MODELLING SIMULATION AND OPTIMISATION
OF
MULTI-COMPONENT BATCH DISTILLATION

A thesis submitted for the degree of
Doctor of Philosophy

BY
Ir. SURACHMAN GUMAY M.Sc

Department of Chemical & Process Engineering

UNIVERSITY OF SURREY

August 1990
SUMMARY

In this thesis rigorous models for simulating the operation of multi-component batch distillation with a hypothetical start-up procedure are derived and solved by a novel analytical derivative technique. The conventional backward derivative technique which usually solves the model only from the steady-state total reflux condition is also extended to include the solution from the hypothetical start-up condition. Both techniques are shown to give identical results.

Simulation and optimisation of a ternary system with slop recycle are analysed by using one of the above rigorous models and solution techniques. Nine modes of operation for handling the recycle slops are developed and a basic mode of operation for evaluating the economic efficiency is defined as the reference. The objective function chosen for the analysis is the profit per cycle time rather than the total product per cycle time. The results of analysis show that the right choice of mode of operation is more significant than the right choice of the constant reflux ratio of the operation.

An explicit short-cut model for estimating the instantaneous overhead composition of multi-component batch distillation is successfully derived. The performance of the short-cut model is acceptably accurate and offers some advantages of speed over other published models. The short-cut model is shown to be very powerful for solving the problem of optimal reflux profile.
ACKNOWLEDGEMENT

I would like to take this opportunity to thank every one who in one way or the other has helped me with my research project. In particular, I sincerely like to thank my respected supervisor DR. J. A. Lamb for all the guidance and encouragement he has given me throughout this work. My own interest in optimisation studies was first stimulated while undertaking M.Sc course in Energy Engineering at the University of Surrey under his supervision.

I also wish to thank my employer, Universitas Sriwijaya, for financing my study leave in England.

Lastly but not the least, I would like to thank my wife, Anna, and my child, Bima. This study would not be completed but for their understanding and support.

Surachman Gumay
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
<td>1</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>ii</td>
</tr>
<tr>
<td>Contents</td>
<td>iii</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Background</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Objective</td>
<td>3</td>
</tr>
<tr>
<td>1.3 Applications</td>
<td>3</td>
</tr>
<tr>
<td>2. Literature Reviews</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Modelling of multi-component batch distillation</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Optimisation of multi-component batch distillation</td>
<td>22</td>
</tr>
<tr>
<td>2.3 Conclusions</td>
<td>35</td>
</tr>
<tr>
<td>3. Further Development of Dynamic Models</td>
<td>37</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>37</td>
</tr>
<tr>
<td>3.2 Primary assumptions</td>
<td>38</td>
</tr>
<tr>
<td>3.3 Derivation of the models</td>
<td>39</td>
</tr>
<tr>
<td>3.4 Integration of the dynamic models</td>
<td>50</td>
</tr>
<tr>
<td>3.5 Results and discussions</td>
<td>82</td>
</tr>
<tr>
<td>3.6 Conclusions</td>
<td>93</td>
</tr>
<tr>
<td>4. Optimisation of Ternary System with Recycle Slop</td>
<td>94</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>94</td>
</tr>
<tr>
<td>4.2 Simulation of a simple ternary system</td>
<td>98</td>
</tr>
<tr>
<td>4.3 Simulation of a ternary system with slop recycle</td>
<td>111</td>
</tr>
<tr>
<td>4.4 Objective function</td>
<td>133</td>
</tr>
<tr>
<td>4.5 Direct search with respect to modes of operation</td>
<td>136</td>
</tr>
<tr>
<td>4.6 Direct search with respect to the reflux ratio</td>
<td>140</td>
</tr>
</tbody>
</table>
1. Introduction

1.1 Background

This work is concerned with the modelling, simulation and optimization of multi-component batch distillation. It was inspired by the work of Diwekar et al. (1987), who studied optimal reflux policy determination for multi-component batch distillation columns using their own proposed short-cut column performance model, and by the work of Luyben (1988) on ternary systems with slop recycle.

Diwekar et al. (1987) have successfully used their short-cut model to solve the problem of optimal reflux rate policy, employing a "gradient method in function space" technique. Their short-cut model comprises a system of simultaneous equations attributed to Hengstebeck-Geddes, Fenske, Underwood and Gilliland which could be solved by the Newton-Raphson method. They do not describe how to arrange the routine for the solution of the simultaneous equations or which key components should be chosen as the basis of calculation. The method used involves the solution of an implicit function (Gilliland's correlation) which can lead to computational difficulties in some circumstances. However, they did solve their problem and compared the results with the "rigorous" method of Murty et al. (1980). The comparison was said to be close to each other and they claimed to have improved the computational time due to their short-cut model. They also
tried to optimise a quaternary system by the same technique, but the reported results show an anomaly where the optimum yield for a system having a lower number of trays is greater than that for a system having a higher number.

Luyben (1988) has been studying an interesting and novel practical aspect of optimal batch distillation design and operation where slop recycle in a ternary system is considered. He proposed three modes of operation for handling slop recycle for analysis and reported in detail. He used a semi-rigorous model in his analysis where the heat balance of the system is not considered. Therefore his performance criterion for optimisation is confined to the overall rate of products of specified quality based on total cycle time. The extension of his performance criteria to the rate of profit per cycle time needs a more rigorous model where the heat balance of the system can be accounted for. Various comprehensive rigorous models have appeared in the literature intended for the purpose of simulation. However, their methods of solution force them to start their simulation from the steady state total reflux condition which must be solved by an external routine based on continuous distillation models. This prevents modelling the start-up period of the process as suggested by Luyben (1988), so the start-up time and energy consumption during the time can not be calculated.
1.2 Objective

The objective of this thesis is divided into two parts. The first part deals with the development of a rigorous model to simulate multi-component batch distillation including the start-up periods as suggested by Luyben (1988) and taking heat balance into account. The rigorous model is then used to study some practical aspects of optimal batch distillation design and operation parallel to the work of Luyben (1988), namely Ternary System with Slop Recycle. The four modes of operation suggested by Luyben (1988) are developed further and the performance criterion for optimisation is made more practical, being the profit per cycle time. The second part deals with the development of a short-cut model for multi-component batch distillation as an alternative to the one suggested by Diwekar et al. (1987). The short-cut model is tested by a study on Optimal Reflux Ratio Determination to that of Diwekar et al. (1987) and Murty et al. (1980) and compares the results to theirs.

1.3 Applications

Batch Distillation remains an important separation technique in the manufacture of small-volume, high-value specialty chemicals. It has the advantage of being able to produce a number of products from a single column. Even though batch distillation consumes more energy than continuous
distillation, it provides more flexibility and involves less capital investment. A single column can also handle a wide range of feed compositions, number of components, and degrees of difficulty of separation.

Because of its flexibility, there results a large number of parameters to be considered in order to find the optimal design and operation of Batch Distillation. This work can be used as a guide to determine the right course of choosing the equipment size, and the mode of operation with regard to the variation of feed composition, volatility, product specification and demand.
2.1 Modelling of Multi-Component Batch Distillation

2.1.1 Introduction

Before reviewing the literature on modelling and simulation of multi-component batch distillation, it is necessary to introduce some notions about batch distillation terminologies in this study. Batch Distillation is a separation process based on relative volatilities of the components in the system to be separated. A multi-component batch distillation model deals with a system having more than two components, but this does not preclude it being used for a binary system.

