## Intensification of adsorption-based oxygen concentrators using layered beds

by

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 $\mathrm{in}$ 

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### Abstract

Adsorption-based oxygen concentrators are modular devices that take in air and operate using electricity to produce 95% pure oxygen. These devices consume less unit energy and are more economical when producing oxygen on a small-to-medium scale (< 300 tons  $O_2$  per day), compared to cryogenic distillation. State of the art, commercial oxygen concentrators use low-silica lithium exchanged zeolite (LiLSX) adsorbents in vacuum swing processes to achieve this in the most efficient way possible. In recent times, due to a surge in demand for lithium worldwide, many industries, including adsorbent manufacturers, are faced with rising costs and frequent short supply. This has persuaded many manufacturers of oxygen concentrators to revert to adsorbents like sodium-exchanged zeolites (13X), despite their inferior performance. This presents an opportunity to explore adsorption-processes with multiple adsorbents in various proportions arranged in the form of layers. This thesis aims to present a method to study processes involving layered adsorbent beds, and how such systems can be designed and optimized to minimize energy and maximize productivity.

In this work, two common adsorbents have been chosen - LiLSX and 13X to study the behaviour of layered beds. Isotherms of the two adsorbents are measured between 0-12 bar pressure using volumetry. The experimental data is fit to the Singlesite Langmuir (SSL) equation. First, the two adsorbents are considered individually. Unary and binary breakthrough experiments are performed on the single adsorbent systems. A mathematical model has been developed to describe various steps of an adsorptive separation process. PSA experiments are conducted on a test rig constructed in-house to validate the model. A set of optimization studies are performed to get the purity-recovery, and energy-productivity limits in various processes using the two adsorbents individually.

A two-layer adsorbent bed is considered in this study, consisting of LiLSX and 13X. For any given proportion of LiLSX to 13X, two possible configurations of the layered bed are possible, depending on which adsorbent is placed near the feed end. At all stages in this study, these two configurations have been analyzed independently to check for any differences in performance between them. Breakthrough experiments are performed to understand dynamics of gas flow, temperature and composition across the layered bed. The mathematical model is extended to describe adsorption in a layered bed system. This enhanced model is validated by performing unary and binary breakthrough experiments through the layered beds. PSA experiments are performed on the test-rig to further validate the process model. Optimization studies are performed to understand purity-recovery and energy-productivity limits of layered beds with various proportions of LiLSX. Special emphasis is given to understand the differences between the operation of a small lab-scale column with finite heat transfer and an adiabatic column with no heat transfer. It is found that the order in which the layers are arranged does not matter in systems where heat is removed easily. In large scale columns, which tend to behave more adiabatically, placing the adsorbent with lower  $N_2$  capacity (13X in this case) near the feed end gives higher recovery than the reverse configuration.

## Preface

The test rig used to perform breakthrough and PSA experiments, described in Chapter 4 and Chapter 5 was designed, built and instrumented in the laboratory by the author with assistance from Dr. James A. Sawada. Low-pressure volumetry experiments on LiLSX and 13X were conducted by Dr. Tranh Tai Nguyen, an alumnus of the laboratory. High-pressure volumetry experiments on LiLSX and 13X were conducted by a colleague, Raviraju Vysyaraju. All other computations and experiments and their analysis was performed by the author. To my parents, for always encouraging me to think big, and for believing that knowledge is power.

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# List of Symbols

$\overline{t}$	Dimensionless time
$\overline{v}$	Dimensionless velocity
$\epsilon, \epsilon_p$	particle voidage
$\epsilon_b$	bed voidage
$\eta$	compressor/vacuum pump efficiency
$\gamma$	adiabatic constant
$\mu$	fluid viscosity
Ω	Dimensionless group in column energy balance
П	Dimensionless group in wall energy balance
$\psi$	Dimensionless group in mass balance
$\rho_s$	adsorbent particle density
$ ho_w$	wall density
$\sigma$	Dimensionless group in column energy balance
au	tortuosity
A	Cross-sectional area of column
$b_i$	temperature-dependent equilibrium constant of the gas
$c_i$	fluid phase concentration
$C_v$	flow coefficient of the valve
$C_{pa}$	specific heat capacity of the adsorbed phase
$C_{pg}$	specific heat capacity of the gas phase
$C_{ps}$	specific heat capacity of the adsorbent
$C_{pw}$	specific heat capacity of the column wall
$D_m$	molecular diffusivity

$D_p$	Particle diameter
$h_{in}$	inside heat transfer coefficient
$h_{out}$	outside heat transfer coefficient
$K_w$	thermal conductivity of column wall
$K_z$	effective gas thermal conductivity
L	column length
n	moles
P	pressure
$P_e$	Peclet number
Q	flow rate
$q_i$	solid phase concentration
$q_i^*$	equilibrium solid phase concentration
$q_s$	saturation capacity of the solid
$q_s$	saturation concentration in the solid phase
$R, R_g$	universal gas constant
$r_p$	particle radius
$r_{in}$	column inner radius
$r_{out}$	column outer radius
Т	temperature
t	time
$T_a$	ambient temperature
$T_w$	column wall temperature
U	internal energy
V	volume
$v_0$	inlet velocity
$V_d$	dead volume
y	gas phase composition
$Y_i$	gas phase composition

Z axial coordinate

## Abbreviations

- 13X Na-exchanged X-type zeolites.
- **5A** Ca-exchanged A-type zeolites.
- **ASU** Air separation units.
- **BPR** Back Pressure Regulator.
- **BSF** Bed Size Factor.
- **CaX** Calcium exchanged X-type zeolites.
- **CMS** Carbon molecular sieves.
- CSS Cyclic Steady State.
- ${\bf CV}\,$  Control Valve.
- DCB Dynamic Column Breakthrough.
- HPVA High Pressure Volumetric Apparatus.
- I/O Input Output.
- **LDF** Linear Driving Force.
- LHS Latin Hypercube Sampling.
- LiLSX Lithium exchanges Low-Silica X-type zeolites.
- LiX Lithium exchanged X-type zeolites.
- **LPM** Litres Per Minute.
- MFC Mass Flow Controller.

- **MFM** Mass Flow Meter.
- **MOF** Metal Organic Framework.
- MV Manual Valve.
- NSGA Non-dominated Sorting Genetic Algorithm.
- ${\bf NV}\,$  Needle Valve.
- **PE** Pressure equalization.
- **PSA** Pressure Swing Adsorption.
- $\mathbf{PT}$  Pressure Transmitter.
- **PVSA** Pressure Vacuum Swing Adsorption.
- **RPSA** Rapid Pressure Swing Adsorption.
- **SLPM** Standard Litre per minute.
- **SV** Solenoid Valve.
- **TPDO** Tons per day of Oxygen.
- **TVD** Total Variation Diminishing.
- **US-DOE** US Department of Energy.
- **VSA** Vacuum Swing Adsorption.

# Chapter 1 Introduction

Earth's atmosphere is a mixture of gases composed of nitrogen (78%), oxygen (20.9%), argon (0.9%) and small amounts of carbon dioxide, water vapour and other noble gases. The presence of oxygen in the atmosphere makes Earth habitable and sustains life. Oxygen from the air is separated and concentrated for several applications. Industrially, oxygen is used to increase combustion efficiency, and in steel making, pulp-and-paper production, waste-water treatment, etc. In aquaculture, oxygen ensures optimal feed conversion and high survival rates [1]. Physicians also administer oxygen to supplement oxygen obtained by respiration in patients having chronic lung disorders.

For large-scale operations, oxygen is produced by the cryogenic distillation of air. Air is liquefied to -194°C and distilled to separate the various components [2]. Cryogenic distillation has been in place for more than 75 years and is considered a mature technology. This is the work-horse used in meeting large-scale industrial needs for oxygen. Cryogenic air separation units (ASU) can be designed to produce up to 5000 tons/day of oxygen. It is also worth mentioning that using cryogenic distillation can produce ultra high purity oxygen with a concentration of 99.999%

For small-to-medium scale operations requiring less than 300 tons/day of oxygen, Pressure Swing Adsorption (PSA) processes using nitrogen-selective zeolites are used. These adsorption-based oxygen concentrators are compact modular units that need only air and electricity to operate and consume significantly less unit energy than a cryogenic ASU. These units are especially useful for on-site oxygen generation at remote locations - mining operations, aquaculture farms, etc. These are also used by patients requiring long-term oxygen therapy, either in the form of stationary homebased devices or lighter, portable oxygen concentrators.

### 1.1 Adsorption processes for air separation

There are two mechanisms by which adsorption processes can be used for air separation depending on the nature of the adsorbent used. In equilibrium-based adsorbents, for example, zeolites, the pore sizes are large enough to allow all three major components of air - nitrogen, oxygen and argon molecules to be adsorbed. Zeolites are crystalline materials consisting of alumino-silicate frameworks and charge-balancing metal cations. Zeolites like LiLSX, 13X and CaX, which are most commonly used for adsorption-based air separation, work on this principle. Nitrogen molecules exhibit a higher value of quadrupole moment than oxygen or argon. This increases the affinity of nitrogen molecules to the zeolite. When air is passed through a bed of zeolites, nitrogen is adsorbed more strongly than oxygen and argon. Oxygen-enriched raffinate is obtained while the adsorbed nitrogen is blown down as extract.

Kinetic-based adsorbents separate molecules based on differences in diffusion rates. Carbon molecular sieves (CMS) are examples of such adsorbents. When air is passed through a bed of carbon molecular sieves, oxygen, which has a smaller kinetic diameter, will diffuse into the adsorbent. At the same time, nitrogen will be obtained in a pure form at the other end. Hence, CMS produces high-purity nitrogen, while zeolites are more commonly used for oxygen purification.

Adsorption-based separation processes exploit the changing equilibrium capacities, or the ability to adsorb gas molecules by the adsorbent at various pressures or temperatures. More gas can be adsorbed per unit mass of adsorbent with increasing pressures and decreasing temperatures. To continuously produce concentrated oxygen from the air, a packed bed of a suitable adsorbent is subjected to repeated cycles of pressurization and depressurization. During the pressurization step, air is fed from one end of the packed bed; nitrogen is adsorbed by the solid, and concentrated oxygen is obtained from the other end. During the depressurization (blowdown or evacuation) step, the feed end is opened to release a nitrogen-rich extract stream. This cleans the bed and makes the adsorption sites available for the subsequent feed air stream.

Depending on the high and low pressures used in the pressurization and evacuation steps of the adsorption cycle, there are three different kinds of adsorption systems. In Pressure Swing Adsorption (PSA) cycles, air pressurized above atmospheric levels up to 5 bar is used to pressurize the column. The column is blown down to atmospheric pressure in the next step to remove the adsorbed nitrogen. In Vacuum Swing Adsorption (VSA) cycles, air at atmospheric pressure (1 bar) is used to pressurize the column, followed by evacuation to vacuum pressures of 0.2-0.5 bar. In a third kind of cycle, air pressurized slightly above atmospheric conditions (1.3-1.5 bar) is used in the pressurization step followed by evacuation to moderate vacuum levels, i.e., 0.5 bar [3]. All of the cycles operate using the same principle - exploiting the differences in affinity of the adsorbent to nitrogen at different pressures. However, the kind of process selected will have an impact on the capital and operating expenses of running an oxygen concentrator. The flow rate and levels of compression/evacuation needed will decide the compressor/vacuum pump size, respectively. Moreover, a PSA system operating at high pressure will require piping and vessels of appropriate pressure-rating for safe operation.

#### **1.2** Motivation

In the earliest days of adsorption-based air separation, zeolites 5A and 13X, which contain calcium and sodium ions, were widely used. As the technology developed, efforts were made to use mixed-cation zeolites to influence the shape of the isotherm and produce adsorbents with higher  $N_2$  capacity and improved  $N_2/O_2$  selectivity [4].

The development of Lithium-X (LiX) type adsorbents was a turning point in adsorptive air separation. In particular, Chao's discovery of high-Li exchanged (at least 88% of AlO<sub>2</sub> tetrahedral units associated with Li<sup>+</sup> ions) low-silica (ratio of Si/Al tetrahedral units = 1) zeolites made adsorptive air-separation easier than ever before [4, 5]. Lithium ions initially occupy sites on the zeolite framework that are not accessible by N<sub>2</sub>, O<sub>2</sub> molecules. When Li<sup>+</sup> exchange levels are increased beyond 75%, the ions start occupying sites that are far more accessible to these molecules. Kirner [6] documented this and observed a dramatic, almost linear increase in N<sub>2</sub> capacity of the zeolite adsorbent when Li<sup>+</sup> exchange levels are beyond 75%. As the Si/Al ratio decreases, the number of Li<sup>+</sup> ions to counter the effective structural charge increases. This leads to an increase in N<sub>2</sub> affinity and lowers the amount of O<sub>2</sub> that can be adsorbed [4, 7]. Along with high N<sub>2</sub> capacity, these new high-Li exchanged, low-silica zeolites (also known as LiLSX) exhibit good N<sub>2</sub>/O<sub>2</sub> selectivity as well.



Figure 1.1:  $N_2$  loading at various  $Li^+$  exchange %. Reproduced with permission from [4].

Although there were adsorbents that exhibited higher  $N_2/O_2$  selectivity like calciumexchanged low-silica X-type zeolite (CaLSX), their  $N_2$  working capacity was still considerably low, requiring either deep vacuum during the evacuation step, or high pressures during the compression step. LiLSX is exceptional because of its high  $N_2$ working capacity between pressures 0.5 bar to 1.5 bar. This allows us to design an efficient PVSA process with minimal compression and evacuation costs to produce oxygen at a competitive cost.

In recent years, the push to move towards renewable energy has created a high demand for Li-ion batteries. Currently, there exists a supply-demand gap in Lithium in the commodity market. Although several new Lithium reserves have been discovered, it will be several years before the supply-demand gap is closed. Fig 1.2 shows how the cost of Lithium ore has risen over eight times within one year between 2021-2022 [8].



Figure 1.2: Cost of Lithium hydroxide between 2021-2022 [8].

This price rise has echoed across the entire supply chain, from zeolite manufacturing to the fabrication of oxygen concentrators. The increased prices of LiLSX have forced some operators to switch back to 13X or CaLSX-based adsorption processes despite being less energy efficient than LiLSX. An inherent trade-off exists between capital costs (primarily the cost of adsorbent) and operating costs (primarily the cost of compression or evacuation according to the choice of operating pressures). This lithium crisis motivates us to explore the trade-off in detail for the case of adsorptive air separation.

New approaches are needed to overcome this challenge. One way would be to develop new sorbents that can offer significantly higher  $N_2$  capacities and  $N_2/O_2$  selectivities. Several works highlight using novel metal-organic frameworks (MOFs) that offer superior separation characteristics. Membrane separation processes using unique polymer frameworks are also proposed as an efficient way to separate oxygen from air. Another approach would be to identify steps for improving adsorption processes. For example, drying feed air to remove moisture before feeding to the adsorbents is a necessary but highly energy-consuming step of the separation process. Some waste heat in the  $N_2$  enriched blowdown gas can be used to reduce the energy consumed in drying. This will help reduce the unit energy of  $O_2$  produced. Such incremental improvements can increase the efficiency of  $O_2$  purification.

One of the ways we can explore this trade-off is to consider a packed column with layers of two kinds of adsorbents. The ratio of volume filled with each adsorbent can be varied to study adsorption process performance as a function of this ratio. In this work, two adsorbents have been considered for the layered bed - LiLSX and 13X, and the performance of air separation systems using these two adsorbents is studied as a function of the ratio of each adsorbent in the packed bed.

### 1.3 Thesis Outline

This work aims to study the effect of stacking layers of two different kinds of adsorbents in a packed bed on adsorptive air separation performance. The following steps are carried out to systematically achieve this objective for each adsorbent system.

- Obtaining and describing single-component isotherms of N<sub>2</sub>, O<sub>2</sub> and Ar on LiLSX and 13X for various temperatures across a large range of pressures.
- An experimental test rig was built to perform lab-scale dynamic column breakthrough and PSA experiments.
- Dynamic column breakthrough experiments were performed for both single component and binary mixtures of  $N_2$  and  $O_2$  to understand the nature of competition between these gases on LiLSX and 13X.
- A rigorous mathematical model is built to simulate adsorption dynamics. Simulations of dynamic column breakthrough experiments are compared with the experimental data.
- PSA experiments are conducted on the test rig, and the mathematical model is extended to simulate a 4-step Skarstrom cycle.
- Two optimization studies are conducted using the model one to maximize purity and recovery and the other to maximize productivity and minimize energy.

Chapter 2 reviews the existing literature on adsorption processes for oxygen concentration, with a special emphasis on using multiple adsorbents.

Chapter 3 details the materials and methods used for this study. Details about the design and construction of the experimental test rig and the experimental procedure are provided. Transport equations that form the basis of the detailed model are provided. Routines used for optimization studies and for building the surrogate model are discussed.

Chapter 4 considers single sorbent systems, where columns packed with only a single adsorbent are studied. Two adsorbents are considered for this - LiLSX and 13X. Adsorption isotherms are measured and modelled, dynamic column breakthrough experiments are conducted, and a detailed model is built to simulate these experiments. PSA experiments are conducted and simulated, and optimization studies are done for various pressure ranges.

Chapter 5 considers using two sorbents arranged by stacking them in two layers within the column. The adsorbents considered for this are the same as those in single sorbent systems - 13X and LiLSX. Different proportions of the individual sorbents are studied for their effect on PSA performance. Dynamic column breakthrough and PSA experiments are conducted and simulated using a model that can capture the effect of layering adsorbents. Purity-recovery and energy-productivity optimization studies are done to understand separation performance as a function of pressure ranges and the proportion of high-performing LiLSX.

# Chapter 2 Literature review

The following sections discuss a review of the developments in various aspects of adsorption-based air separation, from its early days to state-of-the-art technology. Choice of adsorbent, adsorption kinetics, choice of adsorption cycle, performance metrics and experimental design are discussed. This is followed by a comprehensive review of earlier works where simultaneous use of multiple adsorbents in air separation have been reported.

### 2.1 Choice of adsorbent

The first step in designing an adsorptive separation process is to find a suitable adsorbent [9]. In distillation processes, selectivity is fixed by the relative volatility of the components in the mixture to be separated. Unlike distillation, an extra degree of freedom is available in adsorption processes by choosing the adsorbent [10]. Selectivity in adsorption processes is largely influenced by the choice of adsorbent and how each component of the mixture interacts with the adsorbent. Ideally, the adsorbent should have a sufficiently large capacity, high selectivity and fast kinetics for efficient operation. The cost and robustness of the adsorbent will decide the ease with which it can be scaled up for commercialization.

Zeolites are synthetic crystalline alumino-silicates and are used as adsorbents for a variety of gas separation processes. By the nature of their crystal structure, zeolites have a specific pore size. Metal cations are introduced to balance the net negative charge present in the framework. These metal cations create non-uniform electrostatic fields around them. Depending on the interaction between the electrostatic fields of the gas molecules and the metal cation, molecules are adsorbed in the zeolite framework to varying degrees [4, 9]. The ratio of silicon to aluminum ions in the framework, and charge, size and location of the metal cation influence the nature of the electrostatic fields.

PSA processes for oxygen production found their biggest utility in substituting air in industrial combustion processes to improve efficiency. In the early days, 5A (Ca-exchanged A-type zeolites) and 13X (Na-exchanged X-type zeolites) were popularly used as adsorbents. With the rapid development of adsorption processes, several improvements in adsorbent design were suggested to incorporate favourable characteristics like higher N<sub>2</sub> capacity, higher N<sub>2</sub>/O<sub>2</sub> selectivity, higher mass transfer rate, improved binder etc. This was followed by the discovery of low silica Li-exchanged Xtype zeolites (LiLSX) that had significantly higher N<sub>2</sub> capacity and N<sub>2</sub>/O<sub>2</sub> selectivity, which altered the adsorbent landscape at that time.



Figure 2.1:  $N_2$  isotherms for LiLSX and 13X

Around the same time, several researchers started to explore zeolite frameworks with two or more kinds of metal cations. Coe et al. [11] found that having a mix of  $\text{Li}^+$  and alkaline earth metal cations like  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  exhibited enhanced N<sub>2</sub> working capacity between 0.2-1 atm pressures as compared to single-cation exchanged adsorbents.

Hutson et al. prepared X-type zeolites having  $Ag^+$  and  $Li^+$  ions mixed in various proportions [12]. In an earlier work, they identified by conducting ab initio molecular orbital calculations that  $N_2$  adsorption is enhanced by weak chemical interactions with the d-orbitals of  $Ag^+$  ions present in the zeolite framework. They varied the amount of  $Ag^+$  ions per unit cell in the crystalline structure and found that increasing the amount of  $Ag^+$  ions increases the equilibrium  $N_2$  capacity. They also conducted PSA simulation studies and concluded that  $Ag^+$  substituted zeolites gave higher productivity (described as kg  $O_2/h/kg$  adsorbent) at the same purity and recovery when compared with a zeolite containing only  $Li^+$  and  $Na^+$  ions.

