THE MODELLING OF
DIFFUSION CONTROLLED
PRESSURE SWING ADSORPTION

by

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A dissertation submitted for the degree of

Doctor of Philosophy

in the

University of Surrey

United Kingdom

18 December 1992
To my loving and caring wife,

SUAN

without whom.....
The work described in this dissertation was carried out in the Chemical and Process Engineering Department, University of Surrey, from January 1986 to December 1989. It is the original and independent work of the author, except where otherwise stated in the text. No part of this dissertation has been submitted for a degree at any other University.

I wish to express my deepest gratitude to my supervisor, Dr. N F Kirkby. His advice and personal friendship to me and my family has made this research possible, especially during the first year of my research when my father passed away. I am forever indebted to him for his excellent guidance, unfailing enthusiasm and tremendous encouragement. Words cannot adequately describe the quality of his supervision.

I am very grateful to BP Research Centre at Sunbury, for financing the entire project.

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To my late father, my mum, brother, sisters and their families, without their support and encouragement the completion of the research would be
made more difficult. Special thanks go to my neighbours, Mr and Mrs Loveridge, for their warmth and kindness.

My wife Suan, has made every stage of my research a meaningful one, thanks to her wholeheartedly especially for the long hours spent proof-reading the drafts. Thanks also go to my daughter Natasha for being patient throughout.

Daniel Ann Keng LIOW

December 1992
SUMMARY

The objective of the present study is to model the separation of nitrogen from air by PSA using carbon molecular sieves. These processes rely on the different rates at which oxygen and nitrogen gain access to the adsorption sites within the carbon, and not solely on the adsorption equilibria between the gaseous and adsorbed phases.

The model of diffusion controlled pressure swing adsorption in this study consists of a set of inhomogeneous, non-linear, first order, partial differential equations (PDEs). These PDEs are derived from convective mass balance equations, mass transfer equations and the equilibrium isotherm equations. The Method of Characteristics is used to reduce the derived set of hyperbolic PDEs to a set of ordinary differential equations (ODEs) in an exact manner.

The adsorption rate and equilibrium isotherm parameters for oxygen and nitrogen are estimated from data published by Hassan, Ruthven and Raghavan (1986). This study also compare their published theoretical and experimental results against the DCPSA model's result. Such comparisons, however are of limited value because the exact conditions and the manner in which the experiment is conducted are not known.

The original idea of performing implicit integration along the characteristics has made the DCPSA model more robust. This means it is more stable and less computer processing time is required when high but realistic values of the overall mass transfer coefficients are used.
The DCPSA model is able to predict the qualitative behaviour of the simple, product release, purge, backfill and bed pressure equalisation cycles. A series of sensitivity analysis of the process parameters on a simple purge cycle are carried out.

The model predicts an extraordinary 'reverse flow phenomenon' during the product release step when low feed rate is introduced at the feed end. This is because when the feed rate is low, the rate of adsorption at the product end is much greater than the gas feed velocity, and additional gas is required to be drawn in from the product end. No published models have reported this phenomenon.

Finally, it is also the intention of the author to develop the DCPSA model such that the model can also be used in future to simulate any other kinetically based, binary adsorbable gas separating process.
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Microfiche of Program Listing
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<td>kmol m$^{-3}$</td>
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<td>Simplified notation of a derivation in Appendix E</td>
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<td>$r_P$</td>
<td>Adsorbent pellet radius</td>
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<td>$R$</td>
<td>Universal gas constant</td>
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<td>Description</td>
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<td>--------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>K</td>
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<tr>
<td>u</td>
<td>Superficial fluid velocity</td>
<td>m s(^{-1})</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
<td>m(^3)</td>
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<tr>
<td>X</td>
<td>Point on a curve</td>
<td>-</td>
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<tr>
<td>z</td>
<td>Position / Distance in column</td>
<td>m</td>
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**Greek**

- \( \alpha \): Simplified notation for the derivation of quadratic equations
- \( \alpha_k \): Simplified notation for the derivation of quadratic equations
- \( \beta \): Simplified notation for the derivation of quadratic equations
- \( \beta_k \): Simplified notation for the derivation of quadratic equations
- \( \gamma \): Simplified notation for the derivation of quadratic equations
- \( \gamma_k \): Simplified notation for the derivation of quadratic equations
- \( \Gamma \): Notation for a curve                   | -          |
- \( \delta t \): Integration step length             | s          |
- \( \delta z \): Distance of an element of a column  | m          |
- \( \Delta t \): Process cycle time                  | s          |
- \( \Delta z \): Discretisation spatial interval     | m          |
- \( \Delta P \): Column pressure drop                | Pa         |
- \( \varepsilon \): Packed column voidage            | -          |
\( \varepsilon_p \)  
Intra particle voidage

\( \lambda \)  
Simplified notation of a derivation in Appendix D

\( \mu \)  
Fluid viscosity \( \text{kg} \ (\text{m} \ \text{s})^{-1} \)

\( \nu \)  
Superficial velocity \( \text{m} \ \text{s}^{-1} \)

\( \rho \)  
Fluid density \( \text{kg} \ \text{m}^{-3} \)

\( \rho_s \)  
Particle density \( \text{g} \ \text{cm}^{-3} \)

\( \sigma \)  
Simplified notation of a derivation in Appendix D

\( \vartheta \)  
Volumetric flow rate \( \text{m}^3 \ \text{s}^{-1} \)

\( \vartheta_0 \)  
Feed volumetric flow rate \( \text{m}^3 \ \text{s}^{-1} \)

\( \vartheta_{\text{cls}} \)  
Volumetric flow rate at close end \( \text{m}^3 \ \text{s}^{-1} \)

\( \vartheta_f \)  
Feed volumetric flow rate \( \text{m}^3 \ \text{s}^{-1} \)

\( \vartheta_p \)  
Product volumetric flow rate \( \text{m}^3 \ \text{s}^{-1} \)

\( \omega \)  
Packed density \( \text{kg} \ \text{m}^{-3} \)

\( \Omega_i \)  
Dimensionless parameter

**Subscript**

0  
Initial

A  
Oxygen component

B  
Nitrogen component

H  
Notation for Hassan et al's parameter

i  
Component i

j  
Coefficients identifier

k  
Coefficients identifier
L Final
m mth partial derivative of Jacobian matrix
t Differential in time
z Differential in distance
(0) Present function value at time t
(1) Required function value at time t + \( \delta t \)
(i) Current integration time step
(N) Current integration spatial position

Superscript

(1) First prediction of predictor-corrector
(2) Second prediction of predictor-corrector
(n) nth prediction of predictor-corrector
<table>
<thead>
<tr>
<th>ABBREVIATIONS</th>
<th>MEANING</th>
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<tr>
<td>BBBPE</td>
<td>Bottom to Bottom Bed Pressure Equalisation</td>
</tr>
<tr>
<td>BEBPE</td>
<td>Both End Bed Pressure Equalisation</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmentt and Teller</td>
</tr>
<tr>
<td>BF</td>
<td>Bergbau-Forschung of Bergwerksverband GmbH</td>
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<tr>
<td>BOC</td>
<td>British Oxygen Corporation</td>
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<tr>
<td>BPE</td>
<td>Bed Pressure Equalisation</td>
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<td>CMS</td>
<td>Carbon Molecular Sieve</td>
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<td>CPU</td>
<td>Central Processing Unit</td>
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<td>DCPSA</td>
<td>Diffusion Controlled Pressure Swing Adsorption</td>
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<tr>
<td>GDC</td>
<td>Gas Donating Column</td>
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<tr>
<td>GRC</td>
<td>Gas Receiving Column</td>
</tr>
<tr>
<td>IAST</td>
<td>Ideal Adsorption Solution Theory</td>
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<tr>
<td>ILE</td>
<td>Instantaneous Local Equilibrium</td>
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<td>LDF</td>
<td>Linear Driving Force</td>
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<tr>
<td>PDEs</td>
<td>Partial Differential Equations</td>
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<td>PI</td>
<td>Proportional plus Integral</td>
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<td>PSA</td>
<td>Pressure Swing Adsorption</td>
</tr>
<tr>
<td>TSA</td>
<td>Thermal Swing Adsorption</td>
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<td>TTBPE</td>
<td>Top to Top Bed Pressure Equalisation</td>
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CHAPTER 1

INTRODUCTION

1.1 Introduction

Pressure Swing Adsorption (PSA) was first described in 1932 [Finlayson and Sharp] as a process for separating gases, which is based on the adsorptive properties of porous solid adsorbents. However the process was not commercially exploited until after the discoveries of synthetic zeolites [Milton, (1959)]. Since then, gas adsorption has made a major impact on the chemical and petrochemical industries as a key separation method. The increasing industrial uses of this novel process promoted studies of the properties of adsorbents and optimisation of plant design. This chapter gives an overview of PSA, the adsorbents used, PSA configurations, an introduction to mathematical modelling of PSA and the objectives of this project.

1.2 An Overview of PSA

Pressure Swing Adsorption is a gas separation process which depends on the following:

1) the type of adsorbent used,
2) the variation of total pressure,
3) the adsorption equilibrium and the rate of adsorption,
4) the cycle configurations, and
5) the total time required for a column to complete a full process cycle.

The process cycle time is normally less than five minutes because the column pressures can be changed rapidly. The shorter cycle time of PSA compared to other gas separation processes, such as Thermal Swing Adsorption (TSA), has led to its increased use. Although cryogenic distillation is still the dominant bulk gas separation techniques used in the chemical and petrochemical industries, the share of the market for PSA will continue to increase as the process improves further. In recent years, PSA has been adopted as the preferred air separation technique over the cryogenic method, especially in cases where the production rates are below 30 tonnes per day. Similarly, PSA separation of high purity hydrogen (99.9999 %) from reformer product gases is more economical than cryogenic means. PSA also competes with other techniques such as liquid absorption and membrane separation processes.

It is known that the largest PSA plant produces over 100,000 Nm$^3$/hr of 99.9999 % hydrogen and the largest oxygen plant produces about 1,000 Nm$^3$/hr of 95 % oxygen. The largest application of the process in terms of the number of plants is the separation of oxygen from air for medical, domicilliary use.

Publications on PSA and other adsorption processes have grown rapidly since the development of Skarstrom's cycle in 1960. By 1970, there were nearly 1,000 patents held on PSA and 4,500 papers in the open literature on
adsorption. A decade later the number of PSA patents had reached 2,000, and is still growing at an exponential rate [Sircar, (1988)].

The economic evaluation of PSA is complicated. However, the energy required for the following purposes constitute the major operating costs:

1) compression of the feed gas to the required adsorption pressure (if necessary),
2) overcoming the system pressure drops during adsorption or desorption, and,
3) the loss or consumption of energy during desorption by pressure reduction.

Depending on the plant throughput and the type of cycle configurations used, the capital cost for a PSA plant includes:

1) compressor or vacuum pump,
2) product specification analyser,
3) pressure columns and piping,
4) adsorbent,
5) remotely activated valves, and,
6) control electronics.

PSA processes are still relatively poorly understood despite their increasing popularity. Detailed mathematical modelling of these cyclic processes and the solution techniques required are indeed extremely complicated and time consuming. However, different models have appeared in the open literature: Turnock and Kadler (1971), Chan, Hill and Wong (1981), Carter and Wyszynski (1983), Fernandez and Kenney (1983),

3
Chihara and Suzuki (1983), Yang and Doong (1985) and Raghavan and Ruthven (1985). Some of these models and their solutions will be discussed in Chapter 2.

1.3 Adsorbents and Adsorptive Separations

Adsorbents are porous solids which allow fluid phase molecules to adhere or 'adsorb' to their surfaces. Many factors affect the amount of adsorbate retained on the adsorbents. These factors include the structure and composition of the surface of the adsorbents, the concentrations of the adsorbates, and the temperature and pressure of the system.

There are two types of adsorption:

1) chemisorption involves the formation of chemical bonds between the surface and adsorbate which are normally very strong and not easily broken again by moderate changes in physical conditions, and,

2) physisorption involves the formation of less strong, physical bonds which are governed by Van der Waal forces and unlike chemisorption, the adsorption of the loosely bonded molecules is readily reversible.

Most microporous materials can be used as adsorbents for gas separation. The two common types of adsorbent used in PSA air separation processes are zeolites and carbon molecular sieves (CMS). Both of these can physisorb all the molecules in air. A more detailed discussion on these two types of adsorbent is presented in Chapter 2.
Two fundamental factors affect the separation which can be achieved:

1) the equilibrium isotherms, and,

2) the rates of adsorption.

The equilibrium isotherm is the relationship between the amount of a component adsorbed on the adsorbent surface and its partial pressure in the gas phase at equilibrium and at a constant temperature. The amount adsorbed normally increases with both increasing partial pressure and decreasing temperature. Hence the adsorbent in an adsorption column can be regenerated by either decreasing the total pressure of the adsorbed system, as for PSA, or increasing the temperature of the adsorbed system, as for TSA. Due to the large heat capacity and poor heat exchange properties of the adsorbent, the regeneration of adsorbent for a TSA system can be very slow. Often the regeneration of the adsorbent may take several hours, which means large quantities of adsorbent per unit throughput. For this reason PSA processes have replaced many TSA processes. Figure 1.1 shows the pure gas isotherms for oxygen and nitrogen on 5A zeolites.

The rate at which a molecule is adsorbed onto an adsorbent surface is generally governed by gas and solid phase mass transfer. During gas phase mass transfer the molecule is transferred by convection to the boundary layer followed by molecular diffusion across the boundary layer. The solid phase mass transfer includes macropore transport, micropore transport or intracrystalline diffusion. The macro- and micropore transport are controlled by molecular and Knudsen diffusion respectively. The micropore transport is also affected by surface diffusion. In the case of CMS, the
Pure Gas Isotherms for Oxygen and Nitrogen on 5A Zeolites

Figure 1.1
rate of adsorption is mainly governed by pore diffusion, hence CMS is manufactured with a carefully controlled pore size distribution.

An ideal adsorbent for PSA is one in which the fastest diffusing component also has the most favorable equilibrium. However, this is rarely the case, for example, the isotherms for both oxygen and nitrogen on Bergbau-Forschung CMS are almost identical, but the rate at which oxygen diffuses into the adsorbent is 30 times faster than the rate at which nitrogen can diffuse [Ruthven, Raghavan and Hassan (1986)]. Typical kinetic and equilibrium data for oxygen and nitrogen on CMS are presented in Figure 1.2. For air on zeolites, the adsorption isotherms favour the slower diffusing nitrogen molecules.

An important feature of an adsorbent for the kinetic type of separation is that the molecular sieving requires the adsorbent to have a very narrow range of pore sizes.

In practice, small particle diameters are preferable since this minimises the diffusional path lengths for macropore transport and hence allows the use of a reasonable proportion of each particle's adsorptive capacity.
Kinetic and Equilibrium Data for Oxygen and Nitrogen on CMS

Kinetic Data

Equilibrium Data

Figure 1.2
1.4 PSA Simple Cycle Configurations

PSA is a dynamic process and consists of many different cycle configurations. The basic configuration is the simple cycle which consists of three common process steps: pressurisation, product release and depressurisation (Figure 1.3). Additional process steps, such as purge, backfill, second cut and co-current depressurisation are used in more complicated cycle configurations. This is done either to improve the regeneration of the adsorption column or to enhance the product release (Section 2.4).

Pressurisation is a process step where the feed gas is compressed into an adsorption column and the pressure rises to the upper operating pressure.
During this time, the more strongly retained components are adsorbed onto the adsorbent surface leaving a zone of gas enriched in the less strongly retained components at the closed end of the column. To avoid fluidisation if the feed flow is vertically upwards, the peak flow rate must be restricted or the adsorbent must be mechanically retained. Movement of the particles is not desirable because of attrition and, in some extreme cases, may lead to remixing of the gases which have just started to separate.

During the product release step, further feed gas is introduced into the column while maintaining the pressure at the upper operating pressure. The gas enriched in the less retained components is released through the opposite end of the column. When the adsorption front reaches the end of the column, the more strongly retained components start to breakthrough into the product stream and the step is terminated.

During product release there is further separation due to the chromatographic effect of the fronts moving at different speeds and changing shape. This effect is the main cause of separation in PSA processes for the purification of an inert or non-adsorbable gas such as hydrogen purification or air drying but is less important for bulk gas separations such as oxygen or nitrogen separation from air.

The normal depressurisation step is the reverse of the pressurisation step; the existing high operating pressure is reduced to the lower operating pressure by exhausting the gas counter-currently to the feed direction. The drop in pressure causes desorption to occur. The gas released is rich
in the more strongly retained components and is usually called the waste
gas. However, this 'waste' stream sometimes contains the desired product.
In some cases, a large pressure change is needed to increase the distance
travelled by the desorption front. In air separation, the waste gas is
normally vented to the atmosphere. In the case where the lower operating
pressure is below atmospheric pressure, a vacuum pump is used.

A simple cycle that consists of these three basic process steps is normally
incapable of producing a commercially viable separation. This is either
because of the poor product concentration obtained or the product yield is
too low even at the optimal operating condition. The product yield in PSA
is normally defined as the ratio of the amount of desired component that
leaves the plant in the product stream to the amount of the same component
in the feed stream.

To achieve a continuous flow of product during the cyclic operation, more
than one column is needed. Figure 1.4 below gives an example of a two bed
simple cycle.

<table>
<thead>
<tr>
<th>Bed A</th>
<th>Product</th>
<th>Release</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed B</td>
<td>1</td>
<td>2</td>
<td>Product</td>
<td>Release</td>
</tr>
</tbody>
</table>

1) Depressurisation 2) Pressurisation

Figure 1.4
Additional steps to improve on the simple cycle configuration by further regeneration or enhancing the product yield are described in Section 2.4.

1.5 Introduction to PSA Modelling

The nature of a model of any process depends largely on the use for which it is required and the complexity and limits of the process. A mathematical model of PSA, in the context of a study of the dynamics and behaviour of an adsorption column under rapid changes of pressure, depends on many factors. Model complexity will depend on the assumptions made, that is, how precisely the system is represented. Increasing the number of assumptions usually decreases the complexity of the model. In general, the task of the modeller is to develop a model which is a close representation of the real system. Ideally the model should be easily understood and is easy to solve. The importance of having an easily understood model is to enable users from a varied background to appreciate the process and to use the model without the need to have an in-depth knowledge of the process.

There are essentially two types of models: the first being the fitting of correlations to existing experimental results and the second is based on an analysis of the physical and chemical principles involved in the process. In the case of PSA, the latter type of model results in systems of partial differential equations (PDEs) which generally have to be solved numerically.
There are different types of PDEs (parabolic, hyperbolic and elliptic; see Section 3.4) and different numerical techniques may have to be used to solve each type. For example hyperbolic equations may be solved quickly and accurately using the Method of Characteristics but this method cannot be applied to parabolic or elliptic equations.

The Method of Characteristics used to solve these hyperbolic equations will be discussed in more detail in Chapter 4. This method of solution has also proven to be an efficient method for the instantaneous local equilibrium model (ILE) of PSA system [Kirkby (1983)], especially when the tracking discontinuities in the concentration profile is essential.

In general, increasing complexity of model greatly increases the computational load required for solution.

1.6 The Present Research

The main objective of this research is to model the separation of nitrogen from air by pressure swing adsorption using carbon molecular sieves. The purpose of the model is to represent the diffusion controlled PSA process by taking into account the mass transfer limitation encountered by the adsorbates, which is ignored by many PSA models.

The ultimate aims of this model are:

1) to study and understand the dynamics and behaviour of PSA,
2) to direct the search for the optimum operating conditions on existing plant,
3) to provide an accurate design tool for a new or revamped plant,
4) to allow the simulation of different types of cycle configurations, and,
5) to allow the study of other similar types of binary gas mixture separation processes under similar conditions.

This dissertation presents the results and conclusions of the work carried out between January 1986 and December 1989. A brief outline of the remaining chapters is as follows:

Chapter 2 presents a literature review on PSA, discusses the kinetics of sorption in solids and some of the recent theoretical models and the assumptions made.

Chapter 3 presents a diffusion controlled model with its assumptions.

Chapter 4 discusses the application of various integration techniques on the derived model, particularly on the technique originated for the present research.

Chapter 5 outlines the software development and the program structure of the current model. This chapter also presents the unique flow reversal phenomena at low feed rate during product release step.

Chapter 6 describes the results of the computer simulation of PSA including bed pressure equalisation cycles.

Chapter 7 summarises the findings of this study and suggests what future work need to be carried out on diffusion controlled PSA.
2.1 Introduction

Adsorption separation processes have been used widely in the petroleum refining and petrochemical industries long before the commercial development of Pressure Swing Adsorption (PSA). Since the commercial development of PSA, the use of adsorption separation in these industries grew even further. The number of PSA processes alone has grown exponentially for the past decade [Sircar (1988)]. Publications on this subject by Ruthven (1984) and Yang (1987) and the reviews on PSA, summarised in Table 2.1, provide guidance and reference.

This chapter aims to review the historical background of PSA, the types of adsorbent used in air separation and some other possible PSA process cycle configurations. Then the kinetics of sorption in porous solids are discussed to support the assumptions used for the derivation of the Diffusion Control Pressure Swing Adsorption (DCPSA) which are presented in Chapter 3. Finally this chapter presents a review of PSA models with the assumptions used.
Table 2.1 General reviews on PSA

<table>
<thead>
<tr>
<th>Year</th>
<th>Author(s)</th>
<th>General Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1968</td>
<td>Domine &amp; Hay</td>
<td>Described PSA in a more general term.</td>
</tr>
<tr>
<td>1973</td>
<td>Lee &amp; Stahl</td>
<td>Concentrated particularly in air separation processes.</td>
</tr>
<tr>
<td>1973</td>
<td>Smith &amp; Armond</td>
<td>Highlight the differences between PSA and cryogenic separation.</td>
</tr>
<tr>
<td>1984</td>
<td>Kenney &amp; Kirkby</td>
<td>A more comprehensive break-down of different types of process steps involved in PSA.</td>
</tr>
<tr>
<td>1984</td>
<td>Cassidy &amp; Holmes</td>
<td>Historical review of PSA.</td>
</tr>
<tr>
<td>1985</td>
<td>Tondeur &amp; Wankat</td>
<td>Described PSA processes in general, their historical background and also included less common but complicated type of cycles configuration.</td>
</tr>
<tr>
<td>1988</td>
<td>Sircar</td>
<td>General background in adsorption processes which include PSA. Also highlight the growing economics trends for PSA.</td>
</tr>
</tbody>
</table>

2.2 Historical Background of PSA

PSA was first described in a patent by Finlayson and Sharp (1932) as a single bed process involving a number of pressurisation and depressurisation steps. A decade later, Kahle (1942) described the first
two bed PSA system, which was used for drying air and removing carbon dioxide from a gas mixture. Although Kahle had later, in 1954, employed a pressure swing into the Sorbogen Process [Reyhing, (1975)], commercial application of PSA technology was not extensively exploited until after the discovery of synthetic zeolites [Milton (1959)]. A year later, Skarstrom (1960), who is widely acclaimed as the inventor of PSA, developed and patented a two bed PSA processes. The successful application of Skarstrom’s PSA cycle in gas drying has certainly resulted in a rise of PSA patents. In 1964, L’Air Liquide built its first hydrogen purification plant capable of producing 0.02 m³/s of 99.95% of hydrogen from cracked ammonia [Guerin de Montaruil and Domine, (1964)] and, in 1970, PSA was first used commercially to produce oxygen from air.

The increasing popularity of gas separation using PSA cycles had a great impact on the development of different adsorbents. For example, the development of a new carbon molecular sieves (CMS) adsorbent by Juntgen and Knoblauch (1971), of Bergbau-Forschung GmbH (BF) further increased the use of PSA in air separation processes. By 1976, the PSA market for nitrogen production from air was dominated by plants using the BF CMS. The rapid growth of the number of PSA plants in the last two decades has certainly stimulated the interest of researchers to develop better theoretical models of this process.

2.3 Adsorbents for Air Separation

A brief introduction of adsorbent properties and their separation
characteristics was given in Chapter 1. This section mainly describes the existing adsorbents used most commonly in air separation. In particular, 5A zeolite is widely used for oxygen enrichment, while carbon molecular sieves dominates nitrogen production.

Although these two types of adsorbents have demonstrated their usefulness in air separation, they have yet to meet the energy efficiency of cryogenic distillation at large scale. To achieve this, these materials need to have a large selective adsorption capacity as well as a selective diffusional resistance both favouring a single component.

In recent years, Union Carbide Corporation has described a number of new adsorbents which may be used for air separation. For example, Ce[Fe(CN)$_6$] was claimed to have a separation factor for oxygen from nitrogen as high as 48 in 10 minutes, in which time about 70% of the equilibrium oxygen loading was achieved, [Mulhaupt & Berwaldt, (1984)].

2.3.1 Zeolites in PSA Air Separation

Zeolites crystals were discovered and named two and a half centuries ago by a Swedish mineralogist [Cronstedt (1756)]. However the credit of its commercial use in PSA air separation processes go to scientists in Union Carbide Corporation who discovered a method of synthesising these highly porous solid crystals [Milton (1959)]. Publication of zeolite science has grown rapidly since, in particular, Breck (1974) provides an introduction to the properties and applications of zeolites.
Unlike most other adsorbents, zeolite crystals have virtually no pore size
distribution. The crystalline structure is based on a three dimensional
network of AlO$_4$ and SiO$_4$ tetrahedra, which are linked by the sharing of
the oxygen atoms to form cavities. The window and the cavity size of these
crystals can be altered by undergoing a partial or total ion-exchange of
their cations. A common 5A zeolite has a window size of 5.0 Å consisting
of calcium cations whilst a 4A zeolite, with a window size of 4.2 Å, has
a larger combined cation. This is because two sodium cations have to
replace each calcium cation and two sodium cations are larger than one
calcium cation.

Although 34 naturally occurring zeolites and about 100 synthetically
manufactured ones are now identified [Espitalier-Noel (1988)], 5A zeolite
is still the dominant adsorbent used in the process of enriching oxygen
from air.

Despite being the slightly larger molecule, nitrogen is adsorbed
preferentially to oxygen. This is because the nitrogen molecule has a
higher quadropole moment which allows it to form a stronger electrostatic
force with the 5A zeolites.

The rate of adsorption for both nitrogen and oxygen are extremely fast,
therefore oxygen enrichment from air using 5A zeolites are equilibrium
dominated.

The need to further understand and improve the efficiency of utilizing this
highly selective 5A zeolite in air separation had been well demonstrated by many researchers. For example, research carried out by Flores-Fernandez (1978), Kirkby (1983) and Liow (1986) under the guidance of Kenney at Cambridge, and more recently an extension of Kirkby's work by Espitalier-Noel (1988).

Shin and Knaebel (1988) explored the use of 4A zeolites to enrich nitrogen from air. Due to a smaller window size, the rate of adsorption for oxygen in this case is significantly greater than that for nitrogen. The separation becomes kinetically dominated. However, the use of CMS for nitrogen production still dominates the market.

2.3.2 Carbon Molecular Sieves in PSA Air Separation

The chemical industry has manufactured and used activated carbon since about 1909, and its use is now very widespread. Well established applications include water purification, sugar decolourisation, air purification and solvent recovery. Recently, PSA and vapour phase adsorption processes have further increased the demand for carbon derived adsorbents.

The first commercial activated carbons were manufactured by chemical activation of wood char, utilising zinc chloride, phosphoric acid and steam or carbon dioxide. Chemical activation of bone char is used in raw sugar decolourisation. Other different raw materials were also used to manufacture carbon to be used with liquids (e.g. lignite, sulphide black
ash and rice) and with gases (e.g. coconut and chemically charred wood). Activated carbon with a narrow micro-pore size distribution ranging from 4 to 9 Å is referred to as CMS.

CMS provides the possibility of selective separation of mixtures according to the molecular size of the individual components. In 1975, Grant reported the preparation of a 5A carbon sieve suitable for separating larger organic molecules, and two years later, Juntgen (1977), described a process for the manufacture of carbon sieves from coal with a high selectivity for separating nitrogen from air. He also gave a brief account of adsorption mechanisms and pore structures of carbonaceous adsorbents, pointing out that they adsorb selectively non-polar rather than polar components. Furthermore, the distinction between CMS and other activated carbon in terms of their pore volume and pore size distribution has also been presented by Juntgen (1977).

CMS has carefully controlled pore diameters which are tailored to perform a specific separation. The CMS used for PSA air separation, first patented by Bergbau-Forschung of Bergwerksverband GmbH (BF) [Peters and Muenzner, (1971)], are an example of where the pore size distribution must be very tightly controlled, because the oxygen and nitrogen molecules are so nearly the same size. Furthermore, unlike zeolite based PSA processes where the removal of water vapour and carbon dioxide are important, CMS adsorbed and desorbed these two components along with oxygen. This is because the adsorption of water in CMS, in particular, is much weaker than in the zeolites and is not a virtually irreversible competitor, and therefore does not need a thermal swing to remove it again.
In recent years, Calgon Carbon Corporation claimed to have produced a CMS for air separation with oxygen to nitrogen selectivity ratios between 6.5 to 8.5 and diffusion ratios ranging from 9 to 400 [Sutt, (1984)]

2.4 Other PSA Cycle Configurations

The simple cycle, as described in Section 1.4, is not commercially viable and further steps must be included in the cycle to improve product purity, yield and energy consumption. To improve the regeneration of the saturated column, a purge step is normally incorporated into the simple cycle. In a purge step, part of the desired high pressure product from the product release step is re-introduced as a feed into a fully depressurised column (Figure 2.1).

![Further Regeneration Steps Diagram]

*Figure 2.1*
To maintain a constant lower operating pressure during purge, the other end of the regenerating column is left open to allow the waste to leave the system. Since the high pressure product gas is enriched in the less strongly retained component on entering the purge column, it lowers the local partial pressure of the more strongly retained component, providing a driving force for more of this component to desorb leaving a much cleaner column. Kahle was the first to use purge step in PSA (1942), it was also used in the first commercially popular process which was patented by Skarstrom (1960). Nowadays, almost all PSA processes use purge steps as one of several further regeneration steps, especially in cases where high purity product is more important than the yield.

The amount of purge gas used affects both the product purity and the yield. The optimum purge amount usually corresponds to the start of breakthrough of the product gas into the waste line. Above this optimum value, extra product gas is discharged unnecessarily into the waste line, hence reducing the product yield and, in extreme cases, also causing a loss of product concentration. However, if the purge amount is below the optimum value, the adsorbent in the regeneration column will not be fully regenerated, leading to a less pure product. Figure 2.2 below shows an example of a two column purge cycle configuration.

