% O\(_2\) in He used earlier to study the effect of \(k_1\).

![Figure 5.11: Experimental breakthrough results compared with simulation results using Ergun equation for pressure drop for different values of the second Ergun constant \(k_2\). For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results.](image)

Therefore, as discussed in section 5.3, the effect of the second term (convection) in Ergun equation is not significant in the present study due to high bed resistance and hence low gas velocities through the column. Thus, the single parameter Darcy's equation with calibrated \(k_1\) is adequate for analyzing the breakthrough results obtained in this study.
5.4.4.3 Effect of dispersion in inlet blank on breakthrough response at the exit of column

In order to study the effect of mixing in the inlet blank volume on breakthrough simulations, a systematic analysis of breakthrough results was performed by introducing a step change and also considering the blank models, discussed in sections 5.4.1, for the feed gas entering the column. The results are compared again with the same representative experimental run used earlier to study the effect of radial dispersion factor ($\beta$) and Darcy's constant ($k_i$) in section 5.4.4.1 and 5.4.4.2. The radial dispersion factor ($\beta$) obtained in section 5.4.4.1 and experimentally obtained Darcy's constant ($k_i$), which was validated with simulations in section 5.4.4.2, were used in this study. When a step input of feed gas composition through Dankwert’s boundary condition was used at the column entrance, the simulated breakthrough profiles deviated significantly from the experimental results, as shown in Figure 5.12. However, considering the mixing in dead volume near the entrance of the column, the simulated breakthrough profile matched very well with experimental result. Furthermore, the three different methods discussed in section 5.4.1 to represent the blank response in breakthrough simulation were also considered in this study. From Figure 5.12, it is clear that while both TIS and DM models are adequate, by directly using the corrected blank response data to represent the inlet blank it was possible to overcome the deviation in the later part of the predicted breakthrough from the measured response. Therefore, the results in Figure 5.12 provide further justification for choosing the DIB approach to represent the dead volume response at the column inlet in this study.
5.4.4.4 Effect of heat transfer parameter on nonisothermal modeling of breakthrough experiments

The nonisothermal model equations for dynamic breakthrough simulations have been discussed in section 5.4.2. A systematic parametric study was performed in order to analyze the effect of inside heat transfer coefficient \( (h_{\text{in}}) \) on breakthrough simulations. The Darcy's constant \( (k_i = 4136.2) \) and radial dispersion factor \( (\beta = 0.2) \) established from isothermal simulations were kept fixed in the nonisothermal simulations while estimating the effect of inside heat transfer coefficient \( (h_{\text{in}}) \). The specific heat of adsorbate in the adsorbed phase \( (C_{pa}) \) was assumed to be the same as gas phase specific heat \( (C_{pg}) \). The adsorbent specific heat \( (C_{pm}) \) was taken from the literature [Farooq and Ruthven (1990)]. The effective thermal conductivity \( (K_z) \) was taken as five times of gas mixture thermal conductivity \( (K_g) \) [McCabe et al., (1993)].
The same representative experimental run was used for calibrating the inside heat transfer coefficient \( (h_{in}) \). It was observed that the concentration breakthrough obtained from simulation was not sensitive to the inside heat transfer coefficient in the range over which it was varied. The effect of inside heat transfer coefficient \( (h_{in}) \) on temperature breakthrough profiles were investigated and compared with measured temperature profile in the same representative run. The results are shown in Figure 5.13. Since, the concentration breakthrough profiles were not affected by this parameter, they were not included in the figure. It is clear that the inside heat transfer coefficient \( (h_{in}) \) had an affect on temperature breakthrough profile. \( h_{in} \) affected the spread of the profile and had little effect on the peak temperature, as may be seen from Figure 5.13.

![Figure 5.13: Effect of inside heat transfer coefficient \( (h_{in}) \) on adsorption and desorption temperature profile at the middle of the column length compared with experimental temperature measured at the centre of the column for a representative single component breakthrough of 50% O\(_2\) in He. For experimental details, see Table 5.3 and run 2 in Table 5.2. Symbols represent experimental data and lines represent simulation results.](image-url)
Chapter 5. Column Dynamics: Experimental Results, Modeling and Simulation

The best-fit value \( h_{in} = 64.5 \text{ W/m}^2\text{K} \) obtained was kept fixed in the remaining simulations discussed next.

5.5 Dynamic Column Breakthrough (DCB) Experiments and Simulation: Results and Analysis

In order to estimate the gas transport mechanism in 5A zeolite powder (63-75 \( \mu \text{m} \)), a series of single component (50% oxygen in helium) and mixture (oxygen and nitrogen) breakthrough experiments were conducted. The operating conditions specific to each experiment are compiled in Table 5.2 and the common experimental parameters are summarized in Table 5.3.

### Table 5.2: Summary of the breakthrough experiments.

<table>
<thead>
<tr>
<th>Run no</th>
<th>Initial conditions</th>
<th>Inlet pressure (psi)</th>
<th>% ( \text{O}_2 ) in He or ( \text{N}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Purged with He</td>
<td>25</td>
<td>50% in He</td>
</tr>
<tr>
<td>2</td>
<td>Purged with He</td>
<td>30</td>
<td>50% in He</td>
</tr>
<tr>
<td>3</td>
<td>Purged with He</td>
<td>35</td>
<td>50% in He</td>
</tr>
<tr>
<td>4</td>
<td>Purged with He</td>
<td>38</td>
<td>50% in He</td>
</tr>
<tr>
<td>5</td>
<td>Saturated with pure ( \text{N}_2 )</td>
<td>25</td>
<td>21% in ( \text{N}_2 ) (Air)</td>
</tr>
<tr>
<td>6</td>
<td>Saturated with pure ( \text{N}_2 )</td>
<td>30</td>
<td>21% in ( \text{N}_2 ) (Air)</td>
</tr>
<tr>
<td>7</td>
<td>Saturated with pure ( \text{N}_2 )</td>
<td>35</td>
<td>21% in ( \text{N}_2 ) (Air)</td>
</tr>
<tr>
<td>8</td>
<td>Saturated with pure ( \text{N}_2 )</td>
<td>38</td>
<td>21% in ( \text{N}_2 ) (Air)</td>
</tr>
<tr>
<td>9</td>
<td>Saturated with pure ( \text{O}_2 )</td>
<td>25</td>
<td>21% in ( \text{N}_2 ) (Air)</td>
</tr>
<tr>
<td>10</td>
<td>Saturated with pure ( \text{O}_2 )</td>
<td>30</td>
<td>21% in ( \text{N}_2 ) (Air)</td>
</tr>
<tr>
<td>11</td>
<td>Saturated with pure ( \text{O}_2 )</td>
<td>35</td>
<td>21% in ( \text{N}_2 ) (Air)</td>
</tr>
<tr>
<td>12</td>
<td>Saturated with pure ( \text{O}_2 )</td>
<td>38</td>
<td>21% in ( \text{N}_2 ) (Air)</td>
</tr>
</tbody>
</table>

Note:
1. Exit pressure was atmospheric in all the experiments.
2. Feed/cooling water temperature: 25±2 °C.
An average value of 69 µm was used in the simulations. The isothermal and nonisothermal model equations along with the assumptions and boundary conditions to predict the experimental breakthrough profiles have been discussed in sections 3.2 and 5.4.2. In both models, the molecular diffusion in the macropores of 5A zeolite was assumed to be the controlling transport mechanism. In case of the nonisothermal model, the column wall was assumed to be at the same temperature as the circulating water in the jacket of the column. Furthermore, the effect of axial dispersion on the spread of breakthrough curves was analyzed by setting a very large value for the LDF mass transfer rate constant, $k$, in nonisothermal model.

All the simulation results presented henceforth are predictions using parameters obtained from correlations and independent single component experiments. The salient features of these input parameters detailed in section 5.1 to 5.4, are revisited below before presenting the experimental results and model predictions.

(i) Extended Langmuir adsorption isotherm model, with parameters obtained from Langmuir model fit of single component data assuming same saturation capacity for both the adsorbing gases for thermodynamic consistency, has

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column dimensions, cm</td>
<td>10.08 (length) x 1.08 (ID)</td>
</tr>
<tr>
<td>Bed voidage ($\varepsilon$)</td>
<td>0.556</td>
</tr>
<tr>
<td>Particle voidage ($\varepsilon_p$)</td>
<td>0.314</td>
</tr>
<tr>
<td>Adsorbent size ($d_p$)*, µm</td>
<td>63-75</td>
</tr>
<tr>
<td>Adsorbent particle density, g/cc</td>
<td>1.65</td>
</tr>
<tr>
<td>Adsorbate</td>
<td>O$_2$, N$_2$, Air and He</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>binder less 5A zeolite</td>
</tr>
<tr>
<td>Inlet pressure range ($P_H$), psi</td>
<td>25-38</td>
</tr>
</tbody>
</table>

*An average value of 69 µm was used in the simulations.
been used for mixture equilibrium prediction.

(ii) The Darcy's constant, $k_i$, has been directly calibrated against pressure drop experiments conducted in the adsorption column with inert helium.

(iii) Axial dispersion has been estimated from Langer correlation with the radial dispersion factor, $\beta$, obtained by fitting representative experimental concentrative breakthrough profiles for both adsorption and desorption (run 2 in Table 5.2).

(iv) Bed to wall heat transfer coefficient, $h_{in}$, has been similarly obtained by fitting simulation results to the temperature profile measured at the middle of the column in the same representative experimental run 2 in Table 5.2. It was possible to obtain unambiguous estimate of $h_{in}$ since it affected only the temperature profile in the range of interest. Specific heat of adsorbate in the adsorbed phase ($C_{pa}$) has been assumed to be the same as gas phase specific heat ($C_{pg}$). Adsorbent specific heat ($C_{ps}$) was taken from literature [Farooq and Ruthven (1990)].