Although several such novel zeolites continue to appear in academic literature, most manufacturers have found that PVSA systems using LiLSX zeolites give the best oxygen concentration performance. Operating costs drive decisions in choosing an appropriate adsorbent for industrial oxygen concentrators. These efficient LiLSXbased systems produce oxygen with unit energy as low as  $0.2 \text{ kWh/kg O}_2$ . Some of the older systems that continue to be in operation use 13X or 5A zeolites.

Apart from the type of zeolite, there are other factors that inform our choice of adsorbent. Industrial PSA systems typically use larger diameter zeolite sieves (1.3-2 mm). Specialty devices like medical oxygen concentrators have more stringent portability and total weight requirements. Smaller-sized zeolite sieves (0.4-0.8 mm) that offer faster kinetics and improved performance are used in such cases. These smaller sieves are often more expensive than similar ones having larger diameters [4].

Other adsorbents like silver-exchanged titanosilicates (Ag-ETS-10) offer higher  $O_2/Ar$  selectivity, opening the possibility of producing ultra pure oxygen from adsorption-

based processes. Hejazi et al. conducted a materials-to-process study using Ag-ETS-10. In their two-part work, Hejazi et al. show breakthrough experiments and an experimentally validated mathematical model of a VSA system that can produce 99.5% pure O<sub>2</sub> [13, 14].

### 2.2 Adsorption kinetics

Zeolite crystals are usually pelletized with binders like clay, silica or alumina to enhance their structural integrity. The binders allow diffusion of gases into and out of the zeolite crystal. The pelletizing process thus coats the zeolite crystal with an inert material. For gas to be able to adsorb at the zeolite crystal, the gas molecule has to travel from the outer surface of the pellet through an intricate network of pores before it can reach the zeolite crystal. Similarly, gas molecules have to travel through the pores during desorption before they can be released at the outer surface of the pellet. In zeolites, the resistance for gas molecules to travel through the binders' macropores dominate.

Information about adsorption kinetics is important to understand how fast adsorptiondesorption cycles can be implemented to utilize the full range of the working capacity of the adsorbent. This will in turn significantly impact the productivity of the PSA process. The linear driving force (LDF) model can be used to describe the adsorption rate on a zeolite using a lumped mass transfer coefficient.

$$\frac{\partial q_i}{\partial t} = \alpha_i (q_i^* - q_i) \tag{2.1}$$

$$\alpha_i = \frac{c_i}{q_i^*} \frac{15\epsilon_p D_p}{r_p^2} \frac{L}{v_0}$$
(2.2)

The LDF model is a truncated series solution of the pore diffusion model [15]. Under the assumption that the surface concentration of the particle changes slowly, the timederivative terms of surface concentration in the pore diffusion model can be ignored to get the LDF model. This assumption and the LDF model are valid for most equilibrium-based separation applications to describe the adsorption mass transfer. It is also clear that as the particle radius decreases, the resistance to mass transfer decreases, indicating that smaller particles can favour faster cycles.

The LDF model fails when the surface concentration change is rapid enough that the time-derivative terms of the pore diffusion model cannot be ignored. This is true for rapid PSA cycles, where the step times are of the order of a few seconds. Lee and Kim derived a higher-order approximation of the pore diffusion model to be used in such cases [15]. Their modified LDF model is of the following form.

$$\frac{\partial q_i}{\partial t} = \frac{D_p}{r_p^2} (-105q_i + z + 42q_i^*) \tag{2.3}$$

$$\frac{\partial z}{\partial t} = \frac{D_p}{r_p^2} (945)(q_i^* - q_i) \tag{2.4}$$

Jee et al. implemented this modified LDF equation in a model describing a smallscale 2-bed medical  $O_2$  PSA unit [16]. They found that the concentration and temperature profiles obtained from the modified LDF model agreed better with the experimental observations than the regular LDF model.

#### 2.3 Choice of adsorption-cycle

In 1960, C. W. Skarstrom filed a patent for a 2-bed cyclic adsorption process for air dying and oxygen concentration purposes [17]. The cycle featured in the patent, known thereafter as Skarstrom cycle is the first technology used for adsorptive air separation. The adsorption process consists of four steps - feed pressurization, adsorption, blowdown and purge, as shown in Fig. 2.2. The characteristic feature of this cycle is the purge step, also known as light reflux or backflow, in which a portion of the produced  $O_2$  rich gas is fed to the bed's product end at low pressure. This reduces the partial pressure of nitrogen in the bed during desorption and allows  $N_2$  to desorb from the bed more thoroughly. The adsorbent is now clean and ready to adsorb more  $N_2$  in the next feed pressurization step. In addition, Skarstrom also stressed the importance of having faster cycles to reduce the time available for heat fronts to travel along the column.  $O_2$  enriched gas from the adsorption cycle will be at a higher temperature than ambient. When this gas flows through a desorbing bed, the magnitude of temperature reduction is lower. This further enhances the desorption of  $N_2$  from the zeolite.



Figure 2.2: Illustration of Skarstrom cycle as implemented on the experimental test rig

The Skarstrom cycle continues to be popular for  $O_2$  concentration because of its simplicity and effectiveness. Some variations to the basic Skarstrom cycle have also been proposed. An interesting analogy is made by Knaebel and Hill where a PSA system is compared to a pump [18]. As a way of priming the pump, a PSA process would benefit from being fed  $O_2$  rich gas while starting up the cycle, and reach steadystate faster. Specifically, they claim that using light product pressurization instead of feed pressurization gives a higher recovery of oxygen.

Pressure equalization (PE) steps can be introduced in multi-bed systems, where one column is blown down to an intermediate pressure while the removed gas is directed to another column at low pressure. PE steps significantly improve recovery and conserve energy in PSA processes [19]. Such a step allows for gases accumulated in the dead volumes in the equipment to be recycled without being lost in the evacuation steps.

Once the steps of an adsorption cycle are fixed, operating variables like high and low pressures, individual step times, feed, product and purge flow rates can be varied to study their effect on PSA performance. Pressurization and adsorption steps aim to allow as much  $N_2$  to be adsorbed onto the zeolite so that high-purity  $O_2$  enriched gas can be withdrawn from the product end. Once the zeolite is saturated with  $N_2$ , the  $N_2$  wavefront breaks through the column, allowing  $N_2$  to mix with the product gas and contaminate it. Similarly, the blowdown/evacuation and purge steps aim to allow  $N_2$  to be desorbed as much as possible to regenerate the bed and prepare it for the next pressurization + adsorption cycle. In this case, the  $N_2$  concentration wavefront will be pushed back towards the feed end of the column.

In addition to the concentration wavefronts, heat fronts are also generated in PSA cycles. When gases are adsorbed, heat is generated and when they are desorbed, heat is removed. Over several cycles, these repetitive heat swings can lead to a condition called adverse thermal swing [4]. The feed end of the column can get progressively cooler. This affects the process performance, as the capacity of zeolite reduces at lower temperatures. During adsorption steps,  $N_2$  is not sufficiently adsorbed, and in evacuation/blowdown steps,  $N_2$  does not get completely desorbed.

Selection of a process between PSA, VSA and PVSA could depend on the conditions of the feed air, and the shape of the isotherm of the adsorbent. Ackley explains how each adsorbent has an optimum high and low pressure based on the region on the isotherm where the largest difference in  $N_2$  equilibrium capacity is seen for the least change in pressure [4]. This simple metric helps us visualize and see that PSA processes are suited for 13X, VSA processes for CaX and PVSA processes for LiLSX, to ensure optimum utilization.

Jee et al. defined purge-to-feed ratio as the ratio of moles of  $O_2$  in the purge step to the moles of  $O_2$  in the inlet steps [16]. They experimentally demonstrated using the Skarstrom cycle on 13X adsorbent that there exists a limiting purge-to-feed ratio of 0.8-0.9 beyond which very marginal improvements in purity are observed. They also found that the optimum purge-to-feed ratio is coupled with other operating conditions like adsorption pressure, feed flow rate and adsorption step time. At lower adsorption pressure, increasing purge to feed ratio significantly improves purity. As the pressure increases, increasing the purge-to-feed ratio only slightly increases the product purity while significantly decreasing recovery.

Jones et al. introduced Rapid PSA (RPSA) cycles as a way of process intensification [20]. The column is subject to three steps: feed pressurization, closing off the feed valve and counter-current blowdown. Each of these steps is of very short duration in the order of a few seconds, and the product is withdrawn continuously from the product end. Ackley [4] points that this is the class of cycles called the original RPSA, where the high-pressure drop and short cycle times combine and give sufficient bed permeability and internal purging to allow for high purity  $O_2$  to be continuously withdrawn. Kulish and Swank designed a 3-bed system to implement RPSA cycles to produce 2-5 SLPM of oxygen having 96% purity [21]. They used the fact that adsorption is faster than desorption to program an asymmetric cycle.

A related concept is the pulsed PSA process studied by Vemula et al. where a miniaturized adsorbent-bed with small particles is subject to rapid 2-step cycles of adsorption and evacuation for personal medical use [22]. They suggest that for a given particle size, bed length and pressure drop, an optimum combination of adsorption and desorption times exists to maximize product purity. It is worth noting that this
concentrator needs desorption times nearly 10 times that of the adsorption step times for optimum purity values. Despite such a large purge-to-feed ratio, the maximum purity obtained using this concentrator was limited to 40% because of high axial dispersion in the bed.

### 2.4 Performance metrics

The purity of the oxygen produced, defined as the percentage ratio of the number of moles of oxygen in the product to the total number of moles in the product stream is an essential metric to be met by the concentrator. Although the minimum purity required will vary depending on the application, it is generally desirable to produce oxygen having purity > 90%. Since most commercial zeolites exhibit very little to no  $O_2/Ar$  selectivity, producing ultra-pure oxygen is impossible. The maximum purity achieved by adsorption-based concentrators using existing commercial adsorbents is 95%. Most devices are capable of producing oxygen having purity between 90-93%. Figure 2.3 shows the isotherms of  $O_2$  and Ar on two commercial zeolites - LiLSX and 13X. In both adsorbents,  $O_2$  is more strongly adsorbed than Ar. 13X exhibits almost no selectivity between  $O_2$  and Ar, while LiLSX shows a slightly higher selectivity. The product obtained will have the same ratio of moles of  $O_2/Ar$  that was present in the feed air.

A more important performance measure is recovery, which is defined as the ratio of moles of  $O_2$  in the product stream to moles of  $O_2$  sent in the feed stream. This is the parameter that describes the efficiency of the separation process. If the recovery is low, more air needs to be fed into the system to produce the same amount of oxygen compared to a system with high recovery. This will need compressors and/or vacuum pumps that can allow sufficiently large air flow rates, increasing the concentrator's capital and operating costs.

To describe the throughput of the concentrator, productivity expressed in the units of kg  $O_2/kg$  adsorbent/day is often used. Large-scale industrial adsorption systems



Figure 2.3:  $O_2$  and Ar isotherms on LiLSX and 13X

are listed according to their oxygen production capacity, for example, in tons of  $O_2$  produced per day. Assuming that the concentrator operates in such a way that purity is > 90%, we can conclude that higher productivity allows us to produce more  $O_2$  per unit time.

Another performance metric that is especially popular in the field of portable medical oxygen concentrators is the Bed Size Factor (BSF). BSF is equivalent to the inverse of productivity and is often described in units of lbs of adsorbent required to produce one ton of  $O_2$  per day (lbs/TPDO). The smaller the BSF, the lower the mass of adsorbent needed to produce a unit mass of oxygen, resulting in a smaller concentrator.

Electric energy is required to operate compressors and blowers and switch valves continuously to perform adsorption cycles. Very often, the oxygen product produced will be at low pressures (1-1.5 bar for VSA/PVSA), and is re-pressurized using a compressor. This is done to overcome the pressure drop that can take place in a long network of piping to reach the point of application. Data from Benchmark International's Oxygen Solutions Inc. shows the typical energy costs for their concentrators in kWh/kg  $O_2$  [23].

OSI's Dual Bed Concentrators				
	OSI 2000	OSI 3000	OSI 5000	OSI 7000
Discharge flow-rate [kg $O_2/day$ ]	1818	2724	4540	6363
Cost of $\mathrm{O}_2$ generation [kWh/kg $\mathrm{O}_2]$	0.4	0.34	0.3	0.25

Table 2.1: Typical discharge flow-rates and energy required to produce  $O_2$  using commercially available concentrators [23].

Although our goals will be to maximize productivity and minimize energy while maintaining purity, it is impossible to indefinitely push to attain all these goals. It is possible to operate a given concentrator to give various levels of purity by adjusting the adsorption cycle operating conditions like cycle time-steps, pressures and inlet flows. With increasing purity, the recovery steadily drops. Similarly, there exists a relationship between purity and productivity. While it may be possible to increase productivity by reducing cycle times, beyond a certain limit, the adsorbent's kinetic limit will be reached. In large-scale PSA systems, a combination of mass and heat transfer limitations, large pressure drop and adiabatic operation are believed to be the reasons for this limit to exist [24]. This was experimentally demonstrated by Moran and Talu using a small-scale 2-bed PSA system with LiLSX adsorbent [25]. They found that a minimum BSF exists as you vary the cycle times while keeping parameters like product purity, pressure ratio and purge-to-feed ratio constant.

## 2.5 Experimental design, configuration of adsorbent beds

Depending on the application, oxygen concentrators can be fabricated in different ways. Single-column systems are smaller and may be used for applications like personal medical use. However, if we intend to perform Skarstrom-like cycles with the equipment, we will need a product tank to store the produced oxygen and send a portion of it back into the bed for purge. Two column packed bed designs are more popular in larger units. These systems allow for steps like light reflux and pressure equalization where gases can flow from one column to another, instead of needing a product tank.

In academic literature, there are a few examples of experimental demonstration of PSA processes for oxygen concentration. Wilson et al. used a 2-bed system, each bed measuring 1.85 m in length and having a diameter of 104 mm to study the temperature profiles at cyclic steady state. The columns were insulated to minimize heat exchange with the environment [26]. Around the same time, Jee et al. worked with a 2-bed system, bed dimensions being 50 cm length and 2.5 cm diameter [16]. More recently, Moran and Talu also used a similar 2-bed system to study BSF limits, although their beds were much smaller, measuring only 10 cm in length and 1 cm in diameter [25].

There is not a lot of consensus on what should be the preferred bed length-todiameter ratio to avoid axial dispersion. Researchers working to miniaturize oxygen concentrators tend to minimize the amount of adsorbent present to perform rapid PSA cycles. Chai et al. used a packed bed measuring 10 cm in length and 0.4 cm in diameter, having 1 g of LiLSX adsorbent. They could produce high purity oxygen with a recovery of 25-35%, at pressure 3-4 atm, bringing down the BSF value to 25-50 lbs/TPDO [24]. However, it is unclear what is the maximum product flow rate possible. There could also be heat effects that can set in when a similar process is scaled up, and these have not been studied. Similarly, Vemula et al. used a 10 cm x 1.08 cm column for a pulsed PSA process, but they could not obtain purities higher than 40% because of high axial dispersion [22]. The bulk of existing research in this field is found in patent literature, where companies like Air Products & Chemicals Inc. and Praxair Inc. have done extensive studies to develop commercial products. Experimental test rigs of various sizes have been reported in these patents, most confirming to the one-bed or two-bed designs described above. Apart from the standard packed-bed design, there have been attempts to incorporate novel designs to overcome certain limitations associated with packed beds. Chiang and Hong [27] explains that since productivity is limited by mass transfer into the particles, using smaller particles would enhance the mass transfer rate. However, smaller particles would cause a huge pressure drop across the bed. To compensate for this loss, shallower beds having a wide cross-section area must be used. A radial flow adsorber with a thin shell of adsorbent material can overcome this problem without flow distribution concerns even at a large scale. They also found that flowing feed air from inward to outwards gave better purities than the other way around.

Suzuki et al. proposed a piston-style adsorber, where a mechanical piston rapidly pressurizes and depressurizes a packed bed instead of switching valves [28]. Although productivity is quite high, purity is limited to 60%. Based on their results from a miniaturized PSA apparatus, Chai et al. proposed a compact personal oxygen concentrator that can be 'snapped-on' to a compressed air line. Feed flow rate of 67 LPM at 3-4 atm can give 5 LPM of 90%  $O_2$  with 230 g of LiLSX zeolite [24]. In an earlier work, George Keller and Chia-Huei Kuo describe a 2-piston adsorber, where pistons impose cyclic gas flow and pressure variations [29]. By placing the piston on either end of the adsorber column, they could achieve almost complete separation of the air mixture, producing 99% N<sub>2</sub> stream and 95%  $O_2$  stream simultaneously, with recovery approaching 100%.

# 2.6 Multiple adsorbents in adsorptive separation processes

In  $O_2$  PSA systems that take in air without any pre-treatment or drying, it is common to see the use of guard bed layers. Near the feed end of the adsorbent bed, materials like silica gel, alumina or 13X are stacked as a separate layer. Their function is to adsorb water vapour,  $CO_2$  and other contaminants, which can be adsorbed irreversibly to the main zeolite bed. The guard bed layer is sized so that water vapour and  $CO_2$  remain contained within the guard bed over several years in which the concentrator is operated. Since silica gel and alumina have a sufficiently high water capacity and the air being fed to oxygen concentrators is relatively clean, crude calculations were sufficient to size these guard beds. This design continues to be popular even today.

An unintended consequence of using guard beds is the phenomenon of severe axial temperature profiles that can cause cold spots to develop near the feed end of the adsorbent beds. While some variation in the axial temperature profile is expected because of the cyclic adsorption-desorption processes, researchers noted that temperatures as low as -20°C could be attained at the coldest region, which could not be explained by the enthalpy of adsorption and desorption alone. This cold spot also meant that the nitrogen capacity of the bed at the cold spot was enhanced greatly, and a deeper vacuum was needed to be able to completely regenerate the bed in the evacuation step. Collins first documented this effect in their patent and explained that the desorption step creates a refrigeration effect [30]. Cold N<sub>2</sub> passing through the pre-treatment layer cools it by heat transfer. Since 78% of air is N<sub>2</sub>, the volume of N<sub>2</sub> desorbed is significantly larger than that seen in other gas separation processes. The pre-treatment layer stores this 'refrigeration' effect until the next cycle, and this effect accumulates over several cycles to give rise to the cold spot.

A complete understanding of the cold spot phenomena happened much later when Wilson et al. demonstrated experimentally and using simulations that the cold spot only formed in multi-layered adsorbent beds [26]. They explained that the cold spot was due to the interaction between convective heat transfer and the enthalpies of adsorption-desorption. Cold spots can only form in multi-layered adsorbent beds, where the layer near the feed end has significantly lower N<sub>2</sub> capacity than the main layer. If a single-layer adsorbent bed is used, but water vapour is present in the inlet air, it can get adsorbed irreversibly near the feed end and can reduce the N<sub>2</sub> capacity of a portion of the bed, creating a multi-layer bed of sorts. This inert layer acts as a regenerative heat exchanger, and since the moles of gas flowing forward in the bed are always larger than the moles of gas flowing backward, there will be net cooling of the bed near the inlet. Since the inert layer is not associated with any heat of adsorption, the temperature does not rise in the adsorption step, and over time, a severe cold spot could develop.

There have also been attempts to use layered adsorbent beds for separations other than oxygen concentration. Cavenati et al. studied the use of beds composed of a 13X layer to remove  $CO_2$  and a carbon molecular sieve (CMS) layer to remove  $N_2$  from a natural gas feed to produce high purity methane [31]. The layering here functions similar to the way guard beds are implemented in air separation. 13X layer is designed to not allow  $CO_2$  to breakthrough into the CMS layer. They carried out parametric studies by altering the ratio of volumes of each layer to study its impact on purity and recovery. With the help of experiments and simulations, they concluded that there exists an optimum layering ratio that gives the maximum purity. This exists because of the trade-off presented by the two adsorbents. 13X layer should be small enough so that only  $CO_2$  is adsorbed and  $CH_4$  is allowed to pass. A short 13X layer also means more space for the CMS layer, which allows more CH<sub>4</sub> to leave as a light product. Glover and LeVan then conducted sensitivity studies using breakthrough experiments and then applied their findings to arrive at the optimum layering ratio required for maximum purity for the layered bed system proposed by Cavenati et al [32].

A set of two papers by Lu et al. discusses the application of layered beds for air separation process [33, 34]. They considered a two-layered bed and devised a method to simulate and study individually the effects of each layer's selectivity and  $N_2$  capacity. More interestingly, they also considered different cycles to study if the nature of cycles and the flow rates of gas moving in either direction could impact the optimal layering needed for the layered bed. They also proposed that the axial temperature effects impact optimum layering. They arrived at the important conclusion that to maximize the system's efficiency, high-capacity adsorbent should be placed at the discharge end while high-selectivity adsorbent should be placed near the feed end of the bed. In their work that followed this finding, they experimentally demonstrated this effect using a layered bed having two layers - Type-2 of a zeolite material (having base case level of N<sub>2</sub> capacity and N<sub>2</sub>/O<sub>2</sub> selectivity) and Type-1 being a mixture of the same zeolite material with alumina beads in 1:1 ratio (to act like an adsorbent having same N<sub>2</sub>/O<sub>2</sub> selectivity but a reduced N<sub>2</sub> capacity). Similar to what their simulations had predicted, a layered bed having Type-2 near the discharge end gave higher purities than the alternate case. This effect is amplified in simpler cycles with no pressure equalization steps.