Batch distillation is actually a semi batch process where the system is charged once in one cycle time by a fresh feed at the beginning of a batch, while the products can be continually withdrawn from the system and other fresh feed or slop recycles can be introduced to the system during the cycle time. The essential temporal features of the cycle time are the charging period, the start-up period, the topping and feeding period.

Batch distillation is carried out in a tray column consisting of a still or reboiler, a number of trays, a condenser and accumulator with reflux system. For a sophisticated system each tray can be provided with a feed entrance, a side draw
point and a heating or cooling system. During the distillation process, the still, the trays and the accumulator are all filled with liquid and vapor holdup. Vapor flows up from the still through the trays to the condenser where it condenses to a liquid. The liquid then flows to the accumulator. The liquid from the accumulator can be divided into two parts, one part as the top product and the other as reflux which is returned to the column through the top tray. The liquid reflux flows downward through the trays to the still, while coming into contact with the upward vapor flow.

Multi-component batch distillation models consist of a system of differentio-algebraic equations which describes the mass and heat balances of the process and the vapor-liquid equilibria in each tray. The models can be differentiated into three categories, namely rigorous, semi rigorous, and short-cut model.

The essential feature of a rigorous model is that it incorporates complete mass and heat accumulation in all the holdups, mass and heat transfer from the system to the surroundings, and variation of relative volatilities of the components with the operating conditions. A semi-rigorous model is a simplification of a rigorous model with regard to the above essential feature of a rigorous model. There is no real boundary between a rigorous model and a semi-rigorous model. The rigorous model is directed more toward the accuracy of the model, while the semi rigorous model considers
more the importance of computational time.

A short-cut model is the simplest model to describe the material balance of the system using some experience or experimental considerations. It tries to approximate the relationship between the instantaneous composition of the liquid in the accumulator with that of the liquid in the still without involving tray to tray calculation. Therefore, such models usually neglect the heat balance, the tray and the accumulator holdups, and the variation of relative volatilities of the component with temperature and pressure.

2.1.2 Rigorous Model of Multi-Component Batch distillation

The first comprehensive model for multi-component batch distillation was due to Meadows (1963). The model employed heat and material balances as well as volume balances and was limited only by the assumption of ideal trays, constant volume tray and accumulator holdup, adiabatic operation, and negligible vapor holdup. He solved the model using finite difference method starting from the steady state total reflux condition. It was found that the use of finite-difference method for solving the model leads to instability if too large a step size is used, hence high computational times were required. He suggested the future work to develop a more refined method for increasing the speed of the calculation. He also recommended to develop a start-up procedure to allow for calculating heat and time requirements from the point of
first application of heat to the still.

Distefano (1968b) devoted his study mainly to an analysis of various methods of numerically integrating the differential equations comprising a comprehensive mathematical model of multi-component batch distillation. He used the same assumptions as Meadows in his model and started the solution from the steady state total reflux condition. Meadows-Distefano Model can be described as follows. For the condenser-accumulator system, the total mass balance, the component balance and heat balance are respectively

\[ L_o = R \ D \]  

\( \frac{dM_o}{dt} = V_4 - L_4 - D = V_4 - D (R+1) \)  

\( \frac{dM_o X^i_o}{dt} = V_4 Y^i_4 - D (R+1) X^i_o \)  

\( \frac{dM_o h_o}{dt} = V_4 H_4 - D (R+1) h_o - Q_c \)

For an arbitrary tray number \( n \), they are respectively

\( \frac{dM_n}{dt} = V_{n+1} + L_{n-1} - V_n - L_n \)  

\( \frac{dM_n X^i_n}{dt} = V_{n+1} Y^i_{n+1} + L_{n-1} X^i_{n-1} - V_n Y^i_n - L_n X^i_n \)  

\( \frac{dM_n h_n}{dt} = V_{n+1} H_{n+1} + L_{n-1} h_{n-1} - V_n H_n - L_n h_n \)
An analogous description of the reboiler results in the equations

$$\frac{dH_{N+1}}{dt} = L_N - V_{N+1}$$ \hspace{1cm} (8)

$$\frac{dM_{N+1}X^i_{N+1}}{dt} = L_N X^i_N - V_{N+1}Y^i_{N+1}$$ \hspace{1cm} (9)

$$\frac{dM_{N+1}h_{N+1}}{dt} = L_N h_N - V_{N+1}h_{N+1} + Q_B$$ \hspace{1cm} (10)

The molar holdups of liquid in the trays, the still and the accumulator are formulated by

$$N_n = G_n \rho_n$$ \hspace{1cm} (11)

The liquid molar density is a function of temperature, pressure and composition:

$$\rho_n = f(X^t_n, T_n, P_n)$$ \hspace{1cm} (12)

The ultimate success of any distillation model depends upon the accuracy of the vapor-liquid equilibrium relationship employed. The most commonly used form of this relationship for multi-component mixtures is

$$Y^i_n = K^i_n X^i_n$$ \hspace{1cm} (13)
The equilibrium constant as a function of temperature, pressure, and composition is given by

\[ K_n^i = f^i(\bar{X}_n^i, T_n, p_n) \]  \hspace{1cm} (14)

The vapor-liquid equilibrium relationship should satisfy the bubble point calculation as follows

\[ \sum_{i=1}^{NG} y_n^i = 1 \] \hspace{1cm} (15)

The enthalpies of liquid and vapor are each formulated as a function of temperature and composition respectively

\[ h_n = f(\bar{X}_n, T_n) \] \hspace{1cm} (16)

\[ H_n = f(\bar{V}_n, T_n) \] \hspace{1cm} (17)

Distefano (1968a) solved the above model by employing a backward derivative technique to approximate the derivatives of liquid molar holdups and liquid enthalpies from past stored values. This can be formulated by

\[ \frac{dM_n}{dt} \approx \delta_t M_n \] \hspace{1cm} (18)

\[ \frac{dh_n}{dt} \approx \delta_t h_n \] \hspace{1cm} (19)
This technique is reasonable only if the solution starts from the steady state total reflux condition where the initial values of those derivatives are practically zero. The extension of this technique for the solution of a start-up procedure is inhibited by the unknown initial values of those derivatives.

The use of the above approximate derivatives will reduce the number of differential equations of the model by transforming the mass and heat balance equation into a system of difference equations. These difference equations will give the solution for the vapor and the liquid flow of the system. The computational time depends on the solution of the bubble point calculation which must be solved by an iterative technique. Distefano (1968a) suggested that the bubble point calculation need be performed only at the end of an integration step together with the updating of the approximate derivatives, and the vapor and the liquid flow.

Distefano (1968a) method of solution has been tested experimentally by Stewart et al. (1973) who proved that the experimental and the theoretical results were in good agreement. Therefore, Distefano (1968a) method can be used a comparison for any further development of the method of solution.
The work of Distefano (1968a) was popularly followed by Boston et al. (1981) who developed an advanced system known as BATCHFRAC model for the simulation of Batch Distillation operations. They enhanced Distefano's (1968a) model by introducing multiple feed and side product streams. There were no improvements to the method of solution, and the start-up procedure remained untouched.