<table>
<thead>
<tr>
<th>Purge Cycle Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed A</td>
</tr>
<tr>
<td>Bed B</td>
</tr>
</tbody>
</table>

1) Depressurisation
2) Purge
3) Pressurisation

Figure 2.2
Another step which is used to improve the regeneration of the beds is the backfill step. In this case, the waste end of the bed is closed allowing the regeneration column to be partially pressurised (see Figure 2.1). During backfill, the desorption front in the column will be pushed down further towards the closed end. Cycles using a backfill step normally show higher yields than those with a purge step because there is no further waste released during the backfill step. The pressure at the end of the backfill step is called the backfill pressure and its optimum value normally lies about halfway between the upper and lower operating pressures. In PSA cycles used to produce oxygen from air it is common to include both a purge step and a backfill step, and a typical cycle configuration is shown in Figure 2.3 below.

The gas supply for the purge and backfill steps can come from different sources:

1) on-specification product, direct from the product line connected to the product release step.
2) off-specification product, direct from the product line as 1) [Skarstrom, (1960)].
3) from a tank containing gas specially released for regeneration purposes. The gas is fully mixed but off-specification with respect to the normal product, [Marsh, Hoke, Pranmik and Skarstrom, (1964)].

4) from a product buffer tank, where the gas is also fully mixed and on-specification, [Armond & Webber, (1975)].

No additional pressure vessel is needed for methods (1) and (2) and no composition fluctuations will enter the receiving column when using methods (3) and (4). Methods (1), (2) and (4) are all in common use.

At the end of a normal product release step, the concentration front of the more strongly adsorbable components may either start to breakthrough into the product stream or be near the product end of the column. In the latter case, considerable adsorptive capacity at the product end of the column remains unused and represents incomplete use of the adsorbent. The two common ways to enhance the product release step is to use either a second cut step or a co-current depressurisation step (Figure 2.4).
The second cut step is a product release step where all the outlet gas of a donating column (after its normal product release) is fed into another column as feed during the product release step of the receiving column. This step not only improves the product yield but, more importantly it make the process much easier to design because it removes the need to calculate accurately when the concentration front is going to breakthrough. This process step has been patented by BOC Ltd. and is used for oxygen production from air [Armond, (1980)]. To allow for a continuous flow of product, the simplest cycle configuration using second cut involves the use of three columns (Figure 2.5).

<table>
<thead>
<tr>
<th>Cycle Configuration Using Second Cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed A</td>
</tr>
<tr>
<td>Bed B</td>
</tr>
<tr>
<td>Bed C</td>
</tr>
</tbody>
</table>

1) Receive Second Cut 5) Purge
2) Product Release 6) Backfill
3) Donate Second Cut 7) Pressurisation
4) Depressurisation

Figure 2.5

The co-current depressurisation step also increases the yield of the product by releasing the just off-specification gas left at the product end of the column into the product stream after the product release step. An
additional feature of co-current depressurisation is the ability to conserve some pressure energy for the cycle. This step is followed by the normal counter-current depressurisation step which does not now start at the upper operating pressure, hence less energy is lost into the waste line. A disadvantage of this step is that some of the product is produced below the upper operating pressure. Figure 2.6 shows a purge cycle configuration which includes a co-current depressurisation step.

There are many ways to combine the above mentioned individual steps, such that while one column is undergoing further regeneration, another column is enhancing the product release. It is common to combine co-current depressurisation on one column with backfill on another column. The overall effect is to increase the product yield and at the same time conserve some of the pressure energy. This combination is an example of a process called bed pressure equalisation (BPE) (Figure 2.7).
The original version of BPE was where the product end of one column, after product release, is connected to the product end of another column that has just completed a purge step. This configuration will be referred to as top to top BPE (TTBPE). During TTBPE, the column that is at its upper operating pressure is donating the just off-specification gas and performing the task of a co-current depressurisation step and the receiving column, which starts at the lower operating pressure, is backfilled. Other BPE cycle configurations, such as those in Figure 2.7, also have similar advantages.
If only two columns are used in BPE cycle configurations, there will not be a continuous flow of product from the system, as shown in Figure 2.8.

<table>
<thead>
<tr>
<th>Bed A</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed B</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

1) Product release  
2) Co-current depressurisation or Counter-current depressurisation or both  
3) Counter-current depressurisation  
4) Purge  
5) Backfill or Pressurisation or both  
6) Pressurisation

In recent years, BPE cycles have come to the attention of PSA researchers. Hassan, Raghavan and Ruthven (1987) presented the experimental and theoretical study of a Both End BPE (Figure 2.7) cycle without a purge step. However, LaCava, Dominguez and Cardenas (1988) included a purge step in their 6 steps BPE cycle.

2.5 Kinetics of Sorption in Solid

Separation processes in packed columns that are based on sorption in the porous media are affected by the hydrodynamics of the gas flow, adsorption equilibria and interphase heat and mass transfer. These in turn are
influenced by the physical characteristics of the solid adsorbent, such as
the surface properties and the internal structure.

2.5.1 Hydrodynamics of Flow through Packed Column

As a fluid passes through a fixed column of granular material, the
pressure drop, $\Delta P$, across the length of the column, is dependent on:
1) the particle size, $d_p$, its shape, roughness and size distribution,
2) the column length, $L$,
3) the voidage, $\varepsilon$,
4) the physical properties of the fluid, and
5) the superficial fluid velocity, $u$.

Pressure drop was studied by Darcy in 1830 in Dijon and give rise to
Darcy's Law as follows [Coulson, Richardson, Backhurst and Harker, (1978)]:

$$u = K \frac{\Delta P}{L}$$

where $u$ is the average velocity of flow of the fluid, defined as $\frac{1}{A} \frac{dV}{dt}$, and
$K$ is a constant depending on the physical properties of the bed and fluid.

General expressions relating flow rate and pressure drop have also been
developed by Furnas (1929), Chilton and Colburn (1931), Konzeny (1933)
and Carman (1937) [Coulson, Richardson, Backhurst and Harker, (1978)],
and later by Leva (1949) and Ergun (1952).
Pressure drop in a packed column may be significant in cases where the particle size is smaller than 1.0 mm or when PSA operates on a rapid cycle such as those of Keller and Jones (1980). However, pressure drop has not been found to be significant for the slower cycles normally employed in conventional PSA processes. Hassan, Ruthven and Raghavan (1986), for instance, did not report any significant pressure drop for their PSA experiment where BF CMS was used.

Many pressure drop equations such as the Ergun and the Carman-Kozeny equations have been developed from a steady state momentum balance across a non-adsorbable packed column. In PSA, the gas superficial velocities are far from constant, and the use of these theories is yet to be justified. Recent work by Alpay (1992) shows the momentum term is insignificant even in a rapid PSA cycle.

Therefore, in conventional PSA operating with reasonably large particles and slow cycle times which this research model is intended for, the change in pressure over the length of the packed column may be ignored.

2.5.2 Axial Dispersion

Although axial dispersion may be important in some laboratory size packed columns and is included in some theoretical models such as those by Hassan et al (1986) and Liow (1986), it has been ignored in the Diffusion Control Pressure Swing Adsorption (DCPSA) model. This is because the mass transfer coefficients are not calculated from first principles and the effects of
axial dispersion can be rolled into the overall effective mass transfer coefficient, at least to a first approximation. In addition, for most industrial columns, the ratio of column diameter to particle diameter normally exceeds 300 and the bed length to particle diameter ratio is usually well in excess of 1000.

Bono (1989) has discussed briefly the effect of column length, $L$, to the column axial dispersion, $D_L$, by correlating the relationship between axial Péclet number, $\text{Pe}_L = \frac{uL}{D_L}$, and the particle Péclet number, $\text{Pe}_P = \frac{ud_p}{D_L}$. It was shown that for the range of particle size and particle Reynolds number normally encountered, where the particle Péclet number has a value of the order of 0.5 to 2 for liquid systems and 2 for gaseous systems [Levenspiel, (1972)], the value for axial Péclet number is of the order of $L/d_p$ for liquids and $2L/d_p$ for gases. Hence unless the column is short, the contribution of axial dispersion to overall performance is negligible. Liow (1986) showed that, for his experimental apparatus which was 0.987 m long and has an internal diameter of 0.073 m with a mean particle size of 1.77 mm, the importance of axial dispersion increased as the pressure increased for a given fluid superficial velocity. Hence a mass transfer model with axially dispersed plug flow was compared with his experimental results.

2.5.3 Adsorption Equilibrium

The selection of a suitable adsorbent for a given separation is a complex problem. Normally the selection is based on the shape of the adsorption
isotherm, the adsorbent capacity at the appropriate operating conditions and the pore size distribution. The method of adsorbent regeneration is also an important factor. Often the method of regeneration is also determined by the shape of the isotherm.

An adsorption isotherm expresses the equilibrium relationship between the adsorbed and gas phase concentrations for a pure gas, or gas mixture, at constant temperature. Many different types of equilibrium isotherm have been measured experimentally. Similarly, many theories have been proposed, examples of which are the Langmuir, Gibbs and the potential theories. A summary of the derivation of each approach has been given by Young (1987). The most common non-linear isotherm used in PSA theories is the Langmuir Isotherm.

Langmuir first developed his adsorption theory in 1916. The Langmuir isotherm is derived from the assumption that the adsorption system is in dynamic equilibrium, where the rate of adsorption equals the rate of desorption. The theory also assumes that all the vacant sites on the adsorbent are energetically equivalent, each site can hold only one adsorbate molecule and there is no lateral interaction between neighbours.

An extension of Langmuir to a multilayer theory was developed by Brunauer, Emmett, and Teller (1938). However, the BET equation is not used in PSA because vapour pressures in PSA rarely approach the saturated vapour pressure.

In multicomponent systems, the isotherm for a given component may not only
be a function of the partial pressure of that component but may also depend on the partial pressures of the other adsorbable species in the gas phase. To take into account the competition between the various adsorbable species present, a co-adsorption theory based on Langmuir has been developed. This co-adsorption theory has also been used in some PSA models, for example Hassan et al (1986). To predict the co-adsorption effect in their model, the statistical thermodynamics approach by Ruthven, Loughlin and Holborrow (1973) was used.

For the DCPSA model, three isotherm equations were used:

1) the linear isotherm,

2) the Langmuir pure gas isotherm and,

3) the Langmuir co-adsorption isotherm.

Like most PSA models, the presences of argon, water and carbon dioxide are ignored in the DCPSA model due to their insignificant volumes. Furthermore, argon behaves in a similar manner to oxygen or nitrogen depending on the type of adsorbents used.

2.5.4 Mass Transfer

When a fluid passes over a porous adsorbent, mass transfer occurs between the gas and solid phases which involves the diffusion across the external gas film to the surface of the particle, followed by transport within the porous structure of the particle.
There have been many mathematical models developed to describe the diffusion into porous adsorbents. Bono (1989) has broadly classified them into lumped parameter and diffusion models and gave a detailed review of each of them.

In lumped parameter models, all the mass transfer resistances experienced during the adsorption process are lumped into a single overall mass transfer parameter. In this case the mass transfer driving force is expressed in terms of the difference in the adsorbate concentration between the bulk fluid and the mean concentration inside the adsorbent pellets. Diffusion models describe the transport in terms of individual diffusion mechanisms, whether they are the solid diffusion, surface diffusion, macro- and micro- pore diffusion or the combination of these. Diffusion models require adsorbate concentration to be a function of position within the pellets.

Both the lumped parameter and the diffusion transport mechanism assumptions have been used in PSA modelling. Liow (1986) has accounted for pore diffusion in his model and compared his model results with Kirkby’s (1983) ILE model. The improvement of Liow’s model over Kirkby’s model on qualitative and quantitative agreement with experiment results has suggested the possible importance of mass transfer limitations in oxygen production using zeolites.

Although complicated and more realistic, diffusion equations can be used for kinetically controlled PSA systems, the normal approach for taking mass transfer limitations into account in PSA modelling is to use the lumped
parameter as the overall mass transfer coefficient, $K_{eq}$, and assume a linear driving force (LDF) between the bulk gas and the adsorbed phase. This is a compromise between the level of theoretical detail and the practicality of measuring the model parameters reliably and accurately. Young (1987) commented that, for a binary gas separation process, pore diffusion is not important unless the parameter $D_{e}t/r^2$ is below the threshold value of 100, which is not the case for adsorption separation under industrial operating conditions. $D_{e}$ is the adsorbent effective diffusivity, $t_c$ is the total cycle time and $r_p$ is the adsorbent pellet radius.

Bono (1989) has pointed out that there are different types of lumped parameter model depending on the assumptions used to describe the actual linear driving force involved. An example is the work of Glueckauf (1955), where only the internal solid mass transfer was considered. This system can be expressed as:

$$\frac{\partial q_i}{\partial t} = K_{f}a \left( q_{i}^{s} - \bar{q}_i \right) \quad (2.1)$$

where $q_{i}^{s}$ is the adsorbate concentration of component i at solid surface, $t$ is the time of adsorption, $a$ is the external area for mass transfer per unit volume, $\bar{q}_i$ is the mean amount of component i adsorbed within the solid, and $K_f$ is a pseudo-film mass transfer coefficient.

The model is completed by coupling the fluid and solid concentrations at
the particle surface through the adsorption isotherm. Glueckauf (1955) has shown that for spherical particles the above equation with \( K_S = 15D_e / r_p \), where \( D_e \) is the effective pore diffusivity and \( r_p \) is the particle radius, gives an accurate approximation of Fickian diffusion for adsorbates with linear or mildly non-linear isotherms. A detailed discussion on the LDF is also given by Young (1987).

In CMS processes two principal resistances will contribute to the overall resistance,

1) the external film resistance, \( k_e \) (which is dependent on the local particle Reynolds number), and,

2) the intra-particle diffusional resistances, \( k_i \) (which will not be dependent on the local fluid velocity).

These two resistances can be combined to produce a single overall mass transfer resistance (see Appendix A for detail derivation of the lumped parameter LDF model).

There are many semi-empirical correlations which combine all the resistances into a single mass transfer coefficient, for example, Wilson and Geankopolis (1966) and Wakao and Funakiri (1978). These lumped models can be used to include the external film mass transfer. In the case of Wakao and Funakiri (1978), axial dispersion is also included in their lumped mass transfer parameters.

Nakao and Suzuki (1983) showed that during steps in which pressure changes, the overall mass transfer rate was dependent on the process cycle times
used and suggested empirical cyclic correction factors to the overall mass transfer coefficient. Hassan et al (1986), adopted the use of correction factors for their LDF model to fit their model to their experimental results. However, their application of these correction factors was not fully justified because they adopted the frozen solid assumption for their pressure-changing steps.

Although most of the kinetically controlled models in PSA assumed mass transfer resistances to be totally diffusion controlled, LaCava, Dominguez and Cardenas (1988), claimed that diffusion alone was inadequate to predict the uptake of some gases on CMS. They proposed a different type of mechanism where the gas molecules had to first cross an energy barrier before entering the micro-pore cavity. A modified Langmuir kinetic expression was found to be a good approximation to their experiments for some conditions. The disadvantage of this model is the need to know more process parameters, such as the activation energy and the average heats of adsorption.

2.5.5 Heat Transfer

Most PSA models ignore the energy balance and assumed isothermal operation. For a large plant where the variation of temperature at a fixed point in the column can exceed 100 K [Young (1987) and Espitalier-Noel (1988)], the inclusion of an energy balance is clearly essential. A temperature variation of up to 25 K was observed by Espitalier-Noel for his laboratory experiment on air separation using zeolite adsorbent. However, no obvious
trends were observed in the variation of plant performance with a changing process temperature.

Young and Cen (1986) have shown that, for a steady state PSA separation of 50/50 % \( \text{H}_2/\text{CO} \) with activated carbon, the best separation occurs under the hypothetical isothermal condition where 90.79% of CO is recovered compared to the worst separation achieved by adiabatic operation where only 78.96% of CO was recovered.

Although Chihara and Suzuki (1983) have presented a model on non-isothermal PSA for air drying by activated aluminium, no attempt has been made to compare their simulation results with other models on the same PSA process but with an isothermal assumption.

The heat of adsorption on zeolites is generally higher than that on carbon because of both the electrostatic and Van de Waals forces. For adsorbers filled with CMS, there is no report of noticeable temperature variation nor is there any evidence in the literature of the effect temperature variation. The model for present research has therefore assumed isothermal operation.

### 2.6 Historical Development in PSA Modelling

A PSA model, in general is derived from a set of convective mass balance, heat balance, mass transfer rate and gas-solid equilibrium isotherm equations. These form a set of coupled partial differential equations
(PDEs) and algebraic equations. PSA models in the literature have usually been solved by one of the following techniques:

1) analytical [Shendalman and Mitchell, (1971)],
2) explicit finite difference [Mitchell and Shendalman, (1973)],
3) finite elements or cell models [Flores-Fernandez, (1978)],
4) the Method of Characteristics [Kirkby, (1983)],
5) orthogonal collocation [Liow, (1986)], and
6) double collocation method [Hassan et al, (1986)].

Shendalman and Mitchell (1971) have developed an idealised equilibrium model which yields an analytical solution. A two bed Skarstrom cycle was used to purify a feed mixture of 1.09% CO\textsubscript{2} in He by adsorbing CO\textsubscript{2} onto silica gel. The model considered the complexities of pressure-changing steps. However, because these steps only occupy small fractions of the total cycle time, and depend only on initial and final states, these steps were considered to be instantaneous. The Method of Characteristics was used to reduce the partial differential mass balance equation to a pair of ordinary differential equations. The model consistently overpredicted the product concentration by 30% when compared with the experimental results. This overprediction was attributed to the use of linear isotherms and it was suggested that mass transfer processes and dispersion may be important.

Turnock and Kadlec (1971) have formulated a numerical model for a single bed process. The bed was packed with 5A zeolites for nitrogen production from a 28.6% nitrogen in methane mixture. The model was based on the
assumption of instantaneous equilibrium with Freundlich isotherms. The model also considered axial pressure gradients through the use of Darcy's Law. The axial pressure gradient was included because of the rapid cycling (below 20 sec.) and the use of fine zeolite particles (42-60 mesh). In addition, the separation factor between the two components was kept constant and the total amount adsorbed was independent of the gas composition. A finite difference method was used to solve the overall material balance equation, while the component balance equations were evaluated by the Method of Characteristics. The simulated product quality was found to agree better with the experimental result at 273 K than at 203 K. Later Kowler and Kadlec (1972) included a purge step in the study and turned it into an optimisation problem. The objective function was a time averaged product concentration.

Mitchell and Shendalman (1973) were the first to publish a numerical model for the Skarstrom cycle. The aim was to reconcile the large difference between the experimental data and their equilibrium theory. Finite mass transfer rates were assumed for the constant pressure steps. The mass transfer rate coefficients were assumed to be constant and independent of pressure. However, for the pressure-changing steps two limiting cases were considered:

1) due to rapid cycling, no gas-solid exchange is allowed (i.e the frozen solid assumption), and
2) instantaneous gas-solid equilibrium is retained.

The Method of Characteristics, in conjunction with finite differences, was used in the solution method. The model clearly shows that the frozen solid assumption predicts much less separation than is actually achieved,
whereas the equilibrium assumption predicts more separation. The predictions of the equilibrium assumption are, however, much closer to the experimental results.

Weaver and Hamrin (1974) described an algebraic model for the process involving the separation of 5.5% deuterium in a hydrogen feed mixture. The model assumed instantaneous gas-solid equilibrium. One major limitation to the model is that the total volume of the gas streams entering and leaving the beds in all steps must be known. And these volumes are assumed to be independent of the cycle number. The model also did not take into account the pressure-changing steps. The experiment and the model agreed to within 20–30%.

Sebastian (1975) included an axial pressure gradient in his model which was developed for the air/5A zeolite system. The Ergun Equation was used to determine this pressure gradient. Sebastian also demonstrated that when an explicit finite difference method was used, marching instabilities can occur in the solution. When using a backward difference method for the depressurisation step, the solution became very stable. However, a second level of iteration was used to minimise the error at a boundary condition.

Waddoups (1975) derived a mass transfer model for a two bed nitrogen/helium PSA system. The feed concentration consisted of 2 to 10% N₂ in He by volume. Activated carbon produced from coconut shells by Sutcliffe Speatman Limited was used as the adsorbent. The model also considered the heat effects generated in the adsorbent during adsorption and desorption.
When the experimental results were compared to a simplified isothermal model, the model fitted the experimental results satisfactorily at low $N_2$ concentration but not when the feed $N_2$ concentration was high.

Flores-Fernandez (1978) and Flores-Fernandez & Kenney (1983) applied equilibrium theory to PSA air separation. Both $O_2$ and $N_2$ are considered adsorbable gases on 5A zeolite. The adsorption of $N_2$ was assumed to follow the Langmuir isotherm, whereas the $O_2$ isotherm was linear, and the two were independent. The model also described the pressurisation step. Two methods of solution were used, the cell model and the Method of Characteristics. The Method of Characteristics was used when both $O_2$ and $N_2$ isotherms were assumed to be linear. The formation of concentration discontinuities were also discussed. The comparison between experiment and theory shows that the gas-solid equilibrium is nearly reached during the rapid pressurisation of the zeolite bed. Large amounts of nitrogen and oxygen are transferred rapidly to the adsorbed phase. The failure of the frozen solid assumption during bed pressurisation is clearly demonstrated by these results.

Chan, Hill and Wong (1981) extended the original Shandelman and Mitchell analytical solution, from a single adsorbable component in an inert carrier to a binary adsorbable feed mixture. A more detailed solution for effluents from all steps was obtained. Their analytical solution reduces to that of Shandelman and Mitchell when the Henry's constant for the carrier gas is zero. The model also considered the pressure-changing steps.
Chihara and Suzuki (1983) proposed a non-isothermal, non-equilibrium model. The model was based on air drying on activated alumina. A single adsorbable component in an inert carrier gas was assumed. The model also assumed a frozen solid during pressure-changing steps. In addition, thermal equilibrium was assumed between the gas and solid. The adsorption equilibrium coefficients of the linear isotherms were considered to be temperature dependent. For this linear driving force model, the implicit Crank-Nicolson method [Davis, (1984)] was used. The model fitted well with the experimental result obtained for air drying on silica gel [Chihara and Suzuki, (1983)], but the mass transfer coefficients are two to three times higher than those measured independently. These mass transfer coefficients were estimated by a method developed by Nakao and Suzuki (1983), where the mass transfer rate was shown to be dependent on the cycle time used. The use of empirical cyclic correction factors to the mass transfer coefficients were suggested.

Raghavan, Hassan and Ruthven (1985) have presented a model that includes axial dispersion. The model also considered the kinetic effect where the mass transfer coefficients are a function of column pressure. This was later extended to consider adsorption of a single trace component without velocity variation. In both cases, adsorption during the pressure-changing steps was ignored. The method of orthogonal collocation was used to reduce the derived PDEs to sets of ODEs. Later, a model for kinetically controlled bulk gas separation using BF CMS on a four step PSA purge cycle was developed [Raghavan and Ruthven (1985)]. The model assumed linear isotherms. In this case, the rate coefficient for the linear driving force expressions is the same for the two constant pressure
steps. This is a reasonable assumption for a system in which micro-pore diffusion is the dominant mass transfer resistance. For the pressure-changing steps, two further assumptions were assumed:

1) at the end of depressurisation, the concentration of the separating gases (O₂ and N₂) along the bed, is calculated by multiplying the bed concentration by the pressure ratio, and

2) the solid phase concentrations remain frozen.

If the orthogonal collocation method was used, the derived model would result in a system of ordinary differential equations coupled with a system of non-linear algebraic equations. Such a combination of equations may lead to stiffness (see Chapter 4 for definition) and stability problems. Therefore the method of double collocation was applied so that all the equations would be reduced to a large set of algebraic equations. Hassan et al (1986) further extended this model by allowing for non-linear isotherms.

Liow (1986) has proposed a model for oxygen enrichment from air on 5A zeolites. Mass transfer resistance and co-adsorption effects were included. These assumptions are rather unusual for a system where the rates of adsorption are so extremely fast. The isotherms were based on ideal adsorption solution theory (IAST) and could simulate systems with up to four beds. An orthogonal collocation method was used to solve the model, and the model was shown to have good agreement with experimental results.

Cen and Yang (1985 & 1986) and Doong and Yang (1986 & 1987) have reported a number of PSA models [refer to Yang, (1987)]. They include models with a
linear driving force (LDF) as well as mono-disperse (for adsorbent such as activated carbon) and bi-disperse pore diffusion (for zeolite adsorbents). Instantaneous thermal equilibrium between gas and solid was used in these models. The rate coefficients of the LDF model were considered to be fitted parameters. The pore diffusion model was simplified by assuming a parabolic concentration profile within the solid particles. Thus no integration was required along the radial coordinate in the particles. An implicit finite difference method was used to solve the LDF model. When the LDF model was used for a four steps cycle separating a five components mixture, the computation time for each cycle was up to 10 minutes on a VAX 780. When the mono-disperse model was used for a binary mixture separation based on a five steps cycle, much lower computational times of approximately 1 minute per cycle were required. In the bi-disperse model, the inclusion of the micro-pore diffusion made the system of equations stiff. A finite difference scheme was used to reduce the system of PDEs to ODEs. An Euler integration technique for the ODEs was attempted but found inadequate due to the small time steps required for a stable solution. A variable order, variable step Gear's routine was thus used [Gear, (1971)].

Alpay (1992) has developed a new hybrid method called orthogonal collocation on finite elements, for solving his PSA model. This method avoids the use of high order polynomials when dealing with stiff systems.
2.7 Conclusion

Since the commercial development of PSA, the use of adsorption separations in the chemical industries has become increasingly popular. The need for a theoretical understanding of PSA processes has therefore become increasingly important. Furthermore, the search for optimal operation has led to a number of complicated cycle configurations. This means accurate, robust and flexible models are required. Despite the increase in the speed and the reduction in costs of computers, the resulting sets of stiff differential equations still require efficient numerical integration techniques.

The earlier mathematical models were based on equilibrium theory and the effects of mass transfer resistance were ignored. The validity of equilibrium theory has been confirmed experimentally for air separation on a 5A zeolite by Flores-Fernandez and Kenney (1983). However, as for adsorption of CO₂ on silica gel and air separation on a carbon molecular sieve, kinetic effects were found to be an important factor. Furthermore, the equilibrium theory is restricted to a system where the separation depends on a difference in adsorption equilibrium. This is clearly not the case for air separation on CMS where the adsorption equilibria of O₂ and N₂ are almost identical.

In the earlier models, although it was appropriate for the systems it was applied to, the adsorbable component was assumed to be present only at low concentration in an inert carrier. The gas velocity is thus regarded as constant along the length of the column during product release and purge.
This assumption is certainly not applicable to air separation on CMS adsorbent, because the variation in the gas velocity due to adsorption is significant.

The model by Hassan et al (1986) on air separation using a CMS adsorbent is of particular interest to the present research. However, this model includes a frozen solid assumption for the pressure-changing steps. Furthermore, the linear mass transfer rate coefficients recommended by Nakao and Suzuki (1983) are only applicable when the PSA system reaches steady state.

This research aims to derive a more accurate and robust model in view of the increasing demand of PSA air separation to produce nitrogen. The lack of literature for models on this process also encourages the simulation of a number of the more complicated cycle configurations which are currently in use.

The theory of this model is detailed in Chapter 3. Chapter 4 presents the application of Implicit Euler to the Method of Characteristics for a PSA model and its advantages over the commonly used explicit integration techniques.
CHAPTER 3

THEORY

3.1 Introduction

This chapter lists the assumptions used for the Diffusion Control Pressure Swing Adsorption (DCPSA) model. Some of these assumptions were discussed in Chapter 2. A detail derivation of the model using these assumptions is also included. The method of solution used for solving the model is presented in Chapter 4.

3.2 Model Assumptions

The important assumptions made in the development of this model, are summarised below:

1) the feed gas consists of two adsorbable components with no inerts present,
2) the gas phase follows the ideal gas behaviour,
3) the process operates isothermally,
4) the gas passes through the columns in plug flow,
5) axial dispersion may be neglected,
6) radial diffusion and wall effects may be ignored,
7) there is no pressure drop across the column,
8) a lumped parameter, linear driving force is applicable for mass transfer between the gas and adsorbed phases,
9) linear, Langmuir pure gas and Langmuir binary co-adsorption isotherms may be used to describe the adsorption equilibria, and 10) the columns are completely and uniformly filled with identical spherical adsorbent particles.

3.3 Derivation of Model Equations

Figure 3.1 below shows the essential terms and geometry for the convective mass balances which can be written for oxygen (component A) and nitrogen (component B). All the variables used below are described in the nomenclature list.

\[
\begin{align*}
\theta_0 & \rightarrow \theta_p A \rightarrow \theta_p A + \frac{\partial(\theta_p A)}{\partial z} \delta z \rightarrow \theta_L \\
\kappa & \\
\phi & \rightarrow L \\
\n\end{align*}
\]

note that, \( \theta \) represent the volumetric flow rate at pressure \( P \) and \( p_A \) represent the oxygen partial pressure.

Figure 3.1
Based on a molar flow rate (kmol s\(^{-1}\)), the material balance for component A over an element in the column gives,

Amount In = Amount out + Accumulation wrt time + Rate of adsorption in gas phase

\[
\frac{\partial q_A}{RT} = \left[ \frac{\partial p_A}{RT} + \frac{\partial}{\partial z} \left( \frac{\partial p_A}{RT} \right) \right] \delta z + \frac{\partial}{\partial t} \left( \frac{A \varepsilon \delta z}{RT} \right) + A \omega \delta z \frac{\partial q_A}{\partial t} \tag{3.4}
\]

which on collecting terms gives,

\[
\frac{\partial (\phi p_A)}{\partial z} + A \varepsilon \frac{\partial p_A}{\partial t} + A \omega RT \frac{\partial q_A}{\partial t} = 0 \tag{3.5}
\]

Similarly for nitrogen (component B) balance,

\[
\frac{\partial (\phi p_B)}{\partial z} + A \varepsilon \frac{\partial p_B}{\partial t} + A \omega RT \frac{\partial q_B}{\partial t} = 0 \tag{3.6}
\]

Addition of Equations (3.5) and (3.6) will yield the following mass balance equation,

\[
\frac{\partial \varnothing}{\partial z} = - \left[ A \omega p' + \frac{A \omega RT}{P} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \right] \tag{3.7}
\]

where \( p' = \frac{1}{P} \frac{\partial P}{\partial t} \)

Note that Equation (3.7) may also be obtained purely by an overall mass balance on the original element of the column.

The equation obtained from the difference between Equation (3.5) and Equation (3.6) is,

\[
\frac{\varnothing}{\partial z} + \frac{\partial p_A}{\partial t} = \frac{p_A p'}{\varepsilon} + \frac{\omega RT}{P} \left[ \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right] \frac{\partial q_A}{\partial t} \tag{3.8}
\]
As discussed in Section 2.5.3 and Appendix A, the simplest non-equilibrium theory for adsorption uses a lumped parameter, linear driving force expression as follows:

for oxygen

$$\frac{\partial q_A}{\partial t} = K_{GA} a (p_A - p_A^*)$$

(3.9)

and for nitrogen

$$\frac{\partial q_B}{\partial t} = K_{GB} a (p_B - p_B^*)$$

(3.10)

where $p_A^*$ and $p_B^*$ are the partial pressures in equilibrium with the adsorbed phase.