By far, the most extensive studies on using multiple adsorbents for  $O_2$  concentration come from patent literature. Several patents have been filed between 1990-2005 regarding this subject; some of the relevant ones are summarised in Table 2.3. In contrast to layering, it is also possible to physically mix two or more adsorbents in various proportions to give a new 'mixed' adsorbent. Two patents are relevant in this light - 'Oxygen production by adsorption' by Sircar et al. [35] and 'PSA apparatus and process using adsorbent mixtures' by Ackley et al. [36]. Both methods consider adsorbent mixtures to reduce the overall cost of oxygen production by reducing or eliminating lithium-based zeolites. The former patent considers simple homogeneous mixtures of two adsorbents, while in the latter, mixtures of adsorbents in various proportions are arranged in layers according to their adiabatic selectivity.

In their recent work, Ward et al. considered mixtures of two adsorbents for postcombustion carbon capture applications [37]. Using a composite isotherm model to describe uniform mixtures of two adsorbents in different weight ratios, they employed equilibrium-based models to assess the performance of 76 potential adsorbents and their binary mixtures. The analysis is done as a screening exercise to identify binary combinations of materials that can satisfy the US DOE standards of > 95%purity and > 90% recovery. The binary combinations can be classified based on the shapes of their purity-recovery and energy-working capacity optimization Pareto fronts. They find that if one of the materials in the binary combination satisfies the required purity-recovery requirements, then the binary combination will also satisfy the constraints. Moreover, they also find that certain binary combinations can lower the energy requirements as compared to using just a single adsorbent.

In general, when it comes to using multiple adsorbents, there has been a lot of emphasis on understanding the nature of the axial temperature profiles in the adsorbent beds and placing adsorbents which exhibit the best selectivity at those temperature conditions in the respective zones. A lot of the understanding of axial temperature profiles is based on the practical observations made in industrial-size oxygen concentrators which come with guard bed layers (consisting of alumina or 13X) to remove  $CO_2$  and  $H_2O$ . If there is no guard bed, the water vapour in the feed air adsorbs near the feed end and slowly creeps into the bed, incidentally creating a layer with reduced  $N_2$  capacity near the inlet. In such adsorbent bed configurations, a cold spot can develop near the inlet as explained by Wilson et al. [26]. Many patents [36, 38, 39] which support placing increasing proportions of LiX towards the product end seem to assume that the axial temperature profile will prevail irrespective of placing LiX in the feed end or the product end. However, continuing their work, Wilson and Webley [40] experimentally demonstrated that the cold spot phenomena can only occur in multi-layer beds, where the layer near the feed end has significantly lower  $N_2$ capacity than the main adsorbent. An example of this configuration would be placing 13X near the feed end, followed by LiLSX near the product end. Moreover, they also showed that when the layers are reversed, i.e. LiLSX is placed near the feed end and 13X is placed near the product end, a local hot spot is formed near the interface of the two layers. To our knowledge, no source has compared PSA performance for the two types of layered configurations. More work is needed before we can generalize and claim if one kind of layered configuration is better than the other.

Title	Authors (Assignee)	Premise/Study Setting	Methods	Findings/Claims
Multiple zeolite adsorbent layers in oxygen separation [38]	C. F. Watson, Roger D. Whitley, Michael L. Meyer (Air Products & Chemicals Inc.)	Commercially used high-capacity zeolites lose their selectivity at low temperatures (observed near inlet in large adiabatic columns) and develop a high $O_2$ capacity. More $O_2$ is lost in the evacuation step. Deeper vacuum is needed to regenerate the bed.	The adsorbent bed consists of a pre-treatment layer up to 17% (either alumina or 13X), followed by the air separation adsorbents(CaX, 13X). VSA pilot-plant experiments and simulation studies are used.	Placing low-capacity zeolites near the feed end (e.g., 13X) and high-capacity, high-selectivity zeolites near the product end (e.g., CaA, CaX, LiLSX) takes advantage of the severe axial temperature profile that develops in large beds.
PSA apparatus and process using adsorbent mixture [36]	M. W. Ackley, A. B. Stewart, G. W. Henzler, F. W. Leavitt, Frank Notaro, M. S. Kane (Praxair Technology, Inc.)	To bring down the overall cost of oxygen concnetrators and improve performance, it is possible to substitute a portion of the LiX zeolite with 13X. The adsorbent bed consists of multiple layers, each consisting of 13X and LiX mixed in various proportions.	Equilibrium-based simulation models and a two-bed pilot plant PVSA system, operating between 1.5 bar and 0.3 bar approximately.	Based on the adiabatic separation factor, placing increasing proportions of LiX in warmer regions and increasing proportions of 13X in colder regions of the bed results in improved performance. When moving from an adsorbent system consisting only of LiX, upto 20% of the bed can be substituted with 13X with only a modest decrease in recovery.

Oxygen production by adsorption [35]	Shivaji Sircar, W. E. Waldron (Air Products & Chemicals, Inc.)	The cost of oxygen concentrators can be brought down by using a mixture of less expensive zeolites (13X, CaX etc.) and eliminating lithium-based zeolites.	Simulations of a two-bed 60 ton/day $O_2$ plant operated using a PVSA process between 1.35 atm and 0.4 atm.	Mixing zeolites in different proportions gives the flexibility to alter and produce different 'isotherms by design'. An adsorbent bed consisting of a 1:1 mixture of 13X and CaX can produce $O_2$ at a cost competitive to LiX. However, this comes at the cost of lower recovery and higher energy costs.
Multilayer adsorbent beds for PSA gas separation [41]	M.W. Ackley (Praxair Technology, Inc.)	No commercial zeolite is expected to perform optimally over the wide range of temperatures seen in large columns. Adsorbents can be layered in a bed by finding each adsorbent's adiabatic selectivity and working capacity at the prevailing temperature in the respective zone.	Two figures of merit - adiabatic selectivity and adiabatic working capacity are defined by considering the local temperature, pressures and compositions. Consider three layers in the adsorbent bed - pre-treatment, equilibrium zone and mass transfer zone. Simulations of a 2-bed, 60 tons/day PVSA process between 1.5 bar and 0.3 bar are used.	In the equilibrium zone, it is important to place the adsorbent with higher adiabatic $N_2$ working capacity, since the bulk of the $N_2$ in the feed must be adsorbed and separated here. In the mass transfer zone, it is more important to have $N_2/O_2$ selectivity to reduce the adsorption of concentrated $O_2$ .

Adsorbent process & system using multilayor	F. Notaro, J. T. Mullhaupt, F. W. Loavitt	Multiple layers of adsorbants can be stacked	An adsorption figure of morit is defined as the	In general, placing adsorbonts with lower N
system using multilayer adsorbent beds [39]	Mullhaupt, F. W. Leavitt, M. W. Ackley (Praxair Technology, Inc.)	adsorbents can be stacked optimally to take advantage of the large temperature gradients usually observed in PSA systems.	The adsorption figure of merit is defined as the product of $N_2$ working capacity, selectivity at adsorption conditions, and the ratio of selectivity at adsorption and desorption conditions. Computer simulations are used to get temperature profiles at a steady state. The adsorption figure of merit is computed for several adsorbents as a function of	adsorbents with lower $N_2$ affinity (e.g. 13X) near the feed end, and placing adsorbents with stronger $N_2$ affinity (e.g. LiLSX) near the product end, exploits the prevailing temperature gradients and improves performance.
			temperature and plotted.	

Table 2.3: Summary of patents describing the use of multiple zeolites in air separation

# Chapter 3 Materials and methods

#### 3.1 Materials

Two adsorbents were chosen for this study - low silica, lithium-exchanged X-zeolite (LiLSX) and sodium-exchanged X-zeolite (13X). JLOX-103 LiLSX, having an average particle diameter 1.3-1.7 mm was obtained from JALON Zeolites, China. HP10X20 13X from UOP Italy (Honeywell) having an average particle diameter of 1.3 mm is used. Before packing the adsorbent columns, both materials were placed in a glass tube, adequately insulated at the ends and placed inside a tube furnace for activation. LiLSX is activated at a temperature of 500°C, while 13X is activated at 350°C. The adsorbent is heated and maintained at the respective temperature for 24 hours, while passing about 2 SLPM of moisture-free compressed air through the glass tube.

Dynamic column breakthrough experiments used packaged  $N_2$  (99.995%) and  $O_2$  (99.99%) gases obtained as cylinders from Praxair Canada Inc. Compressed house air (water removed only through compression to 7 bar) with a dew-point of -40°C is used for PSA experiments.

#### **3.2** Isotherm measurements

Pure  $N_2$ ,  $O_2$  and Ar adsorption isotherms on both LiLSX and 13X were measured using the Micromeritrics ASAP 2020 (Norcross, GA, USA) volumetric physi-sorption system. Approximately 200 mg of the zeolite was filled in the cell which was evacuated to desorb any gases that would have been adsorbed. This was followed by the activation of the sample for around 10 hours at their respective activation temperature under a vacuum. Once the activation was complete and the sample was brought to room temperature, volumetric measurement experiments were conducted. At any given pressure and temperature condition, a known amount of gas was dosed into the cell, and sufficient time was given for the gas to be adsorbed by the sample until it reached equilibrium. The corresponding loading for that condition was found by measuring the pressure difference between the initial and final conditions. This was repeated for various pressures between 0.01-1.2 bar for a fixed temperature. For each gas on each adsorbent, a minimum of three different temperatures were considered to get the isotherm data.

Since PSA processes, where the high pressure can go up to 5 bar are of interest, it was also necessary to measure high-pressure isotherms. High-pressure isotherms of  $N_2$ on 13X and LiLSX were measured up to 10 bar using High-Pressure Volumetric apparatus (HPVA) from VTI Instruments (Hialeah, FL, USA). The adsorbent samples were activated accordingly before these experiments as well.

## 3.3 Experimental test rig

An experimental test rig was custom-built for this study, as shown in the schematic diagram in Fig. 3.1. A photograph of the complete set-up is shown in Fig. 3.2. Flatended columns measuring 32.7 cm in length, internal diameter of 3.5 cm and external diameter of 4 cm were procured from McMaster Carr Inc., Canada. Stainless steel tubing having 0.25 inch diameter was used for making connections. Feed and blowdown solenoid valves (SV-1, SV-2, SV-3 and SV-4) having sufficiently large  $C_V$  to allow large volumes of air and exhaust were obtained from Burkert, Germany. Compression fitting parts from Swagelok Inc., Canada were used to make pressure-tight connections. A 2-bed system was constructed with lines allowing for light product reflux from the top of one column to the other and for withdrawing product separately. For the product and light reflux lines, solenoid valves SV-5, SV-6, SV-7, SV-8 from DigiKey Electronics were used. A manual needle valve (NV) is also provided in the reflux line to adjust the volume of gas being refluxed. The test rig was designed and



Figure 3.1: Schematic diagram of the PSA test rig set-up

fabricated to minimize dead volumes as much as possible. The entire assembly was mounted on a large stainless steel panel and was designed to have both a Dynamic Column Breakthrough (DCB) station as well as the 2-bed PSA station. Small range flow controllers and meters (0-2 SLPM) obtained from Alicat Scientific (Tucson, AZ, USA) were used for dynamic column breakthrough experiments. A larger range flow controller (MFC-1) from Parker Hannifin (Cleveland, OH, USA) with a range of 0-10 SLPM was used for PSA experiments. Pressure sensors were purchased from SMC Electric (Missouri, USA).

Six different columns were packed to conduct the experimental campaign. Two



Figure 3.2: Experimental test rig showing both DCB (left) and PSA (right) stations

columns were packed with LiLSX adsorbent and two with 13X. Two others were packed in a layered fashion, where approximately 50% of the volume of the column was packed with LiLSX and the remaining 50% with 13X. A mesh screen separated the two layers to prevent the inter-mixing of the two layers throughout the experiments. Mesh screens were also placed at the two ends of each column to prevent zeolite particles from being carried away with the moving gas, which can potentially affect the operation of valves downstream.

The DCB station has a manual switching valve that can be used to switch between the inert gas ( $O_2$  in this case) and the test gas ( $N_2$  or mixtures of  $N_2$  and  $O_2$ ). For the PSA system, the valve-switching sequence is automated using an Arduino microcontroller. Each valve can be switched open or closed for specific time intervals depending on the adsorption cycle we want to run. A program can be written to implement the cycle and loaded onto the microcontroller. Although the microcontroller gives voltage signals, a relay-board is necessary to give the high voltages needed to switch valves. To accomplish this, the microcontroller, relay board and valve are connected in series.

The product gas is sent to a flow meter followed by an oxygen analyzer to measure the flow rate and concentration of the produced oxygen. This will allow us to calculate the purity and recovery of each run. The Oxy 1900 paramagnetic oxygen sensor from Servomex (East Sussex, UK) is used for concentration detection. Data acquisition of pressures, concentration and flow rates is done simultaneously through the Multifunction I/O device from National Instruments (Austin, TX, USA).

### 3.4 Dynamic column breakthrough experiments

Dynamic column breakthrough (DCB) experiments allow us to study the flow of gases through an adsorbent-packed bed by simplifying experimental conditions before moving on to more complex PSA cycles. The objectives for DCB experiments in this study as follows:

- 1. Verify that the single component loading obtained from DCB experiments matches with those obtained from volumetric experiments.
- 2. Find the nature of binary  $\mathrm{N_2/O_2}$  competition on LiLSX and 13X.
- 3. Obtain the best fit of certain transport properties to numerically model the experiment.



Figure 3.3: Schematic diagram of a DCB experiment

A DCB experiment consists of two parts - adsorption run and desorption run. A relatively inert gas that does not adsorb strongly on the adsorbent is used as the sweep gas. In this case,  $O_2$  has been chosen as the sweep gas. The gas of our interest is the adsorbate gas, which in this case is  $N_2$ . The sweep gas line and the adsorbate gas lines are connected to a switching valve. The switching valve can send either of the gases into the packed bed or to a vent line, as shown in Fig. 3.3. Known quantities of  $O_2$  and  $N_2$  are sent to the packed bed using mass flow controllers MFC-2 and MFC-3 (Alicat Scientific, Tucson, AZ, USA). After passing through the packed bed the gases are sent through a mass flow meter (Alicat Scientific, Tucson, AZ, USA) and to the oxygen analyzer.

The sweep gas was initially flown through the packed bed for a long enough time to remove any adsorbate present in the bed to provide a clean bed. The oxygen sensor was monitored to see if the gas from the packed bed was nitrogen-free. Thermocouple T-1 from Omega Engineering (Laval, QC, Canada) was inserted into the packed bed to monitor if thermal equilibrium was attained. Then, at t=0, the valve was switched to flow N<sub>2</sub> through the packed bed. The flow rate, composition of the outlet gas, and the temperature of the packed bed were monitored. This experiment is associated with a temperature rise because of the exothermic nature of adsorption. The experiment was complete when concentration, flow rate and temperature profiles reached a steady state and the bed temperature returned to the initial value.

Once the adsorption experiment was complete, a desorption experiment was performed. For this, until time t=0, N<sub>2</sub> gas was flowing through the packed bed. At time t=0, the value is switched to allow O<sub>2</sub> to enter the column. As O<sub>2</sub> flows through the column, it desorbs the N<sub>2</sub> gas adsorbed on the bed. This continues until all of the N<sub>2</sub> was desorbed from the adsorbent and O<sub>2</sub> saturates the packed bed. This experiment is associated with heat absorption by the adsorbent, because of which a temperature dip will be observed. The experiment was considered complete when the bed temperature climbed back up to the initial temperature.

Initially, blank runs were done by removing the packed bed and placing a small piece of tubing of negligible volume. This is done to find the inherent dead volume in the DCB test rig. This is important as gas may be accumulated inside these dead volumes, which if not accounted for, might give an incorrect value of the equilibrium loadings on the adsorbent. The blank response must be obtained at the same adsorbate flow rate, pressure and temperature conditions as the packed bed experiments. This data is also required to accurately determine transport properties for modelling purposes.

The oxygen analyzer was calibrated by sending  $O_2$  and  $N_2$  of known concentration from a pressurized gas cylinder. The product flow-meter was also calibrated similarly using several compositions of  $N_2/O_2$  mixtures since the flow output signal was also dependent on composition. The data output from the oxygen analyzer and flow meter are volts of a known range. This data was accordingly processed to find the flow rates in Standard Litre per minute (SLPM) with time.

DCB adsorption and desorption experiments were performed using three columns - Bed-1 filled with LiLSX, Bed-2 filled with 13X and a layered bed filled with a 1:1 ratio of 13X and LiLSX stacked in two layers. The mass of adsorbent in each of these columns is listed in Table 3.1.

Adsorbent	Bed-1 $[g]$	Bed-2 $[g]$	Bed-3 $[g]$
LiLSX	186.38	_	92.56
13X	_	192.69	104.52

Table 3.1: Mass of adsorbent in packed beds

A simple equation to find the accumulation of gases in the packed bed can be used to calculate the equilibrium loading from an adsorption DCB experiment. For the adsorbate gas, the following equation can be written.

$$n_{acc} = n_{in} - n_{out} \tag{3.1}$$

Moles of gases in and out can be found using the ideal gas law as a function of the pressure, temperature and composition. Gas accumulation can be either in the adsorbed phase on the solid adsorbent or in the void spaces of the packed bed and the dead volumes.

$$n_{in} - n_{out} = n_{adsorbed} + n_{acc,voidage} + n_{acc,V_d}$$
(3.2)

This can be written as:

$$\frac{P_{ref}Q_{in}}{R_g T_{ref}} y_{in} t_{\infty} + \int_0^{t_{\infty}} \frac{Q(t)P_{ref}}{R_g T_{ref}} y(t) dt = LA \left[ \epsilon \frac{y_{in}P_{in}}{R_g T_{in}} + (1-\epsilon)q_i^* \right] + V_d \frac{y_{in}P_{in}}{R_g T_{in}} \quad (3.3)$$

Equation 3.3 can be solved for each adsorption experiment to find the equilibrium loading of the heavy component on the solid [42].

Similar equations can be derived for a desorption experiment [43].

$$n_{out} = n_{acc} \tag{3.4}$$

$$n_{out} = n_{adsorbed} + n_{acc,voidage} + n_{acc,V_d}$$
(3.5)

$$\int_{0}^{t_{des}} \left(\frac{y_{out} P_{avg} Q_{out}}{R_g T_{out}}\right) dt = LA \left[ \epsilon \frac{y_{in} P_{avg}}{R_g T_{in}} + (1-\epsilon) q_i^* \right] + V_d \frac{y_{in} P_{avg}}{R_g T_{in}}$$
(3.6)

Wilkins et al. [42] recommend that heavy component loadings be calculated using an adsorption experiment and light component loadings from a desorption experiment. For the adsorption of binary mixtures, the molar flow response of light components may have roll-ups, which makes the calculation of equilibrium loading more complex.

Binary DCB experiments can be performed similarly with slight modifications in the equation. N<sub>2</sub> mass balance remains the same as above. Since  $O_2$  is used as the purge gas, the bed is initially saturated with  $O_2$ . In other words, at the time of the start of the experiment,  $O_2$  is already adsorbed by the solid. This value needs to be subtracted from the solid accumulation term in the mass balance as shown in 3.7.

$$\frac{P_{ref}Q_{in}}{R_gT_{ref}}y_{in}t_{\infty} + \int_0^{t_{\infty}}\frac{Q(t)P_{ref}}{R_gT_{ref}}y(t)dt = LA\left[\epsilon\frac{y_{in}P_{in}}{R_gT_{in}} + (1-\epsilon)(q_i^* - q_{initial}^*)\right] + V_d\frac{y_{in}P_{in}}{R_gT_{in}}$$
(3.7)

where,  $q_{initial}^*$  = equilibrium loading of O<sub>2</sub> at the start of the experiment. This value can be obtained from volumetric experiments to get the adsorbents' O<sub>2</sub> isotherm.

## 3.5 PSA experiments

The laboratory building's air supply at approximately 7 bar pressure was used to feed the PSA test rig as shown in Fig 3.1. The test rig was built to experimentally validate the developed process model.