5.5.1 Single component breakthrough experiments

Experimental results from single component breakthrough measurements conducted at two different inlet pressures (run 2 & 4 in Table 5.2) have been compared with model predictions in Figure 5.14. Both isothermal and nonisothermal simulation results have been reported and also the effect of axial dispersion on breakthrough curves in nonisothermal model is presented. The parameters used in the simulations are summarized in Table 5.4.
Both isothermal and nonisothermal models predicted the experimental concentration breakthrough profiles very well. In other words, the small change in temperature had negligible effect on the concentration breakthrough. However, considering only the axial dispersion and neglecting the pore resistance in nonisothermal model (by assuming a large value for the LDF constant, $k$), the simulation results matched with the nonisothermal simulation results considering...
macro-pore resistance and in contrast neglecting the axial dispersion (high Pe number) led to the significant deviation from both experimental and other simulation results as shown in Figure 5.14 (a) and (c). It was thus confirmed that the axial dispersion controlled the rate of gas transport in 5A zeolite adsorbent powder and macro-pore resistance in very small size adsorbent particles was negligible. As shown in Figure 5.14 (b) and (d), the experimentally measured temperature profile at the middle of the column matched well with the nonisothermal simulation results. The predicted maximum/ minimum temperature was somewhat higher compared to the experimental results. It might be due to conduction along the metal tube used to place the thermocouple wire in the bed.

Table 5.4: Optimum parameters used in isothermal and nonisothermal modeling of breakthrough experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darcy's constant (k_i)</td>
<td>4136.2</td>
</tr>
<tr>
<td>Thermal conductivity of Helium (K_g), W/m/K</td>
<td>0.142</td>
</tr>
<tr>
<td>Thermal conductivity of Oxygen (K_g), W/m/K</td>
<td>0.024</td>
</tr>
<tr>
<td>Thermal conductivity of Nitrogen (K_g), W/m/K</td>
<td>0.24</td>
</tr>
<tr>
<td>Thermal conductivity of air (K_g), W/m/K</td>
<td>0.024</td>
</tr>
<tr>
<td>Effective thermal conductivity (K_z), W/m/K</td>
<td>5 (K_g)</td>
</tr>
<tr>
<td>Specific heat of Helium (C_{pg}), J/kg/K</td>
<td>5193.2</td>
</tr>
<tr>
<td>Specific heat of Oxygen (C_{pg}), J/kg/K</td>
<td>918</td>
</tr>
<tr>
<td>Specific heat of Nitrogen (C_{pg}), J/kg/K</td>
<td>1040</td>
</tr>
<tr>
<td>Specific heat of air (C_{pg}), J/kg/K</td>
<td>1014.4</td>
</tr>
<tr>
<td>Specific heat of adsorbed gas phase (C_{ps}), J/kg/K</td>
<td>(\bar{C}_{ps})</td>
</tr>
<tr>
<td>Specific heat of solid adsorbent (C_{ps}), J/kg/K</td>
<td>862.5</td>
</tr>
<tr>
<td>Inside heat transfer coefficient (h_m), W/m²/K</td>
<td>64.5</td>
</tr>
<tr>
<td>Radial dispersion factor (\beta)</td>
<td>0.2</td>
</tr>
</tbody>
</table>
5.5.2 Binary breakthrough experiments

In order to verify the effect of competitive adsorption of both components in air on equilibrium and kinetics, two different sets of binary breakthrough experiments were conducted by saturating the column with one of the components of the mixture (N₂ or O₂) and then purging with air (21% O₂ and 79% N₂) at four different inlet total pressures between 25 and 38 psi (run 5 to 12 reported in Table 5.2). The extended Langmuir adsorption equilibrium isotherm model with parameters obtained from single component equilibrium data, discussed in section 5.2, was used in the binary simulations. Similar to single component breakthrough modeling, the same Darcy's constant \( k_i \) obtained from independent pressure drop experiments using He gas, as well as radial dispersion factor \( \beta \) and inside heat transfer coefficient \( h_{in} \) obtained from fitting single component concentration breakthrough at the column exit and temperature profile at the middle of the column, respectively, measured in a representative experiment (run 2 in Table 5.2) were used in all binary breakthrough simulations. The parameters are reported in Table 5.4.

The experimental concentration breakthrough profiles measured at the exit of the column and the temperature profiles measured at the middle of the column length for two representative runs are shown in Figure 5.15 for switching the feed gas to air from nitrogen with which the bed was previously saturated, and vice versa. The predictions from the isothermal and nonisothermal simulation models are also included in Figure 5.15. It is important to note that nitrogen was desorbed when oxygen was adsorbed, which resulted in net drop in temperature. The reverse resulted in a net temperature rise. The simulated concentration breakthrough profiles matched well with the experimental results. The isothermal and nonisothermal model predictions were practically overlapping with each other. This is not surprising since
the measured temperature changes were very small. The maximum measured temperature rise/drop were < 1°C and the predictions were slightly more than 1°C; the difference fell well within the experimental uncertainties in measuring such small changes.

Figure 5.15: Binary experimental concentration profiles at the exit and temperature profiles at the middle of the column length are compared with simulation results for two representative experimental runs of N₂-Air breakthrough. For experimental details, see Table 5.3 and Table 5.2.

The simulated and experimental concentration breakthrough profiles for switching to air after saturating the adsorption column with oxygen and the reverse are shown in Figure 5.16 for two representative experimental runs. The temperature
profiles measured at the middle of the columns are also included in the figure along with model predictions. Since there was significantly more adsorption/desorption of nitrogen in this binary exchange experiment than oxygen in the previous case where the perturbation was only 21% oxygen, the heat effects were also more pronounced in these experiments, as expected. The simulated and measured temperature profiles were generally in good agreement. However, similar to the results in Figure 5.14((b) and (d)), the predicted maximum/ minimum temperatures were somewhat higher compared to the experimental results. As argued previously, this could be due to conduction along the metal tube carrying the thermocouple wires and the junction.

It is clear from Figure 5.16 ((a) and (c)) that the nonisothermal model better captured oxygen breakthrough when nitrogen in the air saturated bed was displaced with pure oxygen. That was, however, not the case when oxygen was desorbed i.e., when air broke through in oxygen saturated bed. Under the conditions of the experiments presented in Figure 5.16, the heat effect was small. Although, the simulated isothermal and nonisothermal oxygen desorption profiles were practically congruent, they eluted somewhat earlier than the experimental profiles. The trends were similar but the difference increased between the nonisothermal model and experimental oxygen desorption results in Figure 5.16 due to increased heat effect. The good agreement between the isothermal model and experimental results is a coincidence and, therefore, misleading. The difference observed between nonisothermal simulations and experimental results in Figure 5.15 and 5.16 for oxygen desorption seem to suggest that the competition from nitrogen when it was co-adsorbed with oxygen was somewhat stronger that what was estimated from the extended Langmuir isotherm using parameters obtained from single component isotherms.
5.5.3 Equilibrium data from dynamic column breakthrough (DCB) experiments

In order to verify the mass balance in dynamic breakthrough column experiments, the equilibrium amount adsorbed was calculated from mass balance across the adsorption column using Equations 4.3 and 4.4 for a step change in feed gas concentration during adsorption and desorption breakthrough experiments. The equilibrium amount adsorbed was calculated from mass balance across the adsorption column using Equations 4.3 and 4.4 for a step change in feed gas concentration during adsorption and desorption breakthrough experiments. The

Figure 5.16: Binary experimental concentration profiles at the column exit and temperature profiles at the middle of the column length are compared with simulation results for two representative experimental runs of O₂-Air breakthrough. For experimental details, see Table 5.3 and Table 5.2.

![Graphs showing concentration and temperature profiles for two runs](image-url)
equilibrium data obtained from mass balance in single component breakthrough experiments is compared with the single component adsorption equilibrium data independently measured using constant volume apparatus in Figure 5.17 for both \( \text{O}_2 \) and \( \text{N}_2 \) gases. The equilibrium data obtained from single breakthrough measurements closely matched with the single component equilibrium isotherm data measured using constant volume apparatus. The adsorption equilibrium isotherm data obtained from both adsorption and desorption breakthrough experiments were very close to each other in single component breakthrough experiments. The slightly high adsorption equilibrium capacity obtained in breakthrough experiments compared to the adsorption equilibrium isotherm data measured using constant volume apparatus might be due to assuming a linear pressure drop along the column in Equation 4.3 and 4.4 in order to estimate the moles accumulated in the voidspace in the column packed with small size crushed 5A zeolite particles, which gave high pressure drop along the column.

Figure 5.17: Comparison of adsorption equilibrium isotherm data measured using single dynamic column breakthrough (DCB) experiments and constant volume apparatus. Circles represent DCB data and triangles represent data obtained from constant volume apparatus.
5.6 Chapter Conclusion

In this chapter, it has been shown that the extended Langmuir isotherm with parameters obtained from single component data assuming equal saturation capacity for both gases, Darcy's equation re-calibrated in the particle size range of interest, macro-pore molecular diffusion controlled transport mechanism and enhanced axial dispersion coefficient predicted from Langer correlation that account for the effect of agglomeration when the particle size is very small, all combined into a comprehensive model for adsorption column dynamics could reasonably predict the observed experimental breakthrough behavior of the gas mixture. The fitting parameter, $\beta$, in the Langer correlation and inside heat transfer coefficient, $h_{in}$, were obtained by fitting the adsorption/desorption concentration and temperature breakthrough profiles measured in a representative single component experiment. Further analysis revealed that the macro-pore resistance in the very small adsorbent particles had negligible impact on the column breakthrough response, which appeared to be axial dispersion dominated over intra-particle diffusional resistance. The PPSA experimental results are presented and analyzed in the next chapter.
6.1 Overview of the Chapter

In the previous chapter, axial dispersion, pressure drop and heat transfer were characterized for an adsorber packed with binderless 5A zeolite adsorbent by comparing the experimental results with predictions from modeling and simulation study. Although a macro-pore molecular diffusion controlled transport mechanism was assumed, the spread of the breakthrough profiles was found to be axial dispersion controlled. In this chapter, the experimental and simulation study of a two-step pulsed pressure swing adsorption (PPSA) process is presented. The experimental results of the effects of process parameters namely, adsorption time, desorption time, and inlet column pressure on the performance of the PPSA process are compared with the isothermal and nonisothermal simulation results. Considering the limitations on the use of small-size zeolite adsorbent particles identified in the PPSA study, a three-step VSA process, with a product pressurization step, has been proposed and theoretically investigated for personal medical applications of COPD patients.