Guy (1983) developed a similarly complete model to that of Boston et al. (1981). He used the concepts of constant liquid molar holdup, hydraulic time constant and real tray hydraulics as variations to the constant liquid volume holdup assumption. He also introduced a Murphree tray efficiency instead of the assumption of ideal trays.

The total mass balance, the component balance and heat balance for the condenser-accumulator system and for the reboiler system are practically the same as that of Meadows-Distefano Model. The balances around tray number n are respectively

\[
\frac{dM}{dt}_n = V_{n+1} + L_{n-1} - V_n - L_n + F_n - D_n - D_{vn}
\]

\[
\frac{dM}{dt}_n X^n = V_n Y^n + L_n X^n - (L_n + D_n) X^n - (V_n + D_n) Y^n + F_n X^n
\]

\[
\frac{dM}{dt}_n h^n = V_n H^n + L_n h^n - (L_n + D_n) h^n - (V_n + D_n) H^n + F_n h^n
\]
The instantaneous change of liquid flow is formulated by introducing a Hydraulic Time Constant $\tau_n$.

$$\frac{dL_n}{dt} = -\frac{1}{\tau_n} \left( V_{n+1}^L - V_L^L - L_n + F_n + D_n - D_{vn} \right)$$  \hspace{1cm} (23)

To simulate a real tray instead of an ideal tray, he introduced a Hurphree tray efficiency of the form

$$Y^n_l = Y^n_{l+1} + \eta^n_1 \left( Y^n_{l+1} - Y^n_{l+1} \right)$$  \hspace{1cm} (24)

where

$$Y^n_{l+1} = K^n_1 x^n_1$$  \hspace{1cm} (25)

The Guy's (1983) equation for tray hydraulic which relates the liquid volume holdups with the outlet liquid flow is complicatedly formulated. It is beyond the scope of this review to write all of the formulations. However, the equation can be summarised to have the form as follows

$$G^n = f(L_n^{2/3}, \rho_L, \rho_v, \text{coefficients})$$  \hspace{1cm} (26)

His method of solution for an ideal tray system seems unreasonable when he assumes a constant molar holdup for his simplification, making the R.H.S of equation (23) meaningless. Vapor flows are formulated from heat balance equations by neglecting the enthalpy accumulation. This is at variance with the essential nature of his rigorous model, though it will reduce the computational time. The problem of computational time due to the bubble point calculation remains
unsolved. It is not clear whether his method of solution can be extended to handling a start-up procedure.

2.1.3 Semi-Rigorous Model Of Multi-Component Batch Distillation

An example of a semi-rigorous model of multi-component batch distillation was suggested by Luyben (1971). His model was based on the assumption of constant relative volatilities, constant molar holdups in the trays and in the accumulator, and constant vapor flow with flat profiles, and neglected the heat balance.

The component balance in the accumulator, tray number \( n \) and the still, and the total mass balance in the still are given by

\[ L = L_0 = L_1 \ldots = L_N ; \quad V = V_1 = V_2 \ldots = V_{N+1} \quad (1) \]

\[ M_0 \frac{dX^i}{dt} = V \left( Y^i - X^i \right) \quad (2) \]

\[ M_n \frac{dX^i}{dt} = V \left( Y^i_{n+1} - Y^i_n \right) - L \left( X^i_n - X^i_{n-1} \right) \quad (3) \]

\[ \frac{dM^i_{N+1} X^i_{N+1}}{dt} = L X^i_{N+1} - V Y^i_{N+1} \quad (4) \]

\[ \frac{dM_{N+1}}{dt} = V - L \quad (5) \]
The equilibrium relationship is approximated by the concept of constant relative volatility of the components.

\[ y_n^i = \frac{\alpha_i x_n^i}{\sum_{i=1}^{NC} \alpha_i x_n^i} \]  

Luyben (1971) had tried a simple procedure to simulate the start-period. All the holdups are initially charged with liquid of the same composition. It is not clear how to do it in practice. Presumably it can be done by charging the liquid from the accumulator down to the still. He also suggested another alternative that the system can be assumed to have all the tray holdups initially filled with liquid having the composition in equilibrium with the composition of the liquid in the still.

Domenech and Enjalbert (1980) made a slight modification to the model of Luyben (1971). They still introduced the variation of relative volatilities of the components with temperature and pressure. It was stated that a sub-program is needed to start the solution from the steady state total reflux condition. However, it is also possible to start the solution on the basis of temperature and concentration profiles supplied as data. This implies that their model can be used to simulate a similar start-up procedure to that suggested by Luyben (1971). They solved their model using
Runge-Kutta-Merson with variable step size.

Galindez and Fredenslund (1987) solved the above model using their quasi-steady state approach. The unsteady state process of batch distillation is simulated as a succession of short periods of time in which continuous distillation are carried out. They were able to simulate the start-up procedure as suggested by Luyben (1971).

Domenech and Enjalbert (1978) presented the common semi-rigorous model, namely a model without holdup. All the tray holdups and the accumulator holdups are neglected. The model is composed of an overall mass balance and the component balance equation.

\[
\frac{dM_{N+1}}{dt} = - \frac{V}{R+1}
\]  

(7)

\[
\frac{dX_{N+1}^i}{dt} = - \frac{V}{R+1} \frac{X^i_0 - X^i_{N+1}}{M_{N+1}}
\]  

(8)

The instantaneous compositions of the liquid in the accumulator are obtained by solving a system of non-linear equations.
\[
Y_n = K_n^i X_n^i = \frac{R}{R+1} X_{n-1}^i + \frac{X_o^i}{R+1} \\
\text{for } i = 1, 2, \ldots NC \\
\text{and } n = 0, 2, \ldots N \\
\sum_{i=1}^{NC} K_n^i X_n^i - 1 = 0
\]  

(9)

2.1.4 Short-Cut Model Of Multi-Component Batch Distillation

The general form of total mass balance and the component balance for a short-cut model are as follows

\[
\frac{dB}{dt} = - \frac{V}{R+1} 
\]  

(1)

\[
\frac{dX_s^i}{dt} = \frac{1}{R+1} \frac{V}{B} (X_s^i - X_D^i) 
\]  

(2)

where

\[
X_D^i = f^i \left( X_B^i, R, N, \alpha, \text{consts} \right) 
\]  

(3)

The oldest short-cut model for multi-component batch distillation is perhaps due to Chao Kwang-Chu (1954). The suggested short-cut model is a modification of Brown and Souders' (1933) absorption factor method, originally applied to continuous distillation. The absorption factor for each component is formulated as

\[
S_p^i = \frac{K_a^i V}{D} = K_a^i \alpha_i (R + 1) 
\]  

(4)
A direct relationship between the composition of the liquid in the still and the instantaneous composition of the liquid in the accumulator is given by

$$X_D^i = k^i X_B^i$$

where

$$k^i = \left[ \frac{K^i_n \left( S_F^i \right)^n \left( S_F^i - 1 \right)}{\left( S_F^i \right)^n \left( S_F^i - K^i_n \right) + K^i_n - 1} \right]$$

The summation of the instantaneous composition of the liquid in the accumulator as calculated by equation (2) will usually not equal to unity. He suggested that the composition has to be normalised. There is no suggestion as how to choose the temperature for the calculation of the equilibrium constants used in the model.