Manual valve MV-1 was switched open to allow high-pressure air flow into the test system. MFC-1 was set at the desired flow rate and allowed a fixed number of moles per time to be sent to the PSA rig. SV-2 was opened, keeping other valves closed to allow air into Column-1. Air was let in until the desired high pressure  $(P_H)$  was attained. The time needed for the feed pressurization step  $(t_{press})$  will vary with the inlet flow rate and was found manually by monitoring PT-1. At the end of this step, SV-5 was switched open for the adsorption step where high-purity product was collected and sent through CV-1, BPR and MFM. A portion of the product after the MFM was passed through the O<sub>2</sub> analyzer. Air continued to flow through the column through SV-2 for the light reflux donor step. SV-5 was closed and SV-7, SV-8 were opened. This allows the flow of O<sub>2</sub> enriched gas from Column-1 to Column-2, effectively performing a purge step on Column-2. Then SV-2, SV-7 and SV-8 were closed while opening SV-1 for blowing down Column-1. This was followed by purging Column-1 with top product from Column-2 by opening valves SV-8, SV-7 and SV-1. The cycle sequence was programmed so the two columns could be operated to adsorb-desorb cyclically in a staggered manner, as shown in Table 3.2.

Column-1	Column-2
Feed pressurization	Blowdown
Adsorption	Blowdown continues
Light reflux donor	Light reflux receiver
Blowdown	Feed pressurization
Blowdown continues	Adsorption
Light reflux receiver	Light reflux donor

Table 3.2: PSA experiments - cycle sequence

The back-pressure regulator and the needle valve NV in the reflux line were used to maintain the bed pressure during the adsorption and light reflux steps respectively. The position of NV was adjusted manually by inspecting the pressure history of a bed during the light reflux donor step. The back pressure regulator was similarly adjusted by monitoring PT-1 and PT-2. This sequence was carried out for a minimum of 100 cycles per bed, after which the product concentration and flow rate histories were checked to see if a cyclic steady state has been reached and has remained unchanged for a long time. The latest 1000 seconds of concentration and flow rate data thus obtained were averaged and used to calculate the purity and recovery values.

## **3.6** Modelling PSA process dynamics

#### 3.6.1 Model equations & boundary conditions

A one-dimensional model of an adsorbent column is developed to simulate both PSA experiments. The column is discretized into volume elements. Partial differential equations and boundary conditions describe each step in the PSA process, which can be solved by a solver cyclically until a cyclic steady state is established. This model is based on the work by Haghpanah et al. [44] and incorporates the following assumptions:

- 1. Bulk fluid flow is described by an axially dispersed plug flow model.
- 2. Gas phase obeys the ideal gas law.
- 3. The linear driving force model represents mass transfer into the solid.
- 4. Gradients in pressure, temperature and concentration only exist in the axial direction, not radially.
- 5. Heat transfer between gas and solid phase is instantaneous, and thermal equilibrium is achieved almost instantly.
- 6. Darcy's law accounts for the frictional pressure drop across the column.
- 7. Outer walls of the column are at ambient temperature, and heat is transferred from the solid across the column wall and is dissipated.
- 8. Particle size, particle porosity and bed voidage are uniform across the column.

9. For each kind of adsorbent, specific heat is assumed to be constant throughout the column.

Based on these assumptions, partial differential equations for mass and energy balance can be derived and written as shown in Table 3.3 [44]. Dimensionless groups described in these equations are shown in Table 3.4. The symbols used are explained in the nomenclature section of this thesis.

Overall mass balance	$\frac{\partial \bar{P}}{\partial \tau} = \frac{\bar{P}}{\bar{T}} \frac{\partial \bar{T}}{\partial \tau} - \bar{T} \frac{\partial}{\partial Z} \left( \frac{\bar{P}\bar{v}}{\bar{T}} \right) - \psi \bar{T} \sum_{i=1}^{n_{comp}} \frac{\partial x_i}{\partial \tau} (3.8)$
Component mass balance	$\frac{\partial y_i}{\partial \tau} = \frac{1}{Pe} \frac{\bar{T}}{\bar{P}} \frac{\partial}{\partial Z} \frac{\bar{P}}{\bar{T}} \frac{\partial y_i}{Z} - \frac{\bar{T}}{\bar{P}} \frac{\partial}{\partial Z} \left( \frac{y_i \bar{P}}{\bar{T}} \bar{v} - \frac{y_i}{\bar{P}} \frac{\partial \bar{P}}{\partial \tau} + \frac{y_i}{\bar{T}} \frac{\partial \bar{T}}{\partial \tau} - \psi \frac{\bar{T}}{\bar{P}} \frac{\partial x_i}{\partial \tau} (3.9)$
Mass transfer rate	$\frac{\partial x_i}{\partial \tau} = \alpha_i (x_i^* - x_i)(3.10)$
Local velocity	$\bar{v} = \frac{4}{150} \left(\frac{\epsilon}{1-\epsilon}\right)^2 r_p^2 \frac{P_0}{\mu v_0 L} \left(-\frac{\partial \bar{P}}{\partial Z}\right) (3.11)$
Column energy balance	$\frac{\partial \bar{T}}{\partial \tau} = \Omega_1 \frac{\partial^2 \bar{T}}{\partial Z^2} - \Omega_2 \frac{\partial}{\partial Z} (\bar{v}\bar{P}) - \Omega_3 \bar{T} \sum_{i=1}^{n_{comp}} \frac{\partial x_i}{\partial \tau} + \sum_{i=1}^{n_{comp}} (\sigma_i \frac{\partial x_i}{\partial \tau} - \Omega_4 (\bar{T} - \bar{T}_w) - \Omega_2 \frac{\partial \bar{P}}{\partial \tau} (3.12)$
Wall energy balance	$\frac{\partial \bar{T}_w}{\partial \tau} = \Pi_1 \frac{\partial^2 \bar{T}_w}{\partial Z^2} + \Pi_2 (\bar{T} - \bar{T}_w) - \Pi_3 (\bar{T}_w - \bar{T}_a) (3.13)$

Table 3.3: Model Equations

Danckwert's boundary conditions for an axially dispersed plug flow system are applied for the component mass balance and the column energy balance [44]. Three boundary conditions are generally used to represent the steps of a cyclic adsorption process. These are shown in Fig. 3.4. A summary of the boundary conditions for each of these forms is given in Table 3.6.



Figure 3.4: Basic boundary condition-based configurations which can be modified to give all the constituent steps of a PSA cycle.

This basic framework of boundary conditions can be implemented as such or with slight modifications to simulate the four steps of a Skarstrom cycle.

- 1. Feed pressurization can be visualized as an Open-Closed system, where feed gas is being let into the column at Z = 0 and is used to pressurize the bed. N<sub>2</sub> present in the feed gas will be adsorbed near Z=0, and as the gas moves towards Z = L, the gas gets enriched in O<sub>2</sub>.
- 2. Adsorption is an Open-Open step, where feed gas continues to enter the column at Z = 0, while withdrawing concentrated O<sub>2</sub> product from Z = L.
- 3. Blowdown or evacuation is performed in the Closed-Open boundary condition.

$\bar{T} = \frac{T}{T_0}$	(3.14)	$x_i = \frac{q_i}{q_s}$	(3.18)
$\bar{P} = \frac{P}{P_0}$	(3.15)	$\bar{v} = \frac{v}{v_0}$	(3.19)
$\bar{T}_w = \frac{T_w}{T_0}$	(3.16)	$Z = \frac{z}{L}$	(3.20)
$x_i^* = \frac{q_i^*}{q_s}$	(3.17)	$ au = t \frac{c_0}{L}$	(3.21)
$Pe = \frac{v_0 L}{D_L}$	(3.22)	$\psi = \frac{1 - \epsilon_b}{\epsilon_b} \frac{RT_0 q_s}{P_0}$	(3.24)
$Pe_H = \frac{\epsilon_b v_0 L \rho_g C_{pg}}{K_{\pi}}$	(3.23)		

Table 3.4: Dimensionless groups used in Model Equations

$$K_z$$
  $2r \cdot h \cdot L$ 

$$\Pi_1 = \frac{K_w}{\rho_w C_{pw} v_0 L} \qquad (3.25) \qquad \Pi_2 = \frac{2r_{in}h_{in}L}{\rho_w C_{pw} v_0 (r_{out}^2 - r_{in}^2)} \qquad (3.26)$$

$$\Pi_{3} = \frac{2r_{out}h_{out}L}{\rho_{w}C_{pw}v_{0}(r_{out}^{2} - r_{in}^{2})} \qquad (3.27) \qquad \sigma_{i} = \frac{(-\Delta H_{i})q_{s}}{T_{0}(1 - \epsilon_{b})(\rho_{s}C_{ps} + C_{pa}q_{s}\sum_{i=1}^{n}x_{i}}$$
(3.28)

$$\Omega_1 = \frac{K_z}{\left(\frac{1-\epsilon_b}{\epsilon_b}\right)\left(\rho_s C_{ps} + C_{pa} q_s \sum_{i=1}^n x_i\right)\epsilon_b v_0 L} \tag{3.29}$$

$$\Omega_2 = \frac{C_{pg}}{\left(\frac{1-\epsilon_b}{\epsilon_b}\right)\left(\rho_s C_{ps} + C_{pa}q_s\sum_{i=1}^n x_i\frac{P_0}{RT_0}}$$
(3.30)

$$\Omega_{3} = \frac{(C_{pa}q_{s})}{(\rho_{s}C_{ps} + C_{pa}q_{s}\sum_{i=1}^{n}x_{i})} \quad (3.31) \qquad \qquad \Omega_{4} = \frac{2h_{in}L}{\epsilon_{b}r_{in}v_{0}(\frac{1-\epsilon_{b}}{\epsilon_{b}})(\rho_{s}C_{ps} + C_{pa}q_{s}\sum_{i=1}^{n}x_{i})} \quad (3.32)$$

Step	Z = 0	Z = L
	$P _{Z=0} = P_2 + (P_1 - P_2)e^{-\alpha t}$	$\frac{\partial y_i}{\partial Z} _{Z=L} = 0$
Open-Closed	$D_L \frac{\partial y_i}{\partial Z} _{Z=0} = -v _{Z=0}(y_{i,feed} - y_i _{Z=0})$	$\frac{\partial P}{\partial Z} _{Z=L} = 0$
open closed	$\frac{\partial T}{\partial Z} _{Z=0} = -\epsilon v _{z=0}\rho_g C_{pg}(T_{feed} - T _{Z=0})$	$\frac{\partial T}{\partial Z} _{Z=L} = 0$
	$T_w _{Z=0} = T_a$	$T_w _{Z=L} = T_a$
	$v _{Z=0} = v_{feed}$	$P _{Z=L} = P_2$
Open-Open	$D_L \frac{\partial y_i}{\partial Z} _{Z=0} = -v _{Z=0}(y_{i,feed} - y_i _{Z=0})$	$\frac{\partial y_i}{\partial Z} _{Z=L} = 0$
open open	$\frac{\partial T}{\partial Z} _{Z=0} = -\epsilon v _{Z=0}\rho_g C_{pg}(T_{feed} - T _{Z=0})$	$\frac{\partial T}{\partial Z} _{Z=L} = 0$
	$T_w _{Z=0} = T_a$	$T_w _{Z=L} = T_a$
	$v _{Z=0} = 0$	$P _{Z=L} = P_1 + (P_2 - P_1)e^{(-\alpha t)}$
Closed-Open	$\frac{\partial y_i}{\partial z} _{Z=0} = 0$	$\frac{\partial y_i}{\partial Z} _{Z=L} = 0$
	$\frac{\partial T}{\partial Z} _{Z=0} = 0$	$\frac{\partial T}{\partial Z} _{Z=L} = 0$
	$\frac{\partial P}{\partial Z} _{Z=0} = 0$	$T_w _{Z=L} = T_a$

Table 3.6: Boundary conditions for the typical steps in a cyclic adsorption process

However, since we want to remove  $N_2$  from the bed without contaminating the  $O_2$  product, this step must be done in the counter-current direction. In other words, Z=L acts as the closed end, while Z=0 acts as the open end.

4. Light reflux or purge is in principle similar to the adsorption step and can be implemented as an Open-Open step. The product gas is used here instead of feed gas in the adsorption step. Instead of feeding from Z=0 (as in adsorption), the product gas is fed from Z=L for the reflux step.

#### 3.6.2 Solution methodology for single-layer adsorbent Bed

The column is assumed to be divided into N cells and each cell has a volume  $\Delta V$ . For every quantity, a cell-averaged value of f is given by,

$$f_{(t)} = \frac{1}{\Delta V} \int V_j f(t) dt \tag{3.33}$$

*j* represents the cell index. The spatial derivatives in the model equations are rewritten in algebraic terms by considering values at center of the cell to be  $f_j$ . The



Figure 3.5: Schematic diagram of a column discretized in finite volume.

cell j has boundaries as j-0.5 and j+0.5.

The value of N is kept as 30, since this was found to give the best trade-off between speed and accuracy of solving by Haghpanah et al. [44]. The finite volume method is preferred as it solves the integral form of the transport equations, thus giving better closure of mass, energy and momentum balances. The high-resolution total variation diminishing (TVD) method is used to get the values at cell edges using cell center values.

$$f_{j+0.5} = f_j + \frac{1}{2}\phi(r_{j+0.5})(f_{j+1} - f_j)$$
(3.34)

The successive slope ratio  $r_{j+0.5}$  is defined as:

$$r_{j+0.5} = \frac{f_j - f_{j-1} + \delta}{f_{j+1} - f_j + \delta}$$
(3.35)

The flux limitter function  $\phi$  is given by the Van Leer scheme as follows.

$$\phi(r_{j+0.5}) = \frac{r_{j+0.5} + |r_{j+0.5}|}{1 + |r_{j+0.5}|}$$
(3.36)

These set of equations can be used to write the flux equations for cells numbered j=2,...,N-1. For the cells j=1 and j=N, half-cell approximations are used.

$$f_1 - f_0 = 2(f_1 - f_{0.5}) \tag{3.37}$$

$$f_{N+1} - f_N = 2(f_{N+0.5} - f_N) \tag{3.38}$$

Values of  $f_{0.5}$  and  $f_{N+0.5}$  are calculated from the discretized form of the respective boundary conditions. Now the transport equations have been reduced to a system of coupled ordinary differential equations that can be solved using one of MATLAB's ODE stiff solvers, *ode23s* to simulate each step of the PSA process.





Figure 3.6: Schematic of a 2-layer column discretized in finite volume as implemented in this work.

PSA process steps in a multi-layer adsorbent bed can be simulated similarly. The column is assumed to be divided into N cells where

$$N = n_{grid_1} + n_{grid_2} \tag{3.39}$$

 $n_{grid_1}$  represents the number of cells of adsorbent layer-1, which is placed closer to the feed end of the column.  $n_{grid_2}$  represents the number of cells of adsorbent layer-2, which is placed after layer-1, closer to the product end of the column. The value of N is taken to be 30 or 40, to describe percentage (by volume) ratios of each kind of adsorbent in the layered bed. Adsorbent properties like density, specific heat and isotherm parameters are defined separately for each layer. The discretized form of the transport equations remains the same as in the single sorbent case. The coupled ODEs are solved simultaneously for both layers by calling on the appropriate adsorbent parameters. Once again, MATLAB's stiff ODE solver *ode23s* was used to solve this set of equations and simulate each step of the PSA process.

A [%]	B [%]	$n_{grid_1}$	$n_{grid_2}$	Ν	
25	75	10	30	40	
50	50	15	15	30	
75	25	30	10	40	

Table 3.7: Values of N,  $n_{grid_1}$  and  $n_{grid_2}$  for different percentages of adsorbents

#### **3.6.4** Modelling breakthrough and process experiments

A dynamic column breakthrough experiment, an Open-Open system (like the adsorption step), is simulated first, where the inlet velocity,  $v_0$ , is fixed. The adsorbent is initially saturated with O<sub>2</sub>. At time t=0, N<sub>2</sub> gas at 1 bar pressure is introduced as a step change. This is simulated for a long enough time to capture both the concentration and thermal wavefront breakthroughs. Data about the transient functions like solid phase loading, gas phase composition in the column and temperature are recorded as a function of time and space (for each cell).

For the simulation of a Skarstrom cycle, the bed is initially assumed to be saturated with  $O_2$  at atmospheric pressure. With this initial condition, the 4 steps of the cycle are simulated one after the other. This constitutes one iteration. After the first iteration, the steps are repeated again until at least 25 iterations. At the end of 25 iterations, the mass balance errors for  $N_2$  and  $O_2$  are checked to verify the establishment of a cyclic steady state (CSS). Our simulations assume that CSS has been achieved if mass balance errors are less than 0.5% over five consequent cycles. If the simulation does not satisfy this condition after 25 cycles, the simulation is continued to run until the mass balance error criteria are met or until 100 cycles, whichever is earlier. For the adsorption step, the mass balance can be written as,

moles in 
$$-$$
 moles out  $=$  accumulation (3.40)

moles in 
$$= \frac{A\epsilon}{RT_{\text{feed}}} \int_0^{t_{\text{ads}}} P_0 y_{\text{feed}} v_0 dt$$
 (3.41)

moles out 
$$= \frac{A\epsilon}{R} \int_0^{t_{ads}} \frac{P_0 y_{(t),out} v_t}{T_{(t)}} dt$$
 (3.42)

accumulation = accumulation in fluid phase + accumulation in solid phase (3.43)

accumulation in fluid phase = 
$$\frac{LA}{R} \int_0^L \frac{P_0 y_{(z)} \epsilon}{T_{(Z)}} |_{\text{final}} - \frac{LA}{R} \int_0^L \frac{P_0 y_{(z)} \epsilon}{T_{(z)}} |_{\text{initial}} dz$$
 (3.44)

accumulation in solid phase = 
$$LA \int_0^L (1-\epsilon)q_f|_{\text{final}} dz - LA \int_0^Z (1-\epsilon)q_i|_{\text{initial}} dz$$
 (3.45)

Similar equations can be written for all the steps. The total number of moles in and out for each cycle can be calculated.

$$moles_{in,feed} = moles_{in,press} + moles_{in,ads}$$
 (3.46)

$$moles_{out} = moles_{out,ads} + moles_{out,evac} + moles_{out,LR} - moles_{in,LR}$$
 (3.47)

mass balance error = 
$$\frac{|\text{moles}_{\text{in}} - \text{moles}_{\text{out}}|}{\text{moles}_{\text{in}}} \times 100$$
 (3.48)

For the light reflux step, a virtual buffer tank is considered. From the  $O_2$  produced in the adsorption step, the first few moles which consist of the cleanest  $O_2$  gas are considered the product. A portion of the  $O_2$  produced is stored in the reflux buffer variable, which is then used as the purge gas in the reflux step. To account for this reflux gas, the moles of gas refluxed are subtracted from the total number of moles of gas out.

After reaching CSS, performance metrics are calculated in the following way.

Purity, 
$$Pu = \frac{\text{moles}_{\text{out},O_2}}{\text{moles}_{\text{out},\text{product},\text{total}}}$$
 (3.49)

Recovery 
$$Re = \frac{\text{moles}_{\text{out},O_2}}{\text{moles}_{\text{in,feed},O_2}}$$
 (3.50)

Productivity 
$$Pr = \frac{O_2 \text{ in product collected per cycle [kg]}}{\text{adsorbent mass [kg] × cycle time [day]}}$$
 (3.51)

Energy consumption for each step is calculated using the following correlation.

Energy per step, 
$$En = \frac{1}{\eta} \epsilon_{in}^2 \frac{\gamma}{\gamma - 1} \int_{t=0}^{t=t_{step}} (vP_{out}) \left[ \left(\frac{1}{P_{out}}\right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] dt$$
(3.52)

 $P_{out}$  here represents the pressure at which gas exits the column in each step.  $\eta$  is the efficiency of the vacuum pump or the compressor and  $\gamma$  is the adiabatic constant. In cases where  $P_H > 1$  atm, energy will be consumed in the feed pressurization and adsorption step. When  $P_L < 1$  atm, energy will be consumed in the evacuation and light reflux steps. Energy consumed in the process to produce unit mass of product  $O_2$  is calculated as:

$$Energy = \frac{En_{press} + En_{ads} + En_{evac} + En_{LR} [kWh]}{O_2 \text{ in product } [kg]}$$
(3.53)

### 3.7 Optimization

Given the complex nature of adsorption cycles for air separation, simulations can be used to quickly evaluate various process conditions to find which gives the best performance. Moreover, if we find the performance of the PSA cycle over a sufficiently large space of operating conditions, it is possible to find the performance limits of the adsorbent-cycle combination. This is the premise of using optimization methods for PSA processes.

Genetic algorithm-based tools can be used for this purpose. An initial population consisting of a spread of the decision variables across the search space of interest is given to the optimizer. PSA simulation is run for each combination of decision variables. Depending on the purity, recovery, energy and productivity values, a score is given for each of these runs. Similar to the process of evolution, the optimizer compares these fitness values for each set of decision variables, favours those that give better results, and rejects the ones that give poorer results. For the next generation, decision variables that give more favourable results are picked and 'geneticallyselected', in the hope that they will give similar or better results. The simulation is run for the new generation of decision variables and their scores are evaluated which further helps the optimizer find the best points. This selection process is repeated over several generations until no significant further improvement is seen. In addition to genetic selection, effects like mutation and cross-over are incorporated to ensure that the optimizer efficiently searches the entire range of decision variables without getting stuck in a local minima.