6.2 Experimental Study of Pulsed Pressure Swing Adsorption

6.2.1 Experimental procedure

After verifying all the assumptions in the simulation model by conducting
independent equilibrium, pressure drop and breakthrough experiments, a set of experiments were conducted to demonstrate the performance of the PPSA process using the same adsorption column, in which the pressure drop and breakthrough experiments were measured and detailed in chapter 4 and 5. As mentioned earlier, binderless 63-75 µm 5A zeolite adsorbent particles were used in the PPSA experiments. The schematic of experimental set-up was shown in Figure 4.7 and the detailed description of the experimental set-up was also presented in section 4.4.1. For the two-step single column PPSA experiment, the sequence of valve operation is shown in Table 6.1. In the first step, the solenoid valves SV1, SV2 and SV3 were opened and SV4 was closed for the duration of the adsorption step. This allowed the feed gas to enter the adsorbent bed and maintain the feed end at high pressure \( P_{\text{hi}} \). SV1 was connected to air cylinder where the delivery pressure was adjusted according to the desired \( P_{\text{hi}} \) at the column inlet. Since the product end was at atmospheric pressure \( P_{\text{lo}} \), gas flowed through the bed. In the adsorption step, the feed and product flow rates were measured using MFM1 and MFM3, respectively, and the product oxygen concentration was measured using the oxygen sensor, OA2. In the desorption step, the feed valves SV1 and SV2 and product valve SV3 were closed and the exhaust valve SV4 was opened to atmosphere to desorb the gas adsorbed in the previous high pressure step and prepare the bed for the next adsorption step. The duration of the desorption step was much longer than the adsorption step in order to ensure adequate regeneration of the bed. The desorbed gas composition and flow rates were measured using OA1 and MFM2, respectively. The same procedure of alternative adsorption and desorption was repeated until attaining the cyclic steady state. Valve SV5 and SV6 are not used in the PPSA experiments and remained closed.
The effect of adsorption time \((t_a)\), desorption time \((t_d)\) and inlet column pressure \((P_{in})\) on PPSA process performance was experimentally studied by varying one variable at a time while keeping the other two variables, bed length and adsorbent particle size, unchanged. The experimental results along with the isothermal and nonisothermal simulation results are presented and discussed in the following sections.

### Table 6.1: Valve sequencing for 2-step, single bed PPSA process.

<table>
<thead>
<tr>
<th>Solenoid valve</th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>SV1</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>SV2</td>
<td>√</td>
<td>X</td>
</tr>
<tr>
<td>SV3</td>
<td>√</td>
<td>X</td>
</tr>
<tr>
<td>SV4</td>
<td>X</td>
<td>√</td>
</tr>
<tr>
<td>SV5</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SV6</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

\(\sqrt{\cdot}\): indicates open position;  

\(X\): indicates closed position

### 6.2.2 Parametric study of the PPSA process

Prior to conducting the PPSA experiments, the adsorption column was regenerated at 350°C for 24 hr according to the regeneration procedure discussed in section 4.4.3.1. In all the experiments, the adsorption column was initially saturated with pure oxygen at the atmospheric pressure and room temperature before starting the cyclic operation. In the cyclic process experiments, the gas flow in and out of the column during adsorption and desorption steps was controlled by closing and opening of solenoid valves using National Instruments digital output module (NI 9472) automatically driven by a custom-made program implemented in the LabVIEW software. The closing and opening sequence of valves during the cyclic operation of
Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process

PPSA process, discussed in the previous section and tabulated in Table 6.1, was programmed in LabVIEW software, which executed the cycling continuously without any delay. Data acquisition from all the sensors using National Instruments modules and LabVIEW has been detailed in section 4.4.1. All the PPSA experiments were performed for 75 cycles in order to confirm the attainment of cyclic study state (CSS). The experimental data acquired using LabVIEW software was recorded in Microsoft excel workbook after every 5 cycles to avoid storage of huge amount of experimental data obtained during PPSA process experiments. The cyclic steady state was confirmed by plotting the oxygen product purity obtained in the adsorption step as a function of cycle number, as shown in Figure 6.1. In most of the PPSA experiments, the cyclic steady state was obtained within 50 cycles.

Among the five process parameters affecting the process performance, namely adsorption time \( (t_a) \), desorption time \( (t_d) \), inlet pressure \( (P_H) \), bed length \( (L) \) and adsorbent particle size \( (d_p) \), the effect of the first three parameters were experimentally investigated while keeping the remaining, two parameters constant at 10 cm and 69 µm respectively. Unlike the first three parameters, which were easy to vary, change of bed length and particle size would have resulted in variation of bed resistance and dispersion characteristics of the column. This is because 5A zeolite adsorbent particles below 200 µm had the tendency to form clusters upon packing, which led to the increased pressure drop and dispersion characteristics of the column. Hence, in our range of interest, it was not easy to study the effect of bed length and particle size on PPSA process performance without convoluting the results with secondary effects like change in bed resistance. Therefore, the bed length and particle size were not chosen for the experimental evaluation of PPSA process performance in this study. The adsorption/desorption step duration was varied from the LabVIEW
program and the inlet column pressure was varied by adjusting the delivery pressure on the air supply cylinder. Only one parameter was varied at a time. The experimental results are presented along with the model predictions in section 6.5.

![Figure 6.1: Plot of oxygen mole fraction with cycle number. Cyclic steady state was attained after 30 cycles in the PPSA experiment. The process parameters for the present run were \(L=10.08\) cm, \(d_p=69\) µm, \(P_H=2.131\) bar, \(t_d=3\) s, and \(t_d=10\) s.]

6.3 Modeling and Simulation of the Experimental PPSA Process

In addition to validate the isothermal model developed in chapter 3, a nonisothermal model of two-step PPSA process was also developed for detailed analysis of the results from the experimental parametric study. In the following sections, the key changes to the isothermal model in chapter 3, and the model equations and boundary conditions of the nonisothermal model are discussed.

6.3.1 Isothermal model

In view of the inert and adsorption/desorption experimental runs discussed in chapter 5, some changes were necessary in the way pressure drop and axial dispersion
were characterized earlier in chapter 3. Agglomeration of micron-sized zeolite adsorbent particles resulted in increased axial dispersion in the packed bed, for which Equation 5.24 was used in place of Equation 3.23. The optimum radial dispersion factor in Equation 5.24 was obtained from a representative experimental breakthrough run and was subsequently validated with the additional breakthrough runs. Similarly, the optimum Darcy's constant, obtained from independent pressure drop experiments conducted in the same column and validated with unary and binary breakthrough experiments, was used to simulate the PPSA process. The solution procedure and the cyclic steady state criterion were same in section 3.2.3. The input parameters used to simulate the experimental PPSA runs are summarized in Table 6.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed length (L), cm</td>
<td>10.08</td>
</tr>
<tr>
<td>Bed diameter (Dc), cm</td>
<td>1.08</td>
</tr>
<tr>
<td>Adsorbent particle size (dp), µm</td>
<td>63-75</td>
</tr>
<tr>
<td>Particle voidage (εp)</td>
<td>0.314</td>
</tr>
<tr>
<td>Bed voidage (ε)</td>
<td>0.556</td>
</tr>
<tr>
<td>Darcy's constant (k1)</td>
<td>4136.2</td>
</tr>
<tr>
<td>Effective thermal conductivity (Kz), W/m/K</td>
<td>0.12</td>
</tr>
<tr>
<td>Specific heat of air (Cpg), J/kg/K</td>
<td>1014.4</td>
</tr>
<tr>
<td>Specific heat of adsorbed gas phase (Cpa), J/kg/K</td>
<td>1014.4</td>
</tr>
<tr>
<td>Specific heat of solid adsorbent (Cps), J/kg/K</td>
<td>862.5</td>
</tr>
<tr>
<td>Inside heat transfer coefficient (hin), W/m²/K</td>
<td>64.5</td>
</tr>
<tr>
<td>Radial dispersion factor (β)</td>
<td>0.2</td>
</tr>
<tr>
<td>Adsorbent particle density (ρp), g/cc</td>
<td>1.65</td>
</tr>
</tbody>
</table>

*An average value of 69 µm was used in the simulations.*
6.3.2 Nonisothermal model

The nonisothermal model equations were discussed in section 5.4.2 along with the boundary conditions for adsorption/desorption breakthrough experiments. Similar to the assumption in breakthrough modeling, the adsorption column wall was assumed to be in thermal equilibrium with the water circulating in the jacket. Therefore, the energy balance for the column wall was also neglected in the nonisothermal model of the PPSA processes. This is a reasonable assumption in a small-diameter column where the surface to volume ratio is high. The boundary conditions on energy balance in the adsorption step were similar to the boundary conditions in the column breakthrough model discussed in section 5.4.2 and the boundary conditions for desorption step were obtained from energy balance at the two ends of the column. The initial conditions and boundary conditions for the energy balance equations for the adsorption and desorption steps of the PPSA process were as follows:

Initial conditions

\[
\begin{align*}
  x_A &= 0 \\
  T &= T_0 \\
  T_w &= T_0
\end{align*}
\]

at \( t = 0, \ 0 \leq z \leq L \) \hspace{1cm} (5.20)

Boundary conditions

(i) Adsorption step

\[
\begin{align*}
  -K_z \frac{\partial T}{\partial z} &= \rho_B C_{p_{avg}} u (T_0 - T) \\
  T_w &= T_a \\
  \frac{\partial T}{\partial z} &= 0 \\
  T_w &= T_a
\end{align*}
\]

at \( z = 0^+ \) \hspace{1cm} (5.21)

(i) Desorption step
Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process

\[
\begin{align*}
\frac{\partial T}{\partial z} &= 0 \quad \text{at} \quad z = 0' \quad (6.1) \\
T_w &= T_a \\
\frac{\partial T}{\partial z} &= 0 \quad \text{at} \quad z = L' \quad (6.2) \\
T_w &= T_a
\end{align*}
\]

All the equations along with the initial conditions and boundary conditions were made dimensionless by introducing suitable scaling factors. The dimensionless model equation and boundary condition are given in Appendix B.

The radial dispersion parameter \( \beta \) in Equation 5.24, and Darcy's constant were same as in the isothermal model. The same set of heat transfer parameters, namely specific heat of adsorbed gas phase \( C_{pag} \), specific heat of solid adsorbent \( C_p \), and inside heat transfer coefficient \( h_{in} \), used in modeling of breakthrough experiments and given Table 5.4, were retained in the nonisothermal PPSA process. The input heat transfer parameters used in nonisothermal simulation of PPSA experiments were also included in Table 6.2.