For linear isotherms, $p_A^*$ and $p_B^*$ can be expressed as:

$$p_A^* = \frac{q_A}{k_{A1}}$$

(3.11)

and

$$p_B^* = \frac{q_B}{k_{B1}}$$

(3.12)

For the pure gas Langmuir Isotherm,

$$q_A = \frac{A_m k_{A2} p_A^*}{1 + k_{A2} p_A^*}$$

(3.13)

and

$$q_B = \frac{B_m k_{B2} p_B^*}{1 + k_{B2} p_B^*}$$

(3.14)

where $q_A$ and $q_B$ are defined as the amount of component A and B adsorbed at equilibrium respectively. Also $k_{A1} = k_{A2} q_{A_m}$ and $k_{B1} = k_{B2} q_{B_m}$.
where \( k_{A1} \) and \( k_{B1} \) are the Henry's Law constants and \( k_{A2} \) and \( k_{B2} \) are the Langmuir isotherm constants.

In this case \( p_A^* \) and \( p_B^* \) can be expressed as:

\[
p_A^* = \frac{q_A}{k_{A1} - k_{A2} q_A} \tag{3.15}
\]

and

\[
p_B^* = \frac{q_B}{k_{A1} - k_{B2} q_B} \tag{3.16}
\]

However, if Langmuir binary isotherms (with co-adsorption) are assumed, then

\[
q_A = \frac{q_{A1} k_{A2} p_A^*}{1 + k_{A2} p_A^* + k_{B2} p_B^*} \tag{3.17}
\]

and

\[
q_B = \frac{q_{Bm} k_{B2} p_B^*}{1 + k_{A2} p_A^* + k_{B2} p_B^*} \tag{3.18}
\]

\( p_A^* \) and \( p_B^* \) can then be expressed as:

\[
p_A^* = \frac{q_A k_{B1}}{k_{A1} b_{B1} - q_A k_{A2} b_{B1} - q_A k_{B2} b_{A1}} \tag{3.19}
\]

and

\[
p_B^* = \frac{q_B k_{A1}}{k_{A1} b_{A1} - q_A k_{A2} b_{A1} - q_A k_{B2} b_{A1}} \tag{3.20}
\]

The basic equations to be solved for this research are from Equation (3.7) to Equation (3.10) with the appropriate isotherm equations used (Equation (3.11) to Equation (3.20)). Details of the intermediate algebra for the
derivation of Equation (3.7) and Equation (3.8) are shown in Appendix B.

Hence, the resulting DCPSA model from the above derivation consists of four partial differential equations (PDEs) which have four dependent variables, \( \theta, p_A, q_A \) and \( q_B \). Each of these dependent variables is a function of two independent variables, distance, \( z \) and time, \( t \). The total pressure, \( P \), will be specified as an algebraic function of time for the pressure changing steps, and assumption (1), above implies,

\[
P = p_A + p_B
\]

(3.21)

It should be noted that Equations (3.9) and (3.10) may be directly substituted into Equations (3.7) and (3.8), therefore these equations are a set of inhomogeneous, non-linear, first order, partial differential equations, for which there exists a variety of techniques for their numerical solution, which will be discussed in Chapter 4.

3.4 Classification of the Partial Differential Equations

The best way to classify a system of first order PDEs is to develop the concept of characteristics [Ames, (1977)].

Let the coefficients \( a_1, a_2, a_3, a_4, \ldots, i_1, i_2, i_3, i_4 \) be functions of \( z, t, \theta, q_A, q_B \) and \( p_A \). Consider the simultaneous first order quasilinear system (a quasilinear system of equations is one in which the highest order derivatives occur linearly) which represents the problem encountered by the DCPSA model:
When compared to Equations (3.7) to (3.10), the coefficients become:

\[ a_1 = 1, \quad b_1 = 0, \quad c_1 = 0, \quad d_1 = \frac{A\omega RT}{P}, \quad e_1 = 0, \]
\[ a_2 = 0, \quad b_2 = 0, \quad c_2 = 0, \quad d_2 = -\frac{\omega RT}{\epsilon} \left( \frac{p_A}{P} - 1 \right), \quad e_2 = 0, \]
\[ a_3 = 0, \quad b_3 = 0, \quad c_3 = 0, \quad d_3 = 1, \quad e_3 = 0, \]
\[ a_4 = 0, \quad b_4 = 0, \quad c_4 = 0, \quad d_4 = 0, \quad e_4 = 0, \]
\[ f_1 = \frac{A\omega RT}{P}, \quad g_1 = 0, \quad h_1 = 0, \quad i_1 = -A\omega p', \]
\[ f_2 = -\frac{\omega RT}{\epsilon} \frac{p_A}{P}, \quad g_2 = \frac{\sigma}{A\epsilon}, \quad h_2 = 1, \quad i_2 = p_A p', \]
\[ f_3 = 0, \quad g_3 = 0, \quad h_3 = 0, \quad i_3 = K_{GA} \left( p_A - p_A^* \right), \]
\[ f_4 = 1, \quad g_4 = 0, \quad h_4 = 0 \quad \text{and} \quad i_4 = K_{GB} \left( p_B - p_B^* \right). \]

Assume that the solutions for \( \phi, \quad q_A, \quad q_B \) and \( p_A \) are known from the initial state to some curve \( \Gamma \) (assuming discontinuities do not occur). Then at any boundary point \( X \) of this curve, the continuously differentiable values of \( \phi, \quad q_A, \quad q_B \) and \( p_A \), and their directional derivatives in directions below the curve are known.
Hence, if the solution just above \( X \) is uniquely determined by the information below and on the curve \( \Gamma \), and \( \phi_z, \phi_t, q_{Az}, q_{At}, q_{Bz}, q_{Bt}, p_{Az}, p_{At} \) are also known, then at \( X \) we have eight relations, Equations (3.22) to (3.25) and

\[
\begin{align*}
\phi &= \phi_z dz + \phi_t dt \\
q_A &= q_{Az} dz + q_{At} dt \\
q_B &= q_{Bz} dz + q_{Bt} dt \\
p_A &= p_{Az} dz + p_{At} dt
\end{align*}
\]  

whose matrix form is

\[
\begin{bmatrix}
a_1 & b_1 & c_1 & d_1 & e_1 & f_1 & g_1 & h_1 \\
a_2 & b_2 & c_2 & d_2 & e_2 & f_2 & g_2 & h_2 \\
a_3 & b_3 & c_3 & d_3 & e_3 & f_3 & g_3 & h_3 \\
a_4 & b_4 & c_4 & d_4 & e_4 & f_4 & g_4 & h_4 \\
dz & dt & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & dz & dt & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & dz & dt & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & dz & dt
\end{bmatrix}
\begin{bmatrix}
\phi_z \\
\phi_t \\
q_{Az} \\
q_{At} \\
q_{Bz} \\
q_{Bt} \\
p_{Az} \\
p_{At}
\end{bmatrix}
= 
\begin{bmatrix}
in_1 \\
in_2 \\
in_3 \\
in_4 \\
d\phi_z \\
dq_A \\
dp_A
\end{bmatrix}
\]  

By equating the determinant of the matrix in Equation (3.30) to zero and substituting the coefficients as described above, we have the following characteristic equation,

\[
-(dz)^2 + \frac{\theta}{Ac} (dz \ dt) + 0 (dt)^2 = 0
\]  

which is a quadratic equation in \( dz/dt \). If the curve \( \Gamma \) at \( X \) has a slope such that Equation (3.31) is satisfied, then the derivatives \( \phi_z, \phi_t, q_{Az}, q_{At}, q_{Bz}, q_{Bt}, p_{Az}, p_{At} \) are not uniquely determined by the
values of $\theta$, $q_A$, $q_B$ and $p_A$ on $\Gamma$. The directions specified by Equation (3.30) are called characteristic directions; they may be real and distinct, real and identical, or real according to whether the discriminant

$$\left( \frac{\theta}{\Delta e} \right)^2 - 4 \epsilon_1 x_0$$

is positive, zero, or negative. This is the criterion for classifying a system of equation as hyperbolic, parabolic, or elliptic. They are hyperbolic if Equation (3.32) is positive — that is, has two real characteristic directions; parabolic if Equation (3.32) is zero; and elliptic if there are no real characteristic directions. In this instant, it is clear that Equation (3.32) is positive and therefore the derived set of PDEs for the DCPSA model is a hyperbolic system.

3.5 Conclusion

This chapter has derived a set of partial differential equations (PDEs), which will be used to represent diffusion controlled pressure swing adsorption. The derived set of PDEs is classified as a hyperbolic system.

Since oxygen and nitrogen are known to diffuse at very different rates in BF CMS, these equations are likely to pose difficult problems for a numerical solution scheme. Chapter 4 describes the development of a numerical method capable of solving this problem.
4.1 Introduction

The aims of this chapter are:
1) to discuss the different types of method of solution that have been considered and used in the modelling of DCPSA,
2) to give a detailed discussion on the different types of integration technique used with the Method of Characteristics, and
3) to demonstrate the application of Implicit Euler integration along the characteristics for the DCPSA model.

4.2 Method of Solution

The model of diffusion controlled pressure swing adsorption process is a system of partial differential equations (PDEs), which is derived from a set of mass balance, mass transfer rate and equilibrium isotherm equations, as discussed in Chapter 3. This set of PDEs does not have an analytical solution and must be solved by a numerical technique. In general, a system of PDEs that needs a numerical solution may either be solved by the of finite difference methods (e.g. Method of Lines and Crank-Nicolson), orthogonal collocation, the Method of Characteristics or by finite elements. The choice of a suitable method is highly dependent on the type of the PDEs, which may be classified as either hyperbolic,
parabolic or elliptic [Ames, (1977)], (see Section 3.4).

The Crank-Nicolson method is useful for solving parabolic equations and has been widely used in chemical engineering problems, for example, when dispersion terms are incorporated with mass and heat balance equations. The finite element, or cell method, of solution is widely used in elliptic systems. The Method of Characteristics can be used only on hyperbolic systems. Section 2.6 of Chapter 2 has reviewed the application of different types of method of solution to PSA modelling. Two methods have been used concurrently to solve the DCPSA model: the Method of Lines and the Method of Characteristics. The following section gives a more detailed discussion of these two methods.

4.2.1 Application of the Method of Lines

The Method of Lines has been successfully used in many systems of parabolic PDEs. A recent example of which is its application in the study of diffusive transport across synthetic membranes [Bansal (1988)]. The Method of Lines works on any system in which there are N independent variables, by discretizing the derivatives of any N-1 of these variables, leaving ordinary differential equations (ODEs) in the Nth variable [Davis, (1984)]. In Bansal's work, this method first involves the discretisation of the spatial derivatives, which transforms the PDEs into a set of coupled ODEs in the time domain which can be integrated simultaneously. Several powerful software packages, such as DSS/2 [Schissler, (1976)] are available for this method of solution. The spatial discretisation for DSS/2 is also by finite differences. There is, however, more than one
integration technique available in the time domain, such as the Runge-Kutta and the variable order, variable step length method due to Gear (1971).

Although there were real doubts as to whether the finite difference method could cope with the very high rate of adsorption encountered by the DCPSA model, the Method of Lines was used to attempt to solve the system of PDEs, using DSS/2. The reasons for trying DSS/2 were:

1) to see if it was a possible method of solution for the hyperbolic system of PDEs derived in Chapter 3, and
2) to save writing complete software from scratch if the method is feasible.

The PDEs, Equations (3.8), (3.9) and (3.10), of DCPSA model were first spatially discretise using the classical N point, forward finite difference approximation to obtain the following system of ordinary differential equations in the Nth variable, which is denote by subscript (N):

\[
\frac{\vartheta_{(N)}}{\Delta \epsilon} \left( \frac{p_{A(N)} - p_{A(N-1)}}{\Delta z} + \frac{\partial p_{A(N)}}{\partial t} \right) = p_{A(N)}^{\prime} p_{(N)}^{\prime} + \\
\frac{\omega RT}{\epsilon} \left[ \frac{p_{A(N)}}{P} \left( \frac{\partial q_{A(N)}}{\partial t} \right)_{(1)} + \frac{\partial q_{B(N)}}{\partial t} \right] - \frac{\partial q_{A(N)}}{\partial t} \right]_{(1)}
\]

(4.1)

\[
\frac{\partial q_{A(N)}}{\partial t} \left|_{(1)} = K_{GA} a \left( p_{A(N)} - p_{A(N)}^{*} \right) \right.
\]

(4.2)
where $\Delta z$ is the spatial interval, $(z^N - z^1)/(N - 1)$.

The resulting ODEs system were then solved by the Gear's method.

The system of Equations (4.1) to (4.3) did pose some problems when attempting a solution under DSS/2. Equation (4.2) and Equation (4.3) present no problems and may be evaluated first. Equation (4.1) requires that $\frac{dp_A}{dz}|_{(1)}$ and the volumetric flow rate, $\phi^{(N)}$, are known. $\frac{\partial \theta}{\partial z}$ of Equation (3.7) can be calculated as $\frac{dq_{A(N)}}{dt}|_{(1)}$ and $\frac{dq_{B(N)}}{dt}|_{(1)}$ have already been found from Equations (4.2) and (4.3). For the pressurisation step, the flow rate at the closed end of the column is zero, so it is possible knowing $\frac{\partial \theta}{\partial z}$ for all $z$ to integrate backwards from the closed end of the column to obtain $\theta$ for all $z$. This integration was carried out by using a trapezoidal rule algorithm. $\frac{dp_A}{dz}|_{(1)}$ can be approximated since $p_A|_{(1)}$ is known for all $z$, as $p_A|_{(1)}$ is the solution to the integration of Equation (4.1) from the previous time step.

DSS/2 provides a number of routines for approximating the derivatives of a function by finite difference methods of varying orders of accuracy. In this case a five point (i.e $N = 5$) forward differencing method was employed.

Each point in the column is described by the three coupled ODEs (Equations (4.1), (4.2) and (4.3)) derived from Equations (3.8), (3.9) and (3.10). Supposing the column is to approximated by 100 points along its length then...
a system of 300 ODEs needs to be solved simultaneously, which can be very time consuming.

DSS/2 requires that three FORTRAN subroutines be provided which will:
1) set the initial conditions (INITIAL),
2) calculate the derivatives (DERV), and
3) print the results of the calculation as the integration progresses. (PRINT)

DSS/2 first calls INITIAL to set up the initial conditions and then calls DERV repeatedly to calculate the new temporal derivatives as the integration proceeds. PRINT is called at intervals specified by the user. An extra routine PRPLOT was added so that the progress of the solution could be followed graphically.

This attempt to solve the pressurisation step of the DCPSA model using DSS/2 was unsuccessful because the final integration scheme became unstable and did not converge.

The main reason for the instability is because of the stiffness (Section 4.3.3) in the equations resulting from the differences in the rates at which \( q_A \) and \( q_B \) can change. The hyperbolic equations in the model can give rise to shock waves (discontinuities in the values of the variables or their derivatives), hence finite difference approximations for \( \frac{\partial p}{\partial z} \), even at high order, will give rise to errors.

At this stage the Method of Lines was abandoned in favour of the Method of Characteristics as described below.
4.2.2 Application of the Method of Characteristics

A characteristic is a path or trajectory in the independent variable space for which a partial differential equation is reduced to ordinary differential equations. Lapidus (1962) showed that real characteristics arise only from hyperbolic PDEs.

To identify the characteristics of the system of PDEs derived in Chapter 3, consider a bivariate function \( f(z,t) \), where its total derivative with time is

\[
\frac{Df}{Dt} = \frac{\partial f}{\partial z} \frac{dz}{dt} + \frac{\partial f}{\partial t}
\]

(4.4)

and its total derivative with distance is

\[
\frac{Df}{Dz} = \frac{\partial f}{\partial z} + \frac{\partial f}{\partial t} \frac{dt}{dz}
\]

(4.5)

By comparing Equations (3.8), (3.9) and (3.10) with Equation (4.4) and Equation (3.7) with Equation (4.5), the hyperbolic PDEs may be reduced into eight ODEs as follows:

\[
\frac{dp_A}{dt} = p_A \rho' + \frac{\omega RT}{c} \left[ \frac{p_A}{P} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) - \frac{\partial q_A}{\partial t} \right]
\]

(4.6)

\[
\frac{dz}{dt} = \frac{\theta}{A\epsilon}
\]

(4.7)
\[
\frac{dq_A}{dt} = K_{GA} (p_A - p_A^*) \tag{4.8}
\]

\[
\frac{dz}{dt} = 0 \tag{4.9}
\]

\[
\frac{dq_B}{dt} = K_{GB} (p_B - p_B^*) \tag{4.10}
\]

\[
\frac{dz}{dt} = 0 \tag{4.11}
\]

\[
\frac{d\theta}{dz} = - \left[ \frac{Ae\phi' + A\omega RT}{P} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \right] \tag{4.12}
\]

\[
\frac{dt}{dz} = 0 \tag{4.13}
\]

The p_A characteristics, Equation (4.6), are lines across the distance, time plane with velocity \( \phi/Ae \), whereas both the sets of characteristics arising from the rate of adsorption (Equations (4.8) and (4.10)) have zero velocity, see Figure 4.1 below:
The $\theta$ characteristics, Equation (4.12), however have infinite velocity, which means they do not propagate with time.

Since the initial and boundary values of $\theta$ are always known and $p_A$, $q_A$ and $q_B$ at time $t$ are also known, these sets of characteristics can easily be solved by direct numerical integration. The same trapezoidal algorithm was used as for the Method of Lines (see Section 4.2.1).

4.2.3 Interpretation of the Characteristics

Characteristics should be interpreted with caution. In general, characteristics are neither straight, nor of constant composition [Kirkby (1983)]. For process steps which operate at constant pressure (i.e $p' = 0$), the equations simplify, but the characteristics are still not lines.
of constant composition and are still not necessarily straight or parallel.

Hyperbolic equations are notorious for their general property of allowing shock waves to form and propagate. A shock wave is a line across which the dependent variables (or their derivatives) are discontinuous. In the case of the Equations (3.8) to (3.10), it is possible to state that shock waves will not form spontaneously within the $z, t$ plane because the characteristic velocities are not dependent on $p_A, q_A$ or $q_B$ and therefore characteristics from the same family cannot intersect.

A shock wave for the DCPSA model normally arises when $p_A$ is discontinuous at the origin (i.e. when $z = 0$ and $t = 0$). In most cases, any discontinuities introduced into the $z, t$ plane will propagate with time. It is possible to start an infinite number of characteristics from a discontinuity, each with a different value of $p_A$. All these characteristics have the same velocity and therefore the shock wave propagates at the same velocity as these characteristics (Figure 4.2). Thus, although in this system calculation of the shock wave position does not require additional computation, its existence must be correctly accounted for in the calculation of $q_A$ and $q_B$ along their characteristics, and in the integration of Equation (4.12). It should be noted that, since Equation (4.12) is a function of $p_A$, then $\partial \theta / \partial z$ is also not continuous but $\theta$ is continuous. This is important because if $\theta/Ae$ is undefined at the shock wave, then the characteristic velocities will also be undefined. In addition to this, the shock waves will not necessarily degenerate as a result of their propagation during the non-constant pressure steps of the PSA process.
4.3 Integration Techniques along Characteristics

Different methods of integration were investigated to solve the ordinary differential equations along the characteristics. These include, the explicit Euler, the higher order Adams-Bashforth-Moulton predictor-corrector and the implicit Euler.

In general, integration techniques such as the Runge-Kutta and Gear's variable order, variable step length cannot be used directly along characteristics. This is because intermediate values of all the dependent variables are needed for each integrating step but they are not generally available along characteristics.

The ultimate choice of the method used to solve the DCPSA model depends
upon a number of factors, the most important factors are stability and its accuracy. Quite often these factors also affect the speed of computation and memory requirements of the computer.

4.3.1 Explicit Euler

The use of explicit Euler along characteristics was investigated.

Consider the general initial value problem,

\[ q' = f(t, q) \]  

where  \( q(t_0) = q_0 \),  \( t_0 \leq t \leq t_s \) and  \( S \) is the number of integration steps.

On applying explicit Euler, the evaluated \( q \) at the \((i+1)\)th interval is expressed as,

\[ q(t_{i+1}) = q(t_i) + hf(t_i, q(t_i)) \]  

where \( h = (t_s - t_0)/S \)

This method is explicit because the function, \( f \), is evaluated with known information (i.e. at the left hand side of the sub-interval).

In general, a numerical method is unstable if the global error grows with increasing values of the independent variable. The global error of explicit Euler consists of two parts: first, being first order accurate, the error that results from the Euler method approximation can be large if the step size in the independent variable is large. The second part is the propagation effect of the initial error.
Since the step size must be chosen to meet strict requirements for stability and accuracy, a large number of function evaluation are sometimes required for the solution to converge, hence the cost of computation is high. For less well behaved problems, it is not recommended to be used on its own. However, it may be useful if it is used as a predictor in predictor-corrector schemes.

4.3.2 Low Order Predictor-Corrector Methods

A predictor-corrector is a method that extrapolate the solution from stored values and then corrects the extrapolation using derivative information at the new point. Although for smooth functions, predictor-corrector methods may be more accurate and efficient than the Runge-Kutta methods, there are, however, some disadvantages [Press, Flannery, Reukolsky & Vetterling (1988)], for example:

1) huge amounts of storage space may be required to keep previously integrated information which is needed for subsequent integration steps, especially for the multivariable problem,

2) because the integration uses past information it is necessary to start up the integration procedure with some explicit method,

3) it is difficult to change step size without starting again.

The simplest form of predictor-corrector method is based on two integration functions:

1) the explicit Euler predictor step, and

2) the modified Euler corrector step.
The modified Euler scheme, based on the same Equation (4.14) gives,

\[ q(t_{n+1}) = q(t_n) + \frac{h}{2} [f(t_n, q(t_n)) + f(t_{n+1}, q(t_{n+1}))] \]  \hspace{1cm} (4.16)

where \( n \) is the current iteration number.

This modified Euler is used as a corrector, and may be applied repeatedly, with the re-evaluation of the function \( q(t_{n+1}) \) until the solution converges to some specified tolerance, \( TOL \). For example,

\[ |q^{(n)}_{n+1} - q^{(n-1)}_{n+1}| \leq TOL \]  \hspace{1cm} (4.17)

When this predictor-corrector method was used on the pressurisation step of the DCPSA model, the solution was well behaved until the overall mass transfer coefficients, \( K_{GA} \), was increased to \( 2.5 \times 10^{-10} \) (kmol m\(^{-3}\)N kg s\(^{-1}\)) for oxygen, and \( K_{GB} \), was increased to \( 1.0 \times 10^{-11} \) (kmol m\(^{-3}\)N kg s\(^{-1}\)) for nitrogen. The increase in the mass transfer rates made the system of equations highly unstable. The initial explanation considered was that, being first order accurate, the global errors may have increased with the increase in the overall mass transfer rates.

Several experiments were carried out on the pressurisation step to determine the cause of the instability. The results showed that the solution starts to converge or to stabilise when the step size was made very small (0.1 steps in a 60 seconds process step time). This small step size required unacceptable CPU time, approximately 400 seconds, a 10 fold increase over lower mass transfer rates (Section 4.4.1 illustrates the
application of this lower order predictor-corrector to the system of ODEs at the close end of the column during a pressure changing step).

The requirement for a small step size for the solution to converge, suggests that the instability of the solution may be caused by one or both of the following reasons:
1) the stiffness (Section 4.3.3) of the system of equations, and
2) the accuracy of the integration technique.

Since only a minor modification of the computer code was required to improve the scheme's accuracy, the program was extended to a higher order predictor-corrector method to explore the possibility of improving the speed of solution.

4.3.3 High Order Predictor-Corrector Methods

The principle described above (Section 4.3.1) may be extended to give methods of a higher order. The most popular one is the Adams-Bashforth-Moulton scheme.

Consider again the initial value problem (Equation (4.14)),

\[ q' = f(t,q) \]

If the differential equation is integrated from \( t_1 \) to \( t_{i+1} \), we obtain

\[ q(t_{i+1}) = q(t_1) + \int_{t_1}^{t_{i+1}} f(t, q(t)) \, dt \]  (4.18)
To carry out the integration in Equation (4.18), we can approximate \( f(t, q(t)) \) by a polynomial that interpolates \( f(t, q(t)) \) at \( k \) points, \( t_1, t_{1-1}, \ldots, t_{1-k+1} \). If the Newton backward formula of degree \( k - 1 \) \cite{Barnett & Cronin, (1979)} is used to interpolate \( f(t, q(t)) \), then the Adams-Bashforth formulae are generated \cite{Davis, (1984)} and are of the form

\[
q(t_{i+1}) = q(t_i) + h \sum_{j=1}^{k} b_j f_{i-j+1}
\]  

(4.19)

In the case of a three-step formula, Equation (4.19) become

\[
q(t_{i+1}) = q(t_i) + h \left[ b_{1+1} f_{i+1} + b_{2} f_{i-1} + b_{3} f_{i-2} \right]
\]

Similarly the Adams-Moulton formulae are derived as,

\[
q(t_{i+1}) = q(t_i) + h \sum_{j=0}^{k} b_j f_{i-j+1}
\]

(4.20)

and the corresponding three-step Adams-Moulton formula is

\[
q(t_{i+1}) = q(t_i) + h \left[ b_{0} f_{i+1} + b_{1} f_{i-1} + b_{2} f_{i-2} \right]
\]

On applying Taylor's series expansion about \( t_i \) and with the appropriate algebraic manipulation, the coefficients \( b_j \) in the Adam-Bashforth-Moulton formulae can be obtained. The final three step semi-implicit Adams-Bashforth-Moulton predictor-corrector formulae for a system of equations are given as \cite{Davis, (1984)}:
Predictor (4.21)

\[
q_{i+1}^{(n)} = q_i + \frac{h}{12} \left[ 23f_i - 16f_{i-1} + 5f_{i-2} \right]
\]

and,

Corrector (4.22)

\[
q_{i+1}^{(n+1)} = q_i + \frac{h}{12} \left[ 5f_{i+1}^{+1} + 8f_i - f_{i-1} \right]
\]

The corrector, Equation (4.22), may be applied repeatedly, with the re-evaluation of \( f_{i+1}(t_{i+1}, b_{i+1}^{(n+1)}) \) until the solution converges to some specified tolerance as in Equation (4.17).

Test run results (Section 4.4.1) on the application of this higher order predictor-corrector method have shown that there is no improvement over the instability encountered by the lower order predictor-corrector method. The results also show very little improvement in accuracy.

This outcome has clearly indicated that the instability encountered during high overall mass transfer rates was not an accuracy problem but a stiffness problem.

Stiffness of a system of differential equations is normally best solved by an implicit technique (see section below). However no implicit technique has been used on the Method of Characteristics for PSA applications. Since the use of explicit methods for the DCPSA model was restricted to unrealistically low value of overall mass transfer rates, an implicit Euler technique was developed in an attempt to eliminate the instability problem.
4.3.4 First Order Implicit Methods

With more than one first order differential equation, the possibility of a stiff set of equations arises.

The stiffness of a set of differential equation usually occurs when there are two or more very different scales of the independent variable on which the dependent variables are changing. An alternative way of describing stiffness is to say that certain eigenvalues of the Jacobian matrix, \( \frac{\partial f_i}{\partial q_j} \) (see below), have large negative real parts when compared to others [Davis, (1984)]. These problems require special methods for efficient numerical solution. Various authors have suggested that the cure for stabilizing stiff equations during integration is to adopt implicit methods, where the right hand side of the equation is evaluated at the new function location [Davis (1984), Hall and Watt (1976)]. The simplest form of implicit method is the 'backward' or 'implicit' Euler method.

Again consider Equation (4.14), \( q' = f(t, q) \), application of implicit Euler gives,

\[
q_{1+1}^{(n)} = q_1 + hf(t_{1+1}, q_1^{(n)}) .
\]  

This implicit method is found to be absolutely stable for any system of linear equations. However, being only first order accurate, a small step size is sometimes needed for accuracy. For a linear equation, the final formulation is usually rearranged to be explicit in the solution, \( q_{1+1} \).

In general, differential equations which model physical systems are not
linear with constant coefficients, and many non-linear equations may have to be solved iteratively at each step. One method to overcome this iteration is to linearise the equations as follows:

\[
q_{i+1} = q_i + h \left[ f(t_{i+1}, q_i) + \frac{df}{dq} \left( q_{i+1} - q_i \right) \right] . \tag{4.24}
\]

However, if the computational load for solving the non-linear equations iteratively is small, it is more accurate to do so rather than using Equation (4.24) to linearise it (which is an approximation). In addition, it is not always easy to find \( \frac{df}{dq} \) at \( q_i \), nor is it cost efficient to evaluate the eigenvalues of the Jacobian matrix \( J \) (see paragraph below).

For the DCPSA model, the Newton-Raphson iterative method was used.

If the non-linear equations are linearised by Equation (4.24) then the stiffness is based upon the eigenvalues of the Jacobian matrix \( J \) (which involves the term \( \frac{df}{dq} \) in Equation (4.24)), where

\[
J = \begin{bmatrix}
\frac{df_1}{dq_1} & \frac{df_1}{dq_2} & \cdots & \frac{df_1}{dq_m} \\
\frac{df_2}{dq_1} & \frac{df_2}{dq_2} & \cdots & \frac{df_2}{dq_m} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{df_m}{dq_1} & \frac{df_m}{dq_2} & \cdots & \frac{df_m}{dq_1}
\end{bmatrix} . \tag{4.25}
\]

Hence, at each step during integration, the matrix, \( (1 - Jh) \), has to be inverted to find \( q_{1+1} \). This is called a semi-implicit method. It is not guaranteed to be stable, but it usually is [Davis, (1984)].

When the non-linear equations of the DCPSA model are solved by the
iterative method, the CPU required for running a pressurisation step at high overall mass transfer coefficients is approximately 30 seconds. The computation load for using the iterative method is thus the same as those run with an explicit Euler, at lower overall mass transfer coefficients. This iterative method also avoided the need to evaluate the Jacobian matrix for the DCPSA model, which can be expensive in terms of CPU time.

4.3.5 Second Order Implicit Methods

Whilst first order accurate implicit methods are very robust, most problems will tolerate higher order methods.

A simple second order method was constructed by taking the average of the explicit and implicit first order methods as Equation (4.16) described in Section 4.3.1 [Davis, (1984)]:

\[ q_{1+1} = q_1 + \frac{h}{2} (f_1 + f_{1+1}) \]  

(4.26)

This is simply the trapezoidal rule if the function, \( f \), does not depend on \( q \). Similarly, a semi-implicit scheme for a non-linear function can be constructed as below:

\[ q_{i+1} = q_i + \frac{h}{2} \left[ f(t_{i+1}, q_i) + \frac{df}{dq} \left( (q_{i+1} - q_i) + f(t_i, q_i) \right) \right] \]  

(4.27)

Again Equation (4.27) is an approximate solution which requires the evaluation of Jacobian matrix \( J \) (Section 4.3.3). Therefore, when second
order, semi-implicit Euler was used in the DCPSA model, the linearisation technique was also avoided in favour of the solution obtained by an iterative method.

