

MODELING AND SIMULATION OF PRESSURE SWING ADSORPTION

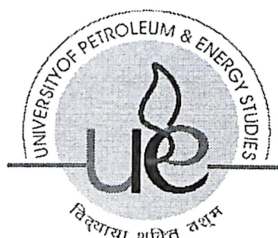
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M. Tech (Process Design)

REPORT ON MAJOR PROJECT (PR0J801)



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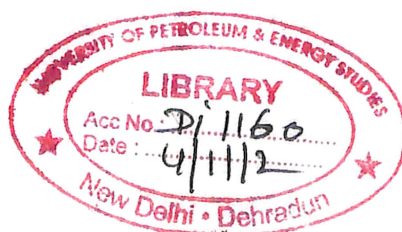
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MODELING AND SIMULATION OF PRESSURE SWING ADSORPTION

A Report submitted in partial fulfillment of the requirements for the Degree of
Master of Technology
(Process Design Engineering)

By
(D.SANTOSH REDDY)

Under the guidance of

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April -2011

CERTIFICATE

This is to certify that the work contained in this thesis titled “MODELING AND SIMULATION OF PRESSURE SWING ADSORPTION ” has been carried out by D Santosh Reddy under our supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

Pressure-swing adsorption (PSA) is a larger class of industrial operations known as separation processes. These involve the separation of a mixture of chemical species into products of a given purity. PSA is a very versatile technology for separation and purification of gas mixtures. A study on a single-bed pressure swing adsorption (PSA) using zeolite 5A was performed for separation of oxygen from air. The effects of various operating parameters such as adsorption pressure, cycle time, production rate on the product purity and recovery were investigated through simulation studies. An equilibrium based isothermal model in conjunction with an LDF (linear driving force) approximation was employed to simulate process performance.

Most of the previous studies dealt with PSA separation by complex multi-bed processes. The project involves developing of a mathematical model and simulation study on Single bed pressure swing adsorption at Nonisothermal conditions. The PSA system which contains a single long bed, utilizes a combination of cyclic adsorption and regeneration steps. The cycle comprises of high pressure adsorption phase and the subsequent low-pressure regeneration phase. In addition the effect of design and operating parameters (cycle time, adsorption pressure, Height of the bed, valve coefficients, valve position etc.) were studied on PSA performance such as purity, recovery and productivity through simulations. It was found that Oxygen purity and recovery both increases when adsorption pressure, productivity increases. Finally It was observed that increasing the cycle time increases the performance of the process.

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Nomenclature

Symbol	Name and Units
A	Cross Sectional Area of the column, m ²
b	Langmuir constant, atm ⁻¹
C	Concentration in the gas phase, mol m ⁻³ .
C _v	Valve coefficient
d _p	Diameter of the particle, m.
k	Mass transfer coefficient, s ⁻¹
K	Henry's law constant
M _i	Molar amount of the component i, mol
n	Number of components
p _i	Partial pressure, atm.
P	Total Pressure, atm.
P _{top}	Total pressure at top side of the valve (Fig 2.1), atm
P _{bottom}	Total pressure at bottom side of the valve (Fig 2.1), atm
q	Solid phase concentration, mol kg ⁻¹ .
q ⁱ	Solid phase concentration of component i in equilibrium with the gas phase, mol kg ⁻¹
q ^{si}	Langmuir constant of component i, mol kg ⁻¹ .
R	Universal gas constant, J mol ⁻¹ K ⁻¹ .
t	Time, s.
T	Temperature, K.
u	Gas velocity, m s ⁻¹ .
y	Mole fraction
L	Length of the bed, m.

Greek symbol

ε	Bed porosity
μ	Viscosity, $\text{kg m}^{-1} \text{s}^{-1}$
ρ	Density, kg m^{-3}

Superscript

*	Equilibrium
---	-------------

Subscripts

b	Bed
c	Cycle
f	Feed
g	Gas phase
i	Component i
p	Product
s	Saturation
w	Waste

CHAPTER 1

Introduction

Over the last few decades, pressure swing adsorption (PSA) processes have emerged successfully as cost-effective alternatives to the traditional gas separation processes, and thus have gained widespread acceptance. Although commercial utilization is widespread, PSA processes still present stiff research challenges in terms of process development, accurate modeling of mass transfer and adsorption phenomena, and adsorbent design, especially for emerging new applications. In this chapter, we highlight such challenges in brief, describe our approach in order to address a few of these, and define the scope of our Project . PSA is relatively inexpensive, capable of producing products of desired purity and especially suitable for handling relatively small throughputs of gas streams (Chihara and Suzuki 1983).

PSA Overview

Separation of gases accounts for a major fraction of the production cost in chemical, petrochemical, and related industries. There has been a growing demand for economical and energy efficient gas separation processes. The new generation of more selective adsorbents developed in recent years has enabled adsorption-based technologies to compete successfully with traditional gas separation techniques, such as cryogenic distillation and absorption. The last few decades have seen a considerable increase in the applications of adsorptive gas separation technologies, such as pressure swing adsorption (PSA). Pressure swing adsorption is a versatile technology for separation and purification of gas mixtures. While initial applications of PSA included gas drying and purification of dilute mixtures, current industrial applications include solvent vapor recovery, air fractionation, production of hydrogen from steam-methane reformer (SMR) and petroleum refinery of f gases, separation of hydrocarbons such as carbon monoxide-hydrogen, carbon dioxide-methane, and n-paraffins separation, and alcohol dehydration. Advent of commercial PSA operations started with the early patents on this subject granted to Skarstrom [12] and Guerin de Montgareuil and Domine [7]. Since then,

PSA has become the state-of-the-art separation technology for applications like air fractionation and hydrogen production. Many of these processes are described in published books and review articles on this subject [6, 8, 9,]. Moreover, Sircar [9] has given an extensive list of publications on PSA which highlights growth in the research and development of PSA technology. PSA processes involve selectively adsorbing certain components of a gas mixture on a microporous-mesoporous solid adsorbent at a relatively high pressure, via gas-solid contact in a packed column, in order to produce a gas stream enriched in less strongly adsorbed components of the feed gas. The adsorbed components are then desorbed from the solid by lowering their gas-phase partial pressures inside the column to enable adsorbent re-usability. Desorbed gases, as a result, are enriched in the more strongly adsorbed components of the feed gas. No external heat is generally used for desorption. The selectivity in a PSA process comes from differences in either adsorption equilibrium or adsorption kinetics between the components to be separated. While a PSA process carries out adsorption at super ambient pressure and desorption at near-ambient pressure level, a vacuum swing adsorption (VSA) process undergoes adsorption at near-ambient pressure, while desorption is achieved under vacuum. Practical PSA/VSA processes are substantially sophisticated with multiple adsorber columns executing a wide variety of non-steady-state operating steps in a non-trivial sequence. Besides adsorption and desorption, such a sequence also involves a multitude of complementary operating steps essential to control product gas purity and recovery, and optimize overall separation efficiency. Each bed undergoes this sequence of steps repeatedly, and thus the entire PSA system operates in a cyclic manner. Some of the advantages of PSA systems and key reasons for recent growth of this technology are as below .

PSA and VSA processes operate at ambient temperatures and do not require any solvent for product recovery or adsorbent regeneration. As a result, their capital expenditure is quite less compared to cryogenic technologies. Primary operating cost for these processes comes from the energy requirements for compression and vacuum generation. Hence, PSA processes are cost-effective compared to traditional technologies, and are especially desirable when lower production rates or lower product purities are required.

- Pressure manipulation serves as an extra degree of thermodynamic freedom, thus introducing significant flexibility in process design as compared with conventional technologies such as distillation, extraction or absorption.
- Numerous microporous-mesoporous adsorbents are available which are specifically tailored and engineered for a particular application, thus exhibiting high selectivity and adsorption capacity which leads to extremely high purity and recovery separation.
- Optimum marriage between a material and a process while synthesizing the separation scheme drives innovation and leads to highly efficient designs for PSA processes.

Theoretical modeling of PSA systems has also been extensively studied to gain a clear understanding of this rather complex process. A summary of the published dynamic models has been compiled by Ruthven [11] and Nikolific et al. [10]. In general, PSA bed model is a set of fairly complex partial differential and algebraic equations (PDAEs) which reflect the transient nature of the process and capture the underlying physics in detail. With such models, it is now possible to accurately predict the dynamic behavior of a PSA process, and to adequately account for all the factors that affect the performance of any given PSA system.

1.1 Non-Adsorptive Gas Separation Processes

Several conventional non-adsorptive gas separation processes such as distillation, chemical and/or physical absorption and membrane separation are available to separate gaseous mixtures in industrial applications. PSA still competes with them because each of the conventional techniques has its own limitations. These limitations are discussed here in brief.

1.1.1 Distillative Separation Process

Distillative separation is one of the major applications which is used in air separation. For separation of air components (nitrogen or oxygen), cryogenic distillation is used extensively. The separation is based on the difference between the boiling points of gas components. Within the rectification column of a cryogenic plant, the gas mixture is cooled down to a very

low temperature. At this low temperature, the gas mixture such as air can be separated in liquid form. The separated liquefied gases leave the column as liquids and have to be stored and transported at low temperatures in the liquid form. For instance, at one atmosphere pressure, nitrogen is liquid at $-196\text{ }^{\circ}\text{C}$. Commercially, higher pressure (8-10 atmosphere) is often required for this process. These pressure/temperature conditions are achieved via multiple steps of compression/expansion and heat exchange. Cold gases exiting column are used to cool air entering it. Nitrogen is more volatile than oxygen and comes off as the distillate product. The main disadvantage of the process is consumption of high energy and higher initial costs. However, at high capacities, the technique is still the most competitive and finds wide application.

1.1.2 Chemical and Physical Absorption

The absorption methods are widely used in the separation of gases using absorbing liquids in chemical and other plants. The gas to be separated is either physically or chemically absorbed in the liquid. In the case of the former, absorption process is governed by solubility and partial pressure gradient. If the gas pressure is low, physical solvents are not that effective. In the case of chemical absorption based processes, the regeneration of the chemical solvents requires substantial energy adding to operational costs of such chemical solvent based-plants. The adsorption techniques find application mostly in removal of contaminants, rather than the separation and recovery. The technique is widely used in gas treatment in petroleum refining and downstream industries.

1.1.3 Membrane Separation Process

Membranes are also useful for gas separations. If the separation process is to be economically competitive, a membrane should be highly permeable and also have higher selectivity for the component to be separated. There is often a trade-off between selectivity and permeability. The diffusion coefficients offered by most polymeric membranes are so low that very thin films are required to produce economically acceptable fluxes. These thin films have fabrication as well as structural problems. The use of porous membranes with higher permeability overcomes the problem of lower flux, but has adverse effect on selectivity. The

main limitations of the conventional membranes are inability to achieve fine separation and loss of process gas to the permeate stream due to poor selectivity. Membrane separation consumes relatively low energy per unit of gas treated and finds application when product purity specifications are not very stringent.