The nonisothermal model equations were also solved using COMSOL® Multiphysics with MATLAB and the results were compared with the experimental results and isothermal model predictions for the effect of change in adsorption time \( t_a \), desorption time \( t_d \) and inlet pressure \( P_H \) on the performance of PPSA process. The comparisons are graphically shown and discussed in section 6.5.

6.4 Estimation of Power Consumption in the PPSA Process

To compare the PPSA process performance with the commercial units, it is important to estimate the power required to run the PPSA process, which represents
the size of compressor as well as the battery required to run the cyclic operation of PPSA process. In a simple two step PPSA process, the only power requirement is by the compressor in the adsorption step to supply the feed air to the column inlet, which was estimated from the theoretical work done by the compressor defined by Equation 6.4. No additional power is required to deliver the gases from the column during adsorption and desorption steps where the high pressure column delivers at atmospheric pressure.

The theoretical work done by a single stroke compressor in the adsorption step to supply the high pressure feed to the column was estimated from the following equation

\[ W = \int_0^{\tau} \frac{\gamma}{\gamma - 1} n_n R g T_{in} \left( \frac{P_{exit}}{P_{in}} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right) \gamma = 1.4 \]

(6.3)

where \( W \) is theoretical work done by the compressor in joule, \( P_{in} \) and \( T_{in} \) are inlet pressure in bars and inlet temperature in K, \( P_{exit} \) is exit pressure of the compressor in bars, \( n_n \) is the number of mole of gas entering the adsorption column, \( \gamma \) is compressibility factor which is the ratio of specific heat under constant pressure to constant volume and \( R_g \) is universal gas constant in J/mol/K. The actual power required by the compressor was estimated from the following equation.

\[ \text{Power}\left(\text{kW/TPD}_{O_2}\right) = \frac{W}{1000\eta C_t TPD_{O_2}}; \eta = 0.72 \]

(6.4)

where \( \eta \) is the efficiency of the compressor, \( C_t \) is cycle time in s and \( TPD_{O_2} \) is tons of oxygen produced per day. Size of the compressor needed to supply the feed gas to the adsorption column, which determines the capacity of the battery and charging frequency, is important in the design of portable oxygen concentrators.
Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process

6.5 Experimental and Simulation Results of Pulsed Pressure Swing Adsorption Process

The performance of pulsed pressure swing adsorption process was investigated in terms of usual indicators namely, purity, recovery and productivity of oxygen. The indicators measured experimentally were compared with the isothermal and nonisothermal simulation results. The power requirement was also theoretically calculated from Equation 6.4 discussed in section 6.4. The effects of varying the process parameters, adsorption time \( t_a \), desorption time \( t_d \) and inlet pressure \( P_H \) on the performance of the PPSA process are discussed in the following sections.

6.5.1 Effect of adsorption step duration on PPSA process performance

The experimentally measured oxygen purity, recovery and productivity are plotted as a function of adsorption time \( t_a \) in Figure 6.2 and compared with isothermal and nonisothermal simulations results of PPSA process for inlet column pressure of 2 bar and desorption step duration of 10 s. The computed compression power requirement to deliver the high pressure feed air to the column is also plotted as a function of adsorption time \( t_a \) in Figure 6.2 (b). The minimum adsorption time \( t_a \) used in these experiments was limited to 1s. The oxygen product purity during adsorption step decreased with increasing adsorption step duration \( t_a \) in case of both experimental study and simulation results. As discussed in section 3.2.2, the nitrogen adsorption in a fast cycling PPSA process was confined to the early part of the bed and the rest of the column was filled with high purity oxygen, which was used to self purge the column in the desorption step instead of the external purge gas used in a
conventional PSA process. An increase of adsorption step duration led to deeper advancement of nitrogen adsorption wave front into the column. An advancing adsorption front also meant to decrease in driving force for mass transfer due to the pressure drop along the column. A very long adsorption step pushed nitrogen towards the product end and it limited the amount of high purity oxygen preserved in the later part of bed, which was useful to self purge the column in the desorption step.

![Graph](Figure 6.2: Effect of adsorption time \(t_a\) on (a) oxygen mole fraction and recovery, and (b) productivity and theoretical power required in PPSA process using binderless 5A zeolite adsorbent. The process parameters are \(L=10.08\) cm, \(d_p=63-75\) µm, \(P_H=2\) bar and \(t_d=10\) s.)
As a result, the oxygen product purity decreased with increasing adsorption step duration, as shown in Figure 6.2 (a). In contrast, oxygen recovery and productivity increased with increasing adsorption step since more of the enriched oxygen conserved in the product end was pushed out of the bed by the advancing nitrogen adsorption front leaving less for self purge. The theoretical power required by the compressor to supply the high pressure feed air to the column decreased with increase of adsorption step duration, which indicates that the increase in oxygen amount in the product was more than proportional to the increase in adsorption step duration.

The isothermal and nonisothermal model predicted the correct qualitative trends. Quantitatively, the isothermal model was closer to the experimental oxygen purity results, whereas nonisothermal model was closer to the experimental recovery results. Productivity predictions from the two models were practically the same and deviated somewhat from the experimental result at high adsorption times.

### 6.5.2 Effect of desorption step duration on PPSA process performance

The effect of varying desorption step duration on process performance indicators has been plotted in Figure 6.3 for an inlet column pressure of 2 bar and adsorption step duration of 2 s. In the figure, the experimentally measured oxygen product purity, recovery and productivity are compared with the isothermal and nonisothermal simulation results. The computed power requirement of the compressor is also included in Figure 6.3 (b). The oxygen product purity increased whereas the oxygen recovery and productivity decreased with increasing desorption step duration. The purpose of the desorption step in a two-step pulsed pressure swing adsorption was to desorb the nitrogen that was adsorbed in the previous step by reducing the column pressure. Nitrogen desorption and removal from the voids was further
facilitated by self purging the bed with the oxygen-rich gas that desorbed from the product end of the bed. Thus, the column was prepared for the selective adsorption of nitrogen from feed air in the subsequent cycle. As discussed in section 3.2.2, longer desorption step led to effective desorption and sweeping of nitrogen in the voids at the

![Graph](image-url)

**Figure 6.3:** Effect of desorption time ($t_d$) on (a) oxygen mole fraction and recovery, and (b) productivity and theoretical power of a PPSA process on binderless 5A zeolite adsorbent. The process parameters are $L=10.08\text{cm}$, $d_p=63-75\text{ µm}$, $P_H=2\text{ bar}$ and $t_a=2\text{ s}$. 

---

*Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process*
feed end of the column due to the increased self-purge effect of the desorbed oxygen from the product end of the column. At the same time, this also meant more loss of oxygen, which could otherwise be collected as product in the next adsorption step. Therefore, the oxygen product purity in adsorption step increased but the recovery and productivity decreased with increasing desorption step duration. Increasing power requirement, expressed on the basis of per TPDO$_2$, with increasing desorption time was the combined effect of decreasing flow of oxygen product and increasing cycle time, which together decreased TPDO$_2$. Similar to the observations in the previous section, here also the isotherm model predicted the experimental oxygen purity very well, but nonisothermal model gave lower purity, as may be seen in Figure 6.3 (a). The recovery from the nonisothermal model was very close to experimental data. Both the models, isothermal and nonisothermal models, predicted the experimentally measured productivity very well as shown in Figure 6.3 (b).

6.5.3 Effect of inlet column pressure on PPSA process performance

For specific adsorption and desorption step durations, the PPSA process performance was investigated and the experimental and simulation results are plotted in Figure 6.4 (a) and (b) as a function of inlet column pressure during adsorption step of PPSA process using the same adsorption column used to measure the pressure drop and breakthrough characteristics. Both the isothermal and nonisothermal simulation results were compared with the experimentally measured process performance in Figure 6.4 (a) and (b). The increase of inlet pressure caused the increase of pressure drop along the column, which governed the gas flow along the column for a constant
bed resistance; the bed resistance was a function of adsorbent particle size. Therefore, the oxygen product purity increased with increase of inlet pressure due to the increase in pressure driving force for solid loading and it resulted in more adsorption of nitrogen in the front end of the column and pushed the high purity oxygen towards the product end. Because of increase in pressure drop for a constant bed resistance, the
gas velocity also increased towards the product end with increase of inlet pressure of the column. Thus, the recovery and productivity also increased with increase of inlet column pressure as shown in Figure 6.4(a) and (b). The power required to deliver the feed air to the column increased with increase of inlet column pressure and it caused the increase in energy consumption, as shown in Figure 6.4(b).

The experimentally measured oxygen product purity is bounded between the predicted oxygen product purity from isotherm and nonisothermal simulations. The experimentally measured oxygen productivity values were in good agreement with both isothermal and nonisothermal simulation results.

6.6 Limitations on Current Experimental Study of PPSA Process.

Limitations of the experimental study of the PPSA process are summarized as follows:

(i) The experimentally measured adsorption and desorption step durations had been limited to >1 s because of limitation on response time of sensors and valves chosen for the current experimental study.

(ii) For a 10 cm long bed and aforementioned limitation on the cycling frequency, the desirable particle size necessary to achieve high oxygen product purity was in the range 20-40 µm. This size range chosen was not readily available in the market. What could be achieved by grinding and sieving 1.6 mm binderless 5A zeolite adsorbent particles was in the range of 63-75 µm.

(iii) Surface roughness and clustering of the crushed zeolite particles led to significantly higher pressure drop than that predicted by Darcy's law with \( k_1 = 150 \) in chapter 3. The axial dispersion was also much higher than the
estimate based on Equation 3.23 used in chapter 3, which is same as Equation 5.23 in chapter 5.

In order to understand which of the above deviations contributed to low oxygen purity, a detailed theoretical study using the nonisothermal PPSA model was conducted where the effect of adsorption step duration on oxygen purity, recovery and productivity was investigated for four different combinations of $k_i$ and axial dispersion coefficient valves. The results are shown in Figure 6.5 together with the experimental results.

A common observation for all the plots in Figure 6.5 (a) is that there is an optimum in oxygen purity for all combinations of the two parameters. The drop in oxygen purity for very short adsorption time was a result of the ineffective pressure swing near the feed-end of the column. The ineffective pressure swing was due to the insufficient adsorption time that limited the penetration of adsorption front deep into the bed and thus the rest of the bed was not affected by the pressure swing near the feed-end of the column.