4.4 Application of Various Integration Techniques on Diffusion Controlled Pressure Swing Adsorption Model's Equations

This section will give a detailed account on how the various numerical integration techniques, mentioned above, were applied to the equations of the DCPSA model. Before deciding which integration techniques were best suited along the characteristic for the DCPSA model, a simplified problem was defined where only Equations (4.6) to (4.11) need to be solved (Section 4.4.1). Application of first and second order implicit Euler on both pressure changing steps and constant pressure steps will be discussed in Sections 4.4.2 and 4.4.3 respectively.

4.4.1 Application of Predictor-Corrector and Gear-Hindmarsh Methods to the System of Ordinary Differential Equations at the Closed End of the Column during Pressure Changing Steps

Since no flow is possible at the closed end of column (by definition), the three partial differential Equations ((3.8) to (3.10)) involved in the formulation can be solved as a set of simultaneous ODEs (Equations (4.6), (4.8) and (4.10)) along the characteristics at the closed end of the column. That is:
With appropriate initial conditions (as discussed in Chapters 5 and 6), this set of ODEs can be solved in principle by all the integration techniques described in Section 4.3.

As shown in the method described in Section 4.3.1, (lower order predictor-corrector method) explicit Euler integration was applied to all three equations (i.e., (4.6), (4.8) and (4.10)) to obtain the first estimate of $q_A$, $q_B$ and $p_A$ at $t + \delta t$. This estimate was then substituted back to the three equations to obtain their derivative at $t + \delta t$ prior to the application of the semi-implicit modified Euler corrector step on all three equations. The integration was iterated until it converged to a set tolerance, otherwise $\delta t$ was reduced. An example of this procedure on Equation (4.8) follows.

Let the subscript $i$ denote the present time, $t$, and subscript $i+1$, be the subsequent time, $t + \delta t$, throughout Section 4.4, then,

\[
q_{A(i+1)}^{(1)} = q_{A(i)}^{(1)} + \frac{d q_A}{d t} \bigg|_{(i)} \delta t
\]  \\

Predictor \hspace{1cm} (4.28)
This method was used to obtain the numerical solution for the ODEs resulting from applying the Method of Characteristics to the PDEs. It has also been used successfully in the set of column end equations, hence it was the first integration technique used in the simulation of simple cycles for DCPSA model. However, it was found to be very inefficient at high values of overall mass transfer coefficients \((K_{GA} \text{ and } K_{GB})\). The CPU time needed to simulate each pressure changing step at high values of overall mass transfer coefficients \((K_{GA} = 2.5 \times 10^{-10} \text{ (kmol m}^3\text{)(N kg s)}^{-1} \text{ for oxygen, and } K_{GB} = 1.0 \times 10^{-11} \text{ (kmol m}^3\text{)(N kg s)}^{-1} \text{ for nitrogen)}\), to converge was 75,000 to 90,000 CPU seconds when run on a Prime 6550 rated at 12 Mips Linpack. This is because of the enormous reduction (approximately 100 fold) in the time step required compared to that when a lower overall mass transfer coefficients were used \((K_{GA} = 2.5 \times 10^{-14} \text{ (kmol m}^3\text{)(N kg s)}^{-1} \text{ for oxygen, and } K_{GB} = 1.0 \times 10^{-15} \text{ (kmol m}^3\text{)(N kg s)}^{-1} \text{ for nitrogen)}\) while all other parameters were the same. (see Appendix I for a typical simple cycle 'standard' simulation data.)

The reason for the large CPU times at high overall mass transfer coefficients was thought to be lack of numerical accuracy since the integration technique is only of second order. A higher order predictor-corrector method was thus thought to be necessary.

A routine based on Adams-Bashforth third order predictor and Adams-Moulton third order corrector method was written (Section 4.3.2). For example,

\[
q_{A(t+1)}^{(2)} = q_{A(t)} + \left( \frac{dq_{A}}{dt}(t) + \frac{dq_{A}}{dt}(t+1) \right) \frac{\delta t}{2}
\]

Corrector (4.29)
the predictor step for the Equation (3.9) is as follows:

\[
q_A^{(1)}_{A(1+1)} = q_A^{(1)} + \frac{\delta t}{12} \left( 23 \frac{dq_A}{dt} \bigg|_{(i)} - 16 \frac{dq_A}{dt} \bigg|_{(i-1)} + 5 \frac{dq_A}{dt} \bigg|_{(i-2)} \right),
\]

(4.30)

and the subsequent calculation is carried out by the corrector is,

\[
q_A^{(2)}_{A(1+1)} = q_A^{(1)} + \frac{\delta t}{12} \left( 5 \frac{dq_A}{dt} \bigg|_{(i+1)} + 8 \frac{dq_A}{dt} \bigg|_{(i)} - \frac{dq_A}{dt} \bigg|_{(i-1)} \right).
\]

(4.31)

Notice that this higher order predictor–corrector method has one obvious disadvantage in that it needs another integration method such as the Euler or modified Euler method to get started. This could be one of the reason why no drastic improvement in computer load was found using this method over the lower order predictor–corrector method described previously.

Since both predictor–corrector methods above required excessive CPU time, it was decided to investigate implicit methods. The Nag Library supplies a variable order, variable step length Gear’s method integrator [D02EBF, Nag Library (1983)]. The routine solves the equations simultaneously with variable order to achieve the required accuracy, and with variable step length to minimize the computer load. Three subroutines need to be supplied by the user, they are:

1) FCN, which evaluates the function \( f_i \), (i.e. the derivatives).
2) PEDERV which evaluates the Jacobian matrix of the system (i.e. the partial derivative \( \partial f_i / \partial q_j \))
3) OUTPUT which allows access to intermediate values of the computed solution.

This method used about a thousand times less CPU time than the explicit
methods described above. However, the Gear-Hindmarsh integration method cannot be used along characteristics in general, due to the need for intermediate values which are not generally available when the families of characteristics of different equations do not coincide.

The main difference between the predictor-corrector methods used, and the Gear's routine is that the former methods used the forward or explicit principle, whereas the latter used the backward or implicit principle.

When both methods were used in simulations of the closed end of the column, there was a problem at lower overall mass transfer coefficients. There is little difference between the two methods in terms of accuracy, stability and CPU usage. However, when both methods were applied on higher overall mass transfer coefficients as before, the Adam-Bashforth-Moulton predictor-corrector method yet again run into an instability problem as experienced by the lower order predictor-corrector method. The solution only become stable when an extremely small step size was taken (approximately 0.01 second step size for a 60 seconds process step time and approximately 1.0 second CPU is required for each time step, giving a total of approximately 6000 seconds CPU).

However, Gear's method had no difficulty in obtaining a stable solution within the same CPU loading as when solving the problem with a lower overall mass transfer coefficients. The total CPU in this case was approximately 3 seconds.

From these simulation results, it can be concluded that high values of overall mass transfer coefficients cause instability in the explicit
numerical methods, and it is the difference in the overall mass transfer coefficients which causes the stiffness.

Implicit methods are well suited to solve stiff problems (Section 4.3.3), and the implicit Gear's routine has been demonstrated to be capability of achieving a stable solution, requiring small CPU times, when compared to the predictor-corrector methods. Hence an implicit method which can be applied generally to the Method of Characteristics was required.

The simplest integration technique along the characteristic is implicit Euler (Section 4.3.3). Although the use of implicit Euler integration techniques for solving stiff problems has been well documented [e.g. (Davis, 1984)], its use with the Method of Characteristics is not well known, and is almost certainly unique in PSA research.

4.4.2 Application of Implicit Euler to the Gas and Solid Phase Equations along the Column on Pressure Changing Steps

The implementation of implicit Euler is illustrated in the following example on the gas phase equation where either linear or Langmuir isotherms were assumed.

The gas phase Equation (4.6) to be solved is,

\[
\frac{\Delta p_A}{\Delta t} = p_A p' + \frac{\omega RT}{c} \left[ \frac{p_A}{P} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) - \frac{\partial q_A}{\partial t} \right]
\]

The implicit Euler method of step length \(\Delta t\) is
\[ p_{A(1+1)} = p_{A(i)} + \left( \frac{dp_A}{dt} \right)_{(i+1)} \delta t \]  

where,

\[ \frac{dp_A}{dt}_{(i+1)} = p_{A(i+1)} \cdot p'_{A(i+1)} + \]

\[ \frac{\omega RT}{\varepsilon} \left[ \frac{p_A(i+1)}{P(i+1)} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \right]_1 - \frac{\partial q_A}{\partial t} \left( p_A(i+1) \right)_{(i+1)} \]  

\[ \frac{\partial q_A}{\partial t} \left( p_A(i+1) \right)_{(i+1)} = K_G A \left( p_A(i+1) - p_{A(i+1)}^* \right) \]  

\[ \frac{\partial q_B}{\partial t} \left( p_B(i+1) \right)_{(i+1)} = K_G B \left( p_B(i+1) - p_{B(i+1)}^* \right) \]  

\[ p_{A(i+1)}^* \] and \[ p_{B(i+1)}^* \] were calculated from the equilibrium isotherm from \( q_A \) and \( q_B \) at time \( t + \delta t \).

On substituting Equations (4.34) and (4.35) into Equation (4.33) gives,

\[ \alpha_1 p_{A(i+1)}^2 + \beta_4 p_{A(i+1)} + \gamma_2 = 0 \]  

Where \( \alpha_1, \beta_4 \) and \( \gamma_2 \) are constants derived in Appendix C.

Substituting Equation (4.36) back into Equation (4.32) gives,

\[ p_{A(i+1)} = p_{A(i)} + \left( \frac{\alpha p_{A(i+1)}^2}{p_A(i+1)} + \beta p_{A(i+1)} + \gamma \right) \delta t \]  

which on rearranging becomes,
\[ ap_{A(i+1)}^2 + bp_{A(i+1)} + c = 0 \]  \hspace{1cm} (4.37)

Again, a, b and c are derived in Appendix C.

Since Equation (4.37) is a simple quadratic equation, the solution for \( p_{A(i+1)} \) is thus,

\[ p_{A(i+1)} = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a} \]  \hspace{1cm} (4.38)

Since there are two real solutions for \( p_{A(i+1)} \) if \( b^2 > 4ac \), a criterion was needed to choose the appropriate solution. As discussed earlier, although more preparatory work is usually needed to use the implicit method, it is more stable, and larger step lengths can be used when stiff problems arise. As for the solid phase, Equations (4.8) and (4.10) are less complicated, a second order implicit modified Euler was used, and the final formulation (for the linear isotherm assumption) was also less complicated than the gas phase equation as shown below:

\[ q_{A(i+1)} = \frac{\sigma}{\lambda} \]  \hspace{1cm} (4.39)

where \( \sigma \) and \( \lambda \) are derived in Appendix D.

With the Langmuir isotherm, the solid phase formulation of the second order implicit method gives rise to a quadratic form, similar to the gas phase formulation (4.37), that is:

\[ dq_{A(i+1)}^2 + eq_{A(i+1)} + f = 0 \]  \hspace{1cm} (4.40)
where $d$, $e$ and $f$ are derived in Appendix D.

Equation (4.40) is quadratic when the Langmuir isotherm assumption is used, hence the solid phase equation is no longer linear. The non-linear form of the gas and the solid phase equations may be linearised using the method described in the Section 4.3.3. The quadratic formulation was used, instead of the linearised form, because the rearrangement given above is exact.

When the isotherms are assumed to be linear or independent pure gas Langmuir equations, it is relatively easy to rearrange the implicit Euler formulae to an explicit form (shown above) and hence calculate directly the gas and adsorbed phase compositions. However, when the isotherms are coupled by co-adsorption effects the rearrangement of the implicit Euler equations, to provide a set of explicit equations for solution is impossible. The complexity of the solid phase problem (Equations (4.8) and (4.10)) is illustrated below:

The co-adsorption isotherm equations of $q_A^*$ and $q_B^*$ are,

$$q_A^* = \frac{k_{A1}^* p_{A}^*}{1 + k_{A2}^* p_{A}^* + k_{B2}^* p_{B}^*}$$  \hspace{1cm} (4.41)

and,

$$q_B^* = \frac{k_{B1}^* p_{B}^*}{1 + k_{A2}^* p_{A}^* + k_{B2}^* p_{B}^*}$$  \hspace{1cm} (4.42)

and inversion, after some rearrangement yields

$$p_{A}^* = \frac{q_A^* k_{B1}^*}{k_{A1}^* k_{B1}^* - q_A^* k_{A2}^* k_{B1}^* - q_B^* k_{B2}^* k_{A1}^*}$$ \hspace{1cm} (4.43)
Applying implicit Euler integration over the time interval from \( t \) to \( t + \delta t \) yields,

\[
q_{A(i+1)} = q_{A(i)} + k_a A(i) k A(i+1) \delta t \left( p_{A(i+1)} - \frac{q_{A(i+1)} k A(i) B_1}{k A(i) B_1 - q_{A(i+1)} k A(i) A_2 B_1 - q_{B(i+1)} k B(i+1) B_2 A_1} \right) \]  

(4.45)

\[
q_{B(i+1)} = q_{B(i)} + k_b B(i) k B(i+1) \delta t \left( p_{B(i+1)} - \frac{q_{B(i+1)} k B(i) B_1}{k B(i) B_1 - q_{A(i+1)} k A(i) A_2 B_1 - q_{B(i+1)} k B(i+1) B_2 A_1} \right) \]  

(4.46)

Solving Equations (4.45) and (4.46) simultaneously with known values of \( p_{A(i+1)} \) and \( p_{B(i+1)} \) \( ( = P_{(i+1)} - p_{A(i+1)} ) \) gives cubic equations.

\[
a_3 q_{A(i+1)}^3 + a_2 q_{A(i+1)}^2 + a_1 q_{A(i+1)} + a_0 = 0 \]  

(4.47)

and

\[
b_3 q_{B(i+1)}^3 + b_2 q_{B(i+1)}^2 + b_1 q_{B(i+1)} + b_0 = 0 \]  

(4.48)

Appendix E gives the detailed derivation of Equations (4.47) and (4.48) and all the expressions for the terms \( a_0 \) to \( b_3 \).

Since the resulting equations are cubic, the Newton-Raphson method (also described in Appendix E) was used to determine numerically the appropriate root. In this work, it was almost always possible to provide a very good starting guess to this procedure and to avoid the possibility of point of inflection at the root. Hence rapid convergence is to be expected.

Chapter 6 gives an example of the simulation of a normal purge cycle where Langmuir isotherms with co-adsorption were assumed.
4.4.3 Application of the Implicit Euler Method to the Constant Pressure Steps

The assumption that there is no pressure change with respect to time, i.e. \( \frac{dP}{dt} = 0 \), reduces Equation (4.6) to a slightly simpler form as follows:

\[
\frac{dp_A}{dt} = \frac{\omega RT}{\varepsilon} \left[ \frac{p_A}{P} \left( \frac{\partial q_A}{\partial t} - \frac{\partial q_B}{\partial t} \right) \right]
\]

(4.49)

However, the formulation for the gas phase equation (Appendix F) using the implicit Euler method was not found to be any simpler than the one used in both the pressurisation and the depressurisation step (Appendix C). In the pressurisation step, when the linear isotherm assumption is used and the feed composition does not vary with time, an analytical solution for the solid phase equations at the feed end of the column is possible. Similarly, for the constant pressure step, an analytical solution for the solid phase equation at the feed end of the column was also formulated (Appendix G).

After some preliminary test runs on the newly developed product release step, again the implicit method was more efficient than the explicit method in terms of both solution stability and computational load, especially for the higher values of overall mass transfer coefficient mentioned above. For high values of the feed volumetric flow rate (e.g. \( \theta_f = 1.013 \times 10^{-4} \text{ m}^3\text{s}^{-1} \)) the concentration profile in the bed after pressurisation will be quickly displaced by the feed (i.e. the bed is saturated at the feed composition), whereas for much lower values of the feed volumetric flow rate (e.g. \( \theta_f = 1.013 \times 10^{-8} \text{ m}^3\text{s}^{-1} \)), a portion of the bed (nearer to the product end) may experience no flow, this is because
the local rate of adsorption is significant compared with the local
defined flow rate (see further discussion in Chapter 5).

4.5 Conclusion

This chapter has presented several numerical techniques that were
implemented along the characteristics. These include:

1) Method of Lines

2) Explicit Euler

3) The simplest, explicit Euler - predictor and modified Euler -
corrector method. The solution obtained from using this technique
became unstable at high but not unrealistic overall mass transfer
coefficients \( K_{GA} = 2.5 \times 10^{-10} \) (kmol m\(^3\))(N kg s\(^{-1}\) for oxygen, and \( K_{GB} = 1.0 \times 10^{-11} \) (kmol m\(^3\))(N kg s\(^{-1}\) for nitrogen).

4) Third order Adam-Bashforth-Moulton predictor-corrector method.
Although there is some improvement in accuracy, no improvement in the
solution's stability was observed.

5) The variable order, variable step length Gear's routine. This
implicit method fulfills both the accuracy and stability criterion.
However it can only be applied on the closed end problem (Section
4.4.1) where all intermediate values are available.

6) The implicit Euler technique. The application of this technique to
PSA modelling is unique and has overcome the problems of an unstable
solution and excessive computational loads. However, it is only
first order accurate. In addition, the implicit equations can be
rather difficult to rearrange to explicit equations. A root searching
routine is then required to solve the explicit equations.
Therefore it is concluded that the implicit Euler technique is the most suitable method for the DCPSA model. Hence the final DCPSA software is based entirely on this implicit technique. The following chapters will describe the software and present the simulation results obtained from using the software to simulate a wide variety of PSA process cycles.
CHAPTER 5

SOFTWARE DEVELOPMENT AND PROGRAM STRUCTURE

5.1 Introduction

This chapter describes the additional process assumptions made in the DCPSA model, that is, the variation of pressure with time, process symmetry, product mixing and the presence of argon. It then explains how the values of the kinetic equilibrium parameters required for the simulations in Chapter 6 were estimated from published literature. It also discusses the boundary conditions for each process step before moving on to describe the phenomena of flow reversal during the product release step, which has not been encountered by other PSA modeller before.

The DCPSA software comprises of 40 Fortran 77 routines. These routines are not described in detail here. A complete program listing is given on the microfiche at the end of this thesis. However a brief description of the program structure with its overall process cycle convergence is given.

5.2 Process Assumptions

In order to apply the various integration techniques along characteristics, described in Section 4.3, to the different process steps in the DCPSA model, it is necessary to make additional process assumptions concerning
the following:
1) variation of pressure with time,
2) process symmetry,
3) product mixing, and
4) presence of argon.

5.2.1 Variation of Pressure with Time

For pressure changing steps, it is necessary to supply an expression for the variation of process pressure with time. For pressurisation and backfill steps, it was assumed that the pressure varied linearly with time. Hence, as the pressure changes from initial operating pressure, $P_i$, to the final operating pressure, $P_f$, in a process time $\Delta t$, the pressure at time $t$, $P(t)$, for pressurisation step is given as,

$$P(t) = P_i + \frac{(P_f - P_i) t}{\Delta t}$$

hence $p'$, which is defined as $\frac{1}{P} \frac{dP}{dt}$ becomes,

$$p' = \frac{P_f - P_i}{(P_f - P_i) t + P_i \Delta t}$$

Note that $P_f$ may be replace by $P_{fB}$, where $P_{fB}$ is the required backfill pressure. Hence if $P_{fB}$ is equal to $P_f$ then the backfill step will completely replace the pressurisation step.
For both co- and counter-current depressurisation, an exponential pressure function was assumed. Hence for the pressure to drop from $P_f$ to $P_i$ in a given process step time, $\Delta t$, the pressure function $P(t)$ is then given by,

$$P(t) = P_f e^{\frac{t}{\Delta t} \ln \left( \frac{p_i}{p_f} \right)}$$

and $p' = \frac{1}{\Delta t} \ln \left( \frac{p_i}{p_f} \right)$.

The use of a linear pressure function for pressurising the column and an exponential pressure function for depressurising the column were shown to be a good approximation by the experimental results obtained by Espitalier-Noel (1988) on a column filled with SA zeolite. An additional advantage of using the exponential pressure function is that, $p'$ is now a constant which improves the computational speed. In the constant pressure steps, product release and purge, $p'$ is zero.

Table 5.1 defines the pressure at the end of each process step encountered in PSA cycles, where the initial pressure, $P_i$ of a process step in any cycle is defined as the final pressure, $P_f$, from the previous step.
Table 5.1  Final Pressure of Each Possible Process Step

<table>
<thead>
<tr>
<th>Final Operating Pressure, $P_f$</th>
<th>Pressure Changing Process Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_n$</td>
<td>Pressurisation</td>
</tr>
<tr>
<td>$P_D$</td>
<td>Co current Depressurisation</td>
</tr>
<tr>
<td>$P_L$</td>
<td>Depressurisation</td>
</tr>
<tr>
<td>$P_B$</td>
<td>Backfill</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_H$</td>
<td>Constant Pressure</td>
</tr>
<tr>
<td></td>
<td>Process Step</td>
</tr>
<tr>
<td>$P_L$</td>
<td>Product Release</td>
</tr>
<tr>
<td></td>
<td>Purge</td>
</tr>
</tbody>
</table>

5.2.2  Process Symmetry

The simulations carried out in the present work have assumed that the process is completely symmetrical, where within any complete cycle, all the columns involved will have the same mass balance, are of the same size and contain identical adsorbent.

The assumption of process symmetry greatly simplifies the process simulations because the final state of the column (gas and adsorbed phase compositions) automatically becomes the initial conditions for the next step. Simulation of unsymmetrical operation would require $n$ times the
computational load (where \( n \) is the number of columns) and great care in carrying forward initial and boundary conditions.

Although there is no strong evidence in the literature showing that symmetrical operation is the best possible way to utilise the adsorbent efficiently during PSA operation.

However, Kirkby (1983) has carried out a study of unsymmetrical operation on both a purge cycle and a backfill cycle, and concluded that, even when there are minor differences in the amounts of adsorbent in each column, the optimum mass balance will be significantly unsymmetrical. In such cases, the optimum performance for unsymmetrical operation is substantially better than the best production obtainable from the same plant when operated symmetrically. The results suggested that it is thus important to ensure that for symmetrical operation, the adsorbent loading for each column should be as accurate as possible and suitable throttles always fitted so that the fine tuning can be maintained.

5.2.3 Product Mixing

In a PSA plant, gas for adsorbent regeneration usually comes either directly from part of the desired high pressure product of the product release step (direct purging) or from a buffer tank (mixed purging), where full product mixing is possible. Similarly, during backfill steps, gas entering the column can come from either source.
In the model, it is assumed that the gas for these steps comes from a buffer tank. This is because, when total product mixing is assumed, the transfer of shock waves between the columns is eliminated. This reduces the computational effort and memory requirements.

The Simulation of direct transfer would involve boundary conditions in which both the composition and the flow rate of the gas transferred could vary with time.

Espitalier-Noel (1988) studied direct purging and concluded that, slightly less purge is required to optimise the product concentration or yield when direct purge is assumed and confirmed this experimentally. The maximum oxygen concentration was the same in both cases. He also showed that, at above optimum purge amounts, the mixed purge source was marginally superior. No results regarding the additional computational load were reported.

Since the differences between direct and mixed purging are minor and the simulation of transfer of concentration and velocity profiles is much more complex and time consuming, direct transfer is not considered further.

5.2.4 Presence of Argon

The present model is based on the assumption that the feed consists of two adsorbable components, nitrogen and oxygen. This is because the diffusivity in carbon molecular sieve for both nitrogen and argon are very
similar [Chihara, Suzuki and Kawazoe, (1978)]. Hence for the simulation of air separation using CMS, the presence of argon is assumed to be negligible. Argon is also claimed to have very similar isotherms to oxygen both in terms of being highly linear and that similar amounts are adsorbed per unit volume for 5A zeolite [Kirkby (1988)]. The assumption that the air composition consists only of nitrogen and oxygen was also made by Hassan et. al. (1986) in their CMS based PSA model.

5.3 Parameter Estimation from the Model of Hassan et. al. (1986)

The values of the adsorption parameters and overall mass transfer coefficients, used for the modelling, were generated from the work published by Hassan et al (1986). Other physical and process parameters used were also selected mostly from the same work by Hassan et. al. when similar types of cycle configurations were used.

Hassan et. al. (1986) present theoretical and experimental results for nitrogen separation from air using the Bergbau-Forschung carbon molecular sieve. In their model they consider a purge cycle but, unlike the present work, they simulate only the product release and purge steps and their purge cycle did not allow for a continuous flow of product (see Figure 5.1).
For depressurisation they assume that the adsorbed phase concentration profile does not move, and that the gas phase mole fractions are fixed and that only the total pressure changes. For pressurisation they assume that the adsorbed phase profile is again frozen but that the gas phase profile is compressed into a zone at the top of the column, of length \(\frac{L_p}{P_f}\), and that the rest of the column is filled with air at \(P_f\). Both these sets of assumptions are, taken separately, highly dubious, but the errors introduced may, by coincidence, cancel.

Like the present work, Hassan et. al. assume Langmuir isotherms. From independent measurements, the values of the constants are given as follows.

- Equilibrium constant for oxygen, \(K_A = 9.25\)
- Equilibrium constant for nitrogen, \(K_B = 8.90\)
- Saturation constant for oxygen and nitrogen, \(q_A = q_{BS} = 2.64 \times 10^3 \text{ mol cm}^{-3}\)
- Particle density, \(\rho_s = 0.9877 \text{ g cm}^{-3}\)
- Bed voidage, \(\varepsilon = 0.4\)
It should be noted that Hassan et. al. do not explicitly state what the volumetric basis of $q_{AS}$, $q_{BS}$ and $\rho_S$ is, but from their overall balances it is clear that a unit volume of solid is intended.

From these values, the parameter values for the present model were determined as follows:

**Adsorbent packed density:**

\[
\omega = (1 - \epsilon) \rho_S \quad \text{kg m}^{-3} \text{ column}
\]
\[
= (1 - 0.4) \times 987.7 \quad \text{kg m}^{-3} \text{ column}
\]
\[
= 593 \quad \text{kg m}^{-3} \text{ column}
\]

**Isotherm parameters:**

Hassan et. al. uses,

\[
q_A^* = \frac{b_{A} q_{AS} C_A}{1 + b_{A} C_A + b_{B} C_B}, \quad \text{where } K_A = b_{A} q_{AS}, \text{ and}
\]
\[
q_B^* = \frac{b_{B} q_{BS} C_B}{1 + b_{A} C_A + b_{B} C_B}, \quad \text{where } K_B = b_{B} q_{BS}
\]

Note that $C_A$ and $C_B$ are in mol cm$^{-3}$ of gas phase.

From the above values, $b_A$ and $b_B$ have thus become,
\[ b_A = \frac{K_A}{q_{AS}} = \frac{9.25}{2.64 \times 10^{-3}} = 3.504 \times 10^3 \text{ cm}^3 \text{ mol}^{-3} \]

and

\[ b_B = \frac{K_B}{q_{BS}} = \frac{8.90}{2.64 \times 10^{-3}} = 3.371 \times 10^3 \text{ cm}^3 \text{ mol}^{-3} \]

The basis of the DCPSA model is somewhat different; the adsorbed amounts \( q_A \) and \( q_B \) are amounts of adsorbate per unit mass of clean adsorbent (kmol kg\(^{-1}\)), and instead of gas phase concentrations \( C_A \) and \( C_B \), partial pressures \( p_A \) and \( p_B \) (Pa) are used. Hence for independent pure gas isotherms of the form,

\[ q_A = \frac{k_{A1} p_A}{1 + k_{A2} p_A} \]

and

\[ q_B = \frac{k_{B1} p_B}{1 + k_{B2} p_B} \]

the relationships required to establish \( k_{A1} \), \( k_{B1} \), \( k_{A2} \) and \( k_{B2} \) for use in the present work are described as follows:

\[ q_A^* = \frac{q_{AH}^*}{\rho_S} \]

\[ q_B^* = \frac{q_{BH}^*}{\rho_S} \]

\[ p_A = C_A^* RT \]

\[ p_B = C_B^* RT \]

Where \( R = 8.3143 \times 10^6 \) Pa cm\(^3\) mol\(^{-1}\) K\(^{-1}\) and \( T = 298 \) K

Thus the independent pure gas isotherm constant for the DCPSA model are,
\[ k_{A1} = \frac{K_A}{\rho S RT} = \frac{9.25}{0.9877 \times 8.3143 \times 10^6 \times 298} = 3.780 \times 10^{-9} \text{ kmol kg}^{-1} \text{ Pa}^{-1} \]

\[ k_{B1} = \frac{K_B}{\rho S RT} = \frac{8.90}{0.9877 \times 8.3143 \times 10^6 \times 298} = 3.637 \times 10^{-9} \text{ kmol kg}^{-1} \text{ Pa}^{-1} \]

\[ k_{A2} = \frac{b_A}{RT} = \frac{3.504 \times 10^3}{8.3143 \times 10^6 \times 298} = 1.414 \times 10^{-6} \text{ Pa}^{-1} \]

\[ k_{B2} = \frac{b_B}{RT} = \frac{3.371 \times 10^3}{8.3143 \times 10^6 \times 298} = 1.361 \times 10^{-6} \text{ Pa}^{-1} \]

These parameter values, when used in the present work, represent the same pure gas isotherms as used by Hassan et al. These parameter values may also be used in the Langmuir co-adsorption isotherms equations if the isotherms used are assumed to have the following form:

\[ q^*_A = \frac{k_{A1}P_A}{1 + k_{A2}P_A + k_{B2}P_B} \]

and

\[ q^*_B = \frac{k_{B1}P_B}{1 + k_{A2}P_A + k_{B2}P_B} \]
Mass transfer coefficients:

In the model by Hassan et. al., the driving force expressions are,

\[
\frac{\partial q_{AH}}{\partial t} = k'_A \left( q^*_A - q_A \right)
\]

and

\[
\frac{\partial q_{BH}}{\partial t} = k'_B \left( q^*_B - q_B \right)
\]

where \(q^*_A\) and \(q^*_B\) are related to \(C_A\) and \(C_B\) by the isotherm expressions discussed above. Hassan et. al. determine the values for \(k'_A\) and \(k'_B\) by using the expressions,

\[
k'_A = \frac{\Omega_A D_A}{r^2}
\]

and

\[
k'_B = \frac{\Omega_B D_B}{r^2}
\]

where \(\Omega_A = \Omega_B = 15\) following the work of Glueckauf (1955), but they are treated as experimentally fitted parameters by Hassan et. al. The published values for the diffusional time constants are,

\[
\frac{D_A}{r^2} = 3.7279 \times 10^{-3} \text{ s}^{-1}
\]

\[
\frac{D_B}{r^2} = 1.1715 \times 10^{-4} \text{ s}^{-1}
\]

and the range of values of the dimensionless parameters \(\Omega\) are determined to be,

\[
11.0 \leq \Omega_A \leq 16.0
\]

\[
49.5 \leq \Omega_B \leq 92.5
\]
The basis for the determination of parameters $\Omega$ is the fitting of their model to their experimental results from a PSA unit.