Trade-offs are built into PSA processes inherently. For example, if we increase the adsorption step time to recover more oxygen, this will be accompanied by a corresponding drop in purity because over time the nitrogen concentration wavefront will break through. Thus, instead of one optimum point, a set of optimal points exists, representing the maximum recovery possible for a given value of purity. The results from optimization studies are represented using Pareto curves, which collect these optimal points. A similar trade-off exists between productivity and energy consumed. As productivity increases, the minimum energy needed to operate the PSA cycle at those conditions increases.

MATLAB's Non-dominated Sorting Genetic Algorithm II (NSGA-II) optimization toolbox is used in this study for these purposes [45]. A random sample population size of 180 is generated for each decision variable using the Latin Hypercube Sampling (LHS) technique. This is used as the initial population, and the optimization is run for 25 generations. For each point, a detailed simulation is run until a cyclic steady state is reached, following which fitness values are obtained.

For purity-recovery optimizations, the fitness functions are defined as follows.

$$f_1 = \frac{1}{P u_{O_2}} \tag{3.54}$$

$$f_2 = \frac{1}{Re_{O_2}} \tag{3.55}$$

The objective is to minimize both  $f_1$  and  $f_2$ .

There is a slight change in the definition of fitness functions for energy-productivity optimizations. We are interested in optimized values of energy and productivity in cases where a target purity has been attained. In this thesis's energy-productivity optimizations,  $O_2$  purity constraint of greater than 90% has been applied. Using penalty functions is a way of building this constraint into the optimizer's algorithm. In this case, fitness functions are defined as:

$$f_1 = A \left[ En \right] + B \left[ max(0, Pu_{const} - Pu_{O_2}) \right]^2$$
(3.56)

$$f_2 = \frac{C}{Pr} + D \left[ max(0, Pu_{const} - Pu_{O_2}) \right]^2$$
(3.57)

The objective is to minimize both  $f_1$  and  $f_2$ .



Figure 3.7: (a) Optimization framework. (b) Result of a typical optimization study. Black points show all points examined while the red points indicate the Pareto curve.
# Chapter 4

# PSA processes for oxygen concentration using a single adsorbent

In this chapter, adsorptive separation processes using a single adsorbent are studied. Two adsorbents have been considered individually for this purpose - LiLSX and 13X. Details of isotherm measurement and fitting, unary and binary dynamic column breakthrough experiments are presented. PSA experiments are conducted to validate the mathematical model developed to describe the separation process. The model is then used to conduct purity-recovery and energy-productivity optimization studies for the two adsorbents.

### 4.1 Isotherm measurements

Adsorption isotherms of  $N_2$ ,  $O_2$  and Ar on LiLSX and 13X are shown in Fig. 4.1 and Fig. 4.2. In both the adsorbents,  $N_2$  exhibited the strongest adsorption, followed by  $O_2$  and then Ar. All three gases are adsorbed more strongly on LiLSX as compared to 13X.  $N_2$  solid loadings up to 10 bar could be obtained using HPVA apparatus. For  $O_2$  and Ar, isotherm points in the low-pressure range from 0.1-1.2 bar were obtained. All isotherms are measured at a minimum of three different temperatures.

On LiLSX,  $N_2$  shows non-linearity above 1 bar, while  $O_2$  and Ar are mostly linear. On 13X, all three gases seem to exhibit mostly linear behaviour. The single-site



Figure 4.1:  $N_2$ ,  $O_2$ , Ar isotherms on LiLSX. Markers are loadings obtained from volumetric experiments. Lines are fitted using the single-site Langmuir model.



Figure 4.2:  $N_2$ ,  $O_2$ , Ar isotherms on 13X. Markers are loadings obtained from volumetric experiments. Lines are fitted using the single-site Langmuir model.

Langmuir (SSL) equation:

$$q_i^* = \frac{q_s b_i c_i}{1 + (b_i c_i)} \tag{4.1}$$

is used to fit the single component loadings on the adsorbents. In this equation,  $q_i^*(\text{mmol/g})$  is the equilibrium solid phase loading at the corresponding gas phase concentration  $c_i(\text{mol/m}^3)$ . The saturation capacity of the solid is represented by  $q_s$ ,  $b_i$  is the temperature-dependent equilibrium constant of the respective gas.  $b_i$  varies with temperature as:

$$b_i = b_{0,i} e^{-\Delta U_i / (R_g T)} \tag{4.2}$$

where  $\Delta U_i$  is the internal energy of component *i*. Equations 4.1 and 4.2 were used to fit the experimental points by varying  $b_{0,i}$  and  $q_s$ . N<sub>2</sub> isotherm points for all temperatures are simultaneously fitted to get the values of  $q_s$ ,  $b_0$  and  $\Delta U_i$ . The  $q_s$ value obtained from this fitting is applied to the O<sub>2</sub> and Ar isotherms. The fitting procedure is repeated to get the  $b_0$  and  $-\Delta U_i$  values of O<sub>2</sub> and Ar as well. The values of the SSL parameters obtained are shown in Table 4.1 and Table 4.2.

Table 4.1: Single-site Langmuir parameters for  $N_2$ ,  $O_2$  and Ar on LiLSX

Parameter	$\mathbf{N}_2$	$O_2$	Ar
$b_0[\mathrm{m}^3/\mathrm{mol}]$	$8.73\times10^{-7}$	$1.23\times 10^{-5}$	$1.43\times10^{-5}$
$q_s[\mathrm{mmol/g}]$	3.164	3.164	3.164
$-\Delta U_i [\mathrm{kJ/mol}]$	23.44	11.74	10.76

Table 4.2: Single-site Langmuir parameters for  $N_2$ ,  $O_2$  and Ar on 13X

Parameter	$N_2$	$O_2$	Ar
$b_0 [\mathrm{m}^3/\mathrm{mol}]$	$3.41\times 10^{-6}$	$1.62\times 10^{-5}$	$1.34\times10^{-5}$
$q_s[\mathrm{mmol/g}]$	3.190	3.190	3.190
$-\Delta U_i [\mathrm{kJ/mol}]$	16.69	9.85	10.18

The values of the isotherm parameters compare well with existing literature. Wu et al. [46] provide detailed experiments performed on a commercial sample of LiLSX to determine isotherm parameters. The values of  $-\Delta U_i$  they obtain for N<sub>2</sub> (24.56 kJ/mol) and O<sub>2</sub> (13.47 kJ/mol) compare reasonably to our parameters. Several factors influence gas adsorption on adsorbent, e.g., extent of Li<sup>+</sup> exchange in the zeolite, quantity of binder used and differences in activation methods. In the light of such uncertainties, the isotherm parameters obtained from both these works are comparable.

Selectivity	$N_2/O_2$	$O_2/Ar$	_
LiLSX	8.0	1.27	
13X	3.34	1.06	

Table 4.3: Selectivity of LiLSX and 13X

Although there is evidence that  $N_2$  and  $O_2$  adsorption on LiLSX is energetically heterogeneous [47], in this study we have chosen to use the simpler single-site Langmuir model.

### 4.2 Dynamic column breakthrough experiments

A series of breakthrough experiments were carried out using  $O_2$  as the purge gas and mixtures of  $O_2$  and  $N_2$  as the adsorbate gas. All experiments were performed at room temperature (22°C to 25°C) and atmospheric pressure, using two columns packed with LiLSX and 13X respectively. Pure component measurements were compared with loadings obtained from volumetry experiments. Binary experiments were conducted to verify if the extended Langmuir model effectively captured the competition between gases. Another goal of the breakthrough experiments is to check if the mathematical model captures the process dynamics sufficiently and to find the fitting parameters that need to be tuned to describe experiments.

#### 4.2.1 Single-component breakthrough measurements

Before starting an adsorption breakthrough experiment, the packed column is purged with a gas that does not adsorb strongly on the adsorbent. In this case,  $O_2$  was used as the purge gas and is flown through the column until no further change in outlet composition and bed temperature is observed. Following this, at t = 0,  $N_2$  gas is introduced to the bed by switching the valve. Adsorption experiments are carried out by flowing  $N_2$  until thermal equilibrium was established, often taking much longer than just reaching constant outlet composition. After the adsorption run, the valve is switched back to flow  $O_2$  through the bed to carry out desorption breakthrough runs. The feed flow rate of both gases was maintained at 500 std cc/min. Temperature profiles are measured using thermocouples approximately 25 cm from the inlet of the bed.

Figure 4.3 shows the breakthrough curves of pure N<sub>2</sub> on both the beds obtained from adsorption and desorption experiments. LiLSX having higher N<sub>2</sub> capacity retains N<sub>2</sub> for a longer time before allowing it to break through in the adsorption experiment, as compared to 13X which has a much lower N<sub>2</sub> capacity. The rise in bed temperature during adsorption is higher for LiLSX (almost 18°C). A moderate rise in temperature is observed in the case of 13X (approximately 5°C). This is consistent with the  $\Delta U_i$ values and the equilibrium capacity.

Similarly, in a desorption experiment, LiLSX takes much longer to desorb, compared to 13X. Since desorption is endothermic, a decrease in bed temperature is expected. A larger dip in temperature is observed in the case of LiLSX compared to 13X. The magnitude of temperature drop for both adsorbents is almost equal to the magnitude of the rise in temperatures seen in adsorption experiments, respectively.

Mass balance calculations were carried out using Eqn. 3.3 and the pure N<sub>2</sub> loadings on each of the adsorbent were found. These are marked as loadings corresponding to  $y_{N_2} = 1$  on Fig. 4.6. It can be seen that these values are comparable to those obtained



Figure 4.3: Adsorption and desorption breakthrough curves from single component dynamic column breakthrough experiments. Markers are experimental data and lines are simulated curves for the respective adsorbents.

from volumetry experiments (lines depict the Extended Langmuir model calculated from isotherm data).

The mathematical model described in Section 3.6 was solved to simulate the breakthrough experiments. Parameters whose values were known reliably were taken as such. Four parameters, namely,  $h_{in}$ ,  $h_{out}$ ,  $C_{ps}$  and  $K_z$  were used as fitting parameters while trying to keep their values as realistic as possible. These values were arrived at by a trial and error process by visually inspecting the experimental and predicted temperature curves. The corresponding values of the fitting variables are reported in Table 4.4.

There is some uncertainty with respect to the values of specific heats of the two adsorbents, and a wide range of values, between 800 to 1400 J/kg/K are reported in literature [16, 43, 44, 48]. Since there is no reliable way to measure this in our lab, this has been treated as a fitting parameter. The composition and temperature

Parameter	Symbol	LiLSX	13X	Units
Column Length	L	0.327	0.327	[m]
Column inner radius	$r_{in}$	0.0175	0.0175	[m]
Column outer radius	$r_{out}$	0.02	0.02	[m]
Bed voidage	$\epsilon_b$	0.37	0.37	[-]
Particle voidage	$\epsilon_p$	0.33	0.33	[-]
Particle radius	$r_p$	0.65	0.65	[mm]
Tortuosity	$\tau'$	3	3	[-]
Adsorbent density	$\rho_s$	960	1025	$[kg/m^3]$
Column wall density	$ ho_w$	7500	7500	$[kg/m^3]$
Specific heat capacity of gas phase	$C_{pg}$	1040	1040	[J/kg/K]
Specific heat capacity of adsorbed phase	$C_{pa}$	1040	1040	[J/kg/K]
Specific heat capacity of adsorbent	$C_{ps}$	850	1100	[J/kg/K]
Specific heat capacity of column wall	$C_{pw}$	500	500	[J/kg/K]
Fluid viscosity	$\mu$	$1.837\times 10^{-5}$	$1.837\times 10^{-5}$	[kg/m/s]
Molecular diffusivity	$D_m$	$7.1833\times10^{-5}$	$7.1833\times10^{-5}$	$[m^2/s]$
Adiabatic constant	$\gamma$	1.4	1.4	[-]
Effective gas thermal conductivity	$K_z$	0.01	0.01	[W/m/K]
Thermal conductivity of column wall	$K_w$	15	15	[W/m/K]
Inner heat transfer coefficient	$h_{in}$	11	11	$[W/m^2K]$
Outer heat transfer coefficient	$h_{out}$	10	10	$[W/m^2K]$
Universal gas constant	R	8.314	8.314	$[Pam^3/(molK)]$
Compression/evacuation efficiency	$\eta$	0.72	0.72	[-]

Table 4.4: Parameters used in process simulations

breakthrough curves obtained from the simulation are shown in Fig. 4.3. Multiple runs were performed for each experiment. The composition and temperature curves obtained from these repetitions are shown in Appendix A. It can be seen that the simulated profiles match well with the experimental profiles.

#### 4.2.2 Binary breakthrough experiments

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Binary breakthrough experiments were carried out by purging the adsorbent columns with  $O_2$  and then introducing mixture of  $N_2$  and  $O_2$  as a step change. Adsorption and desorption experiments were conducted with gas mixtures containing 75%, 50% and 25%  $N_2$ , and the rest  $O_2$  by composition. All gas flow-rates were maintained at 500 sccm. Figures 4.4 and 4.5 show the experimentally obtained composition and temperature curves for LiLSX and 13X respectively. It is observed that mixtures having lower N<sub>2</sub> compositions take a longer time to saturate and break through in adsorption experiments. However, the time taken to completely desorb the N<sub>2</sub> is the same for all compositions. This is characteristic of solute propagation following Langmuir isotherm, where the concentration wave velocity is inversely proportional to the slope of the isotherm,  $\frac{dq^*}{dC}$  [9]. In a desorption experiment, although the initial concentrations are different, as the nitrogen concentration wavefront propagates through the column, the slope of the isotherm at the respective concentration keeps increasing. As the concentration approaches zero, the slope of the isotherm is equal for all cases of initial concentration.



Figure 4.4: Composition and temperature curves obtained from dynamic column breakthrough experiments on LiLSX using a mixture of  $N_2$  and  $O_2$ . Markers are experimental data obtained from binary dynamic column breakthrough experiments. Lines indicate curves obtained from simulations.

From the DCB adsorption runs, mass balance can be done separately for each of



Figure 4.5: Composition and temperature curves obtained from dynamic column breakthrough experiments on 13X using a mixture of  $N_2$  and  $O_2$ . Markers are experimental data obtained from binary dynamic column breakthrough experiments. Lines indicate curves obtained from simulations.

the gases -  $N_2$  and  $O_2$  according to Eqn. 3.3 and Eqn. 3.7 respectively to obtain the competitive equilibrium loadings. These are compared against the loadings obtained from the Extended Langmuir model (lines) in Fig. 4.6. The Extended Langmuir model describes competitive multi-component loading using the following equations.

$$q_i^* = \frac{q_{s,i}b_ic_i}{1 + \sum_{i=1}^{n_{comp}} b_ic_i}$$
(4.3)

It is observed that this model sufficiently describes the competitive loadings for this system over a wide range of compositions. The Extended Langmuir model is thus considered sufficient for describing competitive behaviour in the mathematical model.



Figure 4.6: Markers are experimental data obtained from binary dynamic column breakthrough experiments. Lines represent values calculated using Extended Langmuir Model. Error bars are calculated based on potential errors in calibrating flowrate data with composition.

## 4.3 Experimental validation of process simulations

Process experiments using the Skarstrom cycle were conducted on the test rig using the laboratory building's pressurized air supply. Mass flow controllers were used to supply a fixed rate of air to the packed beds through the feed values. For a given  $P_H$ and feed flowrate  $(Q_F)$  combination, initially, the time needed to pressurize the beds is found manually by trial and error. This gives us the value of  $t_{press}$ .  $t_{ads}$  and  $t_{LR}$  are to serve as inputs to the Arduino micro-controller. The value of  $t_{evac}$  is kept equal to  $t_{press}$  to ensure that one bed is pressurized as the other is being evacuated.

To start an experiment, the step times are programmed into the Arduino microcontroller to set the valve-switching schedule. At t=0, the first cycle of valve switching takes place, and air is let into one of the beds. Initially, both the back pressure regulator (BPR) and the needle valve on the reflux line are kept fully open. Bed pressure is continuously monitored for a couple of cycles. Since the BPR is fully open, a sudden pressure drop will be observed initially during the adsorption and light reflux donor (LRD) steps. Then, BPR is closed slowly to increase resistance to product flow and maintain bed pressure. By observing the bed pressure during adsorption, the position of BPR is fixed so that the column pressure stays at the desired  $P_H$ . Similarly, the reflux line needle valve is closed to keep the donor bed's pressure close to the  $P_H$ . This is important to regulate the quantity of O<sub>2</sub> enriched product sent as reflux.

Each experiment is continued to run for a minimum of 100 cycles, at the end of which the product concentration and flow-rate histories are checked to see if a cyclic steady state has been reached. If not, the experiment is run for 100 more cycles. At the end of the experiment, purity and recovery values are calculated by averaging the values obtained over the last 1000 seconds. Two sets of experimental conditions were chosen - one at  $P_H$  of 3 bar and the other at  $P_H$  of 5 bar, to be run on both the adsorbents - LiLSX and 13X. The details of the step times and feed flow rates are specified in Table 4.5 along with the observed purity and recovery values.

Adsorbent	Experiment		Operating	Conditions		Experi	mental	Detailed	d Model
		$t_{ads} \left[ \mathbf{s} \right]$	$t_{LR}$ [s]	$P_H$ [bar]	$Q_F$ [SLPM]	Purity	Recovery	Purity	Recovery
LiLSX	1 (a)	2	5	5	10.3	94.90%	12.74%	94.21%	20.02%
	2 (a)	5	5	5	10.3	83.47%	30.64%	90.47%	45.86%
	3 (a)	8	5	5	10.3	59.68%	39.07%	66.59%	55.79%
	4 (a)	2	17	3	5	94.61%	5.57%	96.02%	10.77%
	5 (a)	5	17	3	5	93.34%	11.76%	95.11%	25.65%
	6 (a)	8	17	3	5	85.79%	18.45%	84.71%	36.92%
13X	1 (b)	2	5	5	10.3	90.52%	11.65%	94.84%	23.07%
	2 (b)	5	5	5	10.3	70.81%	27.04%	69.07%	42.61%
	3 (b)	8	5	5	10.3	56.67%	33.63%	50.52%	50.04%
	4 (b)	2	17	3	5	86.44%	9.78%	79.78%	12.07%
	5 (b)	5	17	3	5	57.92%	16.66%	49.56%	21.24%
	6 (b)	8	17	3	5	46.67%	20.16%	37.96%	26.56%

Table 4.5: Experimental runs carried out on test rig to validate detailed model

Two experiments are chosen from Table 4.5 - experiment numbers 4(a) and 4(b), and their transient pressure, product flow rate at CSS and evolution of purity with time are shown in Fig. 4.7. The pressure curves in both experiments are almost identical. Despite tuning the BPR and the needle valve in the reflux line, a slight pressure drop is observed in the adsorption + light reflux donor (LRD) steps. We can also see that the pressurization step is quicker in the case of 13X than LiLSX, allowing us to carry out more cycles per unit of time using 13X. The flow rate curves show a clear difference between LiLSX and 13X - product flows in 13X are almost double that seen in LiLSX. Product purity climbs to the steady state value within the first ten cycles in both cases.

The experiments were simulated using the detailed model to verify if the model can closely predict the experimental purity and recovery. Fig 4.8 shows the purity and recovery values plotted for the set of experiments in Table 4.5. As adsorption time increases, purity decreases and recovery increases. In the case of LiLSX, for the same step times and feed flows, higher purities and recoveries are observed than those seen in the case of 13X. It can be seen that there is a reasonably good match between simulated and experimental results of 13X experiments conducted at a  $P_H$  of 3 bar. For LiLSX experiments, a greater mismatch is observed between the experimental and simulated recoveries.

When  $P_H$  is taken up to 5 bar, once again LiLSX gives higher purities and recoveries than 13X respectively. However, a greater mismatch is observed between the experimental and simulated recoveries. This could be because of certain limitations of the test rig. The value of  $t_{press}$  is found manually by trial and error for a given combination of  $Q_F$  and  $P_H$ , leaving room for errors. Ideally, an electronic pressure-based trigger would be employed to switch valves precisely when the target  $P_H$  is reached. The set-point of the BPR is set by tuning a knob, which is quite sensitive to vibrations. It has been observed that the BPR set-point keeps increasing with experiment time, as they are constantly exposed to the vibrations caused by the switching of the



Figure 4.7: Transient pressure and product flow rates from experiment numbers 4(a) & 4(b) in Table 4.5 are shown. Red and green curves correspond to LiLSX and 13X respectively. The two curves in Fig.1.(a) and Fig.1.(b) indicate pressures in the two columns in the test rig. Experimentally observed purity with number of cycles is shown in Fig.3.(a) and Fig.3.(b).

feed and blowdown values. Another major limitation of the test rig is the uncertainty associated with the reflux line. The reflux line is kept small (1/8") diameter) with only a needle value to avoid dead volumes built into the test rig. The absence of a flowmeter in the reflux lines makes estimating the amount of gas leaving the column as reflux difficult. The needle value is useful to throttle flows by observing the bed



Figure 4.8: Plot of purity-recovery for various experiments. Solid markers are experimental data obtained from PSA experiments conducted on the test rig. Broken lines represent values obtained from simulations. The purity error bars shown represent an uncertainty of +/-3% based on observed instrument response in repeated runs of the experiments. Error bars for recovery indicate a +/-10-12% change in recovery calculated based on the difference in product flows from the two adsorbent beds in each experiment. The simulation error band indicates the range of recovery values obtained for an error in any input variables by +/-10%.

pressures when  $Q_F$  is sufficiently low. At very high  $Q_F$  values, the reflux lines are undersized and do not let all of the gas to exit the column. Sensitivity analysis of the model to changes in the input variables by +/- 10% has been conducted to check for the impact of experimental errors on the outcomes. The results of this study have been reported in Appendix B, and reveal that for single sorbent systems, purity and recovery values could be off by up to 10.95% and 5.62% respectively.