It is clear from Figure 6.5 (a) that for bed length and particle size used in the experiments in this study, high oxygen enrichment would require adsorption time of the order of 0.01 s if the pressure drop and axial dispersion estimates used in chapter 3 were valid. The higher bed resistance experienced in this study due to particle clustering was, in fact, helpful to increase the adsorption time where higher oxygen purity could be expected. However, the enhanced axial dispersion that also came with particle clustering prevented the increase in oxygen concentration beyond 38.5%. Furthermore, the high bed resistance led to the low oxygen recovery and productivity due to the low gas velocities through the column. In conclusion, the low performance of two-step PPSA process observed in the present experimental study was a result of
Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process

Figure 6.5: Effect of adsorption time on (a) oxygen mole fraction, (b) recovery and (c) productivity in PPSA process using binderless 5A zeolite adsorbent for four different combinations of Darcy’s constant and axial dispersion estimation. The process parameters are $L=10.08$ cm, $d_p=63-75$ µm, $P_H=2$ bar and $t_d=10$ s.
high bed resistance and enhanced axial dispersion in a 10 cm column packed with very fine binderless 5A zeolite adsorbent particles.

In the present study, the clustering of charged binderless 5A zeolite adsorbent particles led to increase the axial dispersion and pressure drop in the column. Alternative nitrogen selective molecular sieves adsorbents such as aluminophosphates and silicoaluminophosphate (zeolites) are the suitable materials with the less surface charge when crushed to size below 100 micron [Galbraith et al., (2011)]. Hence, these alternative materials may not increase the axial dispersion above the estimates in chapter 3. The other option is using high density structured adsorbents with laminar flow channels, where axial dispersion and pressure drop are low.

6.7 A Novel Three-Step Rapid Vacuum Swing Adsorption Cycle for Reducing Oxygen Concentrator Size

To overcome the above practical limitations in the simple two step PPSA process, a three-step VSA process with product pressurization was theoretically investigated. The bed size was kept at 10 cm, but the adsorbent size was increased to $>250 \, \mu m$ in order to be in the range where there are experimental evidences that clustering of particles will not lead to increased axial dispersion and pressure drop. Thus, the axial dispersion and pressure drop equations used in chapter 3 will be valid.

6.7.1 Process description

The proposed cyclic adsorption process has three steps, namely product pressurization, adsorption and vacuum desorption. The schematic representation of the process is shown in Figure 6.6. In the first step, the column under vacuum is pressurized to the desired atmospheric pressure from the product end of the column.
(z = L) with enriched oxygen stream. In this step, the nitrogen from the vacuum desorption step occupying the voids is pushed to the feed end of the column (z = 0) and the rest of the bed is filled with high purity oxygen. In the second step, the feed air is supplied at the column inlet at a specific feed gas velocity and high purity oxygen product at atmosphere pressure is delivered from the product end. In this step, the pressure at the inlet of the column varies until a steady state flow profile and a fixed pressure across the column are established. During desorption step, the strongly adsorbed nitrogen is desorbed from the solid adsorbent by reducing the column inlet pressure to vacuum. During this step, the column is also self-purged with desorbed oxygen from the product end.

6.7.2 Modeling and simulation of three-step vacuum swing adsorption process

A nonisothermal model is used and all mass and energy balance equations discussed earlier (section 5.4.2) are applicable here. In the model, component A
Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process

represents nitrogen and \( B \) represents oxygen. The initial and boundary condition for the 3-step rapid VSA cycle are:

Initial conditions:

\[
\begin{align*}
    x_A &= 1 \\
    P &= P_v \\
    u_z &= 0 \\
    T &= T_0
\end{align*}
\]

\[\text{at } t = 0, \ 0 \leq z \leq L \quad (6.5)\]

\[
\begin{align*}
    \bar{q}_A &= q_A|_{z=L_T} \\
    \bar{q}_B &= q_B|_{z=L_T}
\end{align*}
\]

Boundary conditions

(i) Product pressurization with enriched oxygen from the product end:

\[
\begin{align*}
    \frac{\partial x_A}{\partial z} &= 0 \\
    \frac{\partial P}{\partial z} &= 0 \\
    u_z &= 0 \\
    \frac{\partial T}{\partial z} &= 0
\end{align*}
\]

\[\text{at } z = 0^+ \quad (6.6)\]

\[
\begin{align*}
    -D_L \frac{\partial x_A}{\partial z} &= u(x_{Ap} - x_A) \\
    P &= P_H - (P_H - P_i)e^{-At} \\
    -K_L \frac{\partial T}{\partial z} &= \rho g \bar{v}_{pg} u(T_0 - T)
\end{align*}
\]

\[\text{at } z = L^+ \quad (6.7)\]

(ii) High pressure adsorption step:

\[
\begin{align*}
    -D_L \frac{\partial x_A}{\partial z} &= u(x_f - x_A) \\
    u_z &= u_0 \\
    -K_L \frac{\partial T}{\partial z} &= \rho g \bar{v}_{pg} u(T_0 - T)
\end{align*}
\]

\[\text{at } z = 0^+ \quad (6.8)\]
Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process

\[
\begin{align*}
\frac{\partial x_A}{\partial z} &= 0 \\
P &= P_{\text{ atm}} \quad \text{at} \quad z = L^- \\
\frac{\partial T}{\partial z} &= 0
\end{align*}
\]

(iii) Reverse evacuation:

\[
\begin{align*}
\frac{\partial x_A}{\partial z} &= 0 \\
P &= P_v + (P_H - P_v)e^{-\lambda_d} \quad \text{at} \quad z = 0^+ \\
\frac{\partial T}{\partial z} &= 0
\end{align*}
\]

\[
\begin{align*}
\frac{\partial x_A}{\partial z} &= 0 \\
u &= 0 \\
\frac{\partial T}{\partial z} &= 0 \quad \text{at} \quad z = L^- 
\end{align*}
\]

In Equation 6.7, \( x_{A_p} \) is average product concentration of component \( A \) obtained in the high pressure adsorption step. The dimensionless forms of the model equations are given Appendix B along with respective boundary and initial conditions. Like in chapter 3, scaling and dimensional analysis were also applied here in to represent the model equations in terms of minimum number of dimensionless groups. The model equations were solved using COMSOL Multiphysics with MATLAB. The cyclic operation was coded in MATLAB. The cyclic steady state (CSS) criterion to terminate the cyclic operation was discussed in chapter 3.

The equilibrium parameters of 5A zeolite adsorbent used in the PPSA experiments and silver exchanged lithium zeolite (Ag-Li-X) used in chapter 3 have been used in this simulation study. Ag-Li-X has high equilibrium selectivity for nitrogen and also has low equilibrium capacity for oxygen. Thus, the superior Ag-Li-X adsorbent, currently available for air separation [Hutson et al., (1999)], has also
been chosen to theoretically demonstrate the potential of the proposed 3-step VSA cycle for miniaturization of oxygen concentrator for personal medical applications.

The process parameters used in this study are summarized in Table 6.3.

### Table 6.3: Summary of parameters used in modeling and simulation of three-step VSA processes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed length (L), cm</td>
<td>10.08</td>
</tr>
<tr>
<td>Bed diameter (Dc), cm</td>
<td>1.08</td>
</tr>
<tr>
<td>Adsorbent particle size (d_p), ( \mu m )</td>
<td>250-1250</td>
</tr>
<tr>
<td>Particle voidage (( \varepsilon_p ))</td>
<td>0.35</td>
</tr>
<tr>
<td>Bed voidage (( \varepsilon ))</td>
<td>0.37</td>
</tr>
<tr>
<td>Common optimum Darcy's constant (k_t)</td>
<td>150</td>
</tr>
<tr>
<td>Specific heat of adsorbed gas phase (C_ps), J/kg/K</td>
<td>( C_{pg} )</td>
</tr>
<tr>
<td>Specific heat of solid adsorbent (C_ps), J/kg/K</td>
<td>862.5</td>
</tr>
<tr>
<td>Inside heat transfer coefficient (h_in), W/m^2/K</td>
<td>64.5</td>
</tr>
<tr>
<td>Adsorbent particle density (), g/cc</td>
<td>1.65(^a), 1.2(^b)</td>
</tr>
</tbody>
</table>

\(^a\) for binderless 5A zeolite,
\(^b\) for Ag-Li-X

### 6.7.3 Simulation results of three-step Rapid VSA processes

The process performance is assessed in terms of oxygen purity, recovery, productivity and power consumption. The effects of process parameters, adsorption step duration, column length to velocity ratio, adsorbent particle size and vacuum pressure, have been discussed in the following sections. The power consumption was estimated from Equation (6.3) and (6.4) discussed in section 6.4.

#### 6.7.3.1 Effect of column length to velocity (\( L/V_0 \)) ratio

The effect of column length to velocity (\( L/V_0 \)) ratio on oxygen recovery, productivity and power consumption is plotted in Figure 6.7 for both 5A zeolite and Ag-Li-X adsorbents for fixed vacuum desorption pressure, adsorbent particle size, and
pressurization and desorption step durations. The adsorption step duration was optimized to obtain maximum oxygen product purity for each $L/V_0$ ratio, which was $>94\%$ in all the cases. The optimum adsorption step duration thus obtained for each $L/V_0$ can be read from the secondary y-axis in Figure 6.7 (a). Oxygen recovery increased with increasing $L/V_0$ ratio for both 5A zeolite and Ag-Li-X adsorbents. The increase of $L/V_0$ ratio increased the residence time of gas molecules, which is evident from the linear increase of optimum adsorption time for both adsorbents in the Figure 6.7(a). The increase of optimum adsorption time with $L/V_0$ in case of 5A zeolite is higher compared to Ag-Li-X for the same set of process parameters. Furthermore, the loss of oxygen in the desorption step was less for an optimum adsorption step and a fixed desorption step duration. Therefore, the oxygen recovery increased with increasing $L/V_0$ ratio for both adsorbents. For 5A zeolite, the exponential increase in recovery up to $L/V_0 = 0.2$ was due to the higher optimum adsorption time compared to Ag-Li-X zeolite. Further increase of $L/V_0$ increased the optimum adsorption time, but the recovery increased only marginally. In case of Ag-Li-X adsorbent, the increase of recovery with $L/V_0$ ratio was linear. The oxygen productivity has an optimum in case of binderless 5A zeolite adsorbent and is nearly constant for Ag-Li-X adsorbent. In case of 5A zeolite, the increase of oxygen productivity with increasing $L/V_0$ up to 0.2, was due to the exponential increase of oxygen moles recovered and marginal increase in optimum adsorption time. Further increase of $L/V_0$ ratio led to a marginal increase of oxygen moles recovered but the increase of optimum adsorption time was higher. As a result, the oxygen productivity dropped with further increase of $L/V_0$ ratio. In case of Ag-Li-X, the gain in oxygen moles recovered with increase of $L/V_0$ ratio was about the same as the decrease in cycling frequency thus the oxygen productivity was approximately constant with change of $L/V_0$ ratio.
Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process