In the present work, the driving force expressions are:

$$\frac{\partial q_A}{\partial t} = K_{gA} a \left( p_A - p_A^* \right)$$

and

$$\frac{\partial q_B}{\partial t} = K_{gB} a \left( p_B - p_B^* \right).$$

In order to compare models, values of $K_{gA}$ and $K_{gB}$ have to be determined from the above data. However since the driving force expressions are different, direct comparisons can be made only at low partial pressure, where all the isotherms are approximately linear. The low partial pressure assumption gives,

$$K_{gA} = \frac{k'B_d q_{dS}}{\rho_s RT} \approx 4.2603 \times 10^{-13} \text{ kmol kg}^{-1} \text{s}^{-1} \text{Pa}^{-1}$$

and

$$K_{gB} = \frac{k'B_d q_{dS}}{\rho_s RT} \approx 1.4091 \times 10^{-11} \text{ kmol kg}^{-1} \text{s}^{-1} \text{Pa}^{-1},$$

Hassan et. al. give their particle size as $\frac{1}{8}$ pellets. Assuming the particles to be spherical with a radius of 1.5875 mm, and given an interparticle voidage of $\epsilon = 0.4$, then the interfacial area per unit volume of column, $a$, is given by,

$$a = \frac{3(1 - \epsilon)}{r_p} \approx 1134 \text{ m}^{-1}.$$

Hence in terms of the present model, the mass transfer parameter values which have been estimated from Hassan et. al. are,
\[ K_{GA} = 1.2426 \times 10^{-14} \frac{\Omega_A}{s} \text{kmol m}^{-1}\text{s}^{-1}\text{Pa}^{-1} \]

\[ K_{GB} = 3.7569 \times 10^{-16} \frac{\Omega_B}{s} \text{kmol m}^{-1}\text{s}^{-1}\text{Pa}^{-1} \]

where \( \Omega_A \) and \( \Omega_B \) are the same as described above.

5.4 Boundary Conditions

For pressure changing steps (i.e. Pressurisation, Co- and Counter-current Depressurisation and Backfill), only one end of the column is open, hence no flow at the closed end is assumed, \( \vartheta_{cls} = 0 \). Thus the three families of characteristics \( (p_A, q_A \text{ and } q_B) \) described in Chapter 3 coincide and can be solved rapidly without needing to locate the position of the characteristics for the subsequent time steps. The feed composition for the pressurisation step is set by the user, and it is usually set to the composition of air.

For Bottom to Bottom Bed Pressure Equalisation (BBBPE) and Both End Bed Pressure Equalisation (BEBPE) steps, the feed came from the corresponding depressurisation step. In these cases, the feed composition was taken as the average composition from the donating depressurisation step. The feed composition for the backfill step was taken as the average composition obtained from the donating step depending on the type of cycle configuration involved (see Section 5.2.3 on perfect mixing).

The boundary conditions for the constant pressure steps arise from specifying the inlet flow rate and composition. The purge inlet volumetric
flow rate was supplied directly by the user depending on the amount of purge needed. This purge inlet rate was assumed to be constant throughout the purge step. The purge composition was assumed to be the average composition obtained during the previous product release step. During the product release step, the initial volumetric flow rate was specified by the user, however, for subsequent cycles, the inlet volumetric flow rate was controlled by the net product amount needed at the product end. At high net product amount, the calculated feed rate for subsequent cycles was kept constant throughout the product release step. When the net product amount is set low and the column starts to exhibit flow reversal at the product end, the feed rate was specified as a function of time in order to prevent flow reversal (see Section 5.5). The feed composition for the product release step was set by the user and was usually set to the same value as the feed composition for the pressurisation step.

The boundary conditions for each process step used in the simulations in Chapter 6 are summarised in Table 5.2 below:

<table>
<thead>
<tr>
<th>Step</th>
<th>Known conditions</th>
<th>Characteristic Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressurisation</td>
<td>$\varphi_L = 0$</td>
<td>$\frac{dz}{dt} = \frac{\varphi}{A\varepsilon}$</td>
</tr>
<tr>
<td></td>
<td>$p' &gt; 0 \text{ &amp; known}$</td>
<td>$\frac{d\varphi}{dz} = - \left[ A\varepsilon p' + \frac{A\omega RT}{p} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \right]$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\frac{dp_A}{dt} = p_A p' + \frac{\omega RT}{\varepsilon} f(q_A, q_B, p_A)$</td>
</tr>
</tbody>
</table>
Product Release $\phi_0$ & $p_{A0}$ known

\[ \frac{dz}{dt} = \frac{\phi}{A_e} \]

$p' = 0$

\[ \frac{d\phi}{dz} = -\frac{A\omega RT}{P} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \]

\[ \frac{dp_A}{dt} = \frac{\omega RT}{\varepsilon} f(q_A', q_B', p_A) \]

Depressurisation $\phi_L = 0$

As pressurisation above

$p' < 0$ & known

Purge $\phi_L$ & $p_{AL}$ known

As product release above

$p' = 0$

Co-current $\phi_0 = 0$

Depressurisation $p' < 0$ & known

As pressurisation above

Backfill $\phi_0 = 0$

As pressurisation above

$p' > 0$ & known

\[ f(q_A', q_B', p_A) = \frac{p_A}{P} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) - \frac{\partial q_A}{\partial t} \]

5.5 Flow Reversal during Product Release

In the course of running the model to simulate a simple cycle, it was discovered that the model for the product release step was violating its own boundary conditions.

It had been assumed initially that product release could be simulated by providing any volumetric flow rate into the bottom of the column, and that this would result in a positive flow out of the top of the column. The
simulations showed that this assumption was not true under all conditions. Consider, for example, a product release step which starts after a rapid pressurisation so that the amount adsorbed in the column is far below being in equilibrium with the gas phase locally or overall in the column. If then the product release step started with a very low volumetric flow rate in at the bottom of the bed, it was found that in some regions of the column the local rate of adsorption was greater than the volumetric flow rate within the column. In this case, the flow rate at the top of the column was calculated to be negative. The model was predicting that gas must be drawn in at both the bottom and top simultaneously in order to maintain a constant total pressure.

This situation is not encountered in practice because feed is drawn on demand so as to maintain a nearly constant positive flow rate out of the top of the column.

Therefore it was decided to reprogram the boundary conditions for the product release step so that if the model predicted that flow reversal had occurred, then that integration step was restarted with an increased volumetric flow rate (the increment was equal to the absolute value of the negative volumetric flow rate experienced), at the bottom of the column. This procedure was repeated with successive increases in flow rate until the flow rate everywhere within the column was positive.

This procedure solved the problem of reverse flow for all times and positions within the column during product release but created a second problem: if the overall amount of product released was to be controlled to
some desired value, it had to be possible to reduce the feed rate again at some later stage of the product release step (once the rate of adsorption had subsided and the inlet flow did not have to be so high in order to prevent reverse flow).

To accommodate this problem, an algorithm was written to integrate the amount of gas entering the column, and to reduce the flow into the column until the current average flow rate into the column was equal to the constant flow rate originally desired for the step.

5.6 Overall Convergence

It is desirable to use the program so that the user can specify the net product amount. An initial guess of the inlet volumetric flow rate during product release has to be specified so that the gross amount of gas released is sufficient to supply gas to the purge and backfill steps and leave exactly the desired amount of net gas released.

A proportional plus integral (PI) control algorithm was used initially because this method had been highly successful on the equilibrium model of Kirkby (1983). The control scheme works as follows: the user supplies a set point amount of net product released per part cycle, and at the end of each part cycle the program applies the PI algorithm to the error between the set point and the actual amount of net product from the just completed cycle. The controller output is a new value of the manipulated variable which, in this case, is the mean inlet flow rate to the next product.
release step. The PI control equation used is shown below:

$$\phi(n+1) = \phi(1) + \text{PGAIN} \left( \sum_{n=1}^{n=n} \text{ERR}(n) + \frac{\text{ERR}(n)}{\text{INACT}} \right)$$

Where

- $\phi(1)$ = the guessed volumetric flow rate for the first time step
- $\phi(n+1)$ = the calculated volumetric flow rate for the next time step
- $\text{ERR}(n)$ = error between the set point and the actual value
- $\text{PGAIN}$ = constant for proportional gain
- $\text{INACT}$ = constant for integral action time

It was discovered that this PI algorithm has several disadvantages amongst which the problem of tuning the controller is especially difficult. For a particular cycle, producing a particular amount of product, optimum controller settings can be found either by trial and error or the Zeigler Nichols closed loop method [Luyben, (1973)]. However, these optimum settings change with product amount and cycle configuration and hence the controller has to be retuned at regular intervals. Meanwhile if a rather too small value of integral action time is used (i.e. too large a value of integral gain) then the integral term produces an oscillatory response which increases greatly the time required to achieve steady state. This oscillatory response may also sometimes require impossibly low feed rates to the product release step and hence cause insurmountable violations of the need to prevent flow reversal.

An alternative method based on polynomial extrapolation was adopted and the PI controller become an optional method for the user. A three point, polynomial extrapolation algorithm, subroutine POLINT, based on Neville's
algorithm [Press et. al. (1988)] was used in favour of a two point linear extrapolation algorithm, subroutine LININT (which is also an additional option for the user). This is because the former was found to be less oscillatory while marching towards steady state. This polynomial algorithm fits a polynomial to approximate the recent history of the set point error, \( \text{ERR}(n) - \text{ERR}(n-2) \), with the inlet volumetric flow rate of product release, \( \theta_p \). Then a new volumetric flow rate for the next cycle is calculated based on this fitted polynomial supplied with the desired, zero, value of set point error. A rapid and stable overall convergence was obtained.

5.7 Program Structure

The final DCPSA software incorporates all the process assumptions described above as well as the following:

1) the assumptions made in deriving the boundary conditions for each process step;

2) the solution originated for the reverse flow phenomena encountered in the product release step; and

3) the process cycle overall convergence methodology which is essential for a dynamic simulation to reach steady state.

The final software consists of a main routine, CPSA, which is illustrated in Figure 5.2, and has the following functions:

1) data is read from a cycle configuration and parameter file, CPSA.DAT (see Appendix I for a typical simple cycle 'standard' simulation configuration file),

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2) all the variables initialised,

3) all the equation constants are calculated from the parameters estimated from the model of Hassan et. al.

4) perform the simulation of the specified PSA cycle from the process step routines:
   - PSR for pressurisation step,
   - PDR for product release step,
   - DPRS for counter-current depressurisation step,
   - CDPRS for co-current depressurisation step,
   - PURGE for purge step, and
   - BCKFL for backfill step.

5) store the output of previous steps for graphic generation and the initial conditions of subsequent steps,

6) perform the overall cycle material balance calculation,

7) execute the selected overall convergence methodology for the simulation to reach steady state, and

8) produce the performance summary report.

Appendix H lists all the routines involved and how they interlink. However, the logic of how each routine is called, and how many times it appears in the calling routine is not described in detail.

A front-end, menu driven FORTRAN program has been written to enable the use of the PSA programs with a minimum of technical understanding of the solution technique used by the model. This user interface program also allows the user to create and edit input data files. Figure 5.3 shows the logic diagram for this user interface program.
Logic Diagram of DCPSA Model Main Routine

Figure 5.2
Figure 5.3
5.8 Concluding Comments

In this chapter, the additional process assumptions have been described that have to be made regarding the variation of pressure with time, process symmetry, product mixing and the presence of argon. The parameters used in the DCPSA model have been derived from the data presented by Hassan et. al. The boundary conditions for both the pressure changing and constant pressure steps have been described. The problem of the flow reversal at low net product amount has been described and a robust solution algorithm presented. Lastly, a polynomial extrapolation technique has been presented which improved the speed and stability of the simulations.

Thus all the additional information required to turn the equations developed in Chapter 3 into a complete simulation of DCPSA has been supplied in this chapter. The results from running the model are presented in the next chapter.
6.1 Introduction

This chapter presents the results and detailed discussion of the simulations run on the DCPSA software. The simulation runs are based on the parameters estimated from the model of Hassan et al. (1986) (see Section 5.3). The simulation runs include the following cycle configurations:
1) simple,
2) purge with counter-current depressurisation (refer as normal purge),
3) purge with co-current depressurisation (refer as co-current purge),
4) backfill,
5) purge and backfill,
6) top to top bed pressure equalisation (TTBPE),
7) bottom to bottom bed pressure equalisation (BBBPE), and
8) both end bed pressure equalisation (BEBPE).

Each simulation run has its own cycle configuration file, which is derived from the 'standard' configuration file used for the simple cycle (see Appendix I). Hence, for the purpose of presenting the results, only those data which are different from the 'standard' configuration file will be mentioned. It should be noted that because the 'standard' configuration file is used as a basis for all other cycle configurations, there are data
in the file which only relate to specific cycle configurations. Therefore these specific data may be ignored by other cycles. All the simulation results are presented on a per part cycle basis.

The figures generated from the simulation results are presented together at the end of this Chapter.

6.2 Simple Cycle Simulation

This section presents the results for the simulation of a simple cycle with operating pressure between 0 and 3 barg. The model was run in control mode 3 (polynomial extrapolation; see Section 5.6), for the calculation of oxygen concentration in the product at an amount of net product per part cycle specified by the user.

6.2.1 Effect of Net Product Amount

Figure 6.1a shows the plotted results of oxygen mole fraction versus net product amount, and Figure 6.1b shows the corresponding nitrogen yield. As expected, when the net product amount increases (i.e. at higher feed rate), with no change in other process conditions, the separation capability reduces approximately exponentially until almost no separation is achieved. In this very high product amount the nitrogen yield approaches 100%.
When the net product amount is low, the feed rate is only slightly faster than the adsorption rate. This allows most of the oxygen in the feed to be adsorbed, thus achieving a higher product purity and fully utilising the adsorptive capacity of the bed. When the feed rate is very low, \(1.0 \times 10^{-6} \text{ m}^3/\text{s}\), the initial rate of adsorption may even be greater than or equal to the feed rate. In this case, for the material to balance, gas will have to be introduced from the product end until the rate of adsorption falls below the feed rate (see Section 5.5 for flow reversal phenomena). To accommodate this flow reversal phenomena, instead of being confined to a fixed feed rate like most PSA models, the DCPSA software can increase the feed rate until there is no more flow reversal (see Figure 6.2).

As the specified net product amount increases, a higher feed rate is required. This means the rate at which oxygen is going into the bed is very much higher than the overall rate of adsorption, thus more unadsorbed oxygen comes out with the product.

Figure 6.1a also shows that for a simple cycle operating at the conditions shown in Appendix I, the best achievable separation in terms of purity is only 92.3% nitrogen and this is achievable at a very low net product amount of \(5.0 \times 10^{-7}\) kmol. However, the separation can be improved to 98.1% of nitrogen concentration in the product by adding on a purge step (see Section 6.3).
6.2.2 Concentration Profiles

Figures 6.3 to 6.5 show the results from a typical simple cycle. Each figure shows both the evolution of the gas phase concentration profile and the family of characteristics underlying the calculation.

1) Pressurisation (Figure 6.3): the step starts with the adsorber saturated with air. The initial concentration profile is then compressed with feed air. As the feed air compresses the saturated profile down to the closed end of the column, oxygen is being adsorbed, leaving a zone of nitrogen rich gas at the closed end of the column. Further increases in pressure would decrease the size of the zone and would increase the nitrogen concentration within it. Below the plateau, the oxygen concentration steadily increases back to the feed end of the column where the adsorbent is virtually in equilibrium with the feed composition. The latter observation has certainly invalidated the frozen solid assumption.

2) Product Release (Figure 6.4): a shock wave (see Section 4.2.3) is generated during the product release step but it diminishes rapidly as it moves along the column with time. However, it should be noted that in general the concentration profile has not changed shape much. The concentration at the product release end is almost constant, that is, no breakthrough of the concentration front has occurred at this rather low product amount.

3) Depressurisation (Figure 6.5): when the gas is discharged through the feed end of the column, the gas in the column moves downward rapidly and the concentration front at the product end is quickly replaced by
the feed composition. During this time, oxygen in the adsorbent slowly desorbs into bulk gas to replace the discharged gas, hence at the end of the depressurisation step, the column consists of a uniform profile which is oxygen rich with respect to feed air. Once again, the simulation of this pressure changing step has indicated that the frozen solid assumption is totally invalid.

6.2.3 Integration Technique

When explicit Euler was first used as an integration technique, the software encountered immense problems in the pressure changing steps which hampered the accurate and efficient calculation of the compositions in the vicinity of a shock wave. However, the use of implicit Euler integration has certainly improved the software's execution efficiency without sacrificing any calculation accuracy. The improvement in CPU time due to the integration technique can be as large as a factor of two hundred times for a simple cycle simulation. The most important observations lie not only on the speed of integration but also on the solution's stability and accuracy (see Table 6.1 below). Based on the observations, this original and novel application of the technique has been applied on all the other cycle configuration simulations in the software development, and explicit Euler integration was no longer used in solving the gas and solid phase equations.
Table 6.1 Comparison Between Explicit and Implicit Euler Integration Technique on a Pressurisation Step Simulation

<table>
<thead>
<tr>
<th>Integration Technique</th>
<th>$O_2$ at Bed End (Zmol)</th>
<th>Total Feed (kmol)</th>
<th>Total $O_2$ in Feed (kmol)</th>
<th>CPU (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explicit</td>
<td>11.7</td>
<td>$1.42 \times 10^{-3}$</td>
<td>$2.99 \times 10^{-4}$</td>
<td>299.7</td>
</tr>
<tr>
<td>Implicit</td>
<td>9.85</td>
<td>$1.47 \times 10^{-3}$</td>
<td>$3.10 \times 10^{-4}$</td>
<td>21.6</td>
</tr>
</tbody>
</table>

6.3 Normal Purge Cycle Simulation

This section presents the results obtained for a series of normal purge cycle simulation runs. The prime objective was to determine the variation of product oxygen concentration with purge flow rate at a given net product amount. The secondary objectives were to determine the effect of net product amount and the type of the adsorption isotherm on the relationship between product oxygen concentration and purge flow rate. The purge flow rate is varied in order to vary the purge amount but the purge step time is kept constant.

The simulation runs use the 'standard' data with the following exceptions,

1) Purge flow rate, $V_{PURGE}$ = Vary from $1.0 \times 10^{-6}$ to $1.0 \times 10^{-2}$ (m$^3$/s)

2) Pressurisation time, $TPS$ = 20 (sec)

3) Depressurisation time, $TDS$ = 20 (sec)

4) Net product amount, $PD_{NET}$ = $1.0 \times 10^{-5}$ and $1.0 \times 10^{-4}$ (kmol)
The variation of pressure with time functions, for both pressurisation (linear) and depressurisation (exponential) can be found in Section 5.2.1.

6.3.1 Effect of Net Product Amount

Figure 6.6a shows two sets of simulation results, each has a constant net product amount, $1.0 \times 10^{-5}$ kmol and $1.0 \times 10^{-4}$ kmol respectively. There is an optimum purge flow rate for each set before the oxygen concentration in the product starts to increase again. These optimum purge flow rates lie between $1.0 \times 10^{-6}$ and $1.0 \times 10^{-4}$ m$^3$/s which correspond to a purge amount per unit time of $8.177 \times 10^{-7}$ and $8.177 \times 10^{-5}$ kmol/s respectively.

At the optimum purge flow rate, the lowest oxygen concentrations in the product were 1.96% and 13.4% respectively. When the purge flow rate is lower than the optimum flow rate, the overall rate of oxygen desorption is low and the column is only partially clean. This is because at low purge flow rates only a small part of the top of the column receives low oxygen purge gas. Low oxygen partial pressures provide the driving force for increased rates of desorption. Therefore oxygen desorption is only enhanced in this small region at the top of the column.

At high purge flow rates, that is, above the optimum, the donating product release step is releasing so much product gas that the product oxygen concentration rises. This is the direct cause of the rise in oxygen concentration in the product. The secondary effect is that the receiving column receives gas of higher oxygen partial pressure, hence the driving
force for oxygen desorption is reduced and the cleaning effect is likewise reduced. It is therefore very important to identify the optimum purge flow rate at each preset net product amount during purge cycle operations.

The effect of net product amount on the normal purge cycle, can be summarised as follows:

1) better separation can be achieved at a lower net product amount, this coincides with the result obtained for simple cycle simulation, where the product oxygen concentration increases as the net product amount increases, and

2) the optimum purge flow rate is larger at higher net product amounts. This is because the adsorptive capability of the adsorbents has not been fully utilised at higher net product amounts. When the feed rate is high during the product release step, the feed rate is much faster than the oxygen adsorption rate, and the product oxygen concentration is increased. This leads to less rapid desorption during the purge step due to a smaller mass transfer driving force for oxygen. Hence the purge step has little effect even within the optimum region. Outside this optimum region, the cleaning effect of the purge step decreases even further for the reasons described above.

Figure 6.6b shows the plot of nitrogen yield versus the purge flow rate on the simulation runs mentioned above. Again the results show the general trends as were obtained for a simple cycle, where the nitrogen yield increases with the increase in net product amount. The figure shows that the nitrogen yield is also dependent on the purge flow rate. However there is no optimum purge amount at constant net product amount.
Hence it is important to identify whether it is the product concentration or the product yield that defines the operating philosophy for the purge cycle. The following points summarise the findings:

1) the lower the net product amount, the better the separation,
2) the higher the net product amount, the better the nitrogen yield,
3) there is an optimum purge flow rate for product purity, and
4) the lower the purge flow rate, the higher the nitrogen yield.

Although no simulation has been carried out to show the effect of purge flow rate at constant purge amount or vice versa, it should be noted that such investigations can be easily carried out using the current model.

6.3.2 Effect of Type of Adsorption Isotherm

Figure 6.7a and Figure 6.7b show the results obtained from running the software with linear isotherm and compared to the results obtained earlier using Langmuir isotherm (Figures 6.6a and 6.6b). The simulation was at a net product amount of $1.0 \times 10^{-5}$ kmol. The results suggest that the DCPSA model is sensitive to the type of isotherm used as far as the product specification is concerned. However the type of isotherm used has a negligible impact on the product yield. No simulation has been carried out using the Langmuir co-adsorption isotherm as far as the variation of purge flow rate is concerned. The model, again, can be used to perform such a simulation.
Figure 6.8 is the plot of product oxygen concentration versus cycle number showing the variation with the three different types of isotherm (linear, Langmuir and Langmuir co-adsorption). The following conclusions were drawn:

1) for the linear isotherm, the simulation took 20 cycles to reach steady-state and the product oxygen concentration is approximately 8.5%. Whereas approximately 35 cycles are required for both the Langmuir pure gas and Langmuir binary co-adsorption isotherms, and their steady-state product oxygen concentrations are 5.5% and 6.5% respectively.

2) the results show that, during the dynamic state, the product oxygen concentration rose temporarily from 8% to 15% for Langmuir binary isotherm, 14% for Langmuir pure gas isotherm and 12.5% for the linear isotherm. These results have demonstrated that the dynamics of using different isotherms are qualitatively similar. It is thus important to have an accurate representation of the isotherm used, especially if the software is used as a design tool for any binary gas adsorption separation.

6.4 Purge Cycle with Co-current Depressurisation Simulation

As discussed in Chapter 2, the co-current depressurisation step is normally used in conjunction with the backfill step. The combination of these two steps constitutes one of the bed pressure equalisation steps. In this section the simulation runs are performed to serve the following purposes:
1) to demonstrate the robustness of the software, and
2) to study the behaviour of purge cycle when using co-current depressurisation as a regeneration step where the co-current gas is as a waste gas. (The co-current depressurisation step is not normally a regeneration step but rather a step which enhances product release, in which case the co-current gas goes out as a product), and
3) to compare the two different types of purge cycles.

The simulation results are generated from the data used for the normal purge cycle.

Figure 6.9 shows the plot of product oxygen concentration versus purge flow rate with two different net product amounts. The results for co-current purge (denoted in the figure by CDPRS) show that the separation behaves in a very similar pattern to that of the normal purge cycle. The figure also shows the direct comparison between the two different types of depressurisation in purge cycles. Both sets of results show that the model favours the normal purge cycle in terms of product purity. However, at high net product amount, the difference between the two cycles is negligible. This difference increases to 2.3% when the net product amount reduces to $1.0 \times 10^{-5}$ kmol per part cycle.

The reason that a higher product oxygen concentration arises for the co-current purge cycle is that when co-current depressurisation commences to regenerate the column, feed composition gas at the bottom of the column travels towards the product end. The oxygen concentration in the gas phase increases as the adsorbed oxygen starts to desorb. As the high oxygen
concentration gas moves towards the product end, it pushes the purer product, left at the end of the product release step, out through the product end. Hence at the end of the co-current depressurisation, the column is left with gas of high oxygen concentration. This certainly does not favour the adsorption of oxygen for the subsequent cycle. This is not the case for a normal purge cycle because when the column starts to regenerate, the purer gas near the product end does not immediately leave the column. Gases that leave the column are those saturated with feed composition near the feed end. As the purer gas at the product end travels towards the feed end, the partial pressure of oxygen in the gas phase becomes less saturated, thus increasing the mass transfer driving force. Under this cycle the adsorbed oxygen will leave the adsorbent more rapidly leaving the column with lesser oxygen components and hence a cleaner column for the subsequent cycle.

The figure shows remarkably little effect when the net product amount is high, $1.0 \times 10^{-4}$ kmol. This is because the adsorptive capability of the adsorbents for both purge cycle types have the same effect, i.e. not being fully utilised at higher net product amounts. When the feed rate is high during the product release step, the feed rate is much faster than the oxygen adsorption rate, and the product oxygen concentration is increased. This leads to less rapid desorption during both the purge steps due to a smaller mass transfer driving force for oxygen. Hence the purge steps have little effect.
6.5 Backfill Cycle Simulation

The simulation results are generated from the 'standard' data shown in Appendix I, used for simple cycle, with the following exceptions:

1) Final Backfill Pressure, \( PH_B \) = Vary from 101.3 to 303.9 (kPa)

2) Process time during backfill, \( T_{BF} \) = Calculated value depending on the final backfill pressure as follows:

\[
T_{BF} = \frac{(PH_B - PLB) \Delta t}{\Delta P},
\]

where \( \Delta P \) is the range of operating pressure, \( \Delta t \) is the process step time and \( PLB \) is the initial backfill pressure (see Section 5.2.1).

3) Net product amount, \( PD_{NET} \) = 1.0 \( \times 10^{-6} \), 1.0 \( \times 10^{-5} \) and 1.0 \( \times 10^{-4} \) kmol.

6.5.1 Effect of Net Product Amount

The software was run to simulate backfill cycles at the three different net product amounts per part cycle. The results are plotted as product oxygen concentration versus backfill pressure in Figure 6.10a and nitrogen yield against backfill pressure in Figure 6.10b. Table 6.2 below, illustrates the performance of the backfill cycles at the three different net product amounts when the backfill pressure is at the upper operating pressure, 303.9 kPa.
Table 6.2 Performance of Backfill Cycles at Different Net Product Amounts

<table>
<thead>
<tr>
<th>Product Amount (kmol/part cycle)</th>
<th>Product Nitrogen (k mol/part cycle)</th>
<th>Product Nitrogen Yield (%)</th>
<th>Contained Nitrogen (k mol/part cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 x 10^-6</td>
<td>98.8</td>
<td>6.9</td>
<td>9.88 x 10^-5</td>
</tr>
<tr>
<td>1.0 x 10^-5</td>
<td>95.4</td>
<td>42.6</td>
<td>9.54 x 10^-4</td>
</tr>
<tr>
<td>1.0 x 10^-4</td>
<td>81.6</td>
<td>86.6</td>
<td>8.16 x 10^-3</td>
</tr>
</tbody>
</table>

When the product nitrogen concentration is compared with the results obtained for a simple cycle, 92%, 91.4% and 81.3% respectively, the inclusion of a backfill cycle has provided a better separation. This is indeed the expected result, since the column is backfilled (pressurised from product end) with gas which is richer in nitrogen than feed gas.

6.5.2 Effect of Backfill Pressure

The effect of backfill pressure on product oxygen concentration and nitrogen yield are summarised as follows (see Figures 6.10a and 6.10b):

1) at low backfill pressure (100 to 130 kPa for net product amounts of 1.0 x 10^-6 and 1.0 x 10^-5 kmol) the product oxygen concentration fall rapidly with decreasing backfill pressure,
2) at intermediate pressure (130 to 275 kPa) there is a slight minimum in product oxygen concentration and slight maximum in nitrogen yield,
3) at high backfill pressure (275 to 304 kPa) the product oxygen concentration rises slightly, and
4) yields are almost independent of backfill pressure, except at very high backfill pressures (274.7 to 303.9 kPa) where the yield decreases as the backfill pressure increases.

The results show that there is an optimum operating region, which lies between 130.2 and 245.8 kPa of the operating pressure. In terms of product oxygen concentration, these optimum region are very shallow but the optimum backfill pressure decreases with decreasing net product amount per part cycle.

Although the separation is very good, 98.8% nitrogen, at low net product amount, $1.0 \times 10^{-6}$ kmol, the product recovery of approximately 6% nitrogen yield is not economical.

The reason for the generation of the optimum region is that, at low backfill pressures, only a small amount of gas with product concentration is introduced into the product end. As the backfill pressure increases, the amount of gas with product concentration entering the product end also increases. This effectively moves a large fraction of the nitrogen from the product release column to the backfill column. This gives the nitrogen a longer residence time in the backfill column which enhances the product concentration and nitrogen yield. However, if the backfill pressure increase further, more gas from the product release step is required. To
maintain a constant net product amount from product release, more gas is required to leave the product end, therefore gas with a higher oxygen concentration starts to break through the product end. When this higher oxygen content gas enters the product end of the backfill step it starts to dilute the purer gas at the product end, thus reducing the effectiveness of the backfill step.

The backfill cycle results when compared to the normal purge cycle at the net product amount of $1.0 \times 10^{-5}$ kmol, show that, although the purge cycle manage to obtain a slightly better separation than the backfill cycle (i.e. 98.1% of nitrogen for normal purge cycle instead of 96.5% obtained by the backfill cycle), an improvement of 9% nitrogen yield is found for the backfill cycle (i.e. 43.0% for backfill cycle and 34.0% for normal purge cycle).