In addition, the models considered in this work use Darcy's law to describe pressure drop across a column, which is more suitable for applications with low Reynold's number. When considering flow through porous solids at higher velocities, it is preferable to use Ergun's equation. This would decrease the flow out during adsorption steps, and could explain the lower recoveries obtained in experiments. This effect does not show up when comparing breakthrough experiments and simulations, since these experiments were conducted at atmospheric pressure and low flow rates of gas, as compared to  $P_H$  values of 3 bar and 5 bar used in PSA experiments.

## 4.4 Optimization studies

Optimization studies were conducted using a Non-dominated sorting genetic algorithm-II (NSGA-II) based multi-objective optimization tool in MATLAB. A population size of 180 points per generation was chosen and run for 25 generations for each set of conditions. Table 4.6 shows each set's range of decision variables. The time required to pressurize the column was fixed at 20 s for all conditions since this was the realistic time needed to pressurize lab-scale columns used in this study while maintaining an inlet velocity that does not exceed the fluidization limit. The feed interstitial velocity's upper limit is 0.3 m/s based on empirical observations of the onset of fluidization in lab-scale columns. The time needed to evacuate the bed is also fixed at 20 seconds for all the cases. Although evacuation can be much faster, especially in the case of PSA where a vacuum pump is not required, experimentally  $t_{press}$  and  $t_{evac}$  need to be maintained equal to be able to run the Skarstrom cycle sequentially on a 2-bed system.

#### 4.4.1 Purity-Recovery optimization

A trade-off exists between purity and recovery in an adsorptive separation process. This can be easily visualized in a light component separation system like  $O_2$  con-

Parameter	VSA	PVSA	PSA
$P_L$ [bar]	0.2	0.5	1
$P_H$ [bar]	1	1.5	5
$t_{ads} + t_{LRD} [s]$	2-100	2-100	2-100
$t_{LRR}$ [s]	1-99	1-99	1-99
$v_0  [\mathrm{m/s}]$	0.001-0.3	0.001-0.3	0.001-0.3

Table 4.6: Range of decision variables used in optimization studies

centration. As we increase  $t_{ads}$ , more product is collected, leading to an increase in recovery. However, simultaneously N<sub>2</sub> concentration wavefront moves closer to the outlet of the bed until it starts breaking through, at which point purity starts to drop. Purity-recovery optimizations are carried out to understand this trade-off and obtain the Pareto front. All points on the Pareto front correspond to the optimum operating conditions representing the maximum achievable recovery for a given purity value.

Three independent optimization studies were conducted for each of the adsorbents - LiLSX and 13X. No constraints were imposed on the purity or recovery of the optimized points, since our interest is in learning the optimum performance across a wide range of purity values.

Fig. 4.9 shows the optimized purity-recovery Pareto fronts for each of the adsorbents - LiLSX and 13X respectively. Three different operating pressure ranges have been considered for VSA, PVSA and PSA cases. In both adsorbents, higher recovery values are attained for VSA, followed by PVSA and PSA conditions. In LiLSX, the improvement in performance in moving from PSA and PVSA processes to VSA processes is more apparent than in the case of 13X, where only a slight improvement in recoveries is seen. This is due to the highly non-linear shape of the N<sub>2</sub> isotherm on LiLSX between the range of 0-1 bar pressure. The corresponding N<sub>2</sub> isotherm on 13X is almost linear up to 5 bar.

In all cases, LiLSX gives higher recovery values for any given purity than 13X, as



Figure 4.9: Pareto curves obtained from Purity-Recovery optimization studies on LiLSX and 13X for VSA, PVSA and PSA cases.

expected. All curves cut off at approximately 95%  $O_2$  purity because of the presence of Ar and the limited  $O_2/Ar$  selectivity offered by the adsorbents. Among the two adsorbents, LiLSX has a slightly higher  $O_2/Ar$  selectivity, which enables it to give higher purity  $O_2$  than 13X. Another interesting effect because of the presence of Ar is that the Pareto curves (except for 13X in VSA) stop at a recovery value of 10-40% at 95% purity and do not go below such recoveries. This is because pure Ar is produced at lower recoveries, and  $O_2$  remains adsorbed within the column.

To compare and understand the performance of each adsorbent under different pressure conditions, points from each Pareto front at an approximate recovery value of 55% are chosen for further examination. The chosen points along with the corresponding decision variables are shown in Table 4.7. For each set of conditions, the detailed simulation was run to get the axial gas composition and solid loading profiles at the end of each step. These results are shown in Fig. 4.10 and Fig. 4.11.

Table 4.7: Optimized conditions for various processes using LiLSX and 13X giving approximately 55% recovery.

		$t_{ads}$ [s]	$t_{LR}$ [s]	$P_L$ [bar]	$P_H$ [bar]	$v_0 \; [{\rm m/s}]$	Purity [%]	Recovery [%]
LiLSX	VSA	35.58	14.16	0.2	1	0.11	95.41	54.99
	PVSA	37.87	16.12	0.5	1.5	0.07	90.18	55.37
	PSA	26.58	10.01	1	5	0.04	77.54	54.82
13X	VSA	56.32	17.38	0.2	1	0.03	66.25	55.43
	PVSA	31.36	11.26	0.5	1.5	0.06	49.31	55.43
	PSA	38.33	10.80	1	5	0.03	48.61	55.43

By observing the gas phase compositions in Fig. 4.10, it is clear that VSA outperforms PVSA and PSA performance, by giving higher purity. At the end of the adsorption + light reflux donor (LRD) step, in the case of VSA, N<sub>2</sub> wavefront has not broken through the column yet, giving a product that is rich in O<sub>2</sub>. In fact, the gas that is collected for reflux from the LRD step is also N<sub>2</sub> free, which helps in cleaning the bed thoroughly. In comparison, the N<sub>2</sub> gas composition wavefronts at the end of adsorption + LRD steps in PVSA and PSA processes have already broken through. This allows us to collect O<sub>2</sub> of reduced purity as product and for reflux purposes. Purity values for LiLSX at the same recovery follow the order: VSA>PVSA>PSA.

This is also true for 13X as can be seen from Fig. 4.11 that the gas phase at the end of adsorption + LRD step is richest in  $N_2$  for the PSA process. In addition, we



Figure 4.10: Axial gas composition and solid loading profiles for LiLSX adsorbent at the end of each step for the optimized conditions shown in Table 4.7.

can also observe the  $N_2$  solid loading at the end of light reflux receiver (LRR) step. In VSA process, length of the bed occupied by  $N_2$  that stays adsorbed at the end of LRR step is least, followed by PVSA and PSA processes. This gives us a peek at why purities follow the order: VSA>PVSA>PSA for 13X.

Although the solid phase loadings in Fig. 4.10 and Fig. 4.11 might make it seem like PSA processes offer a larger differential in equilibrium  $N_2$  capacities, it is important to keep in mind that the pressure differential in PSA processes is much larger (1-5



Figure 4.11: Axial gas composition and solid loading profiles for 13X adsorbent at the end of each step for the optimized conditions shown in Table 4.7.

bar) as compared to PVSA (0.5-1.5 bar) or PSA (0.2-1 bar) processes.

Considering the set of decision variables corresponding to the Pareto fronts, purity values have been plotted against the key variables, the product of  $t_{ads}$  and  $v_0$ , and  $t_{LR}$  in Fig. 4.12. Higher values of purity are obtained when  $t_{ads} \times v_0$  are kept to a minimum, while  $t_{LR}$  must be increased. By observing plots of purity versus  $t_{ads}$ , one can observe that for a given value of  $t_{ads} \times v_0$ , LiLSX can produce product having higher purity than 13X. This is more apparent in the case of VSA and PVSA; in PSA



Figure 4.12: Mapping of decision variables corresponding to the Pareto fronts shown in Fig 4.9

there seems to be no significant difference in the  $t_{ads} \times v_0$  curves. This is because of the superior working capacity afforded by LiLSX between the pressure ranges 0-2 bar as compared to 13X. At higher pressures (1-5 bar as considered for PSA), the differences in working capacity are not sufficient to have a big difference between LiLSX and 13X. Lower  $t_{LR}$  values point that LiLSX needs fewer number of moles of  $O_2$  rich product to be refluxed to give the same purity as 13X.

#### 4.4.2 Energy-Productivity optimization

From a practical viewpoint, it is interesting to know the minimum energy and maximum productivity that can be achieved using a given test rig. This gives us an indication of the cost of the O<sub>2</sub> produced. A purity constraint of > 90% is applied, while there are no constraints on recovery. Energy is recorded in units of [kWh/kg O<sub>2</sub>], while productivity is expressed in [kg O<sub>2</sub> per kg adsorbent per day]. Energy is consumed in PSA processes for compression, VSA processes for evacuation, and for both in PVSA processes.  $P_H$  and  $P_L$  values are checked to appropriately calculate energy values.

Productivity is calculated using the following formula.

Productivity 
$$Pr = \frac{O_2 \text{ in product collected per cycle [kg]}}{\text{adsorbent mass [kg] × cycle time [day]}}$$
 (4.4)

Energy consumption for each step is calculated using the following correlation.

Energy per step, 
$$En = \frac{1}{\eta} \epsilon_{in}^2 \frac{\gamma}{\gamma - 1} \int_{t=0}^{t=t_{step}} (vP_{out}) \left[ \left(\frac{1}{P_{out}}\right)^{\frac{\gamma-1}{\gamma}} - 1 \right] dt$$
(4.5)

 $P_{out}$  here stands for the respective pressure at which gas exits the column in each step.  $\eta$  is the efficiency of the vacuum pump or the compressor. Energy consumed in the process to produce unit mass of product  $O_2$  is calculated as:

$$Energy = \frac{En_{press} + En_{ads} + En_{evac} + En_{LR} [kWh]}{O_2 \text{ in product } [kg]}$$
(4.6)

Compressor and vacuum pump are assumed to be operating at an efficiency of 0.72. Range of the decision variables are same as those used in purity-recovery optimizations and are given in Table 4.6. Once again,  $t_{press}$  and  $t_{evac}$  are maintained as 20 s in all cases.

Fig. 4.13 shows the energy-productivity Pareto curves for the LiLSX and 13X in VSA, PSA and PVSA conditions. LiLSX gives higher productivities at lower energies as compared to 13X. Interestingly, there appears to be a trade-off between lower energy with lower productivity at PVSA conditions, and higher energy at higher



Figure 4.13: Pareto curves obtained from Energy-Productivity optimization studies on LiLSX and 13X for VSA, PVSA and PSA cases. Purity constraint of 290% has been applied.

productivity at PSA conditions. The optimized energy-productivity region for VSA is limited to a small region for both adsorbents. It is clear that LiLSX always gives

higher productivity at lower energy consumption, as compared to 13X.

# Chapter 5

# PSA processes for oxygen concentration using layered beds

This chapter explores adsorptive separation processes using multi-layered beds consisting of two adsorbents - LiLSX and 13X. Following a brief description of the two configurations of the layered bed, dynamic column breakthrough experiments with both pure  $N_2$  and mixtures of  $N_2$  and  $O_2$  are discussed. The results of PSA experiments conducted with the layered beds are reported along with simulation predictions. Purity-recovery optimization studies using layered beds reveal interesting relationships between the amount of LiLSX in the bed and the separation performance. Special emphasis has been given to studying their performance under adiabatic conditions. A discussion of the energy-productivity optimization follows.

### 5.1 Two configurations of the layered bed

A lab-scale column of fixed dimensions is considered. In all experiments performed, a column is packed with two layers of adsorbents, each occupying a volume of approximately 50% of the column. Since the density of the two adsorbents are not equal, there is a slight difference in the mass of adsorbent in each layer, as seen in Table 3.1. Mesh screens separate the two layers and prevent inter-mixing during experiments. Depending on which adsorbent is placed near the feed end, two configurations of the layered bed exist - one in which 13X layer is placed near the feed end, and the other in



Figure 5.1: Four bed configurations considered in this work. (a) and (d) represent single adsorbent beds packed with 13X and LiLSX respectively. (b) and (c) show the two configurations of a layered bed depending on which layer is placed near the feed end.  $T_1$  and  $T_2$  indicate positions where thermocouples are placed to measure temperatures in the two layers in breakthrough experiments.

which LiLSX layer is placed near the feed end, as shown in Fig. 5.1. The configuration in which 13X is placed near the feed end will henceforth be called 13X-LiLSX, and the one in which LiLSX is placed near the feed end will be referred to as LiLSX-13X. Both these configurations have been considered in the experiments and models in this study to find if they affect the process performance. This chapter follows a colour scheme as shown in Fig. 5.1 - blue refers to the 13X-LiLSX configuration while orange refers to the LiLSX-13X configuration.

### 5.2 Dynamic column breakthrough experiments

Similar to the single adsorbent systems, dynamic column breakthrough experiments were performed using  $O_2$  as the purge gas and mixtures of  $O_2$  and  $N_2$  as the adsorbate gas. All experiments were performed at room temperature (22 to 25 °C) and atmospheric pressure. Parameters for the mathematical model were obtained from single adsorbent experiments as shown in Table 4.4. Adsorbent-specific parameters like isotherms, particle density and specific heats of adsorbents were applied separately to each layer. Parameters common to the system, e.g., bed dimensions and heat transfer characteristics were applied uniformly for both layers.

Before starting an adsorption breakthrough run, the column was purged with  $O_2$ gas for a sufficiently long time until the outlet composition consistently showed pure  $O_2$ . At time t = 0, the valve was switched to flow the adsorbate gas mixture into the bed. This was continued until the outlet composition showed pure  $N_2$  and bed temperature returned to the initial value. Then, the desorption run was carried out by switching the valve back to  $O_2$  and was continued until thermal equilibrium was established. The feed flow rate of pure  $O_2$  and the adsorbate mixtures were kept at 500 sccm. Temperatures were measured with time using two thermocouples - one placed in each layer at approximately 5 cm from each end.

#### 5.2.1 Single component breakthrough experiments

Figure 5.2 shows the experimental  $N_2$  composition, bed temperature and outlet flow rate with time for adsorption and desorption experiments using the layered bed and 100%  $N_2$  feed. Experimental data obtained from DCB runs on single adsorbent beds are also given for comparison. The outlet  $N_2$  composition curve of the layered bed falls perfectly in between the two single sorbent curves. Among the two configurations of the layered bed, both curves overlap.

Bed temperatures in the layered bed are measured by two thermocouples - one placed in each layer about 5 cm away from each end. In adsorption experiments, the temperature seen in each layer is almost equal to the spike in temperature observed in the corresponding single sorbent case. In desorption, a slight difference is observed in the temperature drop in the layered beds, when compared with the respective single sorbents. The temperature drop in the layer closest to the feed end - 13X in the blue curve and LiLSX in the orange curve- seems to be equal to the magnitude of



Figure 5.2: Experimental outlet composition, temperature and flow-rate data for both single sorbent and the layered beds using 100% N<sub>2</sub>. In the case of layered beds, temperature is measured by two thermocouples, one placed in each layer.

the temperature drop in the respective single sorbent case. However, for the second layer, the drop in temperature is slightly lower than the respective single sorbents. This is likely due to convective heat transfer between the warmer desorbed gas that is flowing along the second layer, which heats up the adsorbent in the second layer. In adsorption, a counter-effect exists where cooler feed gas flowing along the second layer transfers heat with the bed, causing a drop in the temperature of the second layer. However, this is not seen very explicitly because of the low flow rates of gas moving along the bed during adsorption, leading to a lower convective heat transfer rate. This observation aligns with the qualitative explanation of the 'cold-spot' phenomenon given by Wilson et al. [26].

In adsorption experiments, the outlet flow rate initially drops when the adsorbate is adsorbed. Once the sorbent is saturated with the adsorbate, the outlet flow rate climbs back up and equals the inlet flow rate. The magnitude of flow drop depends on the adsorbent's N<sub>2</sub> capacity - as seen in the difference between the 13X (green) and LiLSX (red) single sorbent curves. In the case of the layered bed, the magnitude of flow drop varies with the layer, depending on the respective N<sub>2</sub> capacity. In desorption experiments, a flow surge is observed when all the adsorbed N<sub>2</sub> gets desorbed and leaves the column. The magnitude of flow surge varies between 2.5 - 3 times the inlet flow, with increasing magnitude corresponding to increased N<sub>2</sub> capacity. The surge magnitude in the layered bed depends on which adsorbent is placed near the feed end - 13X being placed near the feed end (blue) has a lower magnitude of flow surge than LiLSX placed near the feed end (orange).

Figure 5.3 shows the experimental and simulated results of DCB experiments performed on the layered bed with 100% N<sub>2</sub>. The mathematical model for the layered beds uses parameters obtained from single sorbent breakthrough experiments for each layer as shown in Table 4.4. A finer grid consisting of 70 cells (compared to the usual 30) was used to accurately capture the mass of adsorbent in each layer. Although this makes the simulation slow, it was necessary to check if the single sorbent parameters could predict the behaviour of layered beds. The model captures the variation of outlet N<sub>2</sub> composition and bed temperature well. When looking at the bed temperatures specifically, the model can reasonably predict the temperature variation in both layers.

#### 5.2.2 Binary breakthrough experiments

Adsorption and desorption experiments were conducted with gas mixtures containing 75%, 50% and 25%  $N_2$  by composition. The overall mixture has a flow rate of 500 sccm. Figures 5.4, 5.5 and 5.6 show how outlet composition and temperature



Figure 5.3: Composition and temperature histories for two configurations of the layered bed from adsorption and desorption of 100% N<sub>2</sub>. Markers are experimental data. Lines are simulated profiles for the respective adsorbents.

of the two layers change with time for mixtures containing 75%, 50% and 25%  $N_2$  respectively. As expected from single adsorbent experiments, mixtures having lower  $N_2$  compositions take longer to saturate the bed in adsorption breakthrough runs. The time taken to fully desorb  $N_2$  is almost similar for all  $N_2$  compositions. The rise in temperature during adsorption and drop in temperature during desorption increases in magnitude as the  $N_2$  composition in the feed stream increases. The magnitude of each layer's temperature changes is almost the same as that seen in the single sorbent experiments of the respective compositions and adsorbents. The outlet composition breakthrough takes place simultaneously in both the configurations of the layered bed



Figure 5.4: Composition and temperature histories for two configurations of the layered bed from adsorption and desorption of 75% N<sub>2</sub>. Markers are experimental data. Lines are simulated profiles for the respective adsorbents.

- 13X-LiLSX and LiLSX-13X. Once again, it can be seen that the simulated results match the experimental points quite closely.

## 5.3 Experimental validation of process simulations

Similar to the experiments using single sorbents, Skarstrom cycle PSA experiments were conducted using the building's air supply on the experimental test rig. Two columns were filled with identical amounts of LiLSX and 13X, with each of these adsorbents placed as layers. Each column had LiLSX and 13X packed in a 1:1 volume ratio. The columns can be fitted into the test rig as such or after inverting to get the



Figure 5.5: Composition and temperature histories for two configurations of the layered bed from adsorption and desorption of 50% N<sub>2</sub>. Markers are experimental data. Lines are simulated profiles for the respective adsorbents.



Figure 5.6: Composition and temperature histories for two configurations of the layered bed from adsorption and desorption of 25% N<sub>2</sub>. Markers are experimental data. Lines are simulated profiles for the respective adsorbents.

two layered bed configurations: 13X-LiLSX and LiLSX-13X. Mass flow controllers were used to supply a fixed rate of air to each column using the feed valves. For a given  $P_H$  and feed flowrate ( $Q_F$ ) combination, initially, the time needed to pressurize the beds to  $P_H$  is found manually by trial and error. This gives us the value of  $t_{press}$ .  $t_{ads}$  and  $t_{LR}$  are to serve as inputs to the Arduino micro-controller. The value of  $t_{evac}$ is kept equal to  $t_{press}$  to be able to cyclically use the two beds - when one bed is pressurizing, the other gets evacuated.