Theoretical power consumption decreased with increasing L/V₀ ratio due to reduction in the amount of oxygen loss in the desorption step using both adsorbents. Similar to productivity, an exponential drop in power consumption was observed in case of 5A zeolite compared to Ag-Li-X due to the exponential increase of oxygen moles recovered up to L/V₀=0.2. The high recovery and productivity of oxygen and low power consumption using Ag-Li-X adsorbent in three-step VSA process

Figure 6.7: Effect of column length to velocity ratio (L/V₀) on (a) oxygen recovery and adsorption time, and (b) productivity and power consumption in a 3-step product pressurization VSA process using 5A zeolite and Ag-Li-X adsorbent. For all these runs, oxygen product purity was >94%. $L=10\,\text{cm}, \, d_p=250\,\mu\text{m}, \, P_{\text{vac}}=0.2\,\text{bar}, \, t_f=6\,\text{s}$ and $t_d=8\,\text{s}$. Thick lines for 5A zeolite and thin lines for Ag-Li-X adsorbent.
compared to 5A zeolite adsorbent particles for the same set of process parameters was due to the higher nitrogen selectivity and low capacity for oxygen in Ag-Li-X adsorbent.

6.7.3.2 Effect of vacuum desorption pressure

The process performance indicators, oxygen purity, recovery and power consumption have been plotted as a function of vacuum desorption pressure for both 5A zeolite and Ag-Li-X adsorbents in Figure 6.8 for specific L/V₀ ratio, adsorbent particle size and individual step durations. The oxygen product purity decreased and recovery increased with increase of vacuum desorption pressure, as shown in Figure 6.8. The increase of vacuum desorption pressure led to the decrease in working capacity of adsorbent due to the vacuum swing over a smaller pressure range and it led to deeper penetration of N₂ adsorption front farther into the column. Thus, the early breakthrough of N₂ at column exit caused the decrease in oxygen product purity in the adsorption step with increasing vacuum pressure in the desorption step. However, the oxygen recovery increased with increasing vacuum pressure due to decreasing amount of oxygen lost in desorption step. Furthermore, the productivity also increased and power consumption decreased with increasing vacuum desorption pressure, which was also due to the loss of less amount of oxygen in desorption step. The exponential drop in power consumption was also due to the decrease in pressure ratio with increasing vacuum pressure during evacuation step. Therefore, desorption at a very low vacuum pressure is suitable for delivery of high purity oxygen in a three-step VSA process, but at the expense of low recovery and productivity, and high power consumption.
Figure 6.9: Effect of vacuum desorption pressure ($P_{\text{vac}}$) on (a) oxygen purity and recovery, and (b) bed size factor and power consumption in a 3-step product pressurization VSA process using 5A zeolite and Ag-Li-X adsorbent. $L=10$ cm, $d_p=250$ µm, $t_p=6$ s, $t_a=3$ s and $t_d=8$ s. Thick lines for 5A zeolite and thin lines for Ag-Li-X.

6.7.3.3 Effect of adsorbent particle size on three-step VSA process performance

For a specific $L/V_0$ ratio, vacuum pressure and step durations, the effect of adsorbent particle size on performance of three-step VSA process was investigated and the process performance indicators, oxygen purity, recovery, productivity and power consumption have been plotted in Figure 6.9 for both 5A zeolite and Ag-Li-X adsorbent as a function of adsorbent particle size. For adsorbent particles $<750$ µm,
the oxygen product purity was constant and further increase in particle size led to a drop in oxygen purity due to the increase of mass transfer resistance. The oxygen recovery was constant with increase of particles size in case of Ag-Li-X and for the same set of parameters, a minimum was observed in case of 5A zeolite.

Figure 6.9: Effect of adsorbent particle size \( (d_p) \) on (a) oxygen purity and recovery, and (b) productivity and power consumption in a 3-step product pressurization VSA process using 5A zeolite and Ag-Li-X adsorbent. \( L=10 \text{ cm}, P_{\text{vac}}=0.2 \text{ bar}, V_{\text{eff}}=0.5 \text{ m/s}, t_p=6 \text{ s}, t_r=3 \text{ s} \) and \( t_d=8 \text{ s} \). Thick lines for 5A zeolite and thin lines for Ag-Li-X. Solid lines for purity and productivity, and dash lines for recovery and power.

Oxygen productivity and power consumption were also constant for Ag-Li-X adsorbent. Using 5A zeolite, a broad minimum in productivity and maximum is power
Chapter 6. Experimental, Modeling and Simulation Study of PPSA Process

consumption was observed. The oxygen purity and power consumption were lower for Ag-Li-X zeolite. However, the recovery and productivity were significantly higher. Considering the fact that vacuum pumps are more compact and lighter than compressors of comparable capacity, the three-step VSA process appears promising as an option for reducing the oxygen concentrator size for personal medical application of COPD patients.

6.7.4 Estimation of bed size factor

Besides meeting the product purity specifications, the principal parameters for the design of oxygen concentrator are bed size factor (BSF) and oxygen recovery. The latter two are the indicators of adsorber and vacuum pump size in an adsorption based portable oxygen concentrator. Bed size factor is defined as follows:

$$\text{BSF (lb/TPDO}_2\text{)} = \frac{\text{weight of adsorbent}}{\text{ton of O}_2/\text{day}}$$  \hspace{1cm} (6.12)

From the present limited parametric study using Ag-Li-X adsorbent, the optimum bed size factor obtained using a 3-step VSA process is 280.74 lb/TPDO$_2$ at an oxygen product purity of >90% and recovery of 76% for $t_{cyc}=17$ s, $P_{vac}= 0.2$ bar and $d_p=250$ µm. The power consumption was < 6.5 kW/ TPDO$_2$. Therefore, the present 3-step process has a potential to reduce both the size of adsorption column and vacuum pump size in an adsorption based oxygen concentrator for personal medical application.

6.8 Chapter Conclusion

The effect of process parameters, adsorption time, desorption time and inlet column pressure on performance of PPSA process were experimentally studied and
compared with the isothermal and nonisothermal model simulations results. The experimental results were predicted by the isothermal and nonisothermal model simulation results with good accuracy. The performance of PPSA process for air separation was much inferior than expected (from the simulation results in chapter 3) due to the high axial dispersion in the column packed with very small size adsorbent particles. The maximum oxygen product purity obtained experimentally was less than 40%. A three-step VSA process with product gas pressurization and adsorbent particle size in the range not affected by clustering looked promising from the simulation study. The proposed VSA process using Ag-Li-X adsorbent gave higher oxygen recovery of 76% and bed size factor of 280.74 lb/TPDO₂, and lower power consumption (6.5 kW/ TPDO₂) while the oxygen product purity was >90%.
Chapter 7

CONCLUSIONS AND RECOMMENDATION

7.1 Overview of the Chapter

In this chapter, the major conclusions from the theoretical and experimental study conducted in this research project on adsorption based portable oxygen concentrator for personal medical applications are presented. Considering the limitations surfaced in this study, future recommendations are also made for the portable design of oxygen concentrator for personal medical applications.

7.2 Conclusions

Based on the theoretical and experimental study conducted in this project, the following conclusions are drawn:

1. A mathematical model for a two-step pulsed pressure swing adsorption (PPSA) process was developed from considering the common assumptions in the modeling of cyclic adsorption processes. The process performance was thoroughly investigated by solving the dynamic model equations using COMSOL Multiphysics® software and MATLAB® for air separation on both 5A and Ag-Li-X zeolite adsorbents. For both adsorbents, maximum oxygen product purity was determined for several combinations of operating parameters by systematically varying adsorption and desorption times. The optimum desorption time was longer than the optimum adsorption time to ensure proper regeneration of the bed. These optima arose owing to the self-
purging of the bed with the desorbed high purity oxygen from the region ahead of the adsorption front.

2. The results from extensive simulations covering a wide range of operating conditions were consolidated in three graphical design plots for PPSA air separation on 5A and Ag-Li-X zeolite that allow direct determination of the required process parameters and adsorbent volume in order to achieve desired oxygen purity at an oxygen delivery rate of 5 SLPM. For the same combination of process parameters, 5A zeolite gave higher oxygen product purity but lower recovery (and hence higher adsorbent volume) compared to Ag-Li-X zeolite. The extent of size reduction of an oxygen concentrator operated on a PPSA cycle appeared to be constrained by the upper limit of rapid cycling and reduction in adsorbent particles size that were practically achievable.

3. A multi-purpose experimental setup for the investigation of pressure drop characteristics, breakthrough and PPSA measurements was designed and fabricated based on information obtained from a detailed simulation. Fast cycling of the order of ~1 s between adsorption and desorption steps was achieved in the PPSA experiments.

4. The equilibrium adsorption isotherms of O₂ and N₂ on binderless 5A zeolite adsorbent were measured using a specially designed constant volume apparatus that required less than 1 g of adsorbent material to conduct the experiments. From the binary breakthrough results, it appeared that the extended Langmuir adsorption isotherm model using single component parameters, determined from independent single component experiments, represented the equilibrium behavior of oxygen-nitrogen mixture very well.
5. The pressure drop characteristics of an adsorption column, 10 cm in length and 1.08 cm in diameter and packed with a wide range of adsorbent particle sizes, were measured to study the effect of column to particle diameter ratio on pressure drop along the adsorption column. Darcy's law for flow through porous media was used to model the experimental pressure drop results. The constant in Darcy's law had to be adjusted to 4136.2 instead of 150 when the column was packed with binderless 63 µm to 75 µm 5A adsorbent particles. Very small adsorbent particles and large column to particle diameter ratio (=154) chosen in this study were far away from the available data reported in the literature.