6.6 Purge and Backfill·Cycle Simulation

This section describes a single set of simulations in which the net product amount is held constant at $1.0 \times 10^{-5}$ kmol per part cycle. The cycle includes both the purge and backfill steps in that order; the volumetric purge flow rate was varied between $1.0 \times 10^{-6}$ and $1.0 \times 10^{-4}$ m$^3$/s and the backfill pressure was varied between 101.3 and 303.9 kPa. The pressurisation and depressurisation process time are both set at 20 seconds. The backfill process time is calculated as in the backfill cycle simulation (see Section 6.5).
Figure 6.11 shows the product oxygen concentration contours which result from varying the 8 values of backfill pressure with 15 values of purge flow rate. The results confirm the observed results obtained from running purge cycle and backfill cycle independently, that is, there is an optimum product oxygen concentration. This optimum lies in the region of low purge flow rate ($1.5 \times 10^{-6}$ and $5.5 \times 10^{-6}$ m$^3$/s) as well as low backfill pressure (130.2 and 159.2 kPa). As both the purge flow rate and backfill pressure increase beyond the optimum region, the product oxygen concentration increases rapidly. The product oxygen concentration increases further even at and above the purge flow rate of $2.0 \times 10^{-4}$ m$^3$/s. but at this rate it is no longer affected by the backfill pressure. (Above this purge flow rate, the product oxygen concentration further increases with purge flow rate but backfill pressure has little effect.)

Figure 6.12 shows the corresponding contour plots of nitrogen yield. The contours are different from those obtained for product oxygen concentration; no distinct optimum is observed. The general observations are:

1) the nitrogen yield decreases rapidly as the purge flow rate increases,
2) variation of backfill pressure below 274.7 kPa has no effect on nitrogen yield, however, between this backfill pressure and the upper operating pressure 303.9 kPa, nitrogen yield decreases rapidly with the increase of backfill pressure.

These simulation results lead to the conclusion that,

1) it is essential to keep the backfill pressure below 75% of the upper operating pressure so that the nitrogen yield is optimised,
2) There is a region where the oxygen concentration is lower than can be achieved by cycles using purge or backfill alone,

3) The optimum backfill pressure for purge and backfill is approximately 20 kPa lower than for backfill alone, and

4) The optimum purge amount for purge and backfill is also lower than for the purge cycles alone.

6.7 Top to Top Bed Pressure Equalisation Cycle Simulation

As discussed in Section 2.4, if only two columns are used in a Bed Pressure Equalisation (BPE) cycle, there will not be a continuous flow of product (see Figure 2.8). Since the purpose of this simulation is to demonstrate the capability and robustness of the DCPSA software and to study the behaviour of BPE cycles, no attempt is made to simulate a BPE cycle with a continuous flow of product.

Two sets of simulation runs were performed. Constant net product amounts of $1.0 \times 10^{-6}$ and $1.0 \times 10^{-5}$ kmol were used. The purge flow rate used in each case is the optimum purge flow rate, $5.0 \times 10^{-5}$ m$^3$/s, obtained during the normal purge cycle simulation.

In addition to these boundary conditions, the simulation of the Top to Top Bed Pressure Equalisation (TTBPE) cycle is based on the 'standard' data with the following exceptions:

1) Final pressure for co-current depressurisation, PLC = 8 values varying from 303.9 to 101.3 kPa,
2) Initial pressure for normal depressurisation, PHD = Set equal to the final pressure for co-current depressurisation, PLC, on each simulation,

3) Process time for pressurisation step, TPS = 20 sec
4) Process time for product release step, TPR = 40 sec
5) Process time for depressurisation step, TDP = 20 sec
6) Process time for purge step, TPG = 40 sec

Figures 6.13a, 6.13b and 6.13c are the three plots of the backfill pressure, product nitrogen yield and product oxygen concentration versus the co-current depressurisation pressure respectively; obtained from the simulation of TTBPE cycle when the net product amount is kept constant at $1.0 \times 10^{-6}$ kmol.

Figure 6.13a shows that as the pressure in the donating column decreases, the pressure in the backfill column increases almost linearly. No reduction in pressure is possible for the donating column below the pressure in the receiving column unless a compressor is used. The software allows the study of the behaviour of the BPE cycles beyond the normal operating pressure range, and to investigate whether there is any real advantage to be gained by the use of a compressor to induce gas from the donating column.

The results shown on Figures 6.13b and 6.13c and all other BPE simulation results (see later sections) are the maximum and the minimum range values that the simulated process oscillates after it reaches steady state.
From the figures, the results suggest that:

1) the nitrogen yield is not sensitive to the effect of bed pressure equalisation, it only varies between 0.9% and 1.7%. The plot did, however, show that when the co-current depressurisation step reaches its lower operating pressure, the product yield oscillate over a large range and become less stable,

2) the minimum product oxygen concentration lies within the BPE normal pressure range (i.e no compressor is required), and its best separation is 7.09% of oxygen in the product. Again the plot shows a higher product oxygen concentration as the co-current depressurisation step approaches its lower operating pressure.

From these observations it was therefore concluded that there is no advantage in using a compressor to induce further gas from co-current depressurisation once it has reached its equalisation pressure. In fact the simulation suggests that to obtain an optimum separation when operating the TTBPE cycle, it is not necessary to reach its equalisation pressure.

6.7.1 Effect of Net Product Amount

Figures 6.14a, 6.14b and 6.14c are the simulation results of a TTBPE cycle. The simulation run is based on the configuration file used to generate the results for Figure 6.13 with the exception of the net product amount, which has been increased to $1.0 \times 10^{-5}$ kmol. The purpose of these simulations is to study the effect of net product amount on TTBPE cycles.
The results show that,

1) the increase of net product amount does not affect the plot of backfill pressure versus co-current depressurisation pressure. The equalisation pressure is 201.85 kPa.

2) nitrogen yield increases as the co-current depressurisation pressure decreases. This suggests that, as the net product amount increases, nitrogen yield can be improved further even after the equalisation pressure has been reached. However, this improvement cannot be justified because the improvement in the nitrogen yield of 1% will cause a 3% reduction in the purity as shown in Figure 6.14c. The increase in the nitrogen yield is ten times greater than that at the lower net product amount.

3) again there is an optimum product oxygen concentration within the normal BPE operating pressure range. However, the best separation is only 8.16% purity compared to 7.09% at lower net product amount.

6.8 Bottom to Bottom Bed Pressure Equalisation Cycle Simulation

The simulation of the Bottom to Bottom Bed Pressure Equalisation (BBBPE) cycle is based on the data used for the TTBPE run. However, the final normal depressurisation pressure, PLD, is used instead of the final pressure for co-current depressurisation, PLC. Furthermore, this simulation does not include the backfill step.

Figures 6.15a, 6.15b and 6.15c are the three plots obtained from the
simulation of the BBBPE cycle when the net product amount is kept constant at $1.0 \times 10^{-6}$ kmol. The figures plot the pressurisation pressure, product nitrogen yield and product oxygen concentration versus the depressurisation pressure respectively.

Figure 6.15a again shows that the donating and receiving column pressures are linearly related except when virtually all available gas is transferred (using a compressor).

From the figures, the results suggest that:

1) although the plot of nitrogen yield appears rather scattered, it is in fact not as sensitive as that for the TTBPE (Figure 6.13b). The pattern of the scatter plots is due to its plot range which is only 0.6%. The lowest nitrogen yield is 0.86% and the highest is 1.34%.

2) the minimum product oxygen concentration lie within the BPE normal pressure range, and its best separation is 7.12% of oxygen in the product.

Again these observations suggest that there is no advantage in using a compressor to transfer gas from the depressurisation step once it has reached its equalisation pressure. The simulation also suggests that at low net product amount there is little difference between TTBPE and BBBPE cycles.
6.8.1 Effect of Net Product Amount

Figures 6.16a, 6.16b and 6.16c are the simulation results of a BBBPE cycle. The simulation run is based on the configuration file used to generate the results for Figure 6.15 with the exception of the net product amount, which is $1.0 \times 10^{-5}$ kmol. The purpose of this simulation run is to study the effect of net product amount on BBBPE cycles.

The results show that,

1) the increase in net product amount does not affect the plot of pressurisation pressure versus depressurisation pressure. The two curves, Figures 6.15a and 6.16a, are almost identical. The linearity gradient for Figure 6.16a is 1.0061 and its equalisation pressure is 201.93 kPa.

2) nitrogen yield increases as the depressurisation pressure decreases. This suggests that, as the net product amount increases, the nitrogen yield can be improved further even after the equalisation pressure has been reached. However, this improvement may not be justified because the improvement in nitrogen yield of 1% will cause a 0.6% reduction in the purity as shown in Figure 6.16c. The increase in nitrogen yield is approximately eight fold when compared to that of the lower net product amount. When comparing this set of results with the results for the TTBPE, the TTBPE cycle results are more favourable because the TTBPE cycle yields approximately 0.5% more nitrogen.

3) there is an optimum product oxygen concentration within the normal BPE operating pressure range. However, the best separation is only 8.2%
purity compared to 7.12% at lower net product amount. When compared to the TTBPE cycle, there is no difference between both cycle types as far as the product oxygen concentration is concerned.

6.9 Both End Bed Pressure Equalisation Cycle Simulation

The simulation of the Both End Bed Pressure Equalisation (BEBPE) cycle involves the problem of handling the concentration profile in the column. At the end of the product release step, the DCPSA software splits the column horizontally into two separate columns; the top one for co-current depressurisation and the bottom one for counter-current depressurisation. These columns then become the gas donating columns. At the end of the gas donating stage, the two columns re-combine to become the original column, which depressurises further until it reaches the lower operating pressure. This step is then followed by a purge step. At the end of the purge step the column then becomes the receiving stage for BPE.

During the gas receiving stage, the column is pressurised at the feed end as well as backfilled at the product end. Again the column was split in two. At the end of the step the calculated pressurisation pressure and backfill pressure do not normally coincide. Hence an iterative method was implemented in which the position of the split in the receiving column is moved until the pressure in both sections of the column is the same at the end of the step.

The simulation of the BEBPE cycle uses the same data as the TTBPE
simulation so that direct comparisons can be made. The only exception is that the final pressures of the donating column, PLD and PLC, are set equal to each other.

Figures 6.17a, 6.17b and 6.17c are the three plots obtained from the simulation of BEBPE cycle when the net product amount is kept constant at 1.0 x 10^{-6} kmol. The figures show pressure of gas receiving column (GRC), product nitrogen yield and product oxygen concentration versus pressure of gas donating column (GDC) respectively.

From the figures, it is observed that:

1) although the plot of nitrogen yield look rather scattered, it is in fact quite similar to Figure 6.15b for the BBBPE cycle. The pattern on the scatter plots is due to its plot range which is only 1%. The lowest nitrogen yield is 0.91% and the highest is 1.62%.

2) there is a distinctive minimum product oxygen concentration which also lie within the BPE normal pressure range, and its best separation is 6.17% of oxygen in the product. This is by far the best separation for all the BPE cycles encountered so far.

As before, these observations suggest that there is no advantage in using a compressor to induce gas from the GDC once it has reached its equalisation pressure. The simulations also lead to the conclusion that at low net product amount the BEBPE cycle is the superior BPE cycle as far as product oxygen concentration is concerned.
6.9.1 Effect of Net Product Amount

Figures 6.18a, 6.18b and 6.18c are the simulation results of a BEBPE cycle. The simulations run are based on the configuration file used to generate the results for Figure 6.17 with the exception of the net product amount, which is $1.0 \times 10^{-5}$ kmol per part cycle. The purpose of these simulations is to study the effect of net product amount on BEBPE cycles.

The results show that,

1) nitrogen yield is between 9.3% and 10.3%. Again the results scatter within a range of 1%. This therefore clearly suggests that, as the net product amount increases, the only effect is the six-fold increase in nitrogen yield. When compared to other BPE cycles, the difference is small and within 0.5%.

2) there is an optimum product oxygen concentration within the normal BPE operating pressure range. Furthermore, the best separation is 7.0% purity which is 0.8% lower than that of the lower net product amount. When compared to the other two BPE cycles, the improvement is approximately 1.2%.

An interesting outcome from the two product oxygen concentration plots, Figure 6.17c and 6.18c, is that, the optimum oxygen lies relatively close to the upper operating pressure.
6.9.2 Effect of Purge Flow Rate

It is obvious from the results that BEBPE cycle outperforms all other BPE cycles compared so far. It is therefore decided to see the effect of purge flow rate on BEBPE with its net product amount kept at $1.0 \times 10^{-5}$ kmol. Two further simulation runs were conducted, one with purge flow rate of $5.5 \times 10^{-5}$ m$^3$/s and the other with purge flow rate of $4.5 \times 10^{-5}$ m$^3$/s.

The results show that as the purge flow rate decreases, the nitrogen yield increases and the product oxygen concentration decreases. The best separation achieved is 4.54% product oxygen concentration with a nitrogen yield of 10.9%. The results are summarised in Table 6.3 below:

<table>
<thead>
<tr>
<th>Purge Flow Rate $x 10^{-5}$ (m$^3$/s)</th>
<th>Nitrogen Yield (%)</th>
<th>Product Oxygen Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>10.9</td>
<td>4.54</td>
</tr>
<tr>
<td>5.0</td>
<td>10.0</td>
<td>7.00</td>
</tr>
<tr>
<td>5.5</td>
<td>9.36</td>
<td>7.44</td>
</tr>
</tbody>
</table>

6.10 Sensitivity Analysis

A sensitivity analysis was carried out on a number of parameters used in the theory. The parameters chosen were those which could be varied in the design of either the PSA processes or the adsorbent. The sensitivity
The simulation run uses the normal purge cycle with a net product amount of $1.0 \times 10^{-5}$ kmol as a base case. Two sets of runs were then generated, one set with a $+10\%$ and another set with a $-10\%$ on the selected parameters. Plots of product oxygen concentration and nitrogen yield versus the purge amount were used to compare the sensitivity of the parameters. At a purge amount below the optimum purge amount, the sensitivity test is not necessarily meaningful because the model may encounter the flow reversal phenomena during purging. Hence the discussion below only refers to values observed at the optimum purge amount and above.

Figure 6.19a and Figure 6.19b are the sensitivity plots for the column cross section area. The plots show that the DCPSA model is sensitive to the cross section area only by approximately $\pm 0.2\%$ initially in product purity (expressed as a $\%$ of oxygen in the product). But as the purge amount increases the sensitivity increases to $+0.5\%$ and $-0.3\%$. The sensitivity of the nitrogen yield drop from $\pm 2\%$ to $\pm 0.5\%$ as the purge amount increases. The improvement in product purity, when cross section area increases, is mainly due to the reduction in the gas superficial velocity (i.e $A \propto L/\nu$) which favours the separation. On the other hand, the reduction in nitrogen yield is due to the overall reduction in the net product amount as the volume of the column increases.

Figures 6.20a and 6.20b show the result for variation of column voidage. When the cycle is at its optimum purge amount, the model is sensitive to $\pm 0.1\%$ of product purity. These margins gradually change to $+0.3\%$ and $-0.1\%$ as the purge amount increases. As for the nitrogen yield, Figure 6.20b
shows that it varies from ±1% to ±0.5% as the purge amount increases. Therefore, the interesting point about the voidage results is that below the optimum purge amount a reduction of voidage produces more effect on product concentration than increasing the voidage, but above the optimum purge amount the opposite is true. However, the effect on nitrogen yield is symmetrical. The reduction in product purity as the voidage increases is purely due to the increase in the gas superficial velocity which does not favour separation. As for nitrogen yield, the change is insignificant indicating that there is little change in the net product amount.

Figure 6.21a shows that the model is more sensitive to an increase in bed length from base case. For product purity it varies from ±0.2% to +0.6% and −0.4% as the purge amount increases. Again there is little difference for nitrogen yield, it varies from ±2% to ±0.5%, as shown in Figure 6.21b. These results are similar to those for column area (Figures 6.19a and 6.19b).

Figure 6.22a shows that a decrease in the packing density from the base case has a significant effect on the product purity. The sensitivity in the purity increases from +0.2% to +0.5% as the purge amount increases. Figure 6.22b, for the nitrogen yield, confirms that the model is only sensitive to a decrease in the packing density below the base case. The change in nitrogen yield is, however, very small that is less than 0.5%. A decrease in the packing density effectively means an increase in the column voidage. Hence, the gas superficial velocity also increases which is highly undesirable for separation.
Figure 6.23a and Figure 6.23b show the model's sensitivity to variation of the particle radius. It is obvious from the purity plots that a change of ±10% of the radius from the base case causes a change in the product purity. It varied from ±0.15% to ±0.4% as the purge amount increases. Again, changes to the product nitrogen is small, it varied from ±0.5% to less than ±0.1%. Therefore, a variation in the particle radius results in a change in the inter-particle voidage which affects the separation.

The sensitivity tests carried out on the overall mass transfer coefficients for both oxygen (Figure 6.24a and Figure 6.24b) and nitrogen (Figure 6.25a and 6.25b) show very similar results. The model is only sensitive to a 10% increase in the overall mass transfer coefficients from the base case. The effect on both coefficients is a change of +0.2% to +0.6% in the product oxygen concentration as the purge amount increases. The change in the nitrogen yield is less than +0.5%. A decrease in the overall mass transfer coefficient of oxygen, or conversely an increase in the overall mass transfer coefficient of nitrogen, reduces the product purity which confirms the validity of the kinetic model.

In each and every case, the product concentration and nitrogen yield, as predicted by the model were not sensitive to any of the isotherms parameters. The conclusion must be that the process basically never gets near to equilibrium; that is to say that $p^*$ is either too large or too small compared to $p$, hence changing isotherm parameters by 10% (effectively $p^*$ is changed by approximately 10%) has very little effect on $(p - p^*)$ (which is large compared with $p^*$).
Figures 6.26a and 6.26b show the results of the variation in the net product amount. At the optimum purge flow rate of the base case, there is only a slight drop in purity (+0.15% of oxygen) as the net product amount increases. However, as the net product amount decreases, the improvement in purity (-0.4% of oxygen) is larger. Above the optimum, variations of ±10% in the net product amount yield poorer separations than in the base case. In addition, when the net product amount is below the base case, no optimum purge flow rate was observed. This suggests that there is an optimum net product amount, beyond which no improvement in purity is possible. This may be due to the fact that any further reduction in the net product amount will result in a flow reversal which is not desirable. The results for nitrogen yield do not show these effects.

Figures 6.27a and 6.27b represent the results obtained by varying the upper operating pressure. It is clear from the results that the drop in upper operating pressure is undesirable because the product purity can drop as much as 1.5%. Conversely, the improvement in product purity is less than 0.1% for a 10.0% increase in the upper operating pressure. However, nitrogen yield drops by approximately 2%. These observations indicate that the base case upper operating pressure is near to its optimum as far as the product purity is concerned. The results further demonstrate the effects of linear driving force.

The results for the variation of lower operating pressure as shown in Figures 6.28a and 6.28b are very similar to that of Figures 6.27a and 6.27b. In this case, the rise in lower operating pressure is undesirable
for reasons as described above. The variation in nitrogen yield is less obvious in the variation of lower operating pressure.

Figures 6.29a and 6.29b show the results for the variation of cycle time. The change in product purity and nitrogen yield are insignificant. This indicates that fast cyclic processes are insensitive to cycle time.

6.11 Comparison of Purge Cycle Simulation of DCPSA Model with Hassan et. al.'s Work

Figure 6.30 shows the simulation results of a normal purge cycle with different values of $\Omega_A$ and $\Omega_B$ (where the effective sorption rate constant is related to the diffusional time constant by $k = \Omega D/r_p^2$, following Glueckauf and Coates (1947), the value of $\Omega$ is 15; also see Section 5.3). The figure also shows the theoretical (represented by a solid line) and experimental (represented by the symbol 'o') results of Hassan, Ruthven and Raghavan (1986).

The purpose of these simulations is to observe the variation of oxygen concentration in the product with half cycle number and to compare them with the results obtained by Hassan et. al. (1986). It is however important to note that a direct comparison between the DCPSA simulation and the results obtained by Hassan et. al. cannot be made due to differences in the cycle configuration and cycle time. The cycle configuration by Hassan et. al. does not allow for a continuous flow of product and the part cycle time for the configuration is 150 seconds instead of 120 seconds as shown.
in the diagrams below.

Hassan et al. purge cycle configuration

|---------------|---------|-------|--------|

\[\leftarrow 60 \text{ sec} \rightarrow\leftarrow 30 \text{ sec} \rightarrow \leftarrow 60 \text{ sec} \rightarrow\leftarrow 30 \text{ sec}\]

DCPSA normal purge cycle configuration

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Depres.</td>
<td>Purge</td>
<td>Press.</td>
<td>Product Release</td>
</tr>
</tbody>
</table>

\[\leftarrow 20 \text{ sec} \rightarrow\leftarrow 20 \text{ sec} \rightarrow\leftarrow 20 \text{ sec} \rightarrow \leftarrow 60 \text{ sec} \rightarrow\]

The important point to note is that Hassan et al. have shown a good match between the theoretical and experimental results by varying their values of $Q$. They claimed that it is acceptable to vary $Q$ based on the findings of Nakao and Suzuki (1983). However they did not acknowledge that the relationship between $Q$ and cycle time is obtained only after the cyclic adsorption process reaches steady state. Therefore, it is not valid to use the transient state as Hassan et al. have done. As can be seen from Figure 6.30, changing the values of $Q$ also has a great effect on the DCPSA simulation results.
6.12 Conclusion

To summarise,

1) The DCPSA model has been used to simulate eight types of process cycle. These cycles are made up from six distinct steps: pressurisation, product release, counter-current depressurisation, co-current depressurisation, purge and backfill.

2) The model has been used to demonstrate the separation capability of each cycle type, particularly the effect of net product amount on product concentration. As the net product amount increases, the product oxygen concentration also increases.

3) For a simple cycle, the main feature is the sensitivity of the separation capability at a low net product amount. A small variation in net product amount results in a relatively large increase in the product oxygen concentration. The model experiences the flow reversal phenomenon when the net product amount goes below $1.0 \times 10^{-6}$ kmol per part cycle.

4) When the two type of purge cycles are compared, the normal purge cycle is shown to give a better separation, approximately 2.3%, at a net product amount of $1.0 \times 10^{-5}$ kmol per part cycle.

5) Apart from the simple cycle, the model predicts that there is always an optimum operating region:

   a) for both types of purge cycles, the optimum lies within the purge flow rate of $1.0 \times 10^{-6}$ and $1.0 \times 10^{-4}$ m$^3$/s,

   b) for the backfill cycle, the optimum lies within the backfill pressure of 130.2 and 245.8 kPa,
c) for purge and backfill cycles, the optimum lies at a low purge flow rate within the region of $1.5 \times 10^{-6}$ to $5.5 \times 10^{-6}$ $m^3/s$ as well as at a low backfill pressure within the region of 130.2 to 159.2 kPa.

d) for bed pressure equalisation cycles, the optimum lies within the pressure of the donating column (216.9 to 303.9 kPa).

6) It is noted that for the purge and backfill cycle, the product oxygen concentration increases rapidly as both the purge flow rate and the backfill pressure increase beyond the optimum region, as long as the purge flow rate is below $2.0 \times 10^{-4}$ $m^3/s$. Above this purge flow rate, the product oxygen concentration increases further with an increase in the purge flow rate but shows a negligible change with an increase in the backfill pressure.

7) The model simulates the bed pressure equalisation cycles successfully.

8) The sensitivity study is geared towards the physical and the operating parameters. This study has allowed the designer to have a better view of how each individual parameter affects the separation given a fixed set of operating conditions.

9) The use of $\Omega_s$ value as fitting parameters by Hassan et. al. in their model has yet to be fully justified.

Due to the lack of process data and published experimental results, the simulation results are only hypothetical. Hence no quantitative measure should be taken from the results as such. However the behaviour of the model can be accepted as a good indication of how the process can and may behave as suggested by the results.
This chapter has demonstrated the capability and the robustness of the DCPSA model. The following chapter summarises the findings of this research and recommends future work.
Figure 6.1
Simple Cycle

Variable Feed Rate during Flow Reversal

at Low Net Product Amount Per Part Cycle

Figure 6.2
Simple Cycle

Pressurisation Characteristics and Profiles

Gas Phase Characteristics
Plotted in the Distance and Time Plane

Oxygen Composition Versus Distance

Figure 6.3
Figure 6.4
Simple Cycle
Depressurisation Characteristics and Profiles

Distance versus Time

Crack Creep versus Distance

Figure 6.5

154
Normal Purge Cycle

Figure 6.6

155
Normal Purge Cycle

Comparison of Different Isotherms

![Graph of Normal Purge Cycle and Comparison of Different Isotherms]

Figure 6.7

156
Normal Purge Cycle

Comparison of Different Isotherms

Figure 6.8
The Comparison of Normal and Co-Current Purge Cycle

Figure 6.9
Figure 6.10
Purge and Backfill Cycle

Plot of Product Oxygen Concentration versus Backfill Pressure

Figure 6.11
Purge and Backfill Cycle

Plot of Product Nitrogen Yield versus Backfill Pressure

Figure 6.12

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Top to Top Bed Pressure Equalisation Cycle

at Net Product Amount of $10^{-6}$ kmol

**Figure 6.13**
Top to Top Bed Pressure Equalisation Cycle
at Net Product Amount of $10^{-5}$ kmol

Figure 6.14
Bottom to Bottom Bed Pressure Equalisation Cycle

at Net Product Amount of $10^{-6}$ kmol

Figure 6.15
Bottom to Bottom Bed Pressure Equalisation Cycle at Net Product Amount of $10^{-5}$ kmol
Both End Bed Pressure Equalisation Cycle

at Net Product Amount of $10^{-6}$ kmol

Figure 6.17
Both End Bed Pressure Equalisation Cycle

at Net Product Amount of $10^{-5}$ kmol

Figure 6.18.
Normal Purge Cycle

Sensitivity Analysis on Cross-sectional Area

The variation of oxygen composition with purge amount for different column cross section area

![Graph showing oxygen composition variation with purge amount for different column cross section area.]

The variation of percent nitrogen yield with purge amount for different column cross section area

![Graph showing nitrogen yield variation with purge amount for different column cross section area.]

Figure 6.19
Normal Purge Cycle

Sensitivity Analysis on Column Voidage

The variation of oxygen composition with purge amount for different column voidage

![Graph of oxygen composition vs. purge amount](image)

The variation of percent nitrogen yield with purge amount for different column voidage

![Graph of nitrogen yield vs. purge amount](image)

Figure 6.20
Normal Purge Cycle

Sensitivity Analysis on Bed Length

The variation of oxygen composition with purge amount for different column bed length

![Graph showing the variation of oxygen composition with purge amount. The x-axis represents purge amount (x1.0E6 kmol) ranging from 0.0 to 45.0, and the y-axis represents oxygen composition (%) ranging from 1.6 to 5.6. The graph includes lines for +10% BL and -10% BL.]

The variation of percent nitrogen yield with purge amount for different column bed length

![Graph showing the variation of percent nitrogen yield with purge amount. The x-axis represents purge amount (x1.0E6 kmol) ranging from 0.0 to 45.0, and the y-axis represents nitrogen yield (%) ranging from 12 to 42. The graph includes lines for +10% BL and -10% BL.]

Figure 6.21
Normal Purge Cycle

Sensitivity Analysis on Column Packed Density

The variation of oxygen composition with purge amount for different column packed density

![Graph showing the variation of oxygen composition with purge amount for different column packed density.]

The variation of percent nitrogen yield with purge amount for different column packed density

![Graph showing the variation of percent nitrogen yield with purge amount for different column packed density.]

Figure 6.22
Normal Purge Cycle

Sensitivity Analysis on Average Particle Radius

The variation of oxygen composition with purge amount for different average particle radius.

The variation of percent nitrogen yield with purge amount for different average particle radius.

Figure 6.23

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Normal Purge Cycle

Sensitivity Analysis on Overall Mass Transfer Coefficient for Oxygen

The variation of oxygen composition with purge amount for different overall mass transfer coefficient for oxygen

The variation of percent nitrogen yield with purge amount for different overall mass transfer coefficient for oxygen

Figure 6.24
Normal Purge Cycle

Sensitivity Analysis on Overall Mass Transfer Coefficient for Nitrogen

The variation of oxygen composition with purge amount for different overall mass transfer coefficient for nitrogen

![Graph showing the variation of oxygen composition with purge amount for different overall mass transfer coefficients.]

The variation of percent nitrogen yield with purge amount for different overall transfer coefficient for nitrogen

![Graph showing the variation of percent nitrogen yield with purge amount for different overall mass transfer coefficients.]

Figure 6.25

174
Normal Purge Cycle

Sensitivity Analysis on Net Product Amount

Oxygen Composition versus Purge Amount

Nitrogen Yield versus Purge Amount

Figure 6.26

175
Normal Purge Cycle

Sensitivity Analysis on Upper Operating Pressure

Oxygen Composition versus Purge Amount

Nitrogen Yield versus Purge Amount

Figure 6.27

176
Normal Purge Cycle

Sensitivity Analysis on Lower Operating Pressure

Oxygen Composition versus Purge Amount

Nitrogen Yield versus Purge Amount

Figure 6.28

177
Normal Purge Cycle

Sensitivity Analysis on Cycle Time

Oxygen Composition versus Purge Amount

Nitrogen Yield versus Purge Amount

Figure 6.29
Normal Purge Cycle

Comparison of DCPSA Model with Hassan et. al. Work (1986)

Oxygen Mole Fraction Versus Cycle Number

Figure 6.30

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7.1 General Observation and Conclusion

The purpose of deriving this new DCPSA model was to simulate the diffusion controlled PSA process by taking into account the mass transfer limitation encountered by the adsorbates, which has been ignored by many PSA models. The model has been formulated without assuming a frozen solid state during the pressure changing steps. This model allows one to study and to understand the behaviour of PSA processes for many different cycles. This includes one of the most difficult process cycles, both end bed pressure equalisation cycle. No published models have included this cycle. Furthermore, the results shown in Section 6.11 demonstrate the model's ability to fit the theoretical and experimental data obtained by Hassan et. al. (1986), when the correct adsorption parameters are used.

The model presented an extraordinary 'reverse flow phenomenon' during the product release step, which is not reported by other models, when a low feed rate is introduced at the feed end of the column. This is because when the feed rate is low, the rate of adsorption at the product end is much greater than the gas feed velocity and additional gas is required to be drawn in from the product end. This situation is not encountered in practice because feed is drawn in on demand. This reverse flow phenomenon at low feed rate, caused considerable problem to the initial modelling
solution as a constant feed rate was assumed. To counteract the low feed rate problem, a variable feed rate was incorporated in the model making it more robust.

The important assumptions made in the development of this model, are:

1) the feed gas consists of two adsorbable components with no inerts present,
2) the gas phase follows the ideal gas behaviour,
3) the process operates isothermally,
4) the gas passes through the columns in plug flow,
5) axial dispersion is neglected,
6) radial diffusion and wall effects are ignored,
7) there is no pressure drop across the column,
8) a lumped parameter linear driving force is applicable for mass transfer between the gas and adsorbed phases,
9) linear, Langmuir pure gas and Langmuir binary co-adsorption isotherms may be used to describe the adsorption equilibria, and
10) the columns are completely and uniformly filled with identical spherical adsorbent particles.