By assuming constant reflux condition, Chao Kwang-Chu (1954) integrated the mass balance of the system, which resulted in a direct relationship between the amount of the liquid in the still and its compositions

$$X_B^i = X_{B0}^i \left( \frac{B}{B_0} \right)^{k^i - 1}$$

Domenech and Enjalbert (1978) presented another short-cut model. It was stated that the reference equilibrium constant
varies exponentially with tray number by their empirical formula as follows

\[ K_n^r = K_B^r b^{-n+N+1} \]  

(8)

The relationship between the instantaneous composition of the liquid in the accumulator and that of the liquid in the still is calculated by

\[ \chi^i_D = \frac{f^i(b)}{g^i(b)} \]  

(9)

Where

\[ f^i(b) = R \left( \frac{K_B^r \alpha_i}{u} \right)^{N+1} b^{-\frac{NN+N+1}{2}} \]  

(10)

and

\[ g^i(b) = R + 1 + \sum_{n=i}^{N} \left( \frac{K_B^r \alpha_i}{u} \right) b^{-\frac{N(N+1)-n(n-1)}{2}} \]  

(11)

While

\[ u = \frac{R}{R+1} \]  

(12)

The parameter \( b \) in the formula is determined by summing up the all the compositions of the liquid in the accumulator and equalising the summation to unity.

\[ \sum_{i=1}^{NC} \chi^i_D = \sum_{i=1}^{NC} \frac{f^i(b)}{g^i(b)} = 1 \]  

(13)
The latter equation must be solved by an iterative method, and therefore makes their short-cut model not a straight-forward formula.

Diwekar and Madhavan (1986) suggested their short-cut model which is based on the assumption that batch distillation can be considered as continuous distillation with changing feed. That is, for a small interval of time the batch column behaviour is analogous to a continuous column. As such they derived their model from the most widely used short-cut model for continuous distillation. The equations used in the proposed short-cut model are: Hengstebeck-Geddes' equation

\[
X^i_D = \left( \frac{\alpha_i}{\alpha_s} \right)^{C_i} \frac{X^i_D}{X^i_B} \tag{14}
\]

which can be related to the Fenske's equation,

\[
N_{\text{min}} = \frac{\ln \left[ \frac{X^l_k}{X^h_k} + \frac{X^h_k}{X^l_k} \right]}{\ln \alpha_{lh}} \tag{15}
\]

Underwood's equations,

\[
\sum_{i=1}^{NC} \frac{\alpha_i X^i_B}{\alpha_i - \phi} = 0 \tag{16}
\]
\[ R_{\text{min}} + 1 = \sum \frac{\alpha_i^t x^i_{D}}{\alpha_i - \phi} \] (17)

Gilliland's equation,

\[ Y = 1 - \exp \left[ \frac{(1+54.4X)(X-1)}{(11+117.2X)\sqrt{X}} \right] \] (18)

in which

\[ X = \frac{R - R_{\text{min}}}{N + 1} \quad \text{and} \quad Y = \frac{N - N_{\text{min}}}{N + 1} \] (18)

and

\[ \sum_{i=1}^{N_G} x^i_{D} = 1 \] (19)

They apparently treated the above simultaneous equations by reducing them to a one dimensional search in \( C_i \) which they solved using Newton-Raphson's method. This fact of searching in \( C_i \) may result in the value of \( X \) and \( Y \) as calculated by equation (18) running out of range during the search, and therefore the search will fail. However, they did not give explicit arrangement of the solution. Furthermore, they did not give detail as how to choose the light key and the heavy key references of component used in equation (15) and as to whether the references can change during the course of distillation.
2.2 Optimisation of Multi Component Batch Distillation

2.2.1 Introduction

Works on the optimisation of multi-component batch distillation can be divided into two main streams. The first stream treats the optimisation problem as a control problem or variational problem. While the second stream treats it as a design and operation problem or non-linear programming problem.

Control problems of multi-component batch distillation are mainly concerned with the determination of optimal reflux profile for the operation of an existing column. In most cases the objectives considered are of two types. The first one is to minimise the time required to obtain a given amount of product of a given composition. The second one is to maximise the amount of product of a given composition during a specified time. This problem is also known as the "maximum Distillate Problem".

Design and operation problems of multi-component batch distillation deal with the determination of optimal column sizes and wider aspects of modes of operation than simple reflux control. The column design parameters consist of number of trays, still holdup, tray holdups, accumulator holdup, boiler and condenser heat transfer areas. Modes of operation pertain to how a column is operated to achieve the
desired products. The performance criteria for optimisation are usually some formulation of total capacity or profit per cycle time.

2.2.2 Control Problem of Multi-Component Batch Distillation

Works on the control problems of multi-component batch distillation had been reviewed by Rippin (1982). It was stated that reports on the use of optimal reflux profiles in batch distillation began from the work of Converse and Gross (1983). The systems generally studied are binary with constant relative volatility. Ternary systems have been discussed by Robinson (1969), and by Mayur and Jackson (1971). Egly et al. (1979) reported a study of a multi-component system but no detail were given. Robinson (1970) discussed a ten component mixture with constant relative volatilities but for some of the calculations it is treated as an effective binary. The number of trays considered is generally, small-up to 8, with 3 and 5 being common values. Exceptions are Price (1967); 12 trays, Robinson (1970); 30 trays, and Egly (1979) who claimed a capability of handling up to 100 trays. The effect of holdup is generally not treated although it acknowledged to be important. Converse and Huber (1965) attempted to account for it, Robinson (1969) discussed a case with an accumulator holdup to 10% of the reboiler charge. Mayur and Jackson (1970) treated a three tray column with each tray holdup equal to 5% the reboiler charge. Murty et al. (1980) devoted their study to comparing various methods of
solution for the maximum distillate problem.

All the above works employed semi rigorous models to analyse their problems. Diwekar et al. (1987) claimed that the use of semi rigorous method demands much memory and computational time, and therefore they used their short-cut model in their analysis. They solved the maximum distillate problem as an example, and they compared the results of their work with that of Murty et al. (1980). The maximum distillate problem which they studied can be written as:

\[
\max_{\mathbf{R}(t)} \left\{ J = \int_0^T D(t) \, dt = \int_0^T \frac{V}{(R + 1)} \, dt \right\}
\]

subject to the constraint of state equations:

\[
\frac{dB}{dt} = -\frac{V}{R + 1} ; \quad B(O) = B_0
\]

\[
\frac{dX^i_B}{dt} = \frac{1}{R + 1} \frac{V}{B} \left( X^i_B - X^i_D \right) ; \quad X^i_B(O) = X^i_B(0)
\]

\[
X^i_D = f^i\left( \bar{X}_B, R, N, \alpha, \text{consts} \right)
\]

and an isoperimetric constraint of product purity.
Diwekar et al. (1987) claimed to have reduced the dimensionality of equation (3) by choosing component one as a reference and relating any other component \( i \) to the reference component. This can be formulated by

\[
\frac{dX^i_{b}}{(X^i_{D} - X^i_{b})} = \frac{dX^i_{b}}{(X^i_{D} - X^i_{b})} \quad ; \quad X^i_{b_0} = X^i_{p_0}
\]  