1.2 Pressure Swing Adsorption (PSA) Process

The three alternatives discussed earlier suffer from high capital cost and/or large amounts of energy used and are more appropriate to fields where large volumes of gases need to be processed. The advantage of scale then makes the processes economically viable. For the case of medium and small volumes of gas to be processed, other alternatives such as adsorption-based processes may improve the overall economics due to lower operating costs. Adsorption based technologies can reduce the energy needed for the regeneration of the separation agent (adsorbent) and can have a higher degree of automation. The technique can be tailor made for any given separations task through the choice of a suitable adsorbent material. Various adsorption separations are possible such as temperature Swing Adsorption (TSA), Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA), Concentration Swing or Displacement Adsorption etc. PSA is one of the most significant processes for the separation of gases. In some fields, PSA technology has entirely replaced the conventional process; in other fields it has become more and more competitive at larger and larger scales. In general, as energy prices soar, PSA becomes more and more competitive up to large and larger production scales. PSA is adaptable to get the required gas at the right purity, at the desired flow and at low cost. PSA is also implementable at very wide range of capacities from few lpm to millions of cubic meters per day. Therefore, if one is looking for a low-cost, low energy but highly efficient gas separation system in an overall process scheme, a PSA unit may be the right choice.

1.3 Process definition and principle

PSA is a cyclic process where adsorption is carried out at higher pressure and regeneration of adsorbents is achieved by countercurrent depressurization. The separation of gases using this process is based on the differences in adsorption thermodynamics and kinetics between a

given adsorbent material and different gas components present in the gas mixture. At high pressures, few gases have tendency to physically attach to the solid surfaces. Pressure swing adsorption technique is based on a physical, reversible and weak binding of gas molecules on the adsorbent. Adsorbents are selected based on the composition of gas and the objective of separation. Some commonly used adsorbents are zeolite molecular sieves and activated carbons. Even conventional adsorbents such as Alumina and Silica gel have found extensive applications as adsorbents. Some time, more than one adsorbent is used for continuous production of high purity gases (psaplants.com). Hydrogen PSA is one such example and has found extensive usage as refineries turned from hydrogen surplus to hydrogen deficit with environmental regulations demanding lesser and lesser sulfur content in end products. A large number of multi-bed, multi-adsorbent separation system based on PSA are functional in various sectors of industry.

1.4 Mechanism

Depending on the adsorbent-adsorbate system, PSA can be modeled either on the basis of equilibrium or kinetic based separation. If the separation is based on equilibrium selectivity, the more strongly adsorbed components are adsorbed by the adsorbent. The effluent or raffinate contains the less strongly adsorbed species. Separation of oxygen from air is an important example of this class. In case of kinetic based separations, the separation obtained is due to a difference in the diffusion rate of the components. Here the species with higher diffusivity are selectively retained by the adsorbent (Yang, R.T., 2003). Separation of Nitrogen from air is an important example of this class. The optimum process variables and operating conditions to be used depend on the controlling mechanism of the process.

1.5 Industrial applications

Even though PSA process was developed during 1960s, it has witnessed rapid growth in deployment recently as bulk industrial separation application. Pressure Swing Adsorption is a very clean and effective process that has the capacity to remove one, or more gases from another carrier gas. A basic advantage of the pressure swing adsorption units is its low overall cost compared to other gas separation processes like cryogenic separation, membrane

separation. To give an example, for production of industrial gases like oxygen and nitrogen in the capacity range of 20 to 200 ton per day by pressure swing adsorption, PSA is cheaper by at least 10-20% than when produced cryogenically (www.psaplants.com). Some key industrial applications include oxygen, nitrogen, hydrogen purification, gas drying, solvent vapor recovery, fractionation of air, separation between linear and branched hydrocarbons, recovery of aromatic hydrocarbons (Ruthven, D.M., 1984) and alcohol dehydration. PSA is also applicable in novel separations such as purifying coal seam or landfill gases to obtain methane as a valuable fuel and raw material for chemical industries.

1.6 Motivation

Pressure Swing Adsorption is by nature a discrete-continuous process. The adsorbent must cycle through adsorption and desorption steps. In its known applications of bulk gas mixtures and for the purification of gas streams containing low concentration of undesirable components, the PSA systems generally employ multiple adsorber beds to achieve relatively continuous supply of product gases. The high purity, recovery and productivity has pushed the process embodiments to more number of beds and more complex PSA cycle configurations. However, the multiple bed processes are complex and expensive. For simple applications, the complexity and the cost of process can be reduced by single bed PSA process. These simple PSA systems have potentially significantly lower capital and operating costs than multiple-bed systems. This work explores the possibility and performance of such single bed PSA systems.

1.7 Objective of the project

The work involves developing of a mathematical model and application to selected separation systems.

The main objectives of this work are as follows.

1. Developing a dynamic model for PSA process
2. Simulating the model with the help of Aspen ADSIM*
3. Case study
- I. Separation of oxygen using PSA
4. Sensitivity analysis- cycle time, Adsorption pressure, height of the bed, and valve coefficients on the product purity, recovery and productivity

CHAPTER 2

Literature Review

2.1 Introduction

Conventional pressure-swing adsorption (PSA) has been used to separate and purify industrial gases for more than 35 years. In some separations, it has reached high percentage of usage. For example, conventional PSA is responsible for 20% of the world's oxygen production. The technology was first developed by ExxonMobil and Air Liquide in the late 1950s (chemicalprocessing.com). Many of the pressure swing adsorption systems utilize two or more adsorbed beds. For example Skarstrom (1960) and Guerin de Montgareui (1964) proposed a dual bed pressure swing adsorption for separation of air. Carter (1996) assumed the bulk gas is in instantaneous equilibrium with the adsorbent during all four steps in the cycle. Shendalman and Mitchell (1972) were the first to replace the gas adsorbent equilibrium assumption by a linear driving force approximation (to model adsorption kinetics), suggested by Glueckauf and Coates (1947). This linear driving force approximation takes into account the mass-transfer limitations in the processes of adsorption/desorption in adsorbent beds. Since then, a multitude of mathematical models for conventional PSA have been developed (Farooq et al, 1989; Hassan and Ruthven, 1986; Liow and Kenney, 1990; Mendes and Costa, 2001; Raghavan et al, 1985; Shin and Knaebel, 1987; Singh and Jones, 1987; Teague and Edgar, 1999). Few authors studied the equilibrium-based PSA units for oxygen production from air (Fernandez and Kenney 1983; Ruthven, 1984; Hayashi, et al, 1985 and Sircar 2002). Skarstrom cycle has been the basic operation cycle for PSA processes. Most US patents propose modifications to the basic process cycle aimed at improving the recovery of product and thus decreasing the power requirement, which is the major operating cost for a PSA system (Ruthven and Farooq, 1990). These improvements in efficiency are generally achieved by multiple beds in Today's PSA processes. Few authors have studied the effect of process parameters on product purity and recovery for air separation and also suggested the optimized process conditions. (Mendes, et al. 2000, 2001, Alpay et al, 1994 and Jain et al, 2003) The conventional PSA process suffers from low separation efficiency per unit mass of adsorbent material, large capital investments for multiple beds, adsorbent inventory and replacement of

adsorbent material to make up for particle attrition, and associated complexity of the piping network. Current trends in PSA research involve addressing these limitations of conventional PSA by investigating the concept of novel PSA process such as moving bed PSA. PSA is currently used in applications ranging from the production of nitrogen and oxygen from air to dehydration and hydrocarbon recovery. New fast-cycle PSA technology is currently being developed, offering more-compact, less-expensive and more-energy-efficient gas separation equipment. Further Developments in conventional two-bed PSA process are possible by improving the separation efficiency per unit mass of adsorbent material by reducing the size of the adsorbent particles, reducing the complexity of the piping network by using a single adsorption bed and improving the cycle performance (purity, recovery) by long PSA columns as shown in Fig .2.1.

In the present work, the PSA system consists of a single long bed with on-off valves at the two ends. The objective is to study the effect of process parameters through simulations. A single long bed coupled with relatively rapid switching between adsorption and desorption can be used for continuous production, as will be seen later.

2.2 Single bed PSA cycle

The simplest of the PSA systems involve a minimum of two identical beds, one under production phase and another under regeneration. In this work also, we consider a simple single adsorbent PSA with two main steps i.e. adsorption and regeneration as shown in Fig 2.1. However the novelty is in eliminating the need for two or more beds.

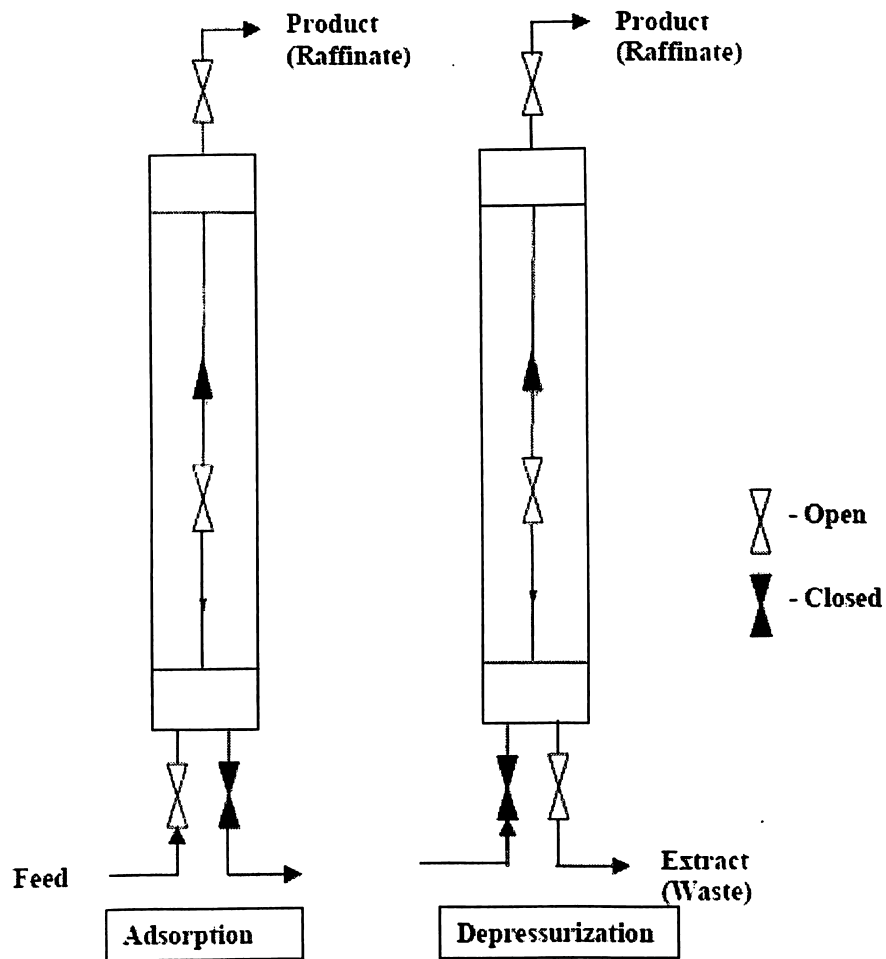


Figure 2.1 Schematic diagram of PSA Cycle

During the adsorption step, high pressure feed gas is fed into the adsorber. The bed gets pressurized, components with higher affinity towards adsorbent get adsorbed on the adsorbent, and the other components are withdrawn as a product (raffinate stream) at the exit (or product) end of the bed. During the depressurization step the adsorbent is regenerated by desorption at the feed end, while the product still continues to be obtained at the product end.