The resulting DCPSA model consists of four partial differential equations. These equations are inhomogeneous, non-linear and first order. The hyperbolic equations in this system were solved by the Method of Characteristics, which identifies trajectories in the distance–time plane along which the partial differential equations can be reduced to ordinary differential equations.
Several integration techniques can be used along the characteristics. Kirkby (1983) used an explicit 4th order Runge-Kutta-Merson method successfully on his instantaneous local equilibrium PSA model. However, when an explicit technique was used in the DCPSA model, it has proven to be unsuitable, particularly when the model encountered high values of overall mass transfer coefficients ($K_{GA} = 2.5 \times 10^{-10} \text{ kmol m}^3\text{(N kg s)}^{-1}$ for oxygen and $K_{GB} = 1.0 \times 10^{-11} \text{ kmol m}^3\text{(N kg s)}^{-1}$ for nitrogen). A higher order explicit technique (Adam-Bashforth-Moulton predictor-corrector method) was also used but no improvement was made. To overcome this, implicit Euler integration along the trajectories of the Method of Characteristics was used.

Although it may be difficult to formulate the equations while using the implicit Euler technique, the equations do not go beyond a third order polynomial, which can be solved by any iterative method. The Newton-Raphson method was used in this case.

By using this implicit technique, the overall performance — in terms of CPU, can improved by approximately 1000 times in some cases. This technique not only made the simulation of the PSA process with high values of overall mass transfer coefficients possible, it also allows the simulation of complicated cycles which require a large number of iterations, an example of which is the both end BPE cycle.

The final model is translated into a software written in FORTRAN. The main features of this software are:

1) read data from a cycle configuration file,
2) perform the specified PSA cycle simulations,  
3) store the results in both tabular and graphical form,  
4) perform a basic control depending on the selected controller mode, and  
5) produce a performance summary report, which includes the material balances for the steps and cycles as a whole.

Eight different cycle configurations have been simulated. In general, the product oxygen concentration increases as the net product amount increases. There is a minimum for the net product amount, below this limit the simulation starts to display the reverse flow phenomena. When this occurs, the feed rate and product rate no longer stay constant. But it is still quite possible to achieve the preset net product amount. This flow reversal has not been described by any other published literature.

Like the equilibrium theory of Kirkby (1983), the simulation of the purge cycles (both co-current and counter-current) also shows that there is an optimum purge amount for the product purity. At low net product amount, \(1.0 \times 10^{-5}\) kmol per part cycle, the model favours the counter-current purge cycle in terms of product purity. At the optimum purge flow rate, the difference in product oxygen concentration between the two purge cycles is approximately 2.3%. However, at high net product amount, \(1.0 \times 10^{-4}\) kmol per part cycle, the difference in product purity between the two cycles is negligible.

For the backfill cycle simulation, the product purity is a function of the backfill pressure. The results show that there is an optimum operating region, which lies between 130.3 and 245.8 kPa of the operating pressure.
In terms of product oxygen concentration, the optimum region is very shallow but the optimum backfill pressure decreases with decreasing net product amount per part cycle. The results further show that the nitrogen yield is almost independent of the backfill pressure, except at very high backfill pressure, 275 to 303.9 kPa, where the yield decreases as the backfill pressure increases.

When comparing the backfill results with those of the normal purge cycle at the net product amount of \(1.0 \times 10^{-5}\) kmol per part cycle, the purge cycle managed to obtain a slightly better separation (98.1% of nitrogen compared to 96.5%). However, for the backfill cycle the nitrogen yield improved by 9% over the purge cycle.

An optimum purge flow rate and backfill pressure for product purity are very well defined for the purge and backfill cycle. The simulation results lead to the conclusion that,

1) it is essential to keep the backfill pressure below 75% of the upper operating pressure in order to optimise the nitrogen yield,
2) there is a region where the oxygen concentration is lower than can be achieved by cycles using purge or backfill alone,
3) the optimum backfill pressure for purge and backfill is approximately 20 kPa lower than for backfill alone,
4) the optimum purge amount for purge and backfill is also lower than for the purge cycles alone, and,
5) the main advantage of running the purge and backfill cycle over the individual cycle, is the improvement in nitrogen yield. The improvement is as high as 32%.
Three bed pressure equalisation cycles, top to top (TTBPE), bottom to bottom (BBBPE) and both end (BEBPE), were simulated. Since only two columns are used in the BPE cycles simulation, there will not be a continuous flow of product. The simulation of BEBPE is particularly difficult, because it requires handling of the concentration profile in the column.

Like the backfill cycle simulation, these BPE simulations also allow the study of the pressure swing adsorption behaviour over the entire operating pressure range. This means that after the columns reach their equalisation pressure, any further reduction in the pressure of the donating column can only be achieved with the use of a compressor.

In general, the results show that as the pressure in the receiving column increases beyond the equalisation pressure, no significant benefit for product purity was observed. Even for nitrogen yield, the benefits are small, the maximum increase is only 2%. In fact for both end bed pressure equalisation, the optimum operating pressure is clearly below the equalisation pressure.

When comparing the three BPEs simulation at net product amount per part cycle of $1.0 \times 10^{-6}$ and $1.0 \times 10^{-5}$ kmol, both the TTBPE and the BBBPE show very similar results for each and every case. However, when these two cycles are compared with BEBPE, the BEBPE gave the best separation both in terms of optimum product purity which is approximately 1.2% purer and optimum nitrogen yield which showed an improvement of 0.5%.
The model was compared with the theoretical and experimental results of Hassan et. al. (1986). It is however important to note that a direct comparison between the DCPSA simulation and the results obtained by Hassan cannot be made due to differences in the cycle configuration and cycle time. The cycle configuration by Hassan et. al. does not allow for a continuous flow of product and the part cycle time for the configuration is 150 seconds instead of 120 seconds.

The important point to note is that Hassan et. al. have shown a good match between the theoretical and experimental results by varying their Ωs values. They claimed that it is acceptable to vary Ωs values based on the findings of Nakao and Suzuki (1983). However they did not acknowledge that the relationship between Ωs values and cycle time is obtained only after the cyclic adsorption process reaches its steady state. It is, therefore, not a valid assumption to use during the transient state by Hassan et. al. The DCPSA model shows that changing the Ωs values has a great effect on the simulation results. These results show the failure of the frozen solid assumption used by Hassan et. al. because the model is effectively dependent on the values of external fitting parameters.

Finally, a series of sensitivity analysis were performed on the physical and operating parameters of the DCPSA model. The results allow one to identify the parameters that affect the process design, so that modification on existing design or improvement to future design is made simpler. It also identifies the best operating parameters to vary, if permitted by the design safety criterion and at low additional operating
cost, to improve the separation.

This research has certainly achieved its objectives:

1) to model a binary mixture of gases that are separated by differences in the intraparticle diffusivities of the two components, the difference in equilibrium capacity being relatively unimportant. The production of nitrogen from air using a carbon molecular sieve is chosen for the simulation.

2) to explore several methods for the efficient solution of the governing equations and boundary conditions with particular reference to an accurate qualitative description with the minimum computational effort.

3) to compare the model against the experimental behaviour of a similar process separating nitrogen from air using carbon molecular sieves.

4) to simulate a variety of process configurations potentially suitable for the recovery of nitrogen from air, in particular the both end bed pressure equalisation cycle.

7.2 Future Work

The model presented in this research is very flexible and robust. However, the understanding of the process is far from complete; it cannot yet be used to design processes to any great accuracy, nor can it be used to predict the performance of novel cycle types with any certainty. The following section therefore suggests the possible future work:

1) based on the sensitivity analysis results, build an experimental rig
that exactly describes the model at its optimum operating condition, concentrating on the simulation of the BEBPE cycle, in particular. Ideally the experimental rig should have an auxiliary probe that can give sensible measurements of the concentration profile accurately and quickly. The measurements will be most useful in examining the role of diffusion in the process and in exploring the effects of mixing the product. This would allow a direct comparison between the model and experimental results during each integration time step. This then allows the study of the model from a different angle, and may help to identify any potential assumptions that should be removed from the model.

2) obtain experimental results that are potentially suitable for the model to test the software fully; adding tuning parameters if necessary.

3) study the breakthrough curves for estimating the rate constants. If this method proved to be difficult, then the use of batch adsorption experiments should be considered. Such as:
   - the use of vacuum microbalance apparatus where the adsorbent is subjected to a small step change in pressure [Daly and Granville, (1980)].
   - the use of a diffusion cell apparatus where the outlet adsorbate concentration is monitored after a step change in the inlet feed concentration [Frost, (1981)].

4) carry out an experiment to observe the possibility of improving separation by changing the feed temperature, if proven to be beneficial, the model should also incorporate the facility of varying the feed temperature.
5) although the DCPSA model has incorporated the facilities of running the simulation with the Langmuir binary co-adsorption isotherms, only a few simulation runs using this type of isotherms have been performed. Hence when compatible experimental results are available, more simulation runs should be performed using this Langmuir binary co-adsorption isotherms option to see its effect on the model.

6) develop an auto tuning algorithm to read data from an on-line configuration file and to perform a search for an optimum operating conditions.

7) derive a method to simulate a well tuned 'rigorous' (derived) model and then fit it to a 'regress' (approximated by regression equation) model. The main aim is to remove the need for the package to simulate the same large number of cycles which an actual plant would perform in order to reach steady state. This should improve the computational speed.

8) reduce the number of assumptions made if there is a large discrepancy between the experimental and theoretical results. The selection of assumptions to be removed may be easier if the experiment suggested in (1) is proven possible. The isothermal assumption may be removed so that the model can be used for systems that encounter a large temperature variation. For example, the production of oxygen using 5A zeolite.

9) study other possible type of cycle configuration. One particularly interesting simulation that may be run is to vary the purge flow rate of the BPE cycles, so as to see how they can increase the nitrogen product concentration and the recovery of the feed nitrogen. The simulation of Second Cut process cycle may also be run and compared to
that of the backfill cycle to see whether one is more superior to the other.

10) the model may be extended to include the facility of selecting the type of purge or backfill, whether it is directly from a product stream or from a fully mixed buffer tank.

7.3 Concluding Comments

The development of PSA cycles has been hampered by the experimental difficulties of establishing the optimum operating conditions for a process with many adjustable parameters. As the world market for nitrogen expands and the pace of competition to supply this market with PSA generators increases, the need for a more complete mathematical description of PSA has never been greater.

The modelling work in this project will not only help the design and operation of cycles based on existing technology but will also assist the development of new cycles. Multibed cycles are currently very difficult to design on a fully quantitative basis because of the many experimental parameters and yet, what little experience has been gained suggests that the rewards in terms of improved energy efficiency and convenience to the customer will be considerable.
Author's quote:

"To reach the end of the universe is the dream of all scientists. This research has brought me a step closer to the dream. The future work suggested can further advance this dream."
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Lumped Mass Transfer Coefficients and Related Parameters

i) The interfacial area, \( a \), per unit volume of packed column

Assuming all the particles are spherical and the same size, then

\[
a = \frac{4 \pi r_p^2 (1 - \epsilon)}{3} \cdot \frac{3 (1 - \epsilon)}{r_p} = \frac{4 \pi r_p^3}{3}
\]

where \( \epsilon \) is the inter-particle voidage and \( r_p \) is the particle radius.

ii) The external mass transfer coefficient, \( k_e \)

The external mass transfer coefficient, \( k_e \) is normally correlated by expressions involving three dimensionless groups:

1) Sherwood number, \( Sh \), where \( Sh = \frac{2 r_p k_e}{D_m} \)  

2) Schmidt number, \( Sc \), where \( Sc = \frac{\mu}{\rho D_m} \), and

3) Reynolds number, \( Re \), where \( Re = \frac{2 r_p \rho v}{\mu} \)

There are numerous equations relating these groups but two important correlations are considered here: the Ranz–Marshall equation was derived from the results of experimental studies of mass transfer rates for freely falling solid spheres [Ruthven, (1984)],

\[
Sh = 2.0 + 1.1 Sc^{1/3} Re^{1/2}
\]
and more recently, the Wakao-Funazkri equation (1978), which takes into account the axial dispersion during adsorption [Ruthven, (1984)],

\[
\text{Sh} = 2.0 + 0.6 \text{Sc}^{1/3} \text{Re}^{0.6} \quad 3 < \text{Re} < 10^4 . \tag{A6}
\]

Substituting Equations (A2), (A3) and (A4) into Equation (A6) gives,

\[
\frac{2 \rho_p k_e}{D_m} = 2.0 + 0.6 \left( \frac{\mu}{\rho \ D_m} \right)^{1/3} \left( \frac{2 \rho_p \rho \ v}{\mu} \right)^{0.6} . \tag{A7}
\]

It is clear that the external film mass transfer coefficient, \( k_e \), is directly proportional to \( (\text{Re})^{0.6} \).

iii) The internal mass transfer coefficient, \( k_l \)

The original work by Glueckauf (1955) and co-workers has been extensively employed and verified and takes the following form,

\[
k_l = \frac{15 \ D_1}{r_p^2 (1 - \epsilon_p)} \tag{A8}
\]

where \( \epsilon_p \) is the intra-particle voidage and \( D_1 \) is the intra-particle effective diffusivity.

iv) The overall mass transfer coefficient, \( K_g \)

The overall mass transfer coefficient can be expressed in terms of the individual coefficients, provided it is assumed that the external film has negligible volume as follows:

\[
\frac{1}{K_g} = \frac{1}{k_e} + \frac{1}{k_l} \tag{A9}
\]
Substituting Equations (A1) and (A8) to Equation (A9) gives,

\[
\frac{1}{K_g a} = \frac{r_p}{3 k_e (1 - \varepsilon)} + \frac{r_p^2 (1 - \varepsilon_p)}{15 D_1 (1 - \varepsilon)}
\]  

(A10)

Previous work on the carbon molecular sieves used for air separation suggests that it is the intra-particle effective diffusivity, \(D^e\), which is of prime importance in effecting the observed separation. To demonstrate this fact the following values are used for Equation (A10):

\[
\begin{align*}
    r_p &= \text{particle radius} = 1.588 \times 10^{-3} \text{ m} \\
    k_e &= \text{external film transfer coefficient} = 0.0508 \text{ m s}^{-1} \\
    \varepsilon_p &= \text{intra-particle voidage} = 0.5 \\
    \varepsilon &= \text{inter-particle voidage} = 0.4 \\
    \frac{D_1}{r_p^2} &= \text{Diffusional time constant for oxygen} = 3.7279 \times 10^{-3} \text{ s}^{-1}
\end{align*}
\]

Substitution these values into the first term of Equation (A10) gives,

\[
\frac{r_p}{3 k_e (1 - \varepsilon)} = \frac{1.588 \times 10^{-3}}{3 \times 0.0508 \times (1 - 0.4)} = 0.0174 \text{ s}^{-1}
\]

and into the second term gives,

\[
\frac{r_p^2 (1 - \varepsilon_p)}{15 D_1 (1 - \varepsilon)} = \frac{1.0}{15 \times 3.7279 \times 10^{-3} \times (1 - 0.4)} = 14.9 \text{ s}^{-1}
\]

the second term has shown to be approximately 850 times larger than the first term. Hence the external film resistance is negligible and the overall mass transfer parameters should not show any significant dependence on gas velocity.
APPENDIX B

Derivation of the Theory for DCPSA Model

Equations (3.7) and (3.8), which form the basis of the DCPSA model (Section 3.3), were derived as follows.

A mass balance for component A over an element in the column gives Equation (3.5),

\[
\frac{\partial (\varphi p_A)}{\partial z} + A\varepsilon \frac{\partial p_A}{\partial t} + A\omega RT \frac{\partial q_A}{\partial t} = 0 \quad \text{(B1)}
\]

Similarly for nitrogen (Equation (3.6)),

\[
\frac{\partial (\varphi p_B)}{\partial z} + A\varepsilon \frac{\partial p_B}{\partial t} + A\omega RT \frac{\partial q_B}{\partial t} = 0 \quad \text{(B2)}
\]

Expanding Equations (B1) and (B2) gives,

\[
\varphi \frac{\partial p_A}{\partial z} + p_A \frac{\partial \varphi}{\partial z} + A\varepsilon \frac{\partial p_A}{\partial t} + A\omega RT \frac{\partial q_A}{\partial t} = 0 \quad \text{(B3)}
\]

and

\[
\varphi \frac{\partial p_B}{\partial z} + p_B \frac{\partial \varphi}{\partial z} + A\varepsilon \frac{\partial p_B}{\partial t} + A\omega RT \frac{\partial q_B}{\partial t} = 0 \quad \text{(B4)}
\]

Multiplying Equation (B3) by \(p_B\) and Equation (B4) by \(p_A\), and then subtracting one from the other yields,

\[
\varphi \left( \frac{\partial p_A}{\partial z} p_B - \frac{\partial p_B}{\partial z} p_A \right) + A\varepsilon \left( \frac{\partial p_A}{\partial t} p_B - \frac{\partial p_B}{\partial t} p_A \right) + A\omega RT \left( \frac{\partial q_A}{\partial t} p_B - \frac{\partial q_B}{\partial t} p_A \right) = 0 \quad \text{(B5)}
\]
Since the gas mixture consists of only two adsorbable components, then
\[ p_B = P - p_A \]  \hspace{1cm} (B6)
and by applying Equation (B6) to Equation (B5) and expanding gives,
\[
\phi \left( (P - p_A) \frac{\partial p_A}{\partial z} - p_A \left( \frac{\partial P}{\partial z} - \frac{\partial p_A}{\partial z} \right) \right) + A\epsilon \left( (P - p_A) \frac{\partial p_A}{\partial t} - p_A \left( \frac{\partial P}{\partial t} - \frac{\partial p_A}{\partial t} \right) \right) \\
+ A\omega RT \left( (P - p_A) \frac{\partial q_A}{\partial t} - p_A \frac{\partial q_B}{\partial t} \right) = 0 \] \hspace{1cm} (B7)
No pressure gradient across the column was assumed, that is,
\[ \frac{\partial P}{\partial z} = 0 \quad \text{and} \quad \frac{\partial P}{\partial t} = \frac{dP}{dt} \] \hspace{1cm} (B8)
So, by applying Equation (B8) to Equation (B7), considerable simplification is possible as follows,
\[ \phi \frac{\partial p_A}{\partial z} + A\epsilon \left( P \frac{\partial p_A}{\partial t} - p_A \frac{dP}{dt} \right) + A\omega RT \left( P \frac{\partial q_A}{\partial t} - p_A \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \right) = 0 \] \hspace{1cm} (B9)
Division throughout by PAε and making the substitution for p', where
\[ p' = \frac{1}{P} \frac{dP}{dt} \] \hspace{1cm} (B10)
gives Equation (3.8), that is,
\[ \phi \frac{\partial p_A}{\partial z} + \frac{\partial p_A}{\partial t} = p_A p' + \frac{\omega RT}{\epsilon} \left[ p_A \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) - \frac{\partial q_A}{\partial t} \right] \] \hspace{1cm} (B11)
Equation (3.7) may be derived in a similar fashion by adding Equations (B1) and (B2),
\[ \frac{\partial (\phi p_A)}{\partial z} + \frac{\partial (\phi p_B)}{\partial z} + A\epsilon \left( \frac{\partial p_A}{\partial t} + \frac{\partial p_B}{\partial t} \right) + A\omega RT \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) = 0 \] \hspace{1cm} (B12)
Expanding and substituting Equations (B6) and (B10) yields Equation (3.7), that is

\[
\frac{\partial \theta}{\partial z} = - \left[ A \omega p' + \frac{A \omega RT}{P} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \right]
\]  

(B13)

Note that Equation (B13) may also be derived directly from consideration of an overall balance on the original slice of the column, thus

Basis : kmol s\(^{-1}\)

Amount In = Amount out + Accumulation wrt time + Rate of adsorption in gas phase

\[
\frac{\partial P}{\partial RT} = \left[ \frac{\partial P}{\partial RT} + \frac{\partial}{\partial z} \left( \frac{\partial P}{\partial RT} \right) \delta z \right] + \frac{\partial}{\partial t} \left( A e \delta z \frac{P}{RT} \right) + A \omega \delta z \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right)
\]  

(B14)

Collection of the terms and application of Equation (B8) yields Equation (B13) immediately.
APPENDIX C

Derivation of Equation (4.37)

The gas phase equation (Equation (4.6)) gave the following ODE for the rate of change of $p_A$ with time along characteristics of velocity $\phi/\Delta\varepsilon$,

$$\frac{dp_A}{dt} = p_Ap' + \frac{\omega RT}{\varepsilon} \left[ \frac{p_A}{p} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) - \frac{\partial q_A}{\partial t} \right] \quad (C1)$$

Let the subscript (0) denote the known value at time $t$, and subscript (1) denote the required value at time $t + \delta t$.

Application of the implicit Euler method gives,

$$p_{A(1)} = p_{A(0)} + \frac{dp_A}{dt} \bigg|_{(0)} \delta t \quad (C2)$$

Since $dp_A/dt$ in Equation (C1) is now at position 1, Equation (C1) has become,

$$\frac{dp_A}{dt} \bigg|_{(1)} = p_{A(1)p'} + \frac{\omega RT}{\varepsilon} \left[ \frac{p_{A(1)}}{p(1)} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \bigg|_{(1)} - \frac{\partial q_A}{\partial t} \bigg|_{(1)} \right] \quad (C3)$$

where

$$\frac{\partial q_A}{\partial t} \bigg|_{(1)} = K_{GA} \left( p_{A(1)}^* - p_{A(1)} \right) \quad \text{and} \quad (C4)$$

$$\frac{\partial q_B}{\partial t} \bigg|_{(1)} = K_{GB} \left( p_{B(1)}^* - p_{B(1)} \right) \quad \text{and} \quad (C5)$$

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\( p^*_A(1) \) and \( p^*_B(1) \) are the equilibrium adsorbed phase partial pressures at time \( t + \delta t \).

For linear isotherms, \( p^*_A(1) \) and \( p^*_B(1) \) can be expressed as,

\[
\begin{align*}
p^*_A(1) &= \frac{q^*_A(1)}{k_{A1}} \quad \text{(C6)} \\
p^*_B(1) &= \frac{q^*_B(1)}{k_{B1}} \quad \text{(C7)}
\end{align*}
\]

where \( k_{A1} = k_{A2} q_{A_m} \) and \( k_{B1} = k_{B2} q_{B_m} \).

\( q_{A_m} \) and \( q_{B_m} \) are defined as the amount of components A and B adsorbed at monolayer capacity respectively, \( k_{A1} \) and \( k_{B1} \) are the linear isotherm gradients (Henry's Law constants) and \( k_{A2} \) and \( k_{B2} \) are the Langmuir constants (Section 3.3). Note that the calculation of \( q^*_A(1) \) and \( q^*_B(1) \) is explained further in Appendix D.

For the Langmuir isotherm without co-adsorption, \( p^*_A(1) \) and \( p^*_B(1) \) can be expressed as,

\[
\begin{align*}
p^*_A(1) &= \frac{q^*_A(1)}{k_{A1} - k_{A2} q^*_A(1)} \quad \text{(C8)} \\
p^*_B(1) &= \frac{q^*_B(1)}{k_{A1} - k_{B2} q^*_B(1)} \quad \text{(C9)}
\end{align*}
\]
Similarly for the Langmuir isotherm with co-adsorption, \( p_{A(1)}^* \) and \( p_{B(1)}^* \) can be expressed as,

\[
p_{A(1)}^* = \frac{q_{A(1)} k_{B1}}{k_{A1} k_{B1} - q_{A(1)} k_{A2} k_{B1} - q_{B(1)} k_{B2} k_{A1}}
\]

\[
p_{B(1)}^* = \frac{q_{B(1)} k_{A1}}{k_{A1} k_{B1} - q_{A(1)} k_{A2} k_{B1} - q_{B(1)} k_{B2} k_{A1}}
\]

Adding (C4) and (C5) gives,

\[
\frac{\partial q_A}{\partial t} \bigg|_{(1)} + \frac{\partial q_B}{\partial t} \bigg|_{(1)} = K_{GA} a \left( p_{A(1)} - p_{A(1)}^* \right) + K_{GB} a \left( p_{B(1)} - p_{B(1)}^* \right)
\]

\[
= \beta^1 p_{A(1)} + \gamma_1
\]

where \( \beta^1 = \left( K_{GA} - K_{GB} a \right) \)

and \( \gamma_1 = K_{GA} a \left( p_{(1)} - p_{B(1)}^* \right) - K_{GB} a p_{A(1)}^* \).

Multiplying Equation (C12) by \( \frac{\omega RT}{\epsilon p_{(1)}} \), gives,

\[
\frac{\omega RT}{\epsilon p_{(1)}} \left( \frac{\partial q_A}{\partial t} \bigg|_{(1)} + \frac{\partial q_B}{\partial t} \bigg|_{(1)} \right) = \frac{\omega RT}{\epsilon p_{(1)}} \left( \beta^1 p_{A(1)} + \gamma_1 \right)
\]

\[
= \alpha_1 p_{A(1)}^2 + \beta^2 p_{A(1)}
\]

where \( \alpha_1 = \frac{\omega RT \beta^1}{\epsilon p_{(1)}} \).
and \[ \beta_2 = \frac{\omega RT}{e} \frac{\chi_1}{P_{(1)}} \]

Similarly multiplying Equation (C4) by \[ \frac{\omega RT}{e} \], gives,

\[ \frac{\omega RT}{e} \frac{\partial q_A}{\partial t} = \frac{\omega RT}{e} K_{GA} \left( p_{A(1)} - p^*_{A(1)} \right) \]

\[ = \beta_3 p_{A(1)} - \gamma_2 \]

(C14)

where \[ \beta_3 = \frac{\omega RT}{e} K_{GA} a \]

and \[ \gamma_2 = \frac{\omega RT}{e} K_{GA} a \]

On substituting Equations (C13) and (C14) back to Equation (C3) gives,

\[ \frac{dp_A}{dt} \bigg|_{(1)} = p_{A(1)} p'_{(1)} + \alpha_1 p^2_{A(1)} + \beta_2 p_{A(1)} - \beta_3 p_{A(1)} + \gamma_2 \]

\[ = \alpha_1 p^2_{A(1)} \left( p'_{(1)} + \beta_2 - \beta_3 \right) p_{A(1)} + \gamma_2 \]

\[ = \alpha_1 p^2_{A(1)} + \beta_4 p_{A(1)} + \gamma_2 \]

(C15)

where \[ \beta_4 = p'_{(1)} + \beta_2 - \beta_3 \]

Substituting Equation (C15) back into Equation (C2) gives,

\[ p_{A(1)} = p_{A(0)} + \left( \alpha_1 p^2_{A(1)} + \beta_4 p_{A(1)} + \gamma_2 \right) \delta t \]
which on rearranging completes the derivation of Equation (4.37), i.e.,

\[ a p_{A(1)}^2 + b p_{A(1)} + c = 0 \]  

(C16)

where

\[ a = \alpha_1 \delta t \]
\[ b = \beta_4 \delta t - 1 \]
\[ c = \gamma_2 \delta t + p_{A(0)} \]

and

Since Equation (C16) is a simple explicit quadratic equation, the solution for \( p_{A(1)} \) is thus,

\[ p_{A(1)} = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a} \]  

(C17)
Derivation of Equations (4.39) and (4.40)

The solid phase equation (Equation 4.8) gave the following ODE for the rate of change of $q_A$ with time along characteristics of zero velocity,

$$\frac{dq_A}{dt} = K_{ga} (p_A - p_A^*)$$  \hspace{1cm} (D1)

Let the subscript (0) denote the known value at time $t$, and subscript (1) denote the required value at time $t + \delta t$.

Application of the implicit modified Euler method gives,

$$q_{A(1)} = q_{A(0)} + \left( \frac{dq_A}{dt} \bigg|_{(0)} + \frac{dq_A}{dt} \bigg|_{(1)} \right) \frac{\delta t}{2}$$  \hspace{1cm} (D2)

From Equation (D2), $\frac{dq_A}{dt}$ is now to be evaluated at both the 0 and 1 position. For linear isotherms, the equilibrium equation for component A is,

$$p_A^* = k_{A1} q_A$$  \hspace{1cm} (D3)

where $k_{A1} = k_{A2} q_{Am}$

$k_{A1}$ is the linear isotherm gradient (Henry's Law constant) and $k_{A2}$ and $q_{Am}$ are the Langmuir constants (Section 3.3).
Substituting Equation (D3) into Equation (D1) for both time, t and t + \( \delta t \), gives,

\[
\frac{dq_A}{dt} = K_{GA} \left[ P_{A(0)} - \frac{q_{A(0)}}{k_{A1}} \right] \quad (D4)
\]

and

\[
\frac{dq_A}{dt} = K_{GA} \left[ P_{A(1)} - \frac{q_{A(1)}}{k_{A1}} \right] \quad (D5)
\]

Addition of Equations (D4) and (D5), gives,

\[
\frac{dq_A}{dt} + \frac{dq_A}{dt} = \frac{K_{GA} a}{k_{A1}} \left[ (k_{A1} P_{A(0)} - q_{A(0)}) + (k_{A1} P_{A(1)} - q_{A(1)}) \right] \quad (D6)
\]

Since \( P_{A(0)} \) and \( q_{A(0)} \) are known values, and \( P_{A(1)} \) is either known at the feed end of the adsorber column or can be calculated from linear interpolation between existing characteristics, Equation (D6) can be simplified to,

\[
\frac{dq_A}{dt} + \frac{dq_A}{dt} = \alpha + \beta q_{A(1)} \quad (D7)
\]

where

\[
\alpha = \frac{K_{GA} a}{k_{A1}} \left[ k_{A1} P_{A(0)} - q_{A(0)} + k_{A1} P_{A(1)} \right]
\]

and

\[
\beta = -\frac{K_{GA} a}{k_{A1}}
\]
Substituting Equation (D7) back into Equation (D2) gives,

\[ q_{A(1)} = q_{A(0)} + \left( \alpha + \beta q_{A(1)} \right) \frac{\delta t}{2} \]

\[ = \alpha_1 + \beta_1 q_{A(1)} \quad \text{(D8)} \]

where

\[ \alpha_1 = q_{A(0)} + \alpha \frac{\delta t}{2} \]

and

\[ \beta_1 = \beta \frac{\delta t}{2} \]

Rearranging Equation (D8) gives the required Equation (4.39),

\[ q_{A(1)} = \frac{\sigma}{\lambda} \quad \text{(D9)} \]

where

\[ \sigma = \alpha_1 \]

and

\[ \lambda = 1 - \beta_1 \]

For Langmuir isotherms without co-adsorption, \( p^*_A(1) \) can be expressed as:

\[ p^*_A(1) = \frac{q_{A(1)}}{k_{A_1} - k_{A_2} q_{A(1)}} \quad \text{(D10)} \]

Substituting Equation (D10) into Equation (D1) for both time steps, \( t \) and \( t + \delta t \) gives,

\[ \frac{dq_A}{dt} \bigg|_{(0)} = K_{GA} a \left[ p_{A(0)} - \frac{q_{A(0)}}{k_{A_1} - k_{A_2} q_{A(0)}} \right] = \gamma \quad \text{(D11)} \]
Addition of Equations (D11) and (D12) gives,

\[
\frac{dq_A}{dt}(0) + \frac{dq_A}{dt}(1) = \gamma_1 - \frac{K_{GA} A_{A(1)}}{k_{A1} - k_{A2} q_{A(1)}}
\]

where \( \gamma_1 = \gamma + K_{GA} a \ p_{A(1)} \).