However, this argument to reduce the dimensionality of the state differential equation seems incomplete, because it could be extended to the still holdup \( B \) in equation (2), thus reducing the dimensionality to one.

\[
- \frac{dB}{B} = \frac{dX^i_{b}}{(X^i_{D} - X^i_{b})}
\]  

They used their short-cut model for equation (4) and combined the objective function \( J \) with the isoperimetric constraint in equation (5) to an augmented objective function. They did it by introducing a Lagrange Multiplier. Their augmented objective function is

\[
I(R) = \int_{0}^{T} \frac{V}{(R + 1)} \left( 1 - \lambda (X^i_{D} - X^i_{b}) \right) dt
\]  

They solved the optimisation of the augmented objective
function by introducing a Hamiltonian Function as follows,

$$H = -\frac{q^V}{(R + 1)} + \frac{q^V}{(R + 1)B} (X^s - X^d) + \frac{V}{(R + 1)} \left( 1 - \lambda (X^s - X^d) \right)$$ \hspace{1cm} (8)

It was not stated whether the Hamiltonian Function applies for all multi-component systems or just for a binary system in their example. They derived the differential equations of the adjoint vector and then solved the two-point boundary value problem using the Gradient Method in Function Space to iterate the reflux profile as follows,

$$R_{\text{new}} = R_{\text{old}} + \varepsilon \frac{\partial H}{\partial R_{\text{old}}}$$ \hspace{1cm} (9)

The choice of constant $\varepsilon$ is said to be important, but there is no clue given as how to choose it. If $\varepsilon$ is too small the convergence will be slow, on the other hand, if $\varepsilon$ is too high it will cause instability. The sign of $\varepsilon$ is also important, because it will determine whether the problem is maximisation or minimisation.

As one of their sample problems, they solved a binary problem which was already discussed by Hurty et al. (1980) who used a semi-rigorous model and compared their results. It was stated that their results were in close agreement. They also tried to solve a quaternary system, but the results seem to show an anomaly. It was found that the optimum yield for a system having a lower number of tray was greater than that for a
system having higher number of trays.

2.2.3 Design Problem Of Multi-Component Batch Distillation

Publications in this area of study are still rare. The first comprehensive one is perhaps due to Luyben (1971). He demonstrated that batch distillation cycle time, or capacity, can be much more significantly affected by design and operating conditions such as tray holdup, accumulator holdup, initial still charge, number of trays, and reflux ratio. He optimised a binary system by a technique which can be extended to a multi-component system. He used a semi-rigorous model with the assumption of constant relative volatility and equimolal-overflow system for simplification.

A complete batch distillation cycle of the binary system in his study consists of:

1) Start-up

At the beginning of the start-up period, when $t=0$, compositions on all trays and the accumulator holdup are assumed equal to the initial charge composition. He stated that it would perhaps be more realistic to assume that if the feed were charged to the still pot, the initial compositions of the trays and the accumulator holdup would be equal to the composition of the vapor in equilibrium with the feed. The column will not produce any rectification until the vapor
boil-up has worked its way up the column and condensed to form enough liquid to fill the accumulator and the trays. During the period of establishing liquid flows, the still would represent only one equilibrium stage.

The column is run at total reflux until steady state is attained. He defined the equilibration (start-up) time as the time when the rate of change of the accumulator holdup composition is less than certain tolerance.

\[
\frac{dX_i^O}{dt} \bigg|_{t=t_E} < \varepsilon
\]

(1)

2) Overhead product withdrawal

The overhead product is withdrawn at a constant rate as dictated by a desired reflux ratio \( R \). The amount of the overhead product collected up to time \( t \) is formulated as

\[
P_i = \int_{t_E}^{t} \frac{V}{(1 + R)} \, dt
\]

(2)

The corresponding average composition of the overhead product with reference to the light component is

\[
X_{P_i}^i = \frac{1}{P_i} \int_{t_E}^{t} \frac{V \, X_i^O}{(1 + R)} \, dt
\]

(2)

28
The withdrawal of the overhead product is carried out until the average composition drops to a specified purity.

\[
X_{Pz}^a \bigg|_{t=t_{Pa}} \leq X_{Pz}^b
\]  

(3)

3) Bottom product purification

To make on-specification product in the still, it is necessary to continue taking material from the accumulator until enough component has been removed. The material removed (slop) is sent to a rework tankage. It is not clear whether the slop is recycled in his treatment of the problem. The material in the accumulator is included in the slop.

The amount of bottom product left is given by

\[
P_z = \sum_{n=1}^{N+1} N_n
\]  

(4)

And the average composition of the bottom product at any time during the removal of the light component is

\[
X_{Pz}^a = \frac{1}{P_z} \sum_{n=1}^{N+1} N_n X_n^a
\]  

(5)
The stopping criterion for the bottom product purification is
\[ X_{FZ}^2 \bigg|_{t=t_F} \geq X_{FZ}^* \quad (6) \]

4) Product removal and recharging

After the bottom product purification, the column is cleaned and recharged for the next batch. There is no calculation for the estimation of the cleaning and recharging time. Apparently he did not include the cleaning and charging time in the total cycle time.

His design objective or criterion is to maximize capacity which he defined as the total amount of on-specification products produced per unit time. The criterion is formulated as follows:

\[ C = \frac{P_s + P_z}{t_F} \quad (6) \]

This capacity, \( C \), is a non-linear function of many variables, among them are number of tray, reflux ratio, accumulator holdup, tray holdup, initial still charge, boilup rate, relative volatilities and specified purities. The calculation of the capacity based on the above variables are performed by numerical integration of the differentio-algebraic system which is described by his own semi-rigorous model.
The optimization problem of the capacity is solved by a simple direct search technique. The non-linear function of many variables is reduced to a function of only two variables by making others constant. The optimum position is represented on the graphs in the form of a contour-map or a level-curve.

He found that the optimal capacity increases if the number of trays increases with the corresponding decrease in the reflux ratio. The optimal capacity also increases if the tray holdup increases with the corresponding decrease in the accumulator holdup.

Diwekar and Madhavan (1986) presented the optimal design of multi-component batch distillation columns using their own short-cut model. The objective function considered was annual profit expressed as annual sales value of distillate minus annual cost of distillation.

The annual cost of distillation is based on the cost function given by Happel (1958) which consists of amortised costs plus annual running costs. The capital costs are deduced from simplified design concepts and result in an annual cost which is a function of boil-up rate, \( V \), number of trays, \( N \), operating time per batch, \( t \), and charging time per batch, \( t_c \).

\[
\text{Annual cost} = f (V, N, t, t_c)
\]  

where the number of batches per year \( N_b \) is expressed as

\( \ldots \)
The time required for cleaning, recharging and start-up are combined together in $t_c$ as a constant of the system. They claimed that their general optimisation problem had three degrees of freedom. The decision variables can be chosen as either the number of trays, $N$, or reflux ratio, $R$, or the final composition of the still pot, $X_{st}^i$, and the boil-up rate, $V$. They further classified the optimisation problem into the problem with fixed terminal conditions and the problem with free terminal conditions.