The key to the success of the process is in adjusting the step times in such a way that even during the desorption step, the pressure gradient at the product end is favorable to product withdrawal. This could be achieved by a special type of diodic valve within the bed located at a suitable height. This valve allows the flow preferentially in one direction (from

feed towards the product end) and controls the flow of raffinate in reverse direction during depressurization step.

In the proposed process embodiment, the basic process steps and concepts are the same as in a conventional two or more bed PSA process and the attempt is to reduce the hardware and adsorbent inventory. At small capacities, such systems have a potential to be very cost effective and compact.

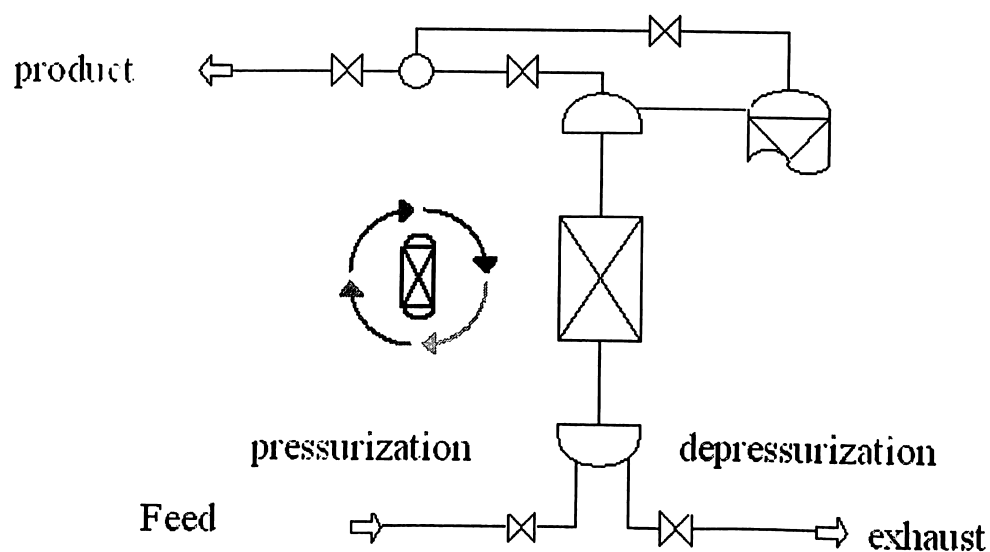


Fig 2.2 Aspen ADSIM Model PSA cycle

CHAPTER 3

Process Modeling

3.1 Introduction

The proposed PSA system consists of a fixed adsorbent bed. The valves at the two ends facilitate implementation of two steps i.e. pressurization and depressurization as shown in Fig.2.1. PSA processes are inherently dynamic in nature i.e. they have no steady state. After a sufficiently large number of cycles, the system reaches cyclic steady state (CSS), at which the conditions within the bed at the start and end of each cycle are identical. Also, the performance is stable, in the cycle-averaged sense.

3.2 Mathematical Modeling

To develop a mathematical model for this process the following assumptions are introduced.

- The fluid is assumed to be in an axial plug flow manner.
- Axial dispersion as well as radial distribution is neglected.
- The system is assumed to operate at Non Isothermal with no conduction.
- Two component system is assumed. For example, while using the mode for air separation (Oxygen or Nitrogen PSA), the presence of argon is neglected. It is assumed that argon goes with oxygen.
- The equilibrium relationships for both the adsorbate components are represented by Langmuir isotherms.
- Mass transfer between fluid and the solid particle is described by linear driving force (LDF) approximation.
- Pressure drop across the adsorbed bed is described by Ergun's Law.
- The gas is assumed as ideal and compressible.

3.3 Governing Equations

Conservation equations were written over a differential element of the bed for a differential time step. The model equations for a general n-component system can be written as follows.

Component Mass Balances

Component balance across an element of width ΔZ is:

Input = Output + Accumulation within the bulk phase + Amount adsorbed on to the adsorbent

$$(\rho Au)_{in} = (\rho Au)_{out} + \varepsilon A \Delta Z \frac{\partial p_i}{\partial t} + (1 - \varepsilon) RT A (\Delta Z) \rho_b \frac{\partial q_i}{\partial t}. \quad 3.1$$

$$\varepsilon \frac{\partial p_i}{\partial t} + \frac{\partial u p_i}{\partial z} + (1 - \varepsilon) RT \rho_b \frac{\partial q_i}{\partial t} = 0, \forall z \in (0, L), \forall t \in (0, t_c), i = 1, 2, \dots \quad 3.2$$

Ideal Gas Law

$$C_i = \frac{p_i}{RT}, \forall z \in (0, L), \forall t \in (0, t_c), i = 1, 2, \dots, n \quad 3.3$$

Adsorption Kinetics and Thermodynamics

The following linear driving force (LDF) model expresses the adsorption rate equation.

$$\frac{\partial q_i}{\partial t} = k_i * (q_i^* - q_i), \forall z \in (0, L), \forall t \in (0, t_c), i = 1, 2, \dots, n \quad 3.4$$

The adsorption equilibrium between the gas and adsorbed phase is expressed by Langmuir model. For n components the isotherms are expressed by the extended Langmuir model.

$$q_i = \frac{q_{si} * b_i * p_i}{1 + \sum_{i=1}^n (b_i * p_i)}, \forall z \in (0, L), \forall t \in (0, t_c), i = 1, 2, \dots, n \quad 3.5$$

Or using Henry's law (Linear isotherm),

$$q_i^* = k_i * C_i, \forall z \in (0, L), \forall t \in (0, t_c), i = 1, 2 \dots n \quad 3.6$$

Pressure Gradient Equation

The steady state momentum balance of gas flow can be expressed in 2 ways. If the gas flows at high velocity through a packed bed, it can be expressed by Ergun's law.

$$-\frac{\partial P}{\partial z} = 150 \frac{\mu(1-\varepsilon)^2}{\varepsilon^3 d_p^2} + 1.75 \frac{(1-\varepsilon)}{\varepsilon^3 d_p} \rho u / u, \forall z \in (0, L), \forall t \in (0, t_c) \quad 3.7$$

If the gas flow is moderate, then it can be expressed by Darcy's Law:

$$-\frac{\partial P}{\partial z} = 150 \frac{\mu(1-\varepsilon)^2}{\varepsilon^3 d_p^2} u, \forall z \in (0, L), \forall t \in (0, t_c) \quad 3.8$$

Valve Equations

Valves play an important role in any PSA process. Generally, valve equations are used for the calculation of flow rates at the ends of a bed in terms of the pressure gradient available across the valves.

$$u|u| = -c_v^2 \left(\frac{p_{top} - p_{bottom}}{\rho_g} \right) \quad 3.9$$

The above equations are solved along with the following stoichiometric equation.

$$\sum y_i = 1, i = 1, 2 \dots n \quad 3.10$$

Initial Conditions

The cyclic steady state performance of the system is independent of the initial conditions used to start the solution of the system. In the present work, the adsorbent across the bed is initially assumed to be saturated at feed condition. The following initial conditions are used to solve the set of differential and algebraic equations.

The initial conditions for Adsorption step is as follows.

$$P_i(z, 0) = P_{if}, y_i(z, 0) = y_{if}, \forall z \in (0, L), \forall t \in (0, t_c), i = 1, 2, \dots, n \quad 3.11$$

These are conditions at the start of simulation of the first cycle. For subsequent cycles, the condition of the bed ensuing at the end of the previous PSA cycle is taken as the initial condition of the bed at the beginning of the new PSA cycle.

$$p_i^{j+1}(z, 0) = p_i^j(z, t_c), y_i^{j+1}(z, 0) = y_i^j(z, t_c), \forall z \in (0, L), i = 1, 2, \dots, n, \\ j = 1, 2, \dots, m \quad 3.12$$

Boundary conditions

The following boundary conditions are used to solve the above set of differential and algebraic equations.

For adsorption step

$$At z = 0, p_i = p_{if}, \forall t \in (0, t_c), i = 1, 2, \dots, n \quad 3.13$$

$$z = L, \frac{\partial p_i}{\partial z} = 0, \forall t \in (0, t_c), i = 1, 2, \dots, n \quad 3.14$$

For depressurization

$$z = L, \frac{\partial p^i}{\partial z} = 0, \forall t \in (0, t_c), i = 1, 2, \dots, n \quad 3.15$$

$$z = 0, \frac{\partial p^i}{\partial z} = 0, \forall t \in (0, t_c), i = 1, 2, \dots, n \quad 3.16$$

The pressures in the feed, raffinate (desired product) and extract (exhaust) tanks are assumed to be constant with time. These are used in the valve equations to relate the total pressure just inside the beds at any time to instantaneous flow velocities across the valves.

3.4 Performance Measures for the PSA Process

The separation performance of a PSA process is measured on the basis of product purity, product recovery and product throughput, once the cyclic steady state is reached. (Nilchan and Pantelides, 1998)

1. Product purity in terms of the desired component is expressed as the ratio between the amount of desired component collected in the product over a cycle and the total amount of the product.

$$purity = \frac{\int_0^{t_c} u(L,t) C_{desired}(L,t) dt}{\int_0^{t_c} u(L,t) \sum_{i=1}^n C_i(L,t) dt} \quad 3.17$$

2. The Recovery of desired component is defined as the ratio of amount of desired component collected in the product stream over a cycle and the amount of desired component fed to the bed over the same cycle.

$$Recovery = \frac{\int_0^{t_c} u(L,t) C_{desired}(L,t) dt}{\int_0^{t_c} u(L,t) C_{desired_i}(0,t) dt} \quad 3.18$$

3. The adsorbent productivity is defined as the amount of desired component produced per unit time and unit weight of adsorbent.

$$Productivity = \frac{\int_0^{t_c} u(L,t)C_{desired}(L,t)dt}{\rho_b L t_c} \quad 3.19$$

The purity and recovery are often expressed in percentage terms. The values calculated as above then need to be multiplied by 100.