6. Unary and binary dynamic column breakthrough experiments were carried to the study the adsorption and desorption kinetics of O₂ and N₂ in binderless 5A zeolite adsorbent. Detailed isothermal and nonisothermal, axially-dispersed plug-flow simulation models of dynamic column breakthrough experiments were also developed. In the model, the experimentally calibrated Darcy's law to represent the pressure drop along the column, extended Langmuir isotherm model to represent the binary equilibrium, Langer co-relation to estimate the enhanced axial dispersion and Linear Driving Force (LDF) mass transfer model with molecular diffusion in the macro-pores of binderless 5A zeolite adsorbent as the assumed transport mechanism were chosen to predict the experimental breakthrough profiles. The effect of mixing in inlet dead volume was considered by using the experimentally measured blank response (DIB method) data in breakthrough modeling. The experimental and simulation results of single and binary breakthrough measurements showed very good agreement. Further analysis revealed that enhanced axial dispersion controlled
the spread of the mass transfer zone in the column. The increased axial dispersion and pressure drop in the column were attributed to the clustering of small-size adsorbent particles, which led to the uneven bed permeability across the column.

7. Experiments were carried out to investigate the performance of a two-step PPSA process for air separation. The significant deviation of PPSA process performance from the simulation study discussed in chapter 3 were due to the high axial dispersion and pressure drop in the experimental column resulting from the clustering of small-size zeolite adsorbent particles. Using the independently established pressure drop, axial dispersion and heat transfer parameters, the isothermal and nonisothermal models of the PPSA process closely predicted the experimental results.

8. Finally, a simple three-step VSA process was theoretically studied for both 5A and Ag-Li-X zeolite adsorbents by considering the practical limitations on pressure drop and dispersion characteristics in pulsed pressure swing adsorption (PPSA) study. The oxygen recovery, bed size factor and power consumption figures obtained for Ag-Li-X adsorbent at oxygen purity >90% looked promising.

7.3 Future Recommendations

After the theoretical and experimental investigation of a simple two-step PPSA process for air separation using small-size adsorbent particles and the theoretical study of a three-step VSA process considering the limitations in two step PPSA process, the following recommendations are made for the further study on oxygen concentrator size reduction:
Chapter 7. Conclusions and Recommendations

1. Based on the promising performance figures obtained from the simulation study, it is highly desirable to experimentally study the performance of three-step VSA process using superior Ag-Li-X adsorbent for air separation.

2. In order to avoid the clustering of small size crushed zeolite adsorbent particles in a simple two-step PPSA process, the substitution/coating of core 5A or Ag-Li-X adsorbent powder on a suitable supporting material, such as Silica (SiO₂), Alumina (Al₂O₃) and Ferrous oxide (Fe₂O₃) may be considered. Furthermore, the use of structured adsorbents, honeycomb, monoliths and fibrous adsorbents, may reduce the axial dispersion and pressure drop along the column. Therefore, these two approaches are highly recommended for further investigation of the two-step PPSA processes.

3. In a rapid pressure swing adsorption process, the mass transfer kinetics and bed pressure drop are strongly dependent on adsorbent particles size. Preliminary simulation results showed that the RPSA process performance can be further improved by layering the adsorption column with different adsorbent particle sizes. A detailed experimental and theoretical analysis of the bed layering in a RPSA process will be a very interesting work.


Bibliography


Bibliography


Hutson N. D., Rege S. U., and Yang R. T. Mixed Cation Zeolites: Li$_x$Ag$_y$-X as a


Krantz W. C., and Sircar S. Pressure Swing Adsorption Process for a Medical Oxygen


Bibliography


APPENDIX A

DIMENSIONLESS EQUATIONS IN CHAPTER 3

Dimensionless equations

Equations (3.5)-(3.9) and (3.12)-(3.20) were made dimensionless by introducing the following dimensionless variables.

\[ P^* = \frac{P}{P_l}; \quad p^*_A = \frac{p_A}{P_l}; \quad \bar{q}^*_A = \frac{\bar{q}_A}{q^*}; \quad \bar{q}^*_B = \frac{\bar{q}_B}{q^*}; \quad q^*_A = \frac{q_A}{q^*}; \quad q^*_B = \frac{q_B}{q^*}; \quad k^*_A = \frac{\tau d^2 q^* p_{avg} RT L_A k_A}{60 \epsilon p_l D_M}; \]

\[ k^*_B = \frac{\tau d^2 q^* p_{avg} RT L_B k_B}{60 \epsilon p_l D_M}; \quad t^* = \frac{d^2 P_t \left( \frac{\epsilon}{1-\epsilon} \right)^2}{150 \mu L^2} ; \quad z^* = \frac{z}{L}; \quad u^*_z = \frac{150 \mu L}{d^2 P_t} \left( \frac{1-\epsilon}{\epsilon} \right)^2 \]

Substituting these dimensionless variables in the above equations results in the following dimensionless equations:

\[ \frac{\partial p^*_A}{\partial t^*} = \Pi_1 \left[ \frac{0.7}{(\Pi_7 + 1)} + 0.5 \frac{\Pi_7}{\Pi_1} \left( 1 - \frac{1}{\Pi_7} \right) \right] \frac{\partial}{\partial z^*} \left[ p^* \frac{\partial}{\partial z^*} \left( p^*_A \right) \right] - \frac{\partial}{\partial z^*} \left( p^*_A u^*_z \right) \]  
(A1)

\[ \frac{\partial P^*}{\partial t^*} = \frac{\partial}{\partial z^*} \left( P^* u^*_z \right) - \Pi_2 \frac{\partial}{\partial t^*} \left( \bar{q}^*_A + \bar{q}^*_B \right) \]  
(A2)

\[ u^*_z = - \frac{\partial P^*}{\partial z^*} \]  
(A3)

\[ \frac{\partial \bar{q}^*_A}{\partial t^*} = \frac{\Pi_{11}}{(1+\Pi_7)} \frac{\Pi_1}{\Pi_4} \frac{1}{\Pi_3 \Pi_5} k_A^* (q_A^* - \bar{q}_A^*) \]  
(A4)

\[ \frac{\partial \bar{q}^*_B}{\partial t^*} = \frac{\Pi_{11}}{(1+\Pi_7)} \frac{\Pi_1}{\Pi_4} \frac{1}{\Pi_3 \Pi_6} k_B^* (q_B^* - \bar{q}_B^*) \]  
(A5)

\[ q_A^* = \frac{p_A^*}{1 + \Pi_5 p_A^* + \Pi_6 \left( P^* - p_A^* \right)} \]  
(A6)

\[ q_B^* = \frac{P^* - p_A^*}{1 + \Pi_5 p_A^* + \Pi_6 \left( P^* - p_A^* \right)} \]  
(A7)

\[ k_A^* = \left[ 1 + \Pi_5 p_A^* + \Pi_6 \left( P^* - p_A^* \right) \right] \]  
(A8)

\[ k_B^* = \left[ 1 + \Pi_5 p_A^* + \Pi_6 \left( P^* - p_A^* \right) \right] \]  
(A9)
Appendix A: Dimensionless Equations in Chapter 3

\[ P^* \frac{\partial}{\partial z^*} \left( \frac{p^*_A}{P^*} \right) = \frac{1}{\Pi_1} \left[ 0.7 \left( \frac{1}{\Pi_7 + 1} \right) + 0.5 \frac{\Pi_2}{\Pi_1} \left( 1 - \frac{1}{\Pi_7} \right) \frac{\Pi_4}{\Pi_4} \right] \frac{\partial P^*}{\partial z^*} (\Pi_\lambda \Pi_\delta - p^*_A) \]

\[ P^* = \Pi_\delta \]

at \( z^* = 0^+ \)

\[ \frac{\partial}{\partial z^*} \left( \frac{p^*_A}{P^*} \right) = 0 \]

\[ \frac{\partial}{\partial z^*} \left( \frac{p^*_A}{P^*} \right) = 0 \]

\[ P^* = 1 \]

\( (A10) \)

The dimensionless groups in the above dimensionless equations are defined as follows:

\[ \Pi_1 = \frac{150 \mu D_m}{d_p^2 P_L} \left( \frac{1 - \varepsilon}{\varepsilon} \right)^2 \]  

\[ \Pi_2 = \frac{1 - \varepsilon}{\varepsilon} \]  

\[ \Pi_3 = \frac{RT \bar{q}^*}{P_L} \]  

\[ \Pi_4 = \frac{d_o}{L} \]  

\[ \Pi_5 = \frac{b_4}{RT} P_L \]  

\[ \Pi_6 = \frac{b_8}{RT} P_L \] 

\( (A15), (A16), (A17), (A18), (A19), (A20) \)
Appendix A: Dimensionless Equations in Chapter 3

\[ \Pi_7 \equiv \frac{P_{\mu}}{P_L} \]  \hspace{1cm} (A21)

\[ \Pi_8 \equiv \frac{y_{j0}}{\mu} \]  \hspace{1cm} (A22)

\[ \Pi_9 = \frac{t_a P_L}{\mu} \]  \hspace{1cm} (A23)

\[ \Pi_{10} = \frac{t_d P_l}{\mu} \]  \hspace{1cm} (A24)

\[ \Pi_{11} = \frac{60\epsilon}{\tau} \] \hspace{1cm} (A25)

Hence the oxygen product purity, recovery and productivity will be a function of dimensionless groups defined in equations A15–A25; that is,

\[
\begin{align*}
\text{Oxygen purity} & \quad \Pi_1, \Pi_2, \Pi_3, \Pi_4, \Pi_5, \Pi_6, \Pi_7, \Pi_8, \Pi_9, \Pi_{10}, \Pi_{11} \\
\text{Oxygen recovery} & \quad f(\Pi_1, \Pi_2, \Pi_3, \Pi_4, \Pi_5, \Pi_6, \Pi_7, \Pi_8, \Pi_9, \Pi_{10}, \Pi_{11}) \quad (A26)
\end{align*}
\]

For air separation using a specified adsorbent, operating pressures and temperature, the oxygen product purity, recovery and productivity are only a function of five dimensionless groups; the remaining dimensionless groups are dependent on adsorbent properties, feed gas mole fraction and operation pressure, and temperature. Therefore, for air separation using a specific adsorbent it follows that

\[
\begin{align*}
\text{Oxygen purity} & \quad \Pi_1, \Pi_4, \Pi_7, \Pi_9, \Pi_{10} \\
\text{Oxygen recovery} & \quad f(\Pi_1, \Pi_4, \Pi_7, \Pi_9, \Pi_{10}) \quad (A27)
\end{align*}
\]