For a problem with fixed terminal conditions $X_{st}^i$ is fixed. If $V$ is also fixed then the problem becomes a single variable optimisation problem with $N$ or $R$ as decision variables. They optimised the annual cost in equation (7) with respect to the decision variable by Fibonacci search method. For this purpose, they defined the limits on the value of $R$ as follows

$$\frac{1}{10} \leq R \leq R_{max}$$

$R_{max}$ is calculated at the initial condition $X_{bo}^i$ using the limiting value $N_{min}$ which is calculated at the terminal value of $X_{st}^i$.

They treated the problem with free terminal conditions as a multivariable optimisation problem. They solved the problem...
by a successive optimisation strategy, employing Fibonacci search technique in each stage. There was a constraint on $X_{st}^4$ given by

$$0 < X_{st}^4 < X_{so}$$  \hspace{1cm} (10)

The problem with fixed terminal conditions shows that there is an optimal $R$ for the maximum annual profit. For the problem with free terminal condition it is found that sub-optimal position moves according to increasing $V$ and decreasing $X_n^4$.

Luyben (1988) extended his previous study on binary system to a study on ternary system with slop recycle. While there are one slop cut and two products in a binary system, there could be two slop cuts and three products for a ternary system. The first slop cut will contain mostly the light component and the intermediate component. The second slop cut will contain mostly the intermediate and the heavy component.

In his particular study, the first slop cut is recycled back to the next still pot charge. The initial still pot charge consists of all fresh feed for the first batch cycle. Subsequent still pot charges to the second batch cycle consist of some fresh feed and the recycled slop. The total molar charge for each batch is kept constant in this model.
It was found that batch distillation parameters were changing during the first several batches. It took about three batch cycles for a pseudo-steady-state operation to build up. The fresh feed decreased as the slop cuts approached their steady state values.

For the purpose of optimisation Luyben (1988) extended his previous capacity factor used as the performance index for binary systems to ternary systems. He assumed a 30-minute period required to empty and recharge the still pot, so that his capacity factor was formulated as

\[ C = \frac{P_1 + P_2 + P_3}{t_F + 0.5} \]  \hspace{1cm} (11)

The treatment of the optimisation problem employed the same methodology as for the case of binary system in his previous study. It was concluded that there was a function of the number of trays. The capacity was decreased when the relative volatility or the number of trays was reduced.

For future study, he proposed examining alternative operating schemes for slop recycling, variable reflux policy and a wider range of parameters such as feed compositions and relative volatilities. The alternative operating schemes or modes of operation to handle slop recycle are:
(1) saving up a number of slop cuts and doing binary batch distillation on each of the slop cuts,

(2) charging fresh feed to the still pot and feeding the slop cuts into the column to an appropriate tray and at an appropriate time during the course of the next batch, and

(3) using the first slop cut to fill up the reflux drum, and perhaps the column, prior to the start-up under total reflux condition in the next batch cycle.

2.3 Conclusion

Publications on the optimal design and operation of multi-component batch distillation are still rare. Luyben (1988) has initiated a study on optimisation of ternary system with slop recycle using a semi-rigorous model of his own. All alternative modes of operation which he suggested have not been reported. Future development of his study is wide open.

Current methods of solution for rigorous models of multi-component distillation are generally confined to the initial steady-state total-reflux conditions. Whether the methods of solution can be extended to the initial conditions of the start-up period as suggested by Luyben (1988) are still ambiguous.
Previous works on the problem of optimal reflux policy determination mostly employed semi-rigorous models. Diwekar et al. (1987) first reported the use of a short-cut model of his own. There are confusing steps in the application of their model to the problem. Some of the results seem a contradiction. An alternative short-cut model and its corresponding method of solution are necessary to obtain a better result.

Several short-cut models of multi-component batch distillation have appeared in literature. Further development of these short-cut models for the solution of optimal reflux policy determination provides a new field of study.
3 Further Development of Dynamic Models

3.1 Introduction

This chapter is aimed at developing dynamic models of multi-component batch distillation. The models have to satisfy certain conditions in order to extend the optimisation study suggested by Luyben (1988). The condition demands that the models have to be more rigorous, so that a start-up period before the steady state total reflux condition is achieved and a complete heat balance of the system can be taken into account.

Assumptions are made in order to achieve a satisfactory model and to have a better guide in the course of derivation of the model. As a result of this, models with varying degrees of rigor can be developed based on the assumptions of alternative laws governing certain processes.

Two methods of solution are discussed for the purpose of comparison and validation of the models, namely the backward derivative technique and the analytical derivative technique. The backward derivative technique which was employed by Distefano (1968a) and was confirmed experimentally by Stewart et al. (1973) normally starts the solution from the steady-state total reflux condition. Whether the backward derivative technique can be extended to start the solution from the beginning of a start-up period can be demonstrated at
once. The analytical derivative technique is specially
developed to solve this problem of start-up period.

3.2 Primary Assumptions

3.2.1 Configuration of the system

The distillation system which will be analysed is basically
the same as that of Guy (1983). It consists of a reboiler, a
number of trays with multiple-feeds and side-product streams,
a condenser, and an accumulator. The top product and the
reflux are withdrawn from the accumulator. They are divided
by a reflux regulator.

Multiple-feed and side-product streams are provided for at
every stage to maintain the generality of the models for any
type of simulation and optimisation purposes. The
side-product streams can be liquid streams or or vapor streams
or both. While the feeds are assumed to be liquids.

3.2.2 Simplification.

In order to avoid the excessively complicated methods of
solution required by the most rigorous models, some relaxation
of rigour is desirable. Three simplifications which do not
compromise the accuracy too much are:
1) Constant pressure

During distillation process the pressures in the column are assumed constant with respect to time. The pressure profile with respect to the stage number can be either a flat profile or a linear profile with a constant pressure drop over each stage.

2) Negligible vapor holdups

The vapor holdup in each stage is relatively small compared with the corresponding liquid holdup, being less than one percent of the total holdup. Therefore, vapour holdups can be neglected for practical purposes.

3) Perfect mixing

The liquid holdup in each stage is assumed to be perfectly mixed, i.e. there are no temperature or concentration differences within the liquid holdups. The temperature of the equipment items holding the liquid in each stage is assumed the same as the liquid temperature.

3.3 Derivation Of The Models

The basic laws which control a distillation process are the laws of vapor-liquid equilibria and the conservation of mass, heat and momentum. Since the assumption of constant pressure
has been made in each stage, the law of conservation of momentum will not be discussed in detail.

3.3.1 Mass Balances

First of all, it is assumed that there are no chemical reactions involved during the process, so that the mass balances can be performed in molar units. The vapor and liquid flow are assumed to have been initially established during the period of start-up preparation. Mass balances of the system can be formulated in terms of both overall balances and component balances as follows.