Cyclic Steady State Condition

At cyclic steady state (CSS), the conditions at the end of each cycle are identical to those at its start in both gas and solid phases across the entire bed. Mathematically, the conditions for the CSS can be expressed in terms of the variables C_i and q_i .

$$C_i(z,0) = C_i(z t_c) \quad \forall z \in (0, L) \quad , i=1, 2 \dots n \quad 3.20$$

$$q_i(z,0) = q_i(z t_c) \quad \forall z \in (0, L) \quad , i=1, 2 \dots n \quad 3.21$$

At CSS, the molar amount $M_{i,f}$ of each component 'i' fed to the bed over a cycle is equal to the sum of the amounts $M_{i,p}$ and $M_{i,w}$ collected in the product (raffinate) and waste (extract) respectively. In practice, this is not exactly true due to the use of numerical solution, discretization of space and time and associated truncation and round off errors. This overall mass balance can be used as a check on numerical consistency as follows.

3.5 Numerical method

Aspen ADSIM uses a set of partial differential equations (PDEs), ordinary differential equations (ODEs) and algebraic equations, together with the appropriate initial and boundary conditions, to fully describe the adsorption column. Spatial derivatives are discretized using algebraic approximations, and a set of ordinary differential equations and algebraic equations (DAEs) results. The spatial derivative terms within the partial differential equations are first- or second-order derivatives of some distributed variable, such as concentration, temperature or molar flux.

The approximations are defined over a fixed, uniform grid of points (nodes); the distributed variables are defined for each node by means of variable sets. The resulting system of differential and algebraic equations must be solved simultaneously since they are coupled. In a sense, the dependent variables at each node march in time along parallel lines perpendicular to the spatial axis, which explains the commonly-used name for this solution technique: the **numerical method of lines**.

Upwind Differencing Scheme 1

- Upwind Differencing Scheme 1 (UDS1) is the preferred option because it is:
- Good all-round performer
- Unconditionally non-oscillatory
- Unconditionally stable
- Cheapest user of simulation time
- Reasonably accurate

You increase accuracy by increasing the number of nodes. If you need greater accuracy with a minimal increase in simulation time, use the Quadratic Upwind Differencing Scheme. For Upwind Differencing Scheme 1 to achieve the same level of accuracy, the number of nodes has to be increased by a factor of two through four, leading to a similar increase in simulation time. In most cases, use Upwind Differencing Scheme 1 first.

Derivation of Upwind Differencing Scheme 1

Upwind Differencing Scheme 1 is a first-order upwind differencing scheme, based on a first-order Taylor expansion. First-order (convection) term:

$$\frac{\partial \Gamma_i}{\partial x} = \frac{\Gamma_i - \Gamma_{i-1}}{\Delta x}$$

Second-order (dispersion) term is approximated with a second-order accurate central differencing scheme:

$$\frac{\partial^2 \Gamma_i}{\partial x^2} = \frac{\Gamma_{i+1} - 2\Gamma_i + \Gamma_{i-1}}{\Delta x^2}$$

Evaluation of Upwind Differencing Scheme 1

Upwind Differencing Scheme 1 has the following advantages (+) and disadvantages (-):

- + Unconditionally stable (that is, it does not produce oscillations in the solution)
 - + Least simulation time
 - Only first-order accurate
- Gives a large amount of so-called .false. or numerical diffusion. (However, this problem decreases as the number of nodes is increased.)

CHAPTER 4

Results and Discussion

The proposed single bed PSA system and its mathematical model were used to ascertain the possibility of getting desired performance for few separation tasks. In view of the available data on air separation, these tasks were chosen as sample case. The simulation results and observations are presented in this chapter.

Oxygen PSA

PSA technology is widely used for the production of oxygen from air. PSA can produce 90-96% pure oxygen with 30-40% product recovery. The upper limit on purity is not due to inability to remove nitrogen completely, but due to the presence of Argon in the raffinate oxygen. The major application of Oxygen PSA is in the medical sector, biological industry, steel industry, waste water treatment, drinking water supply, glass and chemical industry. In this study, zeolite 5A is used to separate the oxygen from air. Oxygen PSA can be designed using 13 X zeolite as well. The quantity of argon present in the air is small, therefore O₂-Ar can be treated as a single component. The Langmuir isotherms for Nitrogen and Oxygen on zeolite 5A are given in Appendix 1 (Sorial et al., 1983; Cruz et al, 2003; Crittenden et al, 1994, 1995). The oxygen PSA processes is well described and reviewed in literature. Chiang et al., (1994) studied a four-bed PSA process for separating oxygen from air in which a cyclic operation includes six steps consisting of adsorption, pressure equalization, blowdown, purge, product pressurization and feed pressurization. They reported details of the experimental conditions and results including pressure, concentration, purity and recovery. In the present work, simulations are carried out for the two steps single bed process using the parameters of this reported four beds PSA process

Breakthrough Plot

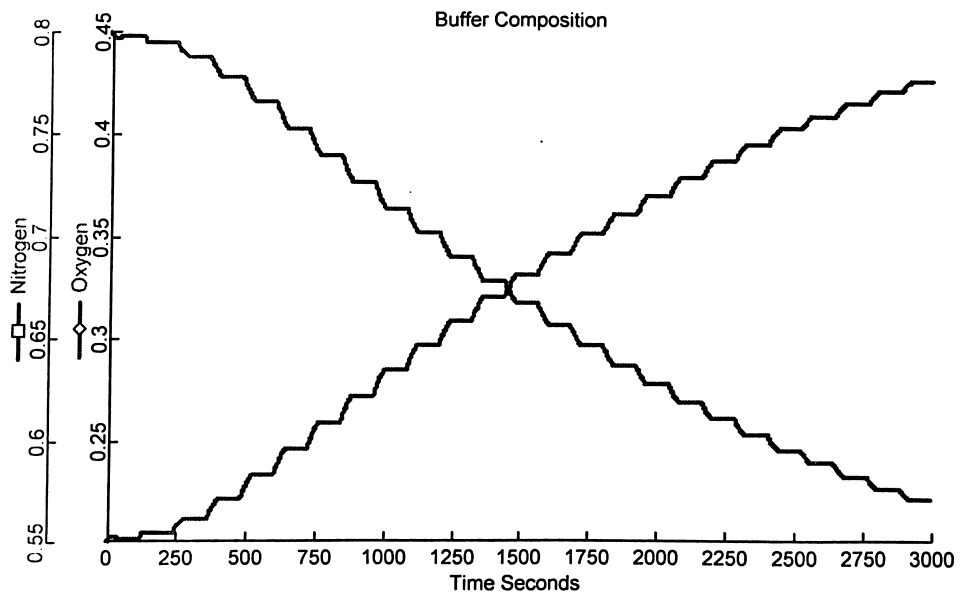
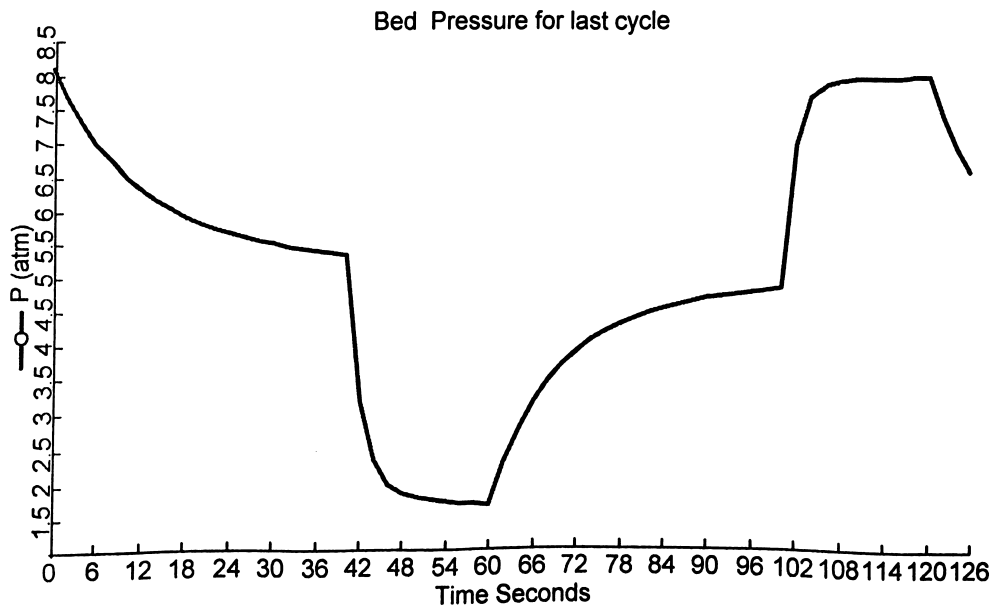


Fig 4.1 Breakthrough plot for oxygen PSA

Pressure and Temperature profile

Fig.4.2.1, 4.2.2 and Fig 4.3.1, 4.3.2 show the pressure and Temperature profiles as they develop along the bed for initial and final cycle