Substitution of Equation (D13) into Equation (D2) yields,

\[
\gamma_2 = \gamma_2(0) + \gamma_2(1) - \frac{K_{GA} A_{A(1)}}{k_{A1} - k_{A2} q_{A(1)}} \frac{\delta t}{2}
\]

where \( \gamma_2 = \gamma_2(0) + \gamma_1 \frac{\delta t}{2} \).

Rearranging Equation (D14) gives the quadratic Equation (4.40),

\[
\frac{dq_A^2}{dt} + eq_{A(1)} + f = 0
\]

where \( d = 2k_{A2} \)

\( e = 2k_{A1} - 2k_{A2} \gamma_2 + \delta t K_{GA} a \)

\( f = 2k_{A1} \gamma_2 \)
Since Equation (D15) is a simple explicit quadratic equation, the solution for \( q_{A(1)} \) is thus,

\[
q_{A(1)} = \frac{-e \pm \sqrt{(e^2 - 4df)}}{2d}
\]

The equivalent derivation for the case of Langmuir co-adsorption isotherms is given in Appendix E.
Application of Implicit Euler to Langmuir Co-adsorption Isotherms

When using the Langmuir Co-adsorption isotherms it is not possible to rearrange the implicit Euler equations to an explicit form because of the coupling between the amounts of A and B adsorbed. This appendix gives the details of the numerical solution employed.

Consider the ordinary differential equations which apply along the two solid phase families of characteristics, namely,

\[
\frac{dq_A}{dt} = K_{GA} \left( p_A - p_A^* \right) \tag{E1}
\]

and

\[
\frac{dq_B}{dt} = K_{GB} \left( p_B - p_B^* \right) \tag{E2}
\]

Let subscript (0) denote the known value at time \( t \), and subscript (1) denote the required value at time \( t + \delta t \).

Application of the implicit Euler method gives,

\[
q_{A(1)} = q_{A(0)} + \frac{dq_A}{dt} \bigg|_{(1)} \delta t \tag{E3}
\]

and

\[
q_{B(1)} = q_{B(0)} + \frac{dq_B}{dt} \bigg|_{(1)} \delta t \tag{E4}
\]
From Equations (E3) and (E4), \( \frac{dq_A}{dt} \) and \( \frac{dq_B}{dt} \) are now to be evaluated at position 1, where,

\[
\frac{dq_A}{dt} \bigg|_{(1)} = K_{GA} \left( p_{A(1)} - p^*_{A(1)} \right) \tag{E5}
\]

and

\[
\frac{dq_B}{dt} \bigg|_{(1)} = K_{GB} \left( p_{B(1)} - p^*_{B(1)} \right) \tag{E6}
\]

The co-adsorption isotherm equations for \( q_A \) and \( q_B \) are,

\[
q_A = \frac{k_{A1}p^*_A}{1 + k_{A2}p_A + k_{B2}p_B} \tag{E7}
\]

and

\[
q_B = \frac{k_{B1}p^*_B}{1 + k_{A2}p_A + k_{B2}p_B} \tag{E8}
\]

Equations (E7) and (E8) after rearrangement yields,

\[
p^*_A = \frac{q_A k_{B1}}{k_{A1}k_{B1} - q_A k_{A2} - q_B k_{A1}} \tag{E9}
\]

and

\[
p^*_B = \frac{q_B k_{A1}}{k_{A1}k_{B1} - q_A k_{A2} - q_B k_{A1}} \tag{E10}
\]

Unlike the linear isotherm or the Langmuir without co-adsorption isotherm, now both \( p^*_A \) and \( p^*_B \) are functions of both \( q_A \) and \( q_B \), and Equations (E3) and (E4) have to be applied simultaneously.
Hence on applying implicit Euler integration over the time interval from \( t \) to \( t + \delta t \) gives,

\[
q_{A(t)} = q_{A(0)} + k_a a \delta t \quad \left( p_{A(t)} - \frac{q_{A(1)} k_{B1}}{k_{A1} k_{B1} - q_{A(1)} k_{A2} k_{B1} - q_{B(1)} k_{B2} k_{A1}} \right) \quad (E11)
\]

\[
q_{B(t)} = q_{B(0)} + k_a a \delta t \quad \left( p_{B(t)} - \frac{q_{B(1)} k_{A1}}{k_{A1} k_{B1} - q_{A(1)} k_{A2} k_{B1} - q_{B(1)} k_{B2} k_{A1}} \right) \quad (E12)
\]

Solving Equations (E11) and (E12) simultaneously with known values of \( p_{A(t)} \) and \( p_{B(t)} \) (\( = p_{(t)} - p_{A(t)} \)) gives equations of the following cubic form,

\[
a_3 q_{A(1)}^3 + a_2 q_{A(1)}^2 + a_1 q_{A(1)} + a_0 = 0 \quad (E13)
\]

\[
b_3 q_{B(1)}^3 + b_2 q_{B(1)}^2 + b_1 q_{B(1)} + b_0 = 0 \quad , \quad (E14)
\]

where the coefficients \( a_0 \) to \( b_3 \) are given by the following expressions:

\[
a_3 = k_{A2} k_a k_{B1}
\]

\[
b_3 = -k_{B2} k_a k_{A1}
\]

\[
a_2 = k_{B1} \left[ k_{A1} \beta - \alpha \left( k_{A1} + k_{GA} a \delta t + Q_k k_{A2} \right) \right]
\]

\[
b_2 = k_{A1} \left[ k_{B1} \beta - \alpha \left( k_{B1} + k_{GB} a \delta t + Q_k k_{B2} \right) \right]
\]

\[
a_1 = Q_k k_{A1} k_{B1} \left[ \beta + \alpha - k_{GB} a \delta t \left( k_{A1} + k_{GA} a \delta t \right) \right]
\]

\[
b_1 = Q_k k_{A1} k_{B1} \left[ \beta - \alpha - k_{GB} a \delta t \left( k_{B1} + k_{GB} a \delta t \right) \right]
\]

\[
a_0 = Q_k^2 k_{A1} k_{A2} k_{GB} a \delta t
\]
and \[ b_0 = Q_B^2 k_{1}^2 k_{1}^2 K_a \delta t \]

where \[ Q_A = q_{A(0)} + K_{gb} a \delta t \]
\[ Q_B = q_{B(0)} + K_{gb} a \delta t \]
\[ \alpha = \left( K_{gb} k_{1} - K_{gb} k_{1} \right) a \delta t \]

and \[ \beta = \left( Q_A k_{gb} k_{2} + Q_B k_{gb} k_{2} \right) a \delta t \]

Extensive investigations did not reveal a suitable factorisation of Equations (E13) and (E14). Therefore these equations were solved by the Newton-Raphson method.

The Newton-Raphson method aims to find a value of \( x \) which satisfies the equation,

\[ f(x) = 0 \quad (E15) \]

Denoting the derivative of the function \( f \) with respect to \( x \) as \( f'(x) \), an iterative procedure is established to find successively better estimates of a root of the Equation (E15), e.g., \( x^{(n)} \), where,

\[ x^{(n)} = x^{(n-1)} - \frac{f' \left( x^{(n-1)} \right)}{f' \left( x^{(n-1)} \right)} \quad (E16) \]

and the initial estimate of \( x \), \( x^{(1)} \), must be supplied externally. If, however, there is an inflexion in \( f(x) \) at the desired root, then this scheme is neither stable nor convergent. This can be overcome by the
introduction of a relaxation factor, $r$, thus Equation (E16) may be replaced by Equation (E17) below:

$$x^{(n)} = x^{(n-1)} - r \frac{f(x^{(n-1)})}{f'(x^{(n-1)})}$$

(E17)

where $r \approx 0.5$.

This scheme is still not unconditionally stable especially if two or more roots are close together. The rate of convergence is dependent on the value of the relaxation factor necessary for stability and the accuracy of the initial guess. However, since it is nearly always possible to get a good initial guess for the solution in the DCPSA model, the use of a relaxation factor was not required.

Application of this method to Equations (E13) and (E14) is straightforward since these equations are readily differentiable in $q_{A(1)}$ and $q_{B(1)}$ respectively. It should be noted that the solution to these equations is coupled to the solution of the gas phase Equation (4.5) because $p_{A(1)}$ appears in Equations (E13) and (E14).
Derivation of the Implicit Euler Method Equation for Equation (4.49)

The ODE along the gas phase characteristics is (Equation (4.49)),

\[
\frac{dp_A}{dt} = \frac{\omega RT}{\varepsilon} \left[ \frac{p_A}{P} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) - \frac{\partial q_A}{\partial t} \right]
\]  \hspace{0.5cm} \text{(F1)}

Let the subscript (0) denote the known value at time \( t \), and subscript (1) denote the required value at time \( t + \delta t \).

Application of the implicit Euler method gives,

\[
P_{A(1)} = p_{A(0)} + \frac{dp_A}{dt} \bigg|_{(1)} \delta t
\]  \hspace{0.5cm} \text{(F2)}

Since \( \frac{dp_A}{dt} \) in Equation (F1) is to be evaluated at position 1, Equation (F1) has become,

\[
\frac{dp_A}{dt} \bigg|_{(1)} = \frac{\omega RT}{\varepsilon} \left[ \frac{p_{A(1)}}{P_{(1)}} \left( \frac{\partial q_A}{\partial t} + \frac{\partial q_B}{\partial t} \right) \bigg|_{(1)} - \frac{\partial q_A}{\partial t} \bigg|_{(1)} \right]
\]  \hspace{0.5cm} \text{(F3)}

Application of Equation (C12) gives,

\[
\left. \frac{\partial q_A}{\partial t} \right|_{(1)} + \left. \frac{\partial q_B}{\partial t} \right|_{(1)} = K_{GA} a \left( p_{A(1)} - p^*_{A(1)} \right) + K_{GB} a \left( p_{(1)} - p_{A(1)} - p^*_{B(1)} \right)
\]

\[
= \beta_1 p_{A(1)} + \gamma_1
\]  \hspace{0.5cm} \text{(F4)}

where \( \beta_1 = \left( K_{GA} a - K_{GB} a \right) \)
and \[ \chi_1 = K_{GA} a \left( P_{(1)}^* - P_{B(1)}^* \right) - K_{GA} a p_{A(1)}^* \]

Application of Equation (C13) gives,

\[ \frac{\omega RT}{\epsilon} \frac{p_{A(1)}}{P_{(1)}} \left( \frac{\partial q_A}{\partial t} \left|_{(1)} \right. \right. + \frac{\partial q_B}{\partial t} \left|_{(1)} \right. \right) = \frac{\omega RT}{\epsilon} \frac{p_{A(1)}}{P_{(1)}} \left( q_A p_{A(1)} + \chi \right) \]

\[ = \beta_1 p_{A(1)}^2 + \beta_2 p_{A(1)} \quad \text{(F5)} \]

where \[ \alpha_1 = \frac{\omega RT}{\epsilon} \frac{\beta_1}{P_{(1)}} \]

and \[ \beta_2 = \frac{\omega RT}{\epsilon} \frac{\chi}{P_{(1)}} \]

Similarly, application of Equation (C14) gives,

\[ \frac{\omega RT}{\epsilon} \frac{\partial q_A}{\partial t} \left|_{(1)} \right. = \frac{\omega RT}{\epsilon} K_{GA} \left( p_{A(1)}^* - P_{A(1)} \right) \]

\[ = \beta_3 p_{A(1)} + \chi_2 \quad \text{(F6)} \]

where \[ \beta_3 = \frac{\omega RT}{\epsilon} K_{GA} a \]

\[ \chi_2 = \frac{\omega RT}{\epsilon} K_{GA} a p_{A(1)}^* \]

Substitution of Equations (F5) and (F6) back to Equation (F3) gives,

\[ \frac{dp_A}{dt} \left|_{(1)} \right. = \alpha_1 p_{A(1)}^2 + \beta_2 p_{A(1)} + \beta_3 p_{A(1)} + \chi_2 \]

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\[
\begin{align*}
\dot{p}_{A1} &= \alpha_1 p_{A1}^2 + \left( \beta_2 - \beta_3 \right) p_{A1} + \gamma_2 \\
&= \alpha_1 p_{A1}^2 + \beta_4 p_{A1} + \gamma_2 \tag{F7}
\end{align*}
\]

where \( \beta_4 = \beta_2 - \beta_3 \).

Now, substitution of Equation (F7) back into Equation (F2) gives,

\[
\begin{align*}
p_{A(1)} &= p_{A(0)} + \left( \alpha_1 p_{A1}^2 + \beta_4 p_{A1} + \gamma_2 \right) \delta t
\end{align*}
\]

which on rearranging becomes,

\[
\begin{align*}
&\alpha_1 p_{A1}^2 + \beta_4 p_{A1} + c = 0 \\
&\text{where } a = \alpha_1 \delta t \\
&b = \beta_4 \delta t - 1 \\
&c = \gamma_2 \delta t + p_{A(0)} \tag{F8}
\end{align*}
\]

Since Equation (F8) is a simple explicit quadratic equation, the solution for \( p_{A(1)} \) is thus,

\[
\begin{align*}
p_{A(1)} &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\
&\tag{F9}
\end{align*}
\]
The Analytical Solution of the Solid Phase Equation at Feed End during Product Release

The adsorption rate equation (i.e. the solid phase equation) for component A along the adsorbed phase characteristic at the feed end of the column \((z = 0)\) is

\[
\frac{dq_A}{dt} = K_{GA}a \left( p_A - p_A^* \right) .
\]  

(G1)

For the linear isotherm assumption, where \(p_A^* = \frac{q_A}{k_{A1}}\), then Equation (G1) becomes,

\[
\frac{dq_A}{dt} = \frac{K_{GA}a}{k_{A1}} \left( k_{A1}p_A - q_A \right) .
\]  

(G2)

If the operating pressure of the product release step is \(P\), and the feed composition is \(y_{AF}\), then the partial pressure \(p_A\) is \(Py_{AF}\).

Let \(\alpha = \frac{K_{GA}a}{k_{A1}}\) and \(\beta = k_{A1}p_A\), then

\[
\frac{dq_A}{dt} = \alpha (\beta - q_A)
\]

which may be integrated directly, if the feed composition is constant, to give,

\[
q_{A(t)} = \beta - (\beta - q_{A(0)}) e^{-\alpha t}
\]  

(G3)

Equation (G3) represents an exact solution for the amount adsorbed as a function of time at the feed end of the column.
**APPENDIX H**

List of FORTRAN Routines for DCPSA Model

<table>
<thead>
<tr>
<th>Routine ID No.</th>
<th>Calling Routine</th>
<th>Called Routine</th>
<th>Subroutines, Function or existing ID No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CPSA</td>
<td></td>
<td>main routine for DCPSA</td>
</tr>
<tr>
<td>2</td>
<td>CLOCK</td>
<td></td>
<td>register current time</td>
</tr>
<tr>
<td>3</td>
<td>PSR</td>
<td></td>
<td>pressurisation step simulation</td>
</tr>
<tr>
<td>4</td>
<td>PDR</td>
<td></td>
<td>product release step simulation</td>
</tr>
<tr>
<td>5</td>
<td>DPRS</td>
<td></td>
<td>depressurisation step simulation</td>
</tr>
<tr>
<td>6</td>
<td>CDPRS</td>
<td></td>
<td>co-current depressurisation step simulation</td>
</tr>
<tr>
<td>7</td>
<td>PURGE</td>
<td></td>
<td>purge step simulation</td>
</tr>
<tr>
<td>8</td>
<td>BCKFL</td>
<td></td>
<td>backfill step simulation</td>
</tr>
<tr>
<td>9</td>
<td>LININT</td>
<td></td>
<td>linear interpolation</td>
</tr>
<tr>
<td>10</td>
<td>POLINT</td>
<td></td>
<td>polynomial interpolation</td>
</tr>
<tr>
<td>11</td>
<td>INOUT</td>
<td></td>
<td>calculate overall material balance</td>
</tr>
<tr>
<td>12</td>
<td>SPLIT</td>
<td></td>
<td>split column profile into two sections for bed pressure equalisation (BPE) simulation</td>
</tr>
<tr>
<td>13</td>
<td>STORE</td>
<td></td>
<td>temporary storage for characteristic handling</td>
</tr>
<tr>
<td>14</td>
<td>GLUE</td>
<td></td>
<td>recombine the split profile after BPE simulation</td>
</tr>
</tbody>
</table>

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List of FORTRAN Routines for DCPSA Model

(Continued)

<table>
<thead>
<tr>
<th>Routine ID No.</th>
<th>Calling Routine</th>
<th>Subroutine, Function or existing ID No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CLOCK</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>PANDPD</td>
<td>linear pressure function, ( P(t) ) and ( p'(t) )</td>
</tr>
<tr>
<td>16</td>
<td>INICON</td>
<td>set initial conditions</td>
</tr>
<tr>
<td>17</td>
<td>PDIDAT</td>
<td>read the initial data for subsequent time steps from data file</td>
</tr>
<tr>
<td>18</td>
<td>NEXACT</td>
<td>closed end analytical solution</td>
</tr>
<tr>
<td>19</td>
<td>EQN</td>
<td>convective balance equations</td>
</tr>
<tr>
<td>20</td>
<td>IMQAB</td>
<td>solid phase equations in implicit form</td>
</tr>
<tr>
<td>21</td>
<td>IMPA</td>
<td>gas phase equations in implicit form</td>
</tr>
<tr>
<td>22</td>
<td>RECHAR</td>
<td>reinitialise data for subsequent time step</td>
</tr>
<tr>
<td>23</td>
<td>RECHYA</td>
<td>rearrange data for subsequent time step such that the characteristics are more evenly spaced in terms of ( \Delta z ) and component A composition</td>
</tr>
</tbody>
</table>

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**List of FORTRAN Routines for DCPSA Model**

(Continued)

<table>
<thead>
<tr>
<th>Routine ID No.</th>
<th>Routine Called</th>
<th>Subroutine, Function or existing ID No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDR</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>CLOCK</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>INICON</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>24</td>
<td>REINTL</td>
<td>reinitialise data for subsequent time step when the number of characteristics is less than a preset number</td>
</tr>
<tr>
<td>25</td>
<td>RENUMB</td>
<td>renumbering the characteristics identifier</td>
</tr>
<tr>
<td>26</td>
<td>PDBOUN</td>
<td>analytical solution for feed end calculation when linear isotherm is used and the feed rate and composition are known</td>
</tr>
<tr>
<td>27</td>
<td>PDEQN</td>
<td>simplified EQN (ID No. 19) due to constant pressure</td>
</tr>
<tr>
<td>IMQAB</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>28</td>
<td>PDIMPA</td>
<td>simplified IMPA (ID No. 21) due to constant pressure</td>
</tr>
<tr>
<td>LININT</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>29</td>
<td>ADDCHR</td>
<td>add more characteristics for subsequent time step</td>
</tr>
<tr>
<td>30</td>
<td>REDUCE</td>
<td>reduce the number of characteristics to save processing time</td>
</tr>
<tr>
<td></td>
<td>RECHYA</td>
<td>23</td>
</tr>
</tbody>
</table>

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List of FORTRAN Routines for DCPSA Model

(Continued)

<table>
<thead>
<tr>
<th>Routine ID No.</th>
<th>Calling Routine</th>
<th>Called Routine</th>
<th>Subroutine, Function or existing ID No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPRS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>C LOCK 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPPAPD</td>
<td>exponential pressure function, P(t) and p'(t)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>INICON</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>REINTL</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EQN</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IMPA</td>
<td>21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IMQAB</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LININT</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RECHYA</td>
<td>23</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CDPRS 6; all the routines called are identical to those called by DPRS (ID No. 5)

PURGE 7; all the routines called are identical to those called by PDR (ID No. 4)

BCKFL 8; all the routines called are identical to those called by PSR (ID No. 3) except no call to routine RECHAR
<table>
<thead>
<tr>
<th>Routine ID No.</th>
<th>Calling Routine</th>
<th>Called Routine</th>
<th>Subroutine, Function or existing ID No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>INOUT</td>
<td></td>
<td>11</td>
<td>overall mass balance calculation</td>
</tr>
<tr>
<td>32</td>
<td>MASBAL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPLIT</td>
<td></td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>LININT</td>
<td></td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>GLUE</td>
<td></td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>REGLUE</td>
<td></td>
<td>rearrange data before two data files are glue back together</td>
</tr>
<tr>
<td>INICON</td>
<td></td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>RECHYA</td>
<td></td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>IMQAB</td>
<td></td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>IMQABC</td>
<td></td>
<td>solid phase equations in second order implicit form</td>
</tr>
</tbody>
</table>

228
<table>
<thead>
<tr>
<th>Routine ID No.</th>
<th>Calling Routine</th>
<th>Called Routine</th>
<th>Subroutine, Function or existing ID No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADDCHR 29</td>
<td></td>
<td>MOIAAF</td>
<td>NAG library routine; used to sort the size of $\Delta z$ from big to small</td>
</tr>
<tr>
<td>REDUCE 30</td>
<td></td>
<td>MOIABF</td>
<td>NAG library routine; used to sort the size of $\Delta z$ from small to big</td>
</tr>
<tr>
<td>IMQABC 34</td>
<td></td>
<td>MNEWT</td>
<td>Newton Raphson iteration algorithm</td>
</tr>
<tr>
<td>MNEWT 37</td>
<td>USRFUN</td>
<td>specific routine required by MNEWT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LUDCMP</td>
<td>specific routine required by MNEWT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LUBKSB</td>
<td>specific routine required by MNEWT</td>
<td></td>
</tr>
</tbody>
</table>
# DCPSA Software Simulation Standard Configuration File

<table>
<thead>
<tr>
<th>Data for Simulation</th>
<th>Variables (and type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIMPLE CYCLE RUN</td>
<td>AT (A)</td>
</tr>
<tr>
<td>3</td>
<td>NSTEP (I)</td>
</tr>
<tr>
<td>1,2,3,0,0,0</td>
<td>IPSR, IPDR, IDPRS, IPURGE, IBCKFL, ICDPRS (I)</td>
</tr>
<tr>
<td>1,1,1,0,0,0</td>
<td>ICP, ICR, ICD, ICG, ICB, ICO (I)</td>
</tr>
<tr>
<td>1</td>
<td>ISO (I)</td>
</tr>
<tr>
<td>9.621D-4 4.000D-1</td>
<td>A (R) E (R)</td>
</tr>
<tr>
<td>0.350D00 5.930D02</td>
<td>BL (R) W (R)</td>
</tr>
<tr>
<td>1.588D-3 1.000D-7</td>
<td>RD (R) TOL (R)</td>
</tr>
<tr>
<td>8.3143D3 2.980D02</td>
<td>R (R) TEMP (R)</td>
</tr>
<tr>
<td>1.86D-13 5.64D-15</td>
<td>RKGA (R) RKGB (R)</td>
</tr>
<tr>
<td>3.0390D5 1.013D05</td>
<td>PHP (R) PLP (R)</td>
</tr>
<tr>
<td>3.0390D5 1.013D05</td>
<td>PHD (R) PLD (R)</td>
</tr>
<tr>
<td>3.0390D5 1.013D05</td>
<td>PHC (R) PLC (R)</td>
</tr>
<tr>
<td>1.0130D5 1.013D05</td>
<td>PHB (R) PLB (R)</td>
</tr>
<tr>
<td>3.0390D5 1.013D05</td>
<td>PPR (R) PPG (R)</td>
</tr>
<tr>
<td>0.2100D0 0.210D00</td>
<td>YAI (R) YAPSR (R)</td>
</tr>
<tr>
<td>0.2100D0 0.210D00</td>
<td>YAPDR (R) YAPUR (R)</td>
</tr>
<tr>
<td>0.2100D0 0.210D00</td>
<td>YABFL (R) YAEQL (R)</td>
</tr>
<tr>
<td>3.780D-9 3.637D-9</td>
<td>SKA (R) SKB (R)</td>
</tr>
</tbody>
</table>
DCPSA Software Simulation Standard Configuration File

(Continue...)

<table>
<thead>
<tr>
<th>Data for Simulation</th>
<th>Variables (and type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.414D-6</td>
<td>SKA2 (R) SKB2 (R)</td>
</tr>
<tr>
<td>6.666D-6</td>
<td>VPROD (R) VPURG (R)</td>
</tr>
<tr>
<td>3.000D01</td>
<td>TPS (R) TPR (R)</td>
</tr>
<tr>
<td>3.000D01</td>
<td>TDP (R) TPG (R)</td>
</tr>
<tr>
<td>2.000D01</td>
<td>TBF (R) TCO (R)</td>
</tr>
<tr>
<td>3.50D-02</td>
<td>DZ (R) NO (I)</td>
</tr>
<tr>
<td>1.000D00</td>
<td>FRACT (R) ICTL (I)</td>
</tr>
<tr>
<td>5.00D-05</td>
<td>PDNET (R) ERRSUM (R)</td>
</tr>
<tr>
<td>0.040D00</td>
<td>PGAIN (R) ACTINT (R)</td>
</tr>
<tr>
<td>51</td>
<td>NCY (I) JCN (I)</td>
</tr>
<tr>
<td>0</td>
<td>IC (I) IFILE (A)</td>
</tr>
<tr>
<td>0</td>
<td>ICODEP (I) ITBPE (I)</td>
</tr>
<tr>
<td>0</td>
<td>IBBPE (I) ITTBB (I)</td>
</tr>
<tr>
<td>0.000D00</td>
<td>PRO (R)</td>
</tr>
</tbody>
</table>

Note

(A) denotes variable is of type character

(I) denotes variable is an integer

(R) denotes variable is double precision
Where:

$AT =$ This field allow the user to enter a title of up to 80 characters for the simulation

$NSTEP =$ The total number of process steps in a simulation cycle

$IPSR, IPDR, IDPRS, IPURGE, IBCKFL, ICDPRS=$ The process step indicators

$ICP, ICR, ICD, ICG, ICB, ICO =$ These indicate the initial data for each subsequent process step,

0 means no initial data required

1 means initial data are required

$ISO =$ Type of isotherm: 0 for linear isotherm

1 for Langmuir pure gas isotherm

2 for Langmuir co-adsorption isotherm

$A =$ Column cross-sectional area, $(m^2)$

$E =$ Packing voidage, (-)

$BL =$ Column length, (m)

$W =$ Column packing density, $(kg/m^3)$

$RD =$ Particle radius, (m)

$TOL =$ Convergence tolerance, (-)

$R =$ Universal gas constant, $(J/kmol K)$

$TEMP =$ Temperature, (K)

$RKGA =$ Mass transfer parameter of component A, $(kmol m/(kg Pa s))$

$RKGB =$ Mass transfer parameter of component B, $(kmol m/(kg Pa s))$

$PHP =$ Final pressure for pressurisation step, (Pa)

$PLP =$ Initial pressure for pressurisation step, (Pa)

$PHD =$ Initial pressure for depressurisation step, (Pa)

$PLD =$ Final pressure for depressurisation step, (Pa)

$PHC =$ Initial pressure for co-current depressurisation step, (Pa)
PLC = Final pressure for co-current depressurisation step, (Pa)
PHB = Final pressure for backfill step, (Pa)
PLB = Initial pressure for backfill step, (Pa)
PPR = Constant pressure for product release step, (Pa)
PPG = Constant pressure for purge step, (Pa)
YAI = Column initial mole fraction of component A, (-)
YAPSR = Feed mole fraction of component A for pressurisation step, (-)
YAPDR = Feed mole fraction of component A for product release step, (-)
YAPUR = Feed mole fraction of component A for purge step, (-)
YABFL = Feed mole fraction of component A for backfill step, (-)
YAEQL = Feed mole fraction of component A for equalisation step, (-)
SKA = Linear isotherm gradient for component A, (kmol/(kg Pa))
SKB = Linear isotherm gradient for component B, (kmol/(kg Pa))
SKA2 = Langmuir isotherm gradient for component A, (Pa^{-1})
SKB2 = Langmuir isotherm gradient for component B, (Pa^{-1})
VPROD = Volumetric feed rate for product release step, (m^3/s)
VPURG = Volumetric purge rate for purge step, (m^3/s)
TPS = Process time for pressurisation step, (s)
TPR = Process time for product release step, (s)
TDP = Process time for depressurisation step, (s)
TPG = Process time for purge step, (s)
TBF = Process time for backfill step, (s)
TCO = Process time for co-current depressurisation step, (s)
DZ = Initial distance step size, (m)
NO = Initial number of fixed spatial discretisation
FRACT = Fractional the product use for purge step
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICTL</td>
<td>Overall convergence controller mode:</td>
</tr>
<tr>
<td></td>
<td>1 for PI controller</td>
</tr>
<tr>
<td></td>
<td>2 for linear interpolation,</td>
</tr>
<tr>
<td></td>
<td>3 for polynomial interpolation,</td>
</tr>
<tr>
<td>PDNET</td>
<td>Target net product amount (controller setpoint), (kmol)</td>
</tr>
<tr>
<td>ERRSUM</td>
<td>Sum of integral error for net product</td>
</tr>
<tr>
<td>PGAIN</td>
<td>Controller proportional gain</td>
</tr>
<tr>
<td>ACTINT</td>
<td>Integral action time constant</td>
</tr>
<tr>
<td>NCY</td>
<td>Number of cycles to be run</td>
</tr>
<tr>
<td>JCN</td>
<td>Starting cycle number</td>
</tr>
<tr>
<td>IC</td>
<td>Indicator for reading initial condition from file</td>
</tr>
<tr>
<td>IFILE</td>
<td>Initial condition file name, up to 8 characters</td>
</tr>
<tr>
<td>ICODP</td>
<td>Indicator for running both co-current and counter-current depressurisation step</td>
</tr>
<tr>
<td>ITBPE</td>
<td>Indicator for running top to top bed pressure equalisation cycle</td>
</tr>
<tr>
<td>IBBPE</td>
<td>Indicator for running bottom to bottom bed pressure equalisation cycle</td>
</tr>
<tr>
<td>ITTBB</td>
<td>Indicator for running both end bed pressure equalisation cycle</td>
</tr>
<tr>
<td>PRO</td>
<td>Percentage of column split for gas donating column</td>
</tr>
</tbody>
</table>