1) Material balance in the condenser-accumulator subsystem

The input to the condenser-accumulator subsystem consists of vapor flow leaving stage number 1, \( V_1 \), and a possible feed flow injected to the accumulator, \( F_0 \), while the output comprises the liquid flow of reflux, \( L_o \), the liquid distillate flow, \( D_{lo} \), and the vapor flow drawn out from the accumulator, \( D_{vo} \). Since the vapor holdup in each stage has been assumed to negligible, then the rate of accumulation comprises only the rate of change of the liquid holdup, \( M_o \), in the accumulator. As a result of this, the overall balance of the system can be expressed by

\[
\frac{dM_o}{dt} = F_o + V_1 - L_o - D_{lo} - D_{vo} \tag{1}
\]
The component material balance in the condenser accumulator subsystem can be derived by the same way. This can be easily done by multiplying each of the flow terms and the liquid holdup in equation (1) by its corresponding mole fraction.

\[
\frac{dM}{dt} = F_X + V_Y - L - D - D_V - D_L
\]  

(2)

2) Material balance in stage number \( n \) subsystem

In stage number \( n \) subsystem, the input consists of the vapor flow leaving stage number \( n+1 \), \( V_{n+1} \), the liquid flow leaving stage number \( n-1 \), \( L_{n-1} \), and a possible feed, \( F_n \). The output comprises the liquid flow leaving for stage number \( n+1 \), \( L_n \), the vapor flow leaving for stage number \( n-1 \), \( V_n \), and the flows of vapor and liquid side product streams, \( D_{v_n} \) and \( D_{l_n} \), respectively. The rate of change of the liquid holdup, \( M_n \), closes the overall material balance in stage number \( n \) as

\[
\frac{dM}{dt} = F_n + V_{n+1} + L_{n-1} - V_n - L_n - D_{v_n} - D_{l_n}
\]  

(3)

The component material balance in stage number \( n \) is found by multiplying all of the flow terms and molar holdup with their corresponding mole fractions, so that

\[
\frac{dM}{dt} = F_n X_n + V_{n+1} Y_{n+1} + L_{n-1} X_{n-1} - (L_n + D_{l_n}) X_n - (V_n + D_{v_n}) Y_n
\]  

(4)
3) Material balances in the reboiler subsystem

The inputs to the reboiler subsystem are the liquid flow leaving stage number \( N \), \( L_N \), and a possible feed flow, \( F_N \). While the output consists of the vapor flow leaving for stage number \( N \), \( V_{N+1} \), the vapor side-product flow, \( D_{vN+1} \), and the liquid side-product flow, \( D_{lN+1} \). The rate of material accumulation comprises only the rate of change of the liquid holdup, \( M_{N+1} \). The overall material balance of the reboiler subsystem is given by

\[
\frac{dM_{N+1}}{dt} = F_{N+1} + L_N - V_{N+1} - D_{lN+1} - D_{vN+1} \quad (5)
\]

Similarly, by multiplying all of the flow terms and the liquid holdup term in equation (5) with their corresponding mole fractions, the component balance of the reboiler subsystem results:

\[
\frac{dM_{N+1}^i}{dt} = F_{N+1}^i X_{F_{N+1}}^i + L_N^i X_N^i - (V_{N+1}^i + D_{vN+1}^i) Y_{vN+1}^i - D_{lN+1}^i X_{lN+1}^i \quad (6)
\]

3.3.2 Heat Balances

Before applying the principle of conservation for the heat balance of the system, it is necessary to introduce several terms of heat flows involved in the process. First of all, the heat flow associated with the vapor and the liquid
carrying them are represented by the products of the vapor flow and the liquid flow with their corresponding molar heat contents or enthalpies, \( \dot{H}_n \) and \( \dot{h}_n \) respectively. The rate of heat loss in each stage are represented by \( \dot{Q}_n \). The rate of heat accumulation in each stage comprises the rate of change of the enthalpy and the sensible heat of the liquid holdup and the equipment items holding it, \( M_n \dot{h}_n + C_p n (T_n - T_R) \).

1) Heat balance in the condenser-accumulator subsystem

The heat input to the condenser-accumulator subsystem consists of the enthalpy flow of the vapor leaving from stage number 1, \( V_1 \dot{h}_1 \), and the enthalpy flow of a possible feed introduced to the accumulator, \( F_0 \dot{h}_F \). Whereas the heat output comprises the enthalpy flow of the vapor, \( \dot{D} \dot{h}_o \), and the total liquid, \( (L_o + D_o) \dot{h}_o \), drawn out of the accumulator, the flow of heat rejected by the coolant, \( \dot{Q}_c \), and heat loss to the surroundings, \( \dot{Q}_q \). The rate of heat accumulation is the rate of change of the liquid holdup enthalpy, \( M_o \dot{h}_o \), and the sensible heat of the equipment containing it, \( C_p o (T_o - T_R) \). The heat balance the condenser-accumulator subsystem can then be expressed by

\[
\frac{d}{dt} \left( M_o \dot{h}_o + C_p o (T_o - T_R) \right) = F_o \dot{h}_F + V_1 \dot{h}_1 - (L_o + D_o) \dot{h}_o - \dot{D} \dot{h}_o - \dot{Q}_c - \dot{Q}_q \tag{7}
\]
2) Heat balance in stage number n subsystem

In stage number n subsystem, the heat input comprises the heat flow associated with the vapor leaving stage number n+1, \( V_{n+1} H_{n+1} \), the liquid leaving stage number n-1, \( L_{n-1} h_{n-1} \), and a possible feed, \( F_h \). Whereas, the heat output consists of the heat flow carried by the liquids, \( (L+D) h \), and by the vapor, \( (V+D) h \), leaving the subsystem, and the heat loss through the wall enclosing the subsystem, \( Q_n \). The rate of heat accumulation is the rate of change of the enthalpy of the liquid holdup and the sensible heat of the equipment items in the subsystem, \( H_n + C (T_n - T_R) \). Thus, the heat balance in the subsystem number n becomes

\[
\frac{d}{dt} \left( H_n h + C (T_n - T_R) \right) = F_h + V_{n+1} H_{n+1} + L_{n-1} h_{n-1} - (V+D) h - Q_n
\]

(8)

3) Heat balance in the reboiler subsystem

The heat input to the reboiler subsystem consists of the heat flow supplied by the heating medium, \( Q_B \), and the heat flow carried by the liquid coming from stage number N, \( L_N h_N \), and by the possible feed, \( F_h \). While the heat output comprises the rate of heat flow associated with the vapor leaving the subsystem, \( V_{N+1} H_{N+1} \), the heat flow associated with side-product streams, \( D_{N+1} h_{N+1} \) and \( D_{N+1} h_{N+1} \), and the rate
of heat loss from the wall enclosing the subsystem, $Q_{N+1}$.