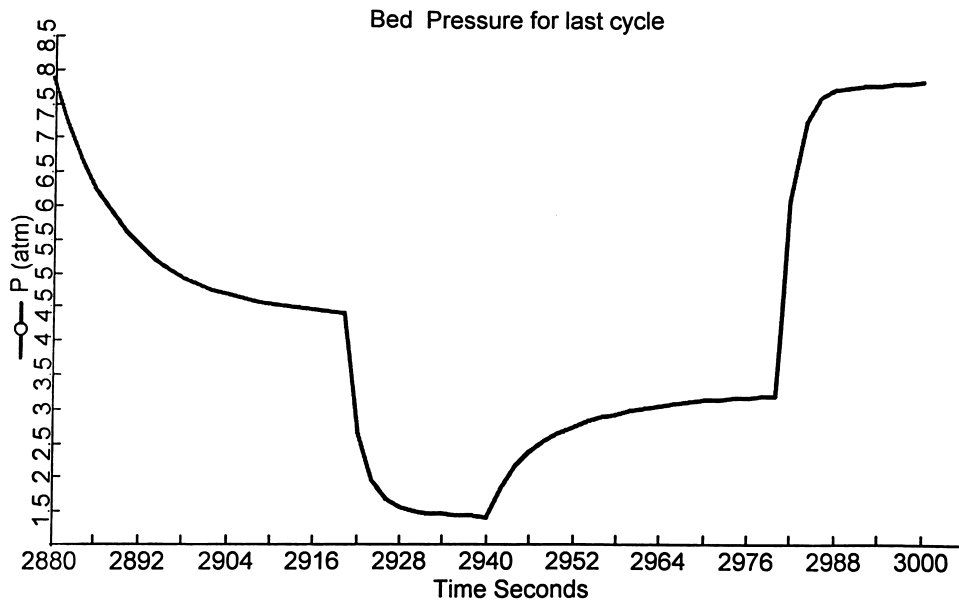


Fig 4.2.2 pressure profile for last cycle

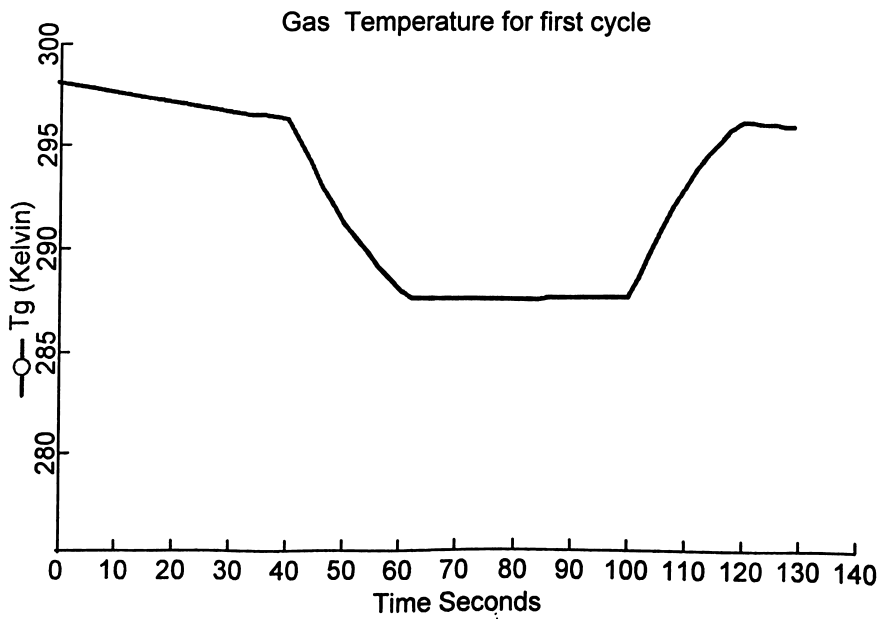


Fig 4.3.1 Temperature profile for first cycle

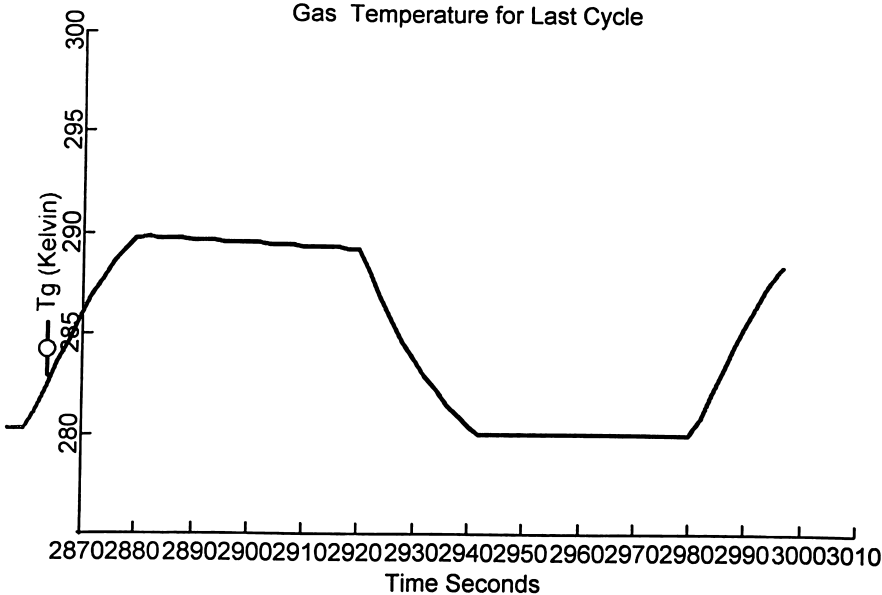


Fig 4.3.2 Temperature profile for last cycle

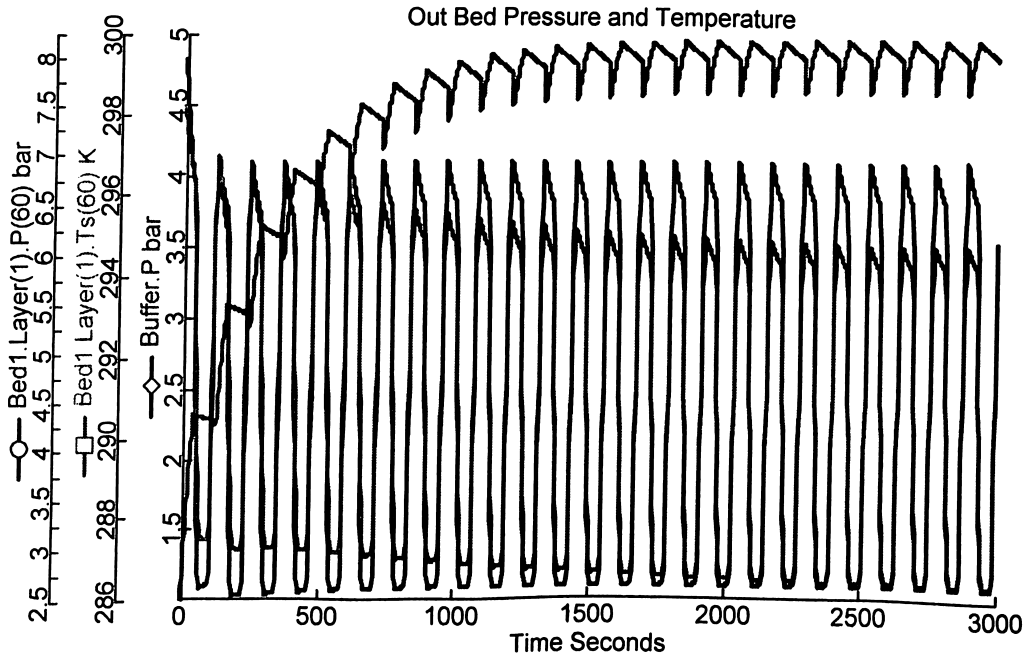


Fig 4.4 out bed pressure and temperature profile

The bed is actually undergoing blowdown, purge and concurrent depressurization simultaneously during this so-called depressurization step. The base case for this simulation is given in appendix 1. In the present simulation, bed is divided into 60 nodes

Effect of parameters on oxygen PSA

Adsorption pressure

Simulation results are shown in Fig 4.4 and Fig 4.5 for various adsorption pressures. It can be observed that if the adsorption pressure increases, the purity and productivity increase, whereas recovery of the product decreases. Selection of the adsorption pressure is based on the equilibrium relationship of the system. An isotherm describes the equilibrium loading of a species, which is dependent on the partial pressure of the species in an adsorption process. If the adsorption pressure increases, more amount of highly adsorbed species is adsorbed. This increases product purity and adsorbent productivity. At the same time, since the bed voids and the solid phase will contain more concentrations of adsorbate species due to high pressure, the depressurization step will generate more extract quantities. This will be at the cost of reduced recovery of the raffinate product.

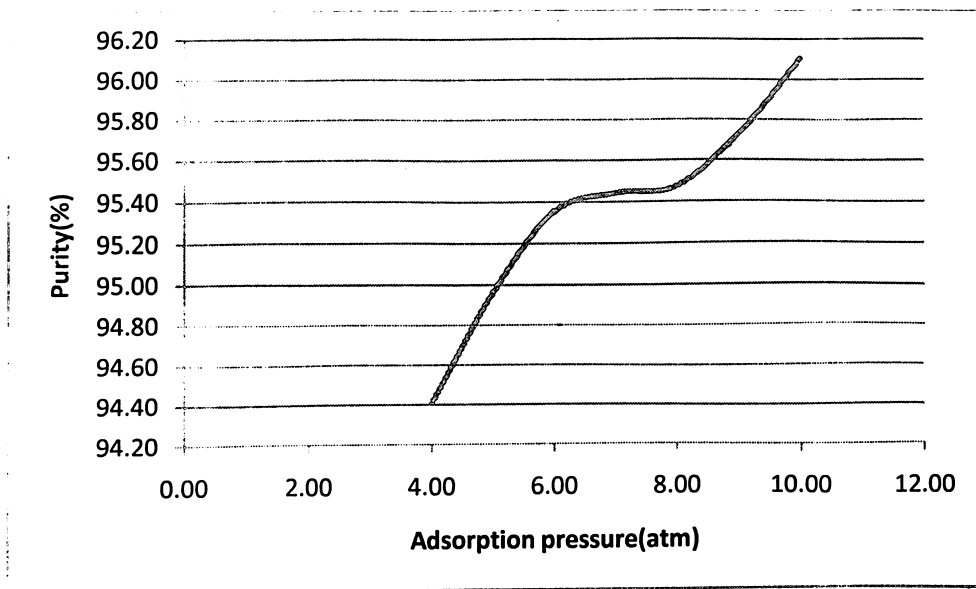


Fig 4.5 Variation of purity with adsorption pressure ($t_c=120$, $L=7m$)

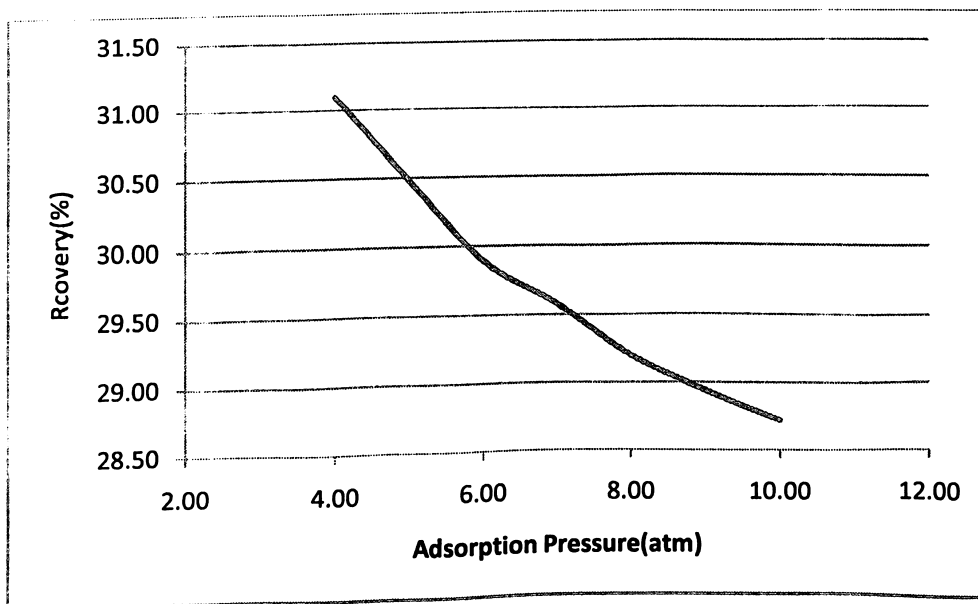


Fig 4.6 Variation of recovery with adsorption pressure ($t_c=120$, $L=7m$)