To start an experiment, the step times are programmed into the Arduino microcontroller to set the valve-switching schedule. At t = 0, the first cycle of valve switching takes place, and air is let into one of the beds. Initially, the back pressure regulator (BPR) and the needle valve on the reflux line are kept fully open. Bed pressure is continuously monitored for a couple of cycles. Since the BPR is fully open, a sudden pressure drop will be observed initially during the adsorption step. Then, BPR is closed slowly to increase resistance to product flow and maintain bed pressure. By observing the bed pressure during adsorption and light reflux donor (LRD) steps, the position of the BPR is fixed so that the column pressure stays at the desired  $P_H$ . Similarly, the needle valve on the reflux line is closed to keep the donor bed's pressure close to the  $P_H$ . This is important to regulate the quantity of O<sub>2</sub> enriched product sent as reflux to the other bed.

Each experiment is continued to run for a minimum of 100 cycles, at the end of which the product concentration and flow-rate histories are checked to see if a cyclic steady state has been reached. If not, the experiment is run for 100 more cycles. At the end of the experiment, purity and recovery values are calculated by averaging the values obtained over the last 1000 s. Two sets of experimental conditions were chosen - one at  $P_H$  of 3 bar and the other at  $P_H$  of 5 bar, to be run on both configurations of the layered bed: 13X-LiLSX and LiLSX-13X. The details of the step times, pressures and feed flow rates are specified in Table 5.1 along with the observed purity and recovery values.

Adsorbent	Experiment		Operati	Operating Conditions		Experi	mental	Detailed Model	
		$t_{ads}$ [s]	$t_{LR}$ [s]	$P_H$ [bar]	$Q_F$ [SLPM]	Purity	Recovery	Purity	Recovery
13X-LiLSX	1 (a)	2	5	5	10.3	91.93%	12.38%	93.79%	20.86%
	2 (a)	5	5	5	10.3	78.55%	27.59%	82.47%	44.10%
	3~(a)	8	5	5	10.3	59.08%	36.60%	59.37%	52.43%
	4 (a)	2	5	3	5	90.39%	5.82%	91.21%	16.14%
	5~(a)	5	5	3	5	61.27%	10.20%	80.39%	35.74%
	6 (a)	8	5	3	5	52.29%	11.70%	61.61%	45.94%
LiLSX-13X	1 (b)	2	5	5	10.3	90.27%	13.15%	94.05%	21.75%
	2 (b)	5	5	5	10.3	71.49%	28.51%	79.11%	44.89%
	3 (b)	8	5	5	10.3	54.95%	36.88%	58.06%	53.65%
	4 (b)	2	5	3	5	79.93%	6.32%	91.89%	17.13%
	5 (b)	5	5	3	5	61.26%	9.76%	73.11%	35.86%
	6 (b)	8	5	3	5	53.41%	11.43%	56.99%	45.92%

Table 5.1: Experimental runs carried out on test rig to validate detailed model


Figure 5.7: Transient pressure and product flow rates from experiment numbers 6(a) & 6(b) in Table 5.1 are shown. Blue and orange curves correspond to the configuration 13X-LiLSX and LiLSX-13X respectively. Each of the two curves in Fig.1.(a) and Fig.1.(b) indicate pressures in the two columns in the test rig. Experimentally observed purity with number of cycles is shown in Fig.3.(a) and Fig.3.(b).

Two experiments are chosen from Table 5.1 - experiment numbers 6(a) and 6(b) are chosen, and their transient pressure, product flow rate at CSS and evolution of purity with time are shown in Fig. 5.7. The pressure curves are close to ideal, with a linear rise in pressure as the air fills up the bed, followed by adsorption and LRD steps at almost constant  $P_H$ . Comparing the pressure and flow curves of the two

configurations, we can see that they are identical. Purity evolution curves indicate the presence of fluctuations in purity value with each cycle - the purities fluctuate between +/-5% of the mean value. This fluctuation becomes apparent by observing the evolution of purities in the single adsorbent cases as shown in Fig. 4.7. This effect was observed in all experiments conducted with the layered beds. Although the reasons for this are not clear, each of the experiments was run for long durations (4-6 hours) to ensure that cyclic steady has been reached.

All experiments were simulated using the detailed, layered bed model to find how accurately the model can predict experimental purity and recovery. Fig. 5.8 shows the purity and recovery values plotted for the set of experiments in Table 5.1. As adsorption time increases, purity decreases and recovery increases. While purities obtained from the detailed model were within +/-5% range of the experimental points, a substantial recovery drop is seen compared to the model predictions. This could be because of the inherent limitations of the test rig and the pressure drop correlation, as was seen in the single adsorbent experiments. The amount of gas transferred between columns during the reflux step cannot be measured, leading to some uncertainty. Sensitivity analysis of the layered bed PSA model to changes in the input variables by +/-10% has been conducted to check for the impact of such experimental errors. The results of this study have been reported in Appendix B, and reveal that for layered bed systems, purity and recovery values could be off by up to 10.42% and 4.81% respectively. This study also reveals that recovery is very sensitive to changes in the reflux time, or the amount of gas used for light reflux. Unlike breakthrough simulations, in simulations of PSA experiments, a regular grid having 30 cells was used to discretize the column since using a finer grid (70 cells) was found to be impractical. Since the purity and recovery depend on the position of the  $N_2$  fronts in the column, some details may be lost by opting for a coarser grid.

In experiments with  $P_H = 3$  bar, both configurations of the layered bed seem to give comparable purity and recovery, except for experiments numbered 4(a) and 4(b),



Figure 5.8: Solid markers are experimental data obtained from PSA experiments conducted on the test-rig. Broken lines represent values obtained from simulations. Experimental purity error bars shown represent an uncertainty of +/-3% based on observed instrument response in repeated runs of the experiments. Error bars for experimental recovery indicate a +/-10-12% change in recovery calculated based on the difference in product flows from the two adsorbent beds in each experiment. Simulation error band indicates the range of recovery values obtained for an error in any of the input variables by +/-10%.

where 13X-LiLSX gives a significantly higher purity (90.39%) than the reverse configuration (79.93%) at the same recovery. In experiments with  $P_H = 5$  bar, there seems to be a trend of 13X-LiLSX configuration giving higher purity for almost the same recovery compared to the LiLSX-13X configuration. The simulations of these experiments do not particularly show any such trend. This could possibly be because of the fact that experiments are run for a long time (100-200 cycles), while simulations are usually run for only 25 cycles to reach cyclic steady state. There is a possibility that the model fails to capture the accumulation of tiny heat effects across the columns, which could lead to the formation of severe axial temperature profiles over such a short period of time. These temperature effects can have an effect on the purity and recovery of lab-scale systems as explained in Section 5.4.2.

#### 5.4 Optimization studies

Optimization studies were conducted for the layered beds in a method similar to the single sorbent case using a Non-dominated sorting genetic algorithm-II (NSGA-II) based multi-objective optimization tool in MATLAB. Table 4.6 shows the range of decision variables used. A population size of 180 points per generation was chosen and run for 25 generations for each set of conditions. The time required to pressurize the column was fixed as 20s for each condition since this was the realistic time needed to pressurize lab-scale columns used in this study while maintaining an inlet velocity that does not exceed the fluidization limit. The feed interstitial velocity's upper limit is 0.3 m/s based on empirical observations of the onset of fluidization in lab-scale columns. The time needed to evacuate the bed is also fixed at 20 s for all cases. Although evacuation can be much faster, especially in the case of PSA where a vacuum pump is not required, experimentally  $t_{press}$  and  $t_{evac}$  need to be maintained equal to be able to run the Skarstrom cycle sequentially on a 2-bed system.

#### 5.4.1 Purity-Recovery optimization

Purity-recovery optimization studies were carried out for the two orientations of the layered bed - 13X-LiLSX and LiLSX-13X. LiLSX is present in three proportions - 25%, 50% and 75% to see if the effect of the addition of LiLSX on performance is linear with respect to the proportion of LiLSX in the column. Three pressure ranges have been considered and Fig. 5.9 shows the Pareto fronts along with the corresponding

single sorbent results.



Figure 5.9: Pareto curves obtained from purity-recovery optimization studies on two configurations of the layered bed: 13X-LiLSX (blue) and LiLSX-13X (orange) with various proportions of LiLSX for VSA, PVSA and PSA cases. Red and green curves correspond to the single sorbent Pareto fronts of LiLSX and 13X respectively.

There is an almost step-wise improvement in recovery in the case of PSA with increasing amounts of LiLSX, where the curves corresponding to increasing amounts of LiLSX seem to be equally spaced out. In PVSA and VSA, this behaviour is significantly non-uniform. Starting from 100% LiLSX, as we move down, the loss in recovery by substituting a part of the LiLSX with 13X is not significant in PVSA and VSA cases. In the case of VSA especially, almost no drop in recovery is seen when moving from 100% LiLSX to 75% LiLSX. This effect is due to the strongly non-linear shape of  $N_2$  isotherm on LiLSX in the 0-1 bar pressure range. To visualize this better, points corresponding to each layered bed Pareto front at approximately 90% purity have been picked and enlisted in Table 5.2. The recoveries obtained in each case are plotted as a function of the amount of LiLSX present in Fig. 5.10.



Figure 5.10: Recovery variation with amount of LiLSX in the bed at conditions giving 90% purity obtained from Pareto fronts shown in Fig. 5.9. Blue and orange curves correspond to 13X-LiLSX and LiLSX-13X configurations respectively.

From Fig. 5.10, it is clear that adding LiLSX in a vacuum process is much more beneficial than in a PSA process. PSA processes have an almost linear improvement with the addition of LiLSX. PVSA and VSA processes show moderate non-linearity in this regard.

In almost all cases shown in Fig. 5.9, the two orientations of the layered bed seem to lie exactly on top of each other, indicating that the order of layering does not matter in the operation of ideal lab-scale columns. Since these columns are small and have sufficient internal heat transfer coefficient  $(h_{in})$  to allow for heat exchange between the

		$t_{ads}$ [s]	$t_{LR}$ [s]	$P_L$ [bar]	$P_H$ [bar]	$v_0 \; [{\rm m/s}]$	Purity [%]	Recovery [%]	
13X-LiLSX	25%	VSA	33.22	10.47	0.2	1	0.063	90.18	55.42
		PVSA	50.86	27.05	0.5	1.5	0.035	90.27	42.99
		PSA	19.20	10.45	1	5	0.048	90.24	39.52
LiLSX-13X	25%	VSA	18.28	7.43	0.2	1	0.112	90.24	53.64
		PVSA	22.28	12.68	0.5	1.5	0.077	90.35	43.77
		PSA	18.58	10.02	1	5	0.047	90.12	39.62
13X-LiLSX	50%	VSA	35.43	9.87	0.2	1	0.075	90.26	60.52
		PVSA	28.12	13.24	0.5	1.5	0.068	90.25	47.90
		PSA	70.96	36.09	1	5	0.014	90.21	42.03
LiLSX-13X	50%	VSA	63.83	22.69	0.2	1	0.042	90.20	59.81
		PVSA	22.49	11.86	0.5	1.5	0.087	90.10	48.44
		PSA	27.83	14.61	1	5	0.034	90.43	42.35
13X-LiLSX	75%	VSA	30.61	7.39	0.2	1	0.105	90.35	66.06
		PVSA	38.27	17.10	0.5	1.5	0.061	90.27	53.10
		PSA	52.32	26.50	1	5	0.022	90.08	46.38
LiLSX-13X	75%	VSA	30.58	8.88	0.2	1	0.105	90.10	65.97
		PVSA	45.21	23.25	0.5	1.5	0.055	90.47	52.37
		PSA	18.49	8.87	1	5	0.053	90.12	47.07

Table 5.2: Optimized conditions corresponding to Pareto fronts for the two configurations of the layered bed giving approximately 90% purity, for use in Fig. 5.10.

packed bed and the ambient, severe axial temperature profiles characteristic of layered beds are not allowed to develop. To further understand how the two configurations behave in various processes, points from the Pareto fronts corresponding to 50% LiLSX giving approximately 90% purity in Fig. 5.9 have been chosen and are enlisted in Table 5.3. Detailed process simulation was run for each of these points to obtain the internal axial gas composition and solid loading profiles, which are shown in Fig. 5.11.

Table 5.3: Optimized conditions for various processes using the two configurations of the layered bed giving approximately 90% purity.

		$t_{ads}$ [s]	$t_{LR}$ [s]	$P_L$ [bar]	$P_H$ [bar]	$v_0 \; [{\rm m/s}]$	Purity [%]	Recovery [%]
13X-LiLSX	VSA	35.43	9.87	0.2	1	0.075	90.26	60.52
	PVSA	28.12	13.24	0.5	1.5	0.068	90.25	47.90
	PSA	70.96	36.09	1	5	0.014	90.21	42.03
LiLSX-13X	VSA	63.83	22.69	0.2	1	0.042	90.20	59.81
	PVSA	22.49	11.86	0.5	1.5	0.087	90.10	48.44
	PSA	27.83	14.61	1	5	0.034	90.43	42.35



Figure 5.11: Axial gas composition and solid loading profiles for the two configurations of the layered bed at the end of each step for the optimized conditions shown in Table 5.3. Blue and orange curves represent the two configurations of the layered beds: 13X-LiLSX and LiLSX-13X respectively.

Figure 5.11 allows us to look inside the column for differences in how the two configurations behave. The gas composition curves indicate that the  $N_2$  wavefronts are positioned further along the bed in the 13X-LiLSX configuration than in the LiLSX-13X case. This is expected since placing LiLSX near the feed end allows for more  $N_2$  capacity to be present near the feed end rather than the product end. The solid loading curves also show a similar trend, where more gas is adsorbed on LiLSX

compared to 13X. It can also be seen that in the VSA process, the gas composition after the evacuation step is rich in  $N_2$  and contains very little  $O_2$ . Thus, little  $O_2$  is lost in the evacuation step in VSA processes as compared to PVSA and PSA processes, giving rise to higher recoveries in the former.



Figure 5.12: Mapping of decision variables corresponding to the Pareto fronts shown in Fig 4.9

Considering the decision variables corresponding to the Pareto fronts of layered beds having 50% LiLSX in Fig. 5.9, purity values have been plotted against the key variables,  $t_{ads} \times v_0$  and  $t_{LR}$  in Fig. 5.12. Similar to what was seen in the single adsorbent case, purity decreases with increase in  $t_{ads} \times v_0$  and increases with increase in  $t_{LR}$ . No consistent trend is observed that points out one configuration as superior to the other, emphasizing once again that in lab-scale, almost isothermal columns, the order in which the two layers are placed does not significantly affect the performance.

#### 5.4.2 Layering in adiabatic columns

It is known that in large-scale industrial columns, the diameter of the packed bed can make it very difficult for heat to enter or exit the column efficiently. In other words, these columns behave adiabatically, and do not allow any heat transfer between the packed bed and the ambient environment. To test the effects of layering in such systems, a purity-recovery optimization routine is done for adiabatic lab-scale columns by making the internal heat transfer coefficient  $h_{in} = 0$ . Fig. 5.13 shows the Pareto fronts obtained from this study.



Figure 5.13: Purity-recovery optimization curves for PSA under adiabatic conditions. Blue and orange curves correspond to 13X-LiLSX and LiLSX-13X configurations respectively.

From Fig. 5.13, it is clear that one orientation of the layered bed - 13X-LiLSX seems to give higher recoveries for any purity than the reverse configuration (LiLSX-13X). A possible reason for this effect is the development of a cold spot in the 13X layer in the 13X-LiLSX configuration, due to the repetitive interactions between convective

Table 5.4: Optimized conditions for adiabatic systems using the four adsorbent configurations giving approximately 90% purity.

		$t_{ads}$ [s]	$t_{LR}$ [s]	$P_L$ [bar]	$P_H$ [bar]	$v_0  [{\rm m/s}]$	Purity [%]	Recovery [%]
LiLSX	Adiabatic	22.71	10.34	1	5	0.04	89.98	48.70
	Finite heat transfer	22.71	10.34	1	5	0.04	92.79	46.66
13X	Adiabatic	22.79	13.23	1	5	0.03	90.15	33.11
	Finite heat transfer	22.79	13.23	1	5	0.03	93.28	31.89
13X-LiLSX	Adiabatic	17.96	9.50	1	5	0.05	89.95	41.74
	Finite heat transfer	17.96	9.50	1	5	0.05	91.32	40.95
LiLSX-13X	Adiabatic	24.65	13.27	1	5	0.03	89.65	39.42
	Adiabatic	24.65	13.27	1	5	0.03	93.45	31.89

heat transfer by the flowing gas and the heating and cooling of the adsorbent due to adsorption-desorption cycles. This has been explained in great detail by Wilson et al. in their two-part work [26, 40]. This cold spot can be severe (5 to 10 °C) and can only form in cases where a layered bed is arranged such that an adsorbent with lower capacity than the main adsorbent is placed near the feed end. The layered bed configuration 13X-LiLSX would be an example of such a system. 13X develops higher  $N_2$  capacity at such low temperatures. In contrast, a hot spot (40 – 50°C) develops in the LiLSX layer in the LiLSX-13X configuration [40]. At such high temperatures, selectivity of LiLSX reduces drastically.

To verify if the difference in performance is because of heat effects, points from the Pareto curves in Fig. 5.13 have been chosen and are listed in Table 5.4. Detailed simulations were run for each of these points for two different conditions - adiabatic  $(h_{in} = 0)$  and finite heat transfer  $(h_{in} = 11 \text{ W/m}^2\text{K})$ . Axial gas composition, solid loading and temperature profiles for these have been extracted and are shown in Fig. 5.14, Fig. 5.15, Fig. 5.16 and Fig. 5.17.

The effect of adiabaticity is severe even in single sorbent systems as seen in Fig. 5.14 and Fig. 5.15. Much higher temperatures are observed in the adiabatic columns (40 - 80 °C), as compared to columns with finite heat transfer (30 - 40 °C) due to accumulation of heat. In layered beds, the axial temperature profiles show the characteristic dip for 13X-LiLSX and peak for LiLSX-13X for both the adiabatic and



Figure 5.14: Axial gas composition and solid loading profiles for LiLSX adsorbent at the end of each step for the optimized conditions shown in Table 5.4. Figures (a), (b), (c) show the profiles obtained from adiabatic processes. Figures (d), (e), (f) show the profiles obtained from corresponding processes allowing finite heat transfer.

finite heat transfer cases, as seen in Fig. 5.16 and Fig. 5.17. The magnitude of the cold and hot spots are respectively lower in the finite heat transfer case, while in the adiabatic case these effects are more apparent and magnified. It can also be seen that there is very little difference in the magnitude of cold-spot between the two heat transfer conditions in 13X-LiLSX configuration; both reaching to about 8 °C. In contrast, there is a clear difference in the magnitude of the hot spot observed between



Figure 5.15: Axial gas composition and solid loading profiles for 13X adsorbent at the end of each step for the optimized conditions shown in Table 5.4. Figures (a), (b), (c) show the profiles obtained from adiabatic processes. Figures (d), (e), (f) show the profiles obtained from corresponding processes allowing finite heat transfer.

the two heat transfer conditions in the case of LiLSX-13X. With finite heat transfer, the hot spot is around 40 °C, while in the adiabatic case, the bed temperature is about 70 °C in the hottest region. This leads us to believe that heat effects are indeed the reason for one configuration of the layered bed outperforming the other. However, contrary to popular opinion, it is not the severity of the cold spot that causes this. Rather, the magnitude of temperature in the hot spot makes LiLSX



Figure 5.16: Axial gas composition and solid loading profiles for the layered bed configuration 13X-LiLSX at the end of each step for the optimized conditions shown in Table 5.4. Figures (a), (b), (c) show the profiles obtained from adiabatic processes. Figures (d), (e), (f) show the profiles obtained from corresponding processes allowing finite heat transfer.

lose its selectivity, leading to poorer performance. Thus, one can conclude that the order in which the layers are placed matters in a large scale adiabatic system. It is beneficial to place the lower  $N_2$  capacity adsorbent (13X in this case) near the feed end, followed by the higher capacity adsorbent (LiLSX). In an ideal lab-scale system, this effect is not obvious because of the ease with which heat can be transferred from



Figure 5.17: Axial gas composition and solid loading profiles for the layered bed configuration LiLSX-13X at the end of each step for the optimized conditions shown in Table 5.4. Figures (a), (b), (c) show the profiles obtained from adiabatic processes. Figures (d), (e), (f) show the profiles obtained from corresponding processes allowing finite heat transfer.

within the packed bed to the environment.

#### 5.4.3 Energy-Productivity optimization

Energy-productivity optimizations are carried out for the lab-scale layered bed columns with finite heat transfer, i.e.,  $h_{in} = 11 \text{ W/m}^2\text{K}$ . A purity constraint of > 90% is applied, while there are no constraints on recovery. Energy is recorded in units of

[kWh/kg  $O_2$ ], while productivity is expressed in [kg  $O_2$  per kg adsorbent per day]. Range of decision variables are same as those used in purity-recovery optimizations and are given in Table 4.6. Once again,  $t_{press}$  and  $t_{evac}$  are maintained as 20 s in all cases.