If the oxygen product purity is maximized with respect to the durations of the adsorption and desorption steps, two additional independent equations are generated that can be used to eliminate the dimensionless groups \( \Pi_9, \Pi_{10} \). Hence, the oxygen product purity, recovery and productivity mainly will depend on only three dimensionless groups namely \( \Pi_1, \Pi_4, \Pi_7 \).
Appendix A: Dimensionless Equations in Chapter 3

\[
\begin{align*}
\text{Oxygen purity} & \\
\text{Oxygen recovery} & \equiv f(\Pi_1, \Pi_4, \Pi_7) \\
\text{Productivity} & \\
\end{align*}
\]

Therefore, from the above equation, the effect of process parameters, bed length and particle size, can be studied in terms of dimensionless groups $\Pi_1$ and $\Pi_4$ for a constant value of the other dimensionless group $\Pi_7$, which is only a function of the maximum pressure in the cycle.
APPENDIX B

DIMENSIONLESS FORM OF NONISOTHERMAL MODEL EQUATIONS

The dimensionless forms of Equations (5.15), (5.17)-(5.22) and (3.5)-(3.9) are obtained by introducing the following dimensionless variables:

\[ \bar{P} = \frac{P}{P_r}; \quad \bar{T} = \frac{T}{T_r}; \quad \bar{T}_w = \frac{T_w}{T_r}; \quad \bar{x}_i = \frac{\bar{q}_i}{q_i}; \quad \bar{x}_i^* = \frac{q_i^*}{q_i}; \quad \bar{u}_z = \frac{u_z}{u_r}; \quad \bar{Z} = \frac{z}{L}; \quad \bar{r} = \frac{u_r}{L} \]

\[ \frac{\partial \bar{y}_A}{\partial \bar{r}} = \frac{1}{Pe} \left( \frac{\partial^2 \bar{y}_A}{\partial \bar{Z}^2} + \frac{1}{\bar{P}} \frac{\partial \bar{y}_A}{\partial \bar{Z}} \frac{\partial \bar{P}}{\partial \bar{Z}} \frac{1}{\bar{T}} \frac{\partial \bar{y}_A}{\partial \bar{Z}} \right) - \bar{u}_z \frac{\partial \bar{y}_A}{\partial \bar{Z}} + \phi \bar{T} \left( y_A - 1 \right) \frac{\partial \bar{x}_A}{\partial \bar{r}} + y_A \frac{\partial \bar{x}_A}{\partial \bar{r}} \]

(B1)

\[ \frac{\partial \bar{P}}{\partial \bar{r}} = -\bar{P} \frac{\partial \bar{u}_z}{\partial \bar{Z}} - \bar{u}_z \frac{\partial \bar{P}}{\partial \bar{Z}} + \bar{P} \frac{\partial \bar{T}}{\partial \bar{Z}} - \phi \bar{T} \frac{\partial \bar{r}}{\partial \bar{r}} (x_A + x_B) + \frac{\bar{P}}{\bar{T}} \frac{\partial \bar{T}}{\partial \bar{r}} \]

(B2)

\[ \frac{\partial \bar{T}}{\partial \bar{r}} = \frac{1}{Pe_H} \frac{\partial^2 \bar{T}}{\partial \bar{Z}^2} - \pi_x \bar{u}_z \frac{\partial \bar{T}}{\partial \bar{Z}} + \sum_{i=1}^{N} \left( \pi_{x,i} \frac{\partial \bar{x}_i}{\partial \bar{r}} - \pi_x \left( \bar{T} - \bar{T}_w \right) \right) \]

(B3)

\[ \frac{\partial \bar{T}_w}{\partial \bar{r}} = \pi_x \frac{\partial^2 \bar{T}_w}{\partial \bar{Z}^2} + \pi_x \left( \bar{T} - \bar{T}_w \right) - \pi_x \left( \bar{T}_w - \frac{T_w}{T_r} \right) \]

(B4)

\[ \frac{\partial \bar{x}_i}{\partial \bar{r}} = \alpha_i (x_i^* - x_i) \quad \alpha_i = \frac{Lk_i}{u_r} \]

(B5)

\[ \bar{u}_z = -\gamma \frac{\partial \bar{P}}{\partial \bar{Z}} \]

(B6)

\[ x_i^* = \frac{\beta_i \bar{P}}{\bar{T}} x_i \]

(B7)
Appendix B: Dimensionless Form of Non–Isothermal Model Equations

Initial conditions

\[
\begin{align*}
    y_A &= y_{A0} \\
    \bar{P} &= \eta_1 \\
    x_A &= x_{A0} \\
    x_B &= x_{B0} \\
    \bar{T} &= \frac{T_a}{T_R} \\
    \bar{T}_w &= \frac{T_0}{T_R}
\end{align*}
\]

at \( \tau = 0, \ 0 \leq Z \leq 1 \) \( \text{(B8)} \)

Adsorption (section 5.4.2 and section 6.3.2)

\[
\begin{align*}
    -\frac{1}{Pe} \frac{\partial y_A}{\partial Z} &= \frac{u_0}{u} (y_{A0} - y_A) \\
    -\frac{1}{Pe \mu} \frac{\partial \bar{T}}{\partial Z} &= \pi_7 \left( \frac{T_0}{T_R} - \bar{T} \right) \\
    \bar{T}_w &= \frac{T_a}{T_R}
\end{align*}
\]

at \( Z = 0^*; \ * \text{in section 6.8.2} \) \( \text{(B9)} \)

\[
\begin{align*}
    \bar{P} &= \eta_2 - (\eta_2 - \eta_1) e^{-\frac{u_0^*}{T_R}} \\
    (or) \\
    \bar{u}_z &= \frac{u_0^*}{u_0}
\end{align*}
\]

Desorption (section 6.3.2)

\[
\begin{align*}
    \frac{\partial y_A}{\partial Z} &= 0 \\
    \frac{\partial \bar{T}}{\partial Z} &= 0 \\
    \bar{T}_w &= \bar{T}_u \\
    \bar{P} &= \frac{P_L}{P_R}
\end{align*}
\]

at \( Z = L^- \) \( \text{(B10)} \)
Appendix B: Dimensionless Form of Non–isothermal Model Equations

\[
\begin{align*}
\frac{\partial y_A}{\partial Z} &= 0 \\
\frac{\partial T}{\partial Z} &= 0 \\
\bar{T}_w &= \frac{T_a}{T_R} \\
\bar{P} &= \eta_l + (\eta_2 - \eta_l) e^{-\frac{a_l}{\bar{T}_R}} \quad \text{at } Z = 0^+ \\
\frac{\partial y_A}{\partial Z} &= 0 \\
\frac{\partial T}{\partial Z} &= 0 \\
\bar{T}_w &= \bar{T}_a \\
\bar{u}_z &= 0 \quad \text{at } Z = L^- \\
\frac{\partial y_A}{\partial Z} &= 0 \\
\frac{\partial T}{\partial Z} &= 0 \\
\frac{\partial \bar{P}}{\partial Z} &= 0 \\
\bar{u}_z &= 0 \quad \text{at } Z = 0^- \\
-\frac{1}{Pe} \frac{\partial \bar{T}}{\partial Z} &= \bar{u}(y_{A0} - y_A) \\
-\frac{1}{Pe_H} \frac{\partial \bar{T}}{\partial Z} &= \alpha_y \left( \frac{T_0}{T_R} - \bar{T} \right) \quad \text{at } Z = L^- \\
\bar{P} &= \eta_2 - (\eta_2 - \eta_l) e^{-\frac{a_l}{\bar{T}_R}} \\
\end{align*}
\]

Reverse Pressurization (section 6.8.2)

The dimensionless equations contain the following dimensionless groups:

\[
\begin{align*}
\alpha_i &= \frac{k_i L}{u_o} \\
\beta_i &= \frac{b_i P_R}{R_i T_R} \quad ; \quad b_i = b_i^0 e^{-\frac{M_i}{BT}} \\
\gamma &= \frac{k_f P_R}{\mu u_k L} \\
\end{align*}
\]
Appendix B: Dimensionless Form of Non–isothermal Model Equations

\[ \eta_1 = \frac{P_L}{P_R} \]

\[ \eta_2 = \frac{P_H}{P_R} \]

\[ Pe = \frac{u_L H}{D_L} \]

\[ Pe_H = \frac{\varepsilon \Delta u_R L}{K_z} \]

\[ \phi = \frac{1 - \varepsilon}{\varepsilon} \frac{q_R T_R}{P_R} \]

\[ \pi_1 = \frac{K_v}{L \rho_w u_R c_{pw}} \]

\[ \pi_2 = \frac{2 r h_1 L}{\rho_w C_{pw} u_R \left( r_o^2 - r_i^2 \right)} \]

\[ \pi_3 = \frac{2 r h_o L}{\rho_w C_{pw} u_o \left( r_o^2 - r_i^2 \right)} \]

\[ \pi_4 = \frac{\rho_g C_{pf} {L}}{\lambda} \]

\[ \pi_5 = \left( \frac{1 - \varepsilon}{\varepsilon} \right) \frac{\Delta H_d q_x}{\lambda T_R} \]

\[ \pi_6 = \frac{2 h L}{\lambda \varepsilon r_i u_R} \]

\[ \pi_7 = \frac{\rho_g C_{pf} u_o}{\varepsilon \lambda u_R} \]
APPENDIX C

EQUILIBRIUM DATA OF NITROGEN AND OXYGEN ON BINDERLESS 5A ZEOLITE

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### Appendix C: Equilibrium Data of Nitrogen and Oxygen on Binderless 5A zeolite

#### Oxygen

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<th>Temperature (K)</th>
<th>Pressure (bar)</th>
<th>Amount adsorbed (mmol/cc)</th>
<th>Temperature (K)</th>
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#### Single component Langmuir isotherm parameters

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<th>Adsorbate</th>
<th>$q_s$ (mol/cc)</th>
<th>$b_o$ (cc/mol)</th>
<th>$\Delta U$ (Kcal/mol)</th>
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