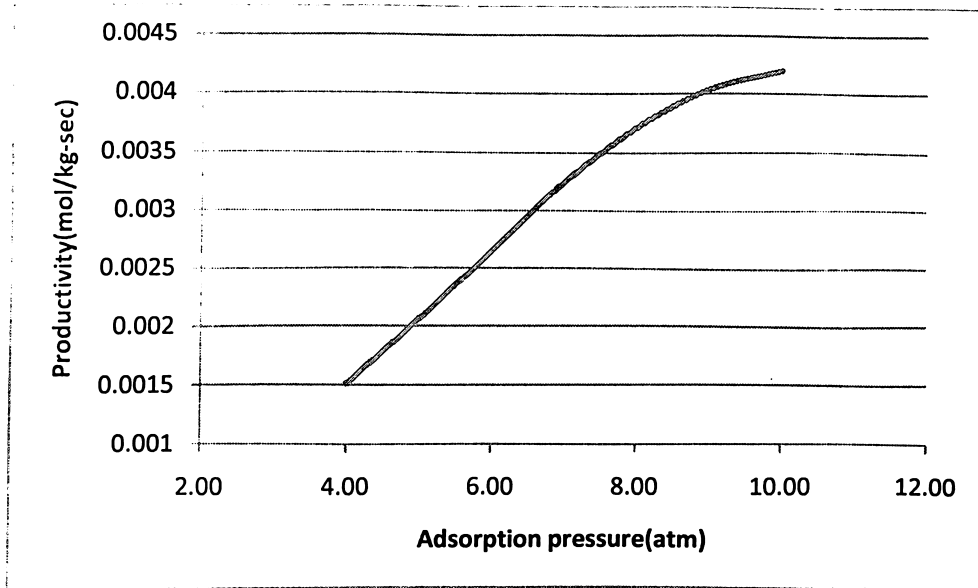


Fig 4.7 Variation of productivity with adsorption pressure ($t_c=120$, $L=7m$)

Cycle Time

The cycle time of the process controls the rate of pressurization and depressurization of the bed. In the present model, it is assumed that both the pressurization and depressurization times are equal. As the cycle time increases, bed reaches and crosses the break through point during adsorption step. If the cycle time is increase further, the purity of the product decreases due to saturation of the bed towards the later part of the adsorption step and significant breakthrough of the undesired component.

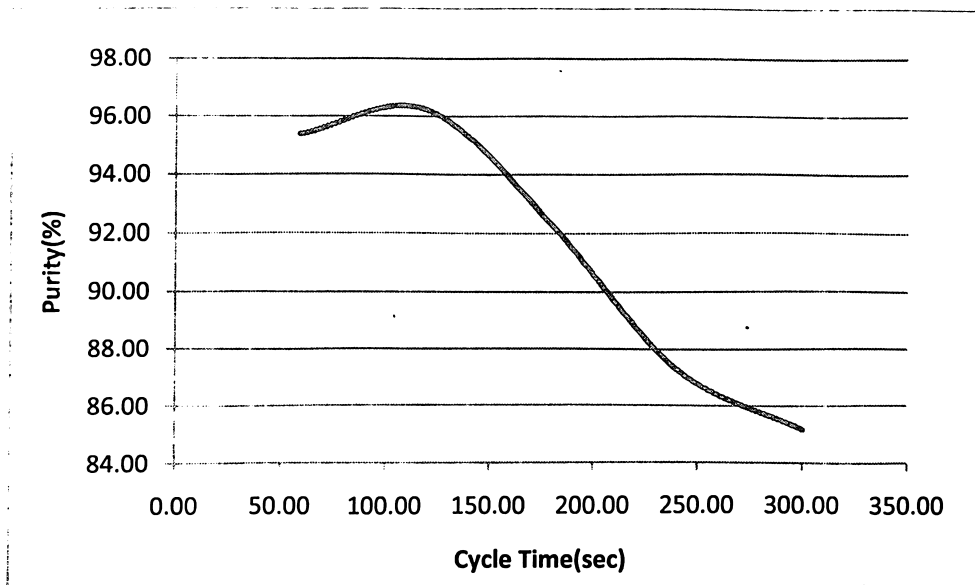


Fig 4.8 Variation of purity with cycle time(Pads =8, L=7m)

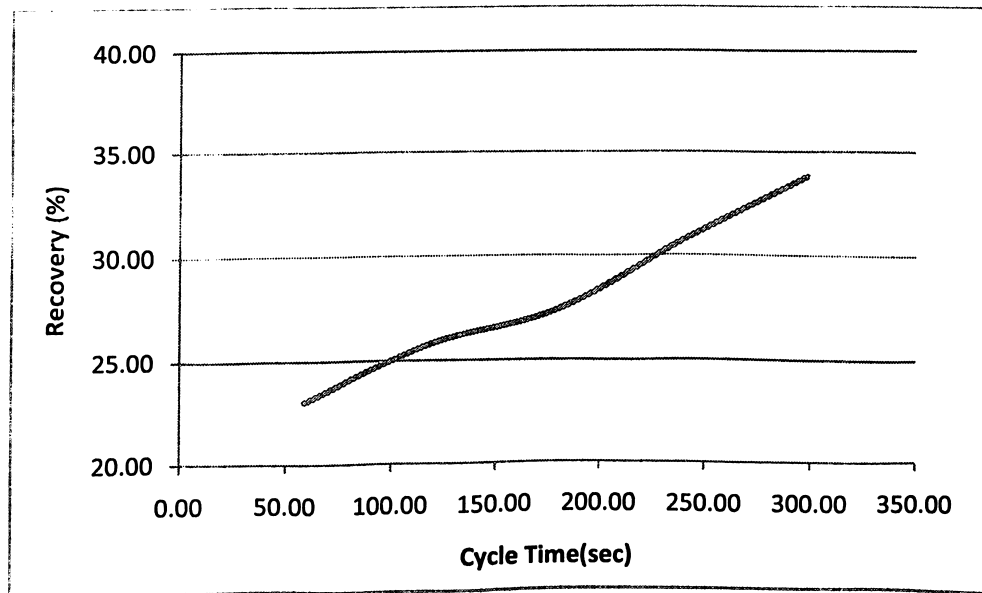


Fig 4.9 Variation of Recovery with cycle time (Pads =8, L=7m)

Simulation results are shown in Fig 4.7, Fig 4.7 and Fig 4.9 for various cycle times. It can be observed that the product purity and adsorbent productivity first increases and then decreases with cycle time due to the saturation of bed, whereas recovery of the product increases when the cycle time increases. Thus, an optimum cycle time is to be chosen for maximization of purity, recovery and productivity

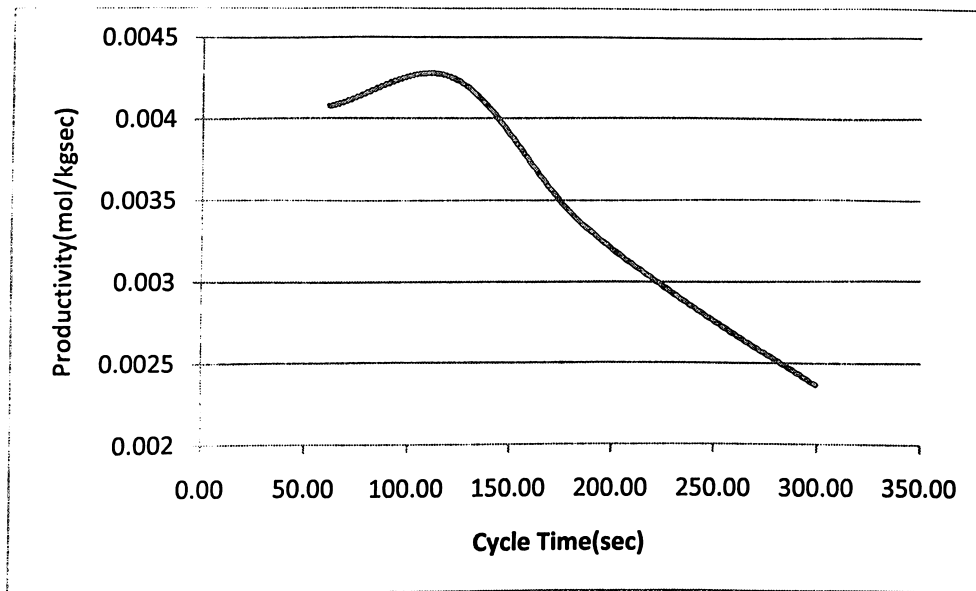


Fig 4.10 Variation of Productivity with cycle time (Pads =8, L=7m)

The increase in product purity for operation at low cycle time is surprising. It seems to be because of the following reason. At low cycle times, the bed does not get sufficient time for regeneration through desorption aided by low pressures and product purge. For non-linear isotherms, desorption is that much more time consuming than adsorption. Small desorption times due to small PSA cycle times cause accumulation of undesired component in the bed to a higher level and affect product purity.

Length of the column

Long bed is useful for continuous production. There is that much more inventory of raffinate in the bed during desorption step to continue supplying product during desorption step although the feed is stopped. Also, due to the long bed, appropriate pressure gradients exist along the bed for this purpose. These pressure gradients give the continuous production. Purity and productivity variations are shown in Fig 4.8 and Fig 4.9. It can be observed that with the increase in the height of the column, purity increases and then decreases slightly whereas productivity and recovery decreases as the height increases. Therefore the selection of bed height is also an important parameter for getting a better performance.