Figure 5.18: Pareto curves obtained from energy-productivity optimization studies on two configurations of the layered bed: 13X-LiLSX (blue) and LiLSX-13X (orange) with various proportions of LiLSX for VSA, PVSA and PSA cases. Red and green curves correspond to the single sorbent Pareto fronts of LiLSX and 13X respectively.

Fig. 5.18 shows the Pareto fronts obtained from these optimization studies for the layered bed containing various proportions of LiLSX. Similar to what was seen in purity-recovery optimizations, the improvement in productivity with increasing amounts of LiLSX seems to be uniformly progressive in PSA, and not very uniform in VSA and PVSA. The curves for the two configurations of the layered bed overlap, or fall within close range of each other in all cases, further indicating that the order of layering does not have an effect in ideal lab-scale systems. Another observation that can be made is that PVSA systems operate using the least energy, while productivity can be maximized by employing PSA systems. Interestingly, PVSA system with 75% LiLSX seems to give a higher productivity for a marginal increase in energy, as compared to 100% LiLSX.

In conclusion, it can be seen that the performance of layered beds, especially the variation in performance as a function of the amount of LiLSX present depends to a great extent on the range of pressures where the bed is operated. If an existing concentrator is a single-sorbent LiLSX system operating in VSA or PVSA modes, substituting a portion of bed with 13X will degrade the performance only slightly. Another way to look at this is, if an existing concentrator is a single-sorbent 13X system operating in VSA or PVSA modes, substituting a portion of this is, if an existing concentrator is a single-sorbent 13X system operating in VSA or PVSA modes, substituting a portion of the bed with LiLSX will give a steep increase in performance for a small cost. If these substitutions were to take place in a PSA system, the small improvement in performance might not justify the effort involved in re-packing the beds.

# Chapter 6 Conclusions

#### 6.1 Summary

In this work, processes for oxygen concentration using layered beds were investigated by using two adsorbents - LiLSX and 13X. Their performance was studied as a function of amount of LiLSX in the bed in VSA, PVSA and PSA processes.

In Chapter 1, methods for air separation were introduced, and the advantages of adsorption-based  $O_2$  concentration for small to medium scale production units were discussed. The motivation for the problem statement was presented as the rising cost of lithium due to increase in global demand and the need to produce  $O_2$  at an affordable price. In Chapter 2, a comprehensive review of existing literature related to adsorption-based oxygen concentration was provided. Special emphasis was given to the developments in oxygen concentrators with multiple adsorbents. In Chapter 3, the adsorbents used in the study are introduced along with a detailed description of the various methods/instruments used to study them.

In Chapter 4, single adsorbent systems were considered. Pure gas  $N_2$ ,  $O_2$  and Ar isotherms on LiLSX and 13X were experimentally obtained and fit using the Singlesite Langmuir model. Single-component and binary breakthrough experiments were performed. A detailed mathematical model was developed to be able to simulate breakthrough and PSA experiments. The models were experimentally validated using an in-house test rig. Optimization studies were performed to obtain the purityrecovery and energy-productivity Pareto fronts.

In Chapter 5, layered bed adsorbent systems were studied. Following a brief description of the possible configurations of the layered bed, single-component and binary breakthrough experiments were presented. The detailed model was extended to be able to simulate PSA processes in a layered bed, and attempts were made to validate it experimentally using the test rig. Purity-recovery and energy-productivity optimization studies were performed to study adsorption performance as a function of the amount of LiLSX in the layered bed. Special emphasis was given to the effect of adiabatic columns, and reasons as to why one configuration of the layered bed performs better than the other are analyzed.

#### 6.2 Challenges

As part of this work, detailed experimental campaigns were run using the in-house PSA test rig. Although the test rig could perform the basic steps of a PSA process, certain features could be enhanced to get more process data. Improvements like a steady, vibration-proof back pressure regulator (BPR), a way to meter the reflux flow and using valves with larger flow coefficients for product lines can greatly enhance the reliability of the test rig. Enabling a pressure-trigger that can switch valves precisely at the moment  $P_H$  has been attained can give us confidence in the simulation input parameters. Incorporating thermocouples to measure bed temperature at various axial locations in the bed can help in learning about the position of the N<sub>2</sub> fronts and in diagnosing any abnormalities.

Another factor that could potentially pose a problem long-term is the presence of water and organic contaminants in the feed air. Although it has a dew-point of -40°C, the water content in the compressed air is sufficient to adsorb irreversibly in most commercial zeolites. Over time, with several cycles of operation, water may start creeping into the adsorbent bed and deteriorate it. Using packaged gases with lower water content can be helpful if this is found to be an issue. Another way to overcome this challenge is to activate the packed columns before every experimental run.

Packing of columns, especially layered beds needs to be done carefully. Bulk densities of adsorbents need to be measured independently before packing in layers. This will allow us to measure the exact amount of adsorbent to be packed in each layer. It is also important to use sturdy mesh screens that can withstand the rigours of repetitive adsorption-desorption cycles to hold the layers in place.

To improve the detailed model, more data like high pressure  $O_2$  and Ar isotherms will be useful. Isotherm models that incorporate energetic heterogeneity of  $N_2$  on zeolites can be used, at the expense of more computational resources. Validation of the breakthrough model should preferably be done at various pressures to ensure that the fitting parameters and pressure drop correlation are valid throughout the entire range of operating pressures.

#### 6.3 Outlook

In line with the concept of layered beds studied in this work, physical mixtures of adsorbents in various proportions can also be explored. Their performance can be studied as a function of the amount of LiLSX present in the mixture, and can be compared with those offered by layered beds. It is possible that this way of mixing two adsorbents could be easier to implement in large-scale industrial columns, as compared to packing in layers.

In optimization studies, instead of specifying the amount of LiLSX in the layered bed as an input, it can be allowed to vary as one of the decision variables. This will allow the optimizer to pick the optimum ratio that can give the best performance in terms of recovery and energy.

Detailed costing studies are needed to compare the performance of layered beds in VSA, PVSA and PSA processes, in order to find the unit cost of producing oxygen. This costing study should consider various prices of LiLSX, as a wide variation in prices has been observed in recent history. This will serve as the ultimate check to understand at what stage would we be willing to sacrifice a superior adsorbent for a less-expensive one at the cost of separation performance.

### Bibliography

- [1] "Oxygenation in aquaculture," *Linde PLC*, [Online]. Available: https://www. linde-gas.com/en/processes/controlled\_and\_modified\_atmospheres/oxygenation\_ in\_aquaculture/index.html (visited on 06/25/2023).
- "Commercial technologies for oxygen production," National Energy Technology Laboratory (NETL), [Online]. Available: https://netl.doe.gov/research/Coal/energy-systems/gasification/gasifipedia/commercial-oxygen#:~:text=Cryogenic\%20distillation\%20separates\%20oxygen\%20from,removed\%20in\%20molecular\%20sieve\%20adsorbers (visited on 06/25/2023).
- [3] J. Tolley and L. Estupinan, "Energy consumption of pressure swing adsorption vs. vacuum swing adsorption a thermodynamic study," White paper from Benchmark International's Oxygen Solution Inc., Mar. 31, 2022. [Online]. Available: https://osioxygen.com/wp-content/uploads/2022/03/VPSA-White-Paper.pdf (visited on 04/02/2023).
- [4] M. W. Ackley, "Medical oxygen concentrators: A review of progress in air separation technology," *Adsorption*, vol. 25, no. 8, pp. 1437–1474, 2019.
- [5] C. C. Chao, Process for separating nitrogen from mixtures thereof with less polar substances, US Patent 4,859,217, 1989.
- [6] J. F. Kirner, Nitrogen adsorption with highly li exchanged X-zeolites with low Si/Al ratio, US Patent 5,268,023, 1993.
- [7] T. R. Gaffney, "Porous solids for air separation," Curr. Opin. Solid. St. M., vol. 1, no. 1, pp. 69–75, 1996.
- [8] M. McCormick and J. Jacobs, "The \$1.4tn that energy investors risk losing - plus, natural resource inflation in charts," *Financial Times*, May 31, 2022. [Online]. Available: https://www.ft.com/content/209e6f64-31a5-42de-8632c24dfdee1344 (visited on 04/01/2023).
- D. M. Ruthven, Principles of adsorption and adsorption processes. John Wiley & Sons, 1984.
- S. Sircar, "Pressure swing adsorption," Ind. Eng. Chem. Res., vol. 41, pp. 1389–1392, 6 Mar. 2002, ISSN: 0888-5885. DOI: 10.1021/ie0109758. [Online]. Available: https://pubs.acs.org/doi/10.1021/ie0109758.
- [11] C. G. Coe, J. F. Kirner, R. Pierantozzi, and T. R. White, *Nitrogen adsorption with a Ca and/or Sr exchanged lithium X-zeolite*, US Patent 5,152,813, 1992.

- [12] N. D. Hutson, S. U. Rege, and R. T. Yang, "Mixed cation zeolites: LixAgY-X as a superior adsorbent for air separation," *AIChE J.*, vol. 45, no. 4, pp. 724–734, 1999.
- S. A. Hosseinzadeh Hejazi, A. Rajendran, J. A. Sawada, and S. M. Kuznicki, "Dynamic column breakthrough and process studies of high-purity oxygen production using silver-exchanged titanosilicates," *Ind. Eng. Chem. Res.*, vol. 55, no. 20, pp. 5993–6005, 2016. DOI: 10.1021/acs.iecr.6b01560. eprint: https: //doi.org/10.1021/acs.iecr.6b01560. [Online]. Available: https://doi.org/10. 1021/acs.iecr.6b01560.
- S. A. Hosseinzadeh Hejazi, L. Estupiñan Perez, A. Rajendran, and S. Kuznicki, "Cycle development and process optimization of high-purity oxygen production using silver-exchanged titanosilicates," *Ind. Eng. Chem. Res.*, vol. 56, no. 19, pp. 5679–5691, 2017. DOI: 10.1021/acs.iecr.7b00219. eprint: https://doi.org/ 10.1021/acs.iecr.7b00219. [Online]. Available: https://doi.org/10.1021/acs.iecr. 7b00219.
- [15] J. Lee and D. H. Kim, "High-order approximations for noncyclic and cyclic adsorption in a particle," *Chem. Eng. Sci.*, vol. 53, no. 6, pp. 1209–1221, 1998.
- [16] J.-G. Jee, J.-S. Lee, and C.-H. Lee, "Air separation by a small-scale two-bed medical o<sub>2</sub> pressure swing adsorption," *Ind. Eng. Chem. Res.*, vol. 40, no. 16, pp. 3647–3658, 2001.
- [17] C. W. Skarstrom, Method and apparatus for fractionating gaseous mixtures by adsorption, US Patent 2,944,627, 1960.
- [18] K. S. Knaebel and F. B. Hill, "Analysis of gas purification by pressure swing adsorption: Priming the parametric pump," *Sep. Sci. Technol.*, vol. 18, no. 12-13, pp. 1193–1219, 1983.
- [19] A. M. Mendes, C. A. Costa, and A. E. Rodrigues, "Oxygen separation from air by PSA: Modelling and experimental results: Part I: Isothermal operation," *Sep. Purif. Technol.*, vol. 24, no. 1-2, pp. 173–188, 2001.
- [20] R. L. Jones, I. G. E. Keller, and R. C. Wells, *Rapid pressure swing adsorption process with high enrichment factor*, US Patent 4,194,892, 1980.
- [21] S. Kulish and R. P. Swank, *Rapid cycle pressure swing adsorption oxygen con*centration method and apparatus, US Patent 5,827,358, 1998.
- [22] V. R. Rao, S Farooq, and W. Krantz, "Design of a two-step pulsed pressureswing adsorption-based oxygen concentrator," *AIChE J.*, vol. 56, no. 2, pp. 354– 370, 2010.
- [23] "Osi 2000/3000/5000/7000 dual bed concentrator," OSI Oxygen Solutions Inc., Edmonton, [Online]. Available: https://osioxygen.com/wp-content/uploads/ 2020/09/OSI\_dual\_bed.pdf (visited on 04/15/2023).
- [24] S. W. Chai, M. V. Kothare, and S. Sircar, "Rapid pressure swing adsorption for reduction of bed size factor of a medical oxygen concentrator," *Ind. Eng. chem. Res.*, vol. 50, no. 14, pp. 8703–8710, 2011.

- [25] A. Moran and O. Talu, "Limitations of portable pressure swing adsorption processes for air separation," *Ind. Eng. Chem. Res.*, vol. 57, no. 35, pp. 11981– 11987, 2018.
- [26] S. J. Wilson, C. C. Beh, P. A. Webley, and R. S. Todd, "The effects of a readily adsorbed trace component (water) in a bulk separation PSA process: The case of oxygen VSA," *Ind. Eng. Chem. Res.*, vol. 40, no. 12, pp. 2702–2713, 2001.
- [27] A. Chiang and M. Hong, "Radial flow rapid pressure swing adsorption," Adsorption, vol. 1, pp. 153–164, 1995.
- [28] M. Suzuki, T. Suzuki, A. Sakoda, and J. Izumi, "Piston-driven ultra rapid pressure swing adsorption," Adsorption, vol. 2, pp. 111–119, 1996.
- [29] I. G. E. Keller and C.-H. A. Kuo, Enhanced gas separation by selective adsorption, US Patent 4,354,859, 1982.
- [30] J. J. Collins, Air separation by adsorption, US Patent 4,026,680, 1977.
- [31] S. Cavenati, C. A. Grande, and A. E. Rodrigues, "Separation of CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> mixtures by layered pressure swing adsorption for upgrade of natural gas," *Chem. Eng. Sci.*, vol. 61, no. 12, pp. 3893–3906, 2006.
- [32] T. G. Glover and M. D. LeVan, "Sensitivity analysis of adsorption bed behavior: Examination of pulse inputs and layered-bed optimization," *Chem. Eng. Sci.*, vol. 63, no. 8, pp. 2086–2098, 2008.
- [33] Y. Lü, S.-J. Doong, and M. Bülow, "Pressure-swing adsorption using layered adsorbent beds with different adsorption properties: I—results of process simulation," Adsorption, vol. 9, pp. 337–347, 2003.
- [34] Y. Lü, S.-J. Doong, and M. Bülow, "Pressure-swing adsorption using layered adsorbent beds with different adsorption properties: II—experimental investigation," Adsorption, vol. 10, pp. 267–275, 2005.
- [35] S. Sircar and W. E. Waldron, *Oxygen production by adsorption*, US Patent 6,468,328, 2002.
- [36] M. W. Ackley, A. B. Stewart, G. W. Henzler, F. W. Leavitt, F. Notaro, and M. S. Kane, *Psa apparatus and process using adsorbent mixtures*, US Patent 6,027,548, 2000.
- [37] A. Ward, K. Li, and R. Pini, "Assessment of dual-adsorbent beds for CO<sub>2</sub> capture by equilibrium-based process design," *Sep. Purif. Technol.*, vol. 319, p. 123 990, 2023.
- [38] C. F. Watson, R. D. Whitley, and M. L. Meyer, *Multiple zeolite adsorbent layers* in oxygen separation, US Patent 5,529,610, 1996.
- [39] F. Notaro, J. T. Mullhaupt, F. W. Leavitt, and M. W. Ackley, Adsorption process and system using multilayer adsorbent beds, US Patent 5,674,311, 1997.
- [40] S. J. Wilson and P. A. Webley, "Cyclic steady-state axial temperature profiles in multilayer, bulk gas PSA the case of oxygen VSA," *Ind. Eng. Chem. Res.*, vol. 41, no. 11, pp. 2753–2765, 2002.

- [41] M. W. Ackley, *Multilayer adsorbent beds for PSA gas separation*, US Patent 6,152,991, 2000.
- [42] N. S. Wilkins, A. Rajendran, and S. Farooq, "Dynamic column breakthrough experiments for measurement of adsorption equilibrium and kinetics," *Adsorption*, vol. 27, no. 3, pp. 397–422, 2021.
- [43] N. S. Wilkins and A. Rajendran, "Measurement of competitive CO<sub>2</sub> and N<sub>2</sub> adsorption on zeolite 13x for post-combustion CO<sub>2</sub> capture," *Adsorption*, vol. 25, no. 2, pp. 115–133, 2019.
- [44] R. Haghpanah et al., "Multiobjective optimization of a four-step adsorption process for postcombustion CO<sub>2</sub> capture via finite volume simulation," Ind. Eng. Chem. Res., vol. 52, no. 11, pp. 4249–4265, 2013.
- [45] K. Deb, A. Pratap, S. Agarwal, and T. Meyarivan, "A fast and elitist multiobjective genetic algorithm: NSGA-II," *IEEE T. Evolut. Comput.*, vol. 6, no. 2, pp. 182–197, 2002.
- [46] C.-W. Wu, M. V. Kothare, and S. Sircar, "Equilibrium adsorption isotherms of pure N<sub>2</sub> and O<sub>2</sub> and their binary mixtures on LiLSX zeolite: Experimental data and thermodynamic analysis," *Ind. Eng. Chem. Res.*, vol. 53, no. 17, pp. 7195– 7201, 2014.
- [47] C.-W. Wu, M. V. Kothare, and S. Sircar, "Model analysis of equilibrium adsorption isotherms of pure N<sub>2</sub>, O<sub>2</sub>, and their binary mixtures on LiLSX zeolite," *Ind. Eng. Chem. Res.*, vol. 53, no. 31, pp. 12428–12434, 2014.
- [48] K. N. Pai, T. T. Nguyen, V. Prasad, and A. Rajendran, "Experimental validation of an adsorbent-agnostic artificial neural network (ANN) framework for the design and optimization of cyclic adsorption processes," *Sep. Purif. Technol.*, vol. 290, p. 120783, 2022, ISSN: 1383-5866. DOI: https://doi.org/10.1016/ j.seppur.2022.120783. [Online]. Available: https://www.sciencedirect.com/ science/article/pii/S1383586622003422.

## Appendix A: Repeats of single component breakthrough experiments



Figure A.1: Adsorption and desorption profiles from single component dynamic column breakthrough experiments. Circles and triangles are data points obtained from repetitions of the same experiment. Dotted lines are simulated curves for the respective adsorbents.

### Appendix B: Sensitivity studies on PSA simulations

Two experiments were chosen from those performed for the purposes of experimental validation of the model. These points are simulated using the detailed model for the decision variables corresponding to the experiment, called the base case. This is followed by simulations with a + and - 10% change in the value of each of the input parameters. Purity and recovery values for each are tabulated, along with the percentage deviation of new values from the base case values.

#### **B.1** Single sorbent simulation

Experiment 3(b) from Table 4.5 is considered.

Table B.1: Sensitivity study on PSA simulations of single sorbent systems.

	$t_{ads} + t_{LR(D)} \ [s]$	$t_{LR(R)}$ [s]	$P_L$ [bar]	$P_H$ [bar]	$v_0  [{\rm m/s}]$	Purity [%]	Recovery [%]	Purity deviation [%]	Recovery deviation [%]
Base case	13	5	1	5	0.1064	50.52	50.04	-	-
+10%	14.3	5	1	5	0.1064	45.74	52.26	9.45	-4.43
	13	5.5	1	5	0.1064	50.94	47.37	-0.84	5.33
	13	5	1.1	5	0.1064	49.34	50.46	2.33	-0.85
	13	5	1	5.5	0.1064	48.23	49.01	4.52	2.06
	13	5	1	5	0.1170	46.08	49.70	8.78	0.68
-10%	11.7	5	1	5	0.1064	56.06	47.22	-10.96	5.63
	13	4.5	1	5	0.1064	48.96	52.32	3.08	-4.57
	13	5	0.9	5	0.1064	50.53	49.29	-0.02	1.50
	13	5	1	4.5	0.1064	51.56	50.72	-2.06	-1.36
	13	5	1	5	0.0958	54.41	49.75	-7.69	0.58

### B.2 Layered bed simulation

Experiment 3(a) from Table 5.1 is considered.

Table B.2: Sensitivity study on PSA simulations of layered bed systems.

	$t_{ads} + t_{LR(D)}$ [s]	$t_{LR(R)}$ [s]	$P_L$ [bar]	$P_H$ [bar]	$v_0 \; [{\rm m/s}]$	Purity [%]	Recovery [%]	Purity deviation [%]	Recovery deviation [%]
Base case	13	5	1	5	0.1064	59.37	52.43	-	-
+10%	14.3	5	1	5	0.1064	53.18	54.62	10.42	-4.18
	13	5.5	1	5	0.1064	61.80	50.23	-4.10	4.19
	13	5	1.1	5	0.1064	57.26	52.71	3.55	-0.54
	13	5	1	5.5	0.1064	56.81	51.71	4.31	1.36
	13	5	1	5	0.1170	54.58	52.35	8.06	0.15
-10%	11.7	5	1	5	0.1064	68.28	49.91	-15.00	4.81
	13	4.5	1	5	0.1064	57.08	54.62	3.84	-4.19
	13	5	0.9	5	0.1064	61.64	52.22	-3.83	0.39
	13	5	1	4.5	0.1064	61.80	53.07	-4.09	-1.23
	13	5	1	5	0.0958	64.88	52.24	-9.28	0.37