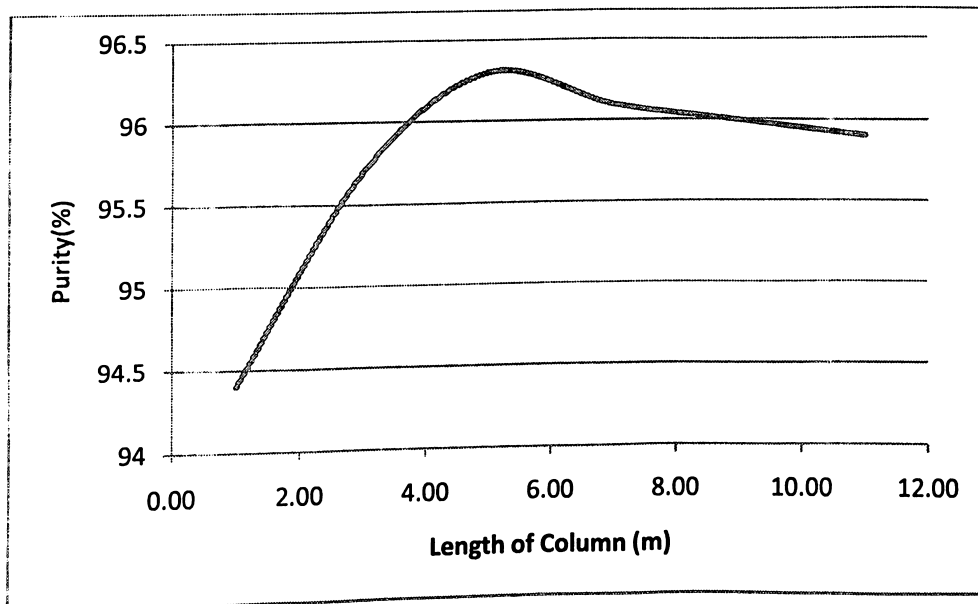


Fig 4.11 Variation of purity with length of the column(Pads=8 atm, L= 7m)

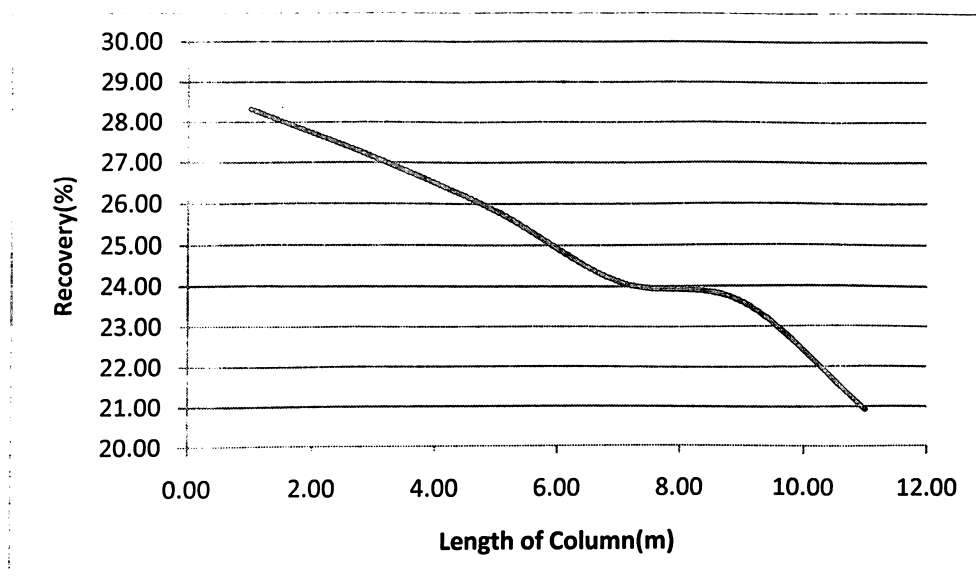


Fig 4.11 Variation of recovery with length of the column(Pads=8 atm, L= 7m)

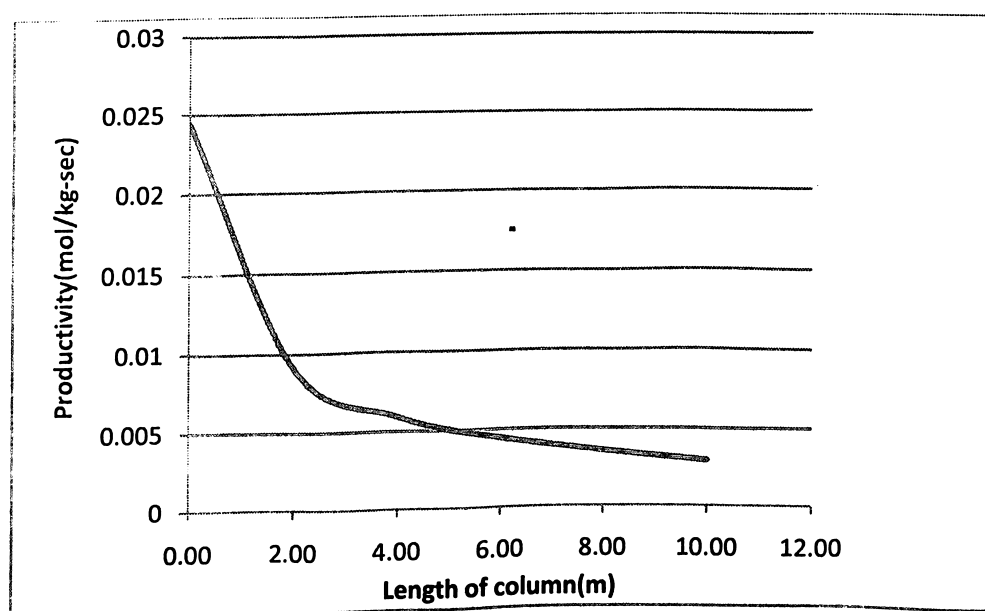


Fig 4.13 Variation of Productivity with length of the column(Pads=8 atm, L= 7m)

Effect of Valve coefficients

There were few studies which give the effect of fluid resistance in the pipelines on the PSA operation. The fluid resistance in the pipelines can be changed by changing one of the valve coefficients C_{V1} , C_{V2} , C_{V3} and keeping the others as constant. The valve coefficients are given in appendix 1. Valve V_1 controls the feed flow rate. When it opens wider, the product flow rate increases and the recovery decreases, while the product purity rises sharply at the beginning and falls slightly later, as shown in Fig 4.13, 4.14 Valve V_2 controls the product flow rate. With its valve coefficient C_v increasing, the product flow rate increases. This will enhance the recovery but lower the product purity, as shown in Fig 4.15

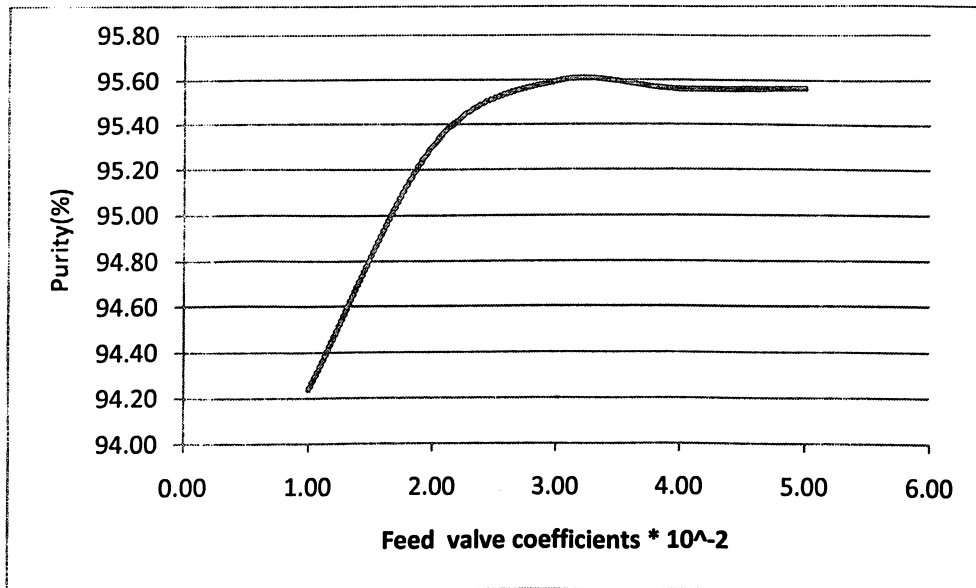


Fig 4.14 Variation of purity with feed valve coefficient ($t_c=120\text{sec}$, $P_{\text{ads}}=8\text{ atm}$, $L=7\text{m}$)

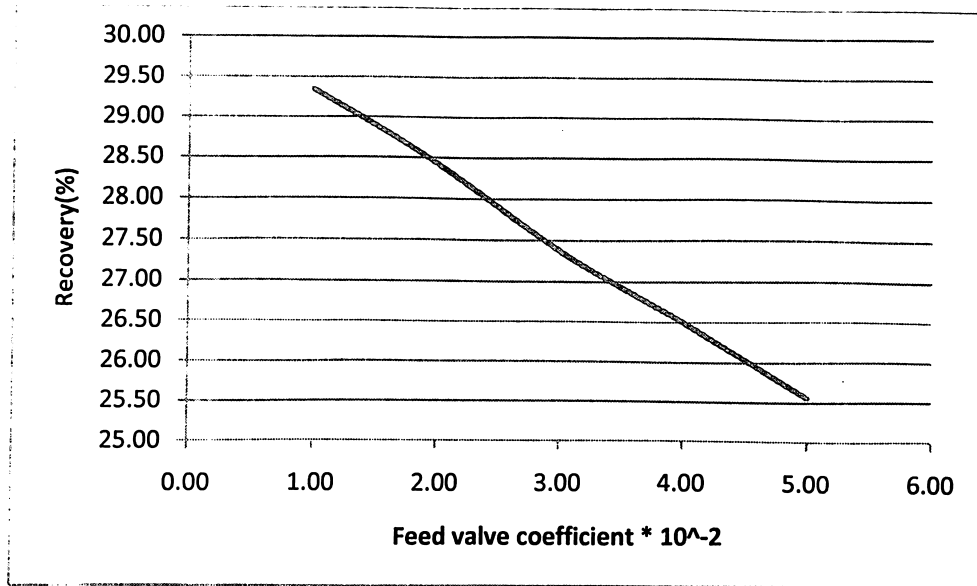


Fig 4.15 Variation of Recovery with feed valve coefficient ($t_c=120\text{sec}$, $P_{\text{ads}}= 8 \text{ atm}$, $L=7\text{m}$)

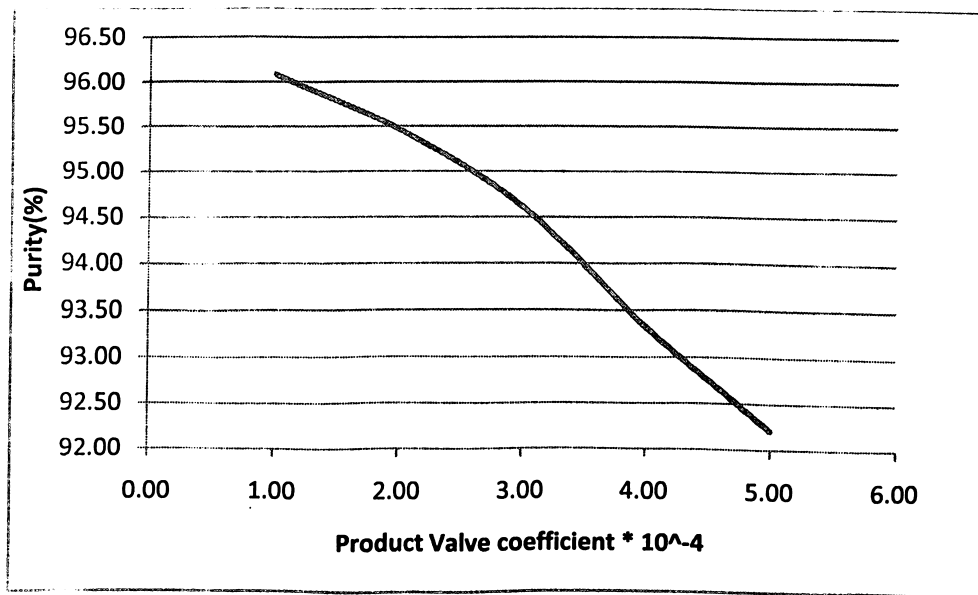


Fig 4.16 Variation of Purity with Product valve coefficient ($t_c=120\text{sec}$, $P_{\text{ads}}= 8 \text{ atm}$, $L=7\text{m}$)

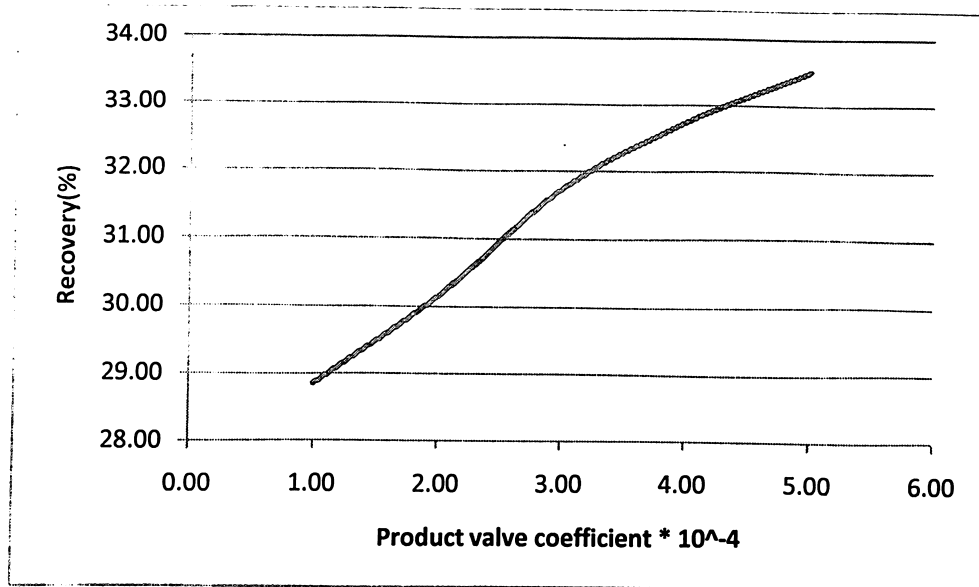


Fig 4.17 Variation of Recovery with product valve coefficient ($t_c=120\text{sec}$, $P_{\text{ads}}= 8 \text{ atm}$, $L=7\text{m}$)

Valve V_3 controls the blow down flow rate. From Fig 4.1, it can be seen that if the valve coefficient C_v increases, the product purity increases and recovery decreases. This is as expected because the blowdown is more complete as the valve allows more flow and uses more purge volume.

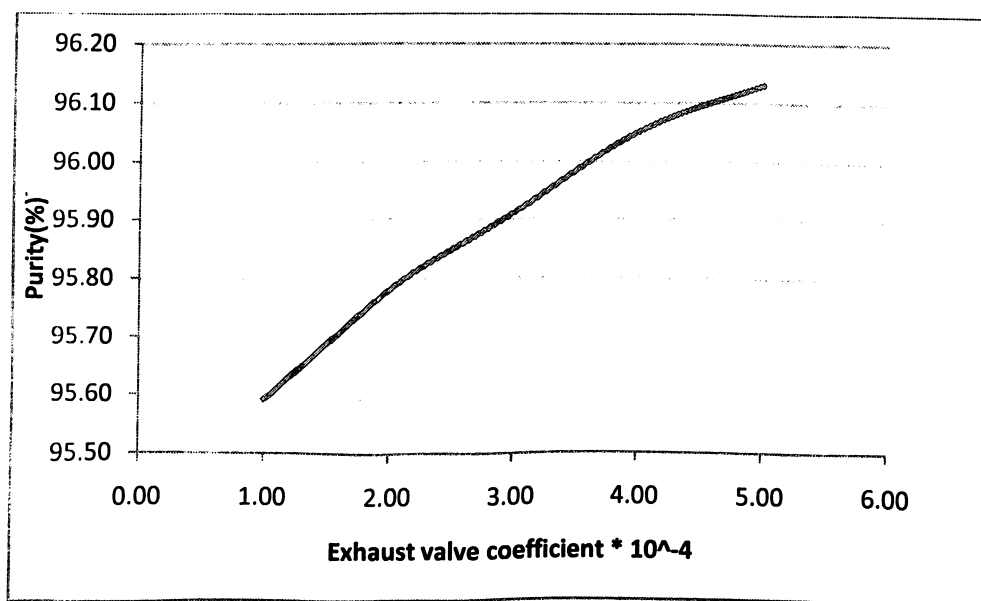


Fig 4.18 Variation of Purity with exhaust valve coefficient ($t_c=120\text{sec}$, $P_{\text{ads}}= 8 \text{ atm}$, $L=7\text{m}$)

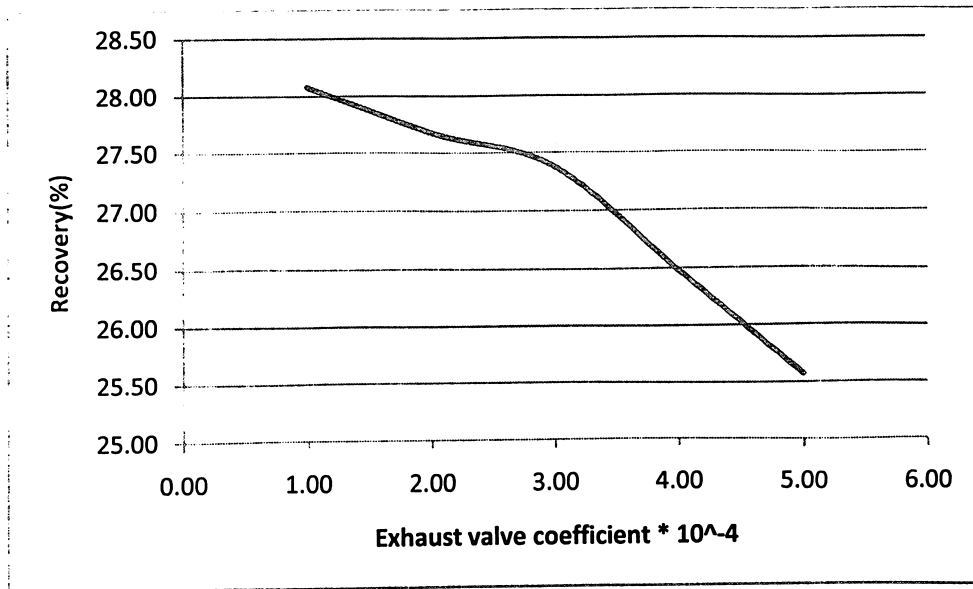


Fig 4.19 Variation of Recovery with Exhaust valve coefficient ($t_c=120\text{sec}$, $P_{\text{ads}}= 8 \text{ atm}$, $L=7\text{m}$)

From the above discussion, the purity and recovery cannot be increased at the same time via regulating the values of C_v , therefore there will be an optimal C_v selection for the valve combination. Single bed PSA thus offers itself as a good candidate for optimizing process control

Conclusion

In this chapter, the model is simulated for oxygen PSA process and also studied the effect of process parameters on PSA performance. In the next chapter, the conclusion of present work and scope of future work is discussed.

CHAPTER 5

Conclusions and future work

In the present work, a concept of single bed PSA process with possibility of continuous product withdrawal was proposed. It seems to be potentially good from economic point of view as well as for simplicity of design. A mathematical model was developed and the process dynamics and performance was studied through simulations of such a process embodiment. The single-bed PSA process is simulated using the parameters from the literature for oxygen PSA. The results indicate that the proposed single bed PSA system can closely match in performance with the corresponding multi-bed systems. The effects of cycle time, adsorption pressure, height of the column and valve coefficients on product purity and recovery were studied. Some of the salient findings on the sensitivity analysis carried out were as follows.

Adsorption pressure: Product purity and productivity increases whereas recovery decreases when the adsorption pressure increases.

Cycle time: Product purity and productivity first increases and then decreases whereas recovery increases monotonically when the cycle time increases.

Length of the Bed: Product purity first increases and then decreases whereas productivity and recovery decrease when the height of the column increases.

Valve coefficients:

Feed valve coefficients: Product purity increases whereas recovery decreases when the feed valve coefficient increases.

Product valve coefficients: Product purity decreases where as product recovery increases when the product valve coefficient increases.

Exhaust valve coefficients: Product purity increases and recovery decreases slightly when the exhaust valve coefficient increases.

The future work will focus on extending of present analysis and testing the present model with other complex systems, such as multi-component separation, Non isothermal operations with gas and solid conduction etc

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Appendix 1

Table A1.1 Design parameters for Oxygen PSA (Ruthven 1984; Chiang et al, 1994; Crittenden, et al, 1995; Ruthven and Farooq, 1990, Jain, et al 2003)

Parameter	Value
Adsorbent	Zeolite 5A
Feed gas composition	21% oxygen, 79% nitrogen
Particle size	1/16 inch (0.00158m)
Bed diameter	0.102 m
Column length	7 m
Bed density	1210 kg m ⁻³
Bed porosity	0.33
Feed temperature	298 K
Viscosity of air mixture	1.8702 X10 ⁻⁵ kg s ⁻¹ m ⁻¹
Density of air mixture	1.2 kg m ⁻³
Mass transfer coefficient for O ₂	0.0032 s ⁻¹
Mass transfer coefficient for N ₂	0.0098 s ⁻¹

Table A1.2 Isotherm parameters for Oxygen PSA

Gas	q_{si} (mol/kg)	b (bar ⁻¹)
N ₂	2.387	0.1498
O ₂	5.714	0.02352

Table A 1.3 Cycle parameters for Oxygen PSA

Parameter	Value
Adsorption pressure	8 atm

Product pressure	1.013 atm
Cycle time	120 s
Feed valve coefficient	0.01
Product valve coefficient	0.0001
Bottom valve coefficient	0.0001