The rate of heat accumulation is the rate of change of the enthalpy of the liquid holdups and the sensible heat of the construction item of the subsystem. From this, the heat balance of the subsystem can be expressed by

$$\frac{d}{dt} \left( N_{M+1} h_{M+1} + C_{PN+1} (T_{N+1} - T_R) \right) = Q_b + F_{N+1} h_{PN+1} + L_N h_N - D_{IN+1} h_{N+1} - (V_{N+1} + D_{IN+1}) h_{N+1} - Q_{N+1} \quad (9)$$

### 3.3.3 Vapor-liquid Equilibria

The equilibrium vapour compositions in each stage, $y_{n}^{i*}$, are functions of the liquid compositions, $x_{n}^{i}$, the stage temperature, $T_n$, and the stage pressure, $p_n$. This relationship can be expressed with the help of an equilibrium constant as follows

$$y_{n}^{i*} = K_{n}^{i} x_{n}^{i} \quad (10)$$

where

$$K_{n}^{i} = K_{n}^{i}( \bar{x}_{n}^{p}, T_n, p_n ) \quad (11)$$

Furthermore, the summation of vapor compositions has to be equal to one, so that
For a system of ideal trays, the vapor composition, $Y_v^i$, is equal to the equilibrium vapor composition, $Y_v^{i\ast}$. While for a system of non-ideal trays, the two terms of vapor composition can be related by a concept of Murphree tray efficiency.

$$Y_v^i = Y_v^{i\ast} + \eta_n^i \left( Y_v^{i\ast} - Y_v^{i+1} \right)$$

The Murphree tray efficiency, $\eta_n^i$, is a complicated function involving the complex interplay of mass transfer and fluid mechanics. In this analysis the concept will not be discussed in detail. The Murphree tray efficiency, $\eta_n^i$, will be the same for each component and constant from tray to tray.

### 3.3.4 Physical Properties

There are several important physical properties directly involved in the analysis, among them are the liquid molar volume, $\rho_n$, the vapor enthalpy, $H_n$, and the liquid enthalpy, $h_n$. All of these are functions of composition, temperature, and pressure which can be expressed in general form as follow

$$H_n = H_n \left( \bar{Y}_n^k, T_n, p_n \right)$$  \hspace{1cm} (14)

$$h_n = h_n \left( \bar{X}_n^k, T_n, p_n \right)$$  \hspace{1cm} (15)
The heat capacities of the equipment in contact with the liquid holdup in each stage, \( C_{p,n} \), are assumed independent of temperature.

### 3.3.5 Heat transfer

The rate of heat loss, \( Q_n \), in each stage can be formulated using a simple driving force which is a temperature difference between the liquid holdup and the surroundings, \( (T_n - T_s) \). The overall heat transfer coefficient and the heat transfer area can be regarded as a combined constant, \( (UA)_n \). As a result of this, the rate of heat loss can then be expressed by

\[
Q_n = (UA)_n (T_n - T_s) \tag{17}
\]

It is assumed that the rate of heat supplied by the heating medium in the reboiler, \( Q_B \), and the rate of heat rejected by the condenser, \( Q_C \), can be controlled to follow the course of the desired operating condition of the process. The control systems governing this will not discussed in this analysis.

### 3.3.6 Holdup Dynamics

There are three kinds of holdup in the system, namely the reboiler holdup, \( M_{N+1} \), the tray holdups, \( M_n \), and the accumulator holdup, \( M_o \). During a normal operation, the
reboiler holdup decreases with time unless there is enough
feed supply to restore it. This dynamical behaviour is
limited predominantly by the material and heat balance in the
reboiler subsystem. Whereas the dynamical behaviour of the
tray holdups is not only limited by their material and heat
balance but also by the momentum balance which involves the
complicated tray fluid dynamics. However, some simplification
of the tray dynamic concept can be made to ease the solution
of the model. In this analysis the accumulator holdup is
assumed to have the same dynamical limitation as the the tray
holdups.

The dynamic behaviour of the tray and the accumulator holdups
can be described by one of the following four models which
have been variously employed by Meadows (1963), Distefano
(1968a), Luyben (1971), Franks (1972), Guy (1983), and
Srivastava (1987):

1) Constant molar holdup model

In this model, the molar holdup in each tray and in the
accumulator is assumed constant. This model can be expressed
in differential form as

\[ \frac{dM}{dt} = 0 \]  

(18)
2) Constant volume holdup model

The volume holdup which can be expressed by the multiplication of the molar holdup and its molar volume, \( H_n \), in each tray and the accumulator is assumed constant. In a differential form, the formulation is

\[
\frac{dM_n}{dt} = 0
\]  

(19)

3) Hydraulic time constant model

In this model, the liquid holdup is proportional to the liquid flow leaving the subsystem. The relationship can be expressed in differential form by using the hydraulic time constant, \( \tau_n \).

\[
\frac{dM_n}{dt} = \tau_n \frac{dL_n}{dt}
\]  

(20)

4) Simplified tray dynamic model

Here, the liquid volume holdup, \( G_n \), is related to the liquid flow, \( L_n \), the cross sectional area of the column, \( A_n \), the weir height, \( L_w \), and the weir constant, \( W_c \):

\[
G_n = A_n \left( L_w + W_c L_n^{2/3} \right)
\]  

(21)
The above models of multi component batch distillations are each a complicated system of differentio-algebraic equations, (D.A.E. system), which comprises: differential equations of the overall material balances, the component balances, and the heat balances, non-linear algebraic equations of the vapor-liquid equilibria, and some explicit formulations of the physical properties of the system. The solution of these D.A.E. systems requires a well-planned algorithm before they can be translated into robust computer routines. Alternative techniques for devising such an algorithm are the following.

3.4.1 Backward Derivative Technique

The backward derivative technique is based on the idea that certain derivatives in a D.A.E. system which do not vary very much with time can be substituted by their approximate backward derivatives of a lower order. As a result of this some of differential equations in the D.A.E. system are reduced into ordinary algebraic equations. This technique has been employed by Distefano (1968a) followed by Franks (1972), Stewart et al. (1973), and Boston et al. (1980).
3.4.1.1 Formulation of the backward derivative approximations

In the above D.A.E. systems of multi-component batch distillation, the derivatives which can be substituted by approximation are all of the stage temperatures, $T_n$, the liquid enthalpies, $h_n$, and the liquid molar holdups, $H_n$, except the reboiler holdup, $H_{N+1}$. The approximate derivatives can be calculated from the current values at time $t$ and the previously stored values at time $t_o$ of the differential variables. The calculation can be carried out by using the following formulae.

$$\frac{dH_n}{dt} \approx \delta T_n = \frac{H_n(t) - H_n(t_o)}{t - t_o}$$ (22)

$$\frac{dT_n}{dt} \approx \delta T_n = \frac{T_n(t) - T_n(t_o)}{t - t_o}$$ (23)

$$\frac{dh_n}{dt} \approx \delta h_n = \frac{h_n(t) - h_n(t_o)}{t - t_o}$$ (24)

3.4.1.2 Modified differential equations of the D.A.E. system

By using the above approximate derivatives the arrangement of the D.A.E. system can be modified. The number of differential equations is reduced. The remaining differential equations comprise mainly the differential equations of the liquid mole
fractions, $X^i_n$, and the reboiler holdup, $M_{N+1}$. The modified system of differential equations can be derived by rearranging the differential equations of the overall material balance and the component balances, equations (1) to (6).

\[
\frac{dX^i_0}{dt} = \frac{1}{H_0} \left\{ F_0 (X^i_0 - X^i) + V_1 (Y^i_1 - X^i_0) - D_{vo} (Y^i_0 - X^i_0) \right\} \quad (25a)
\]

\[
\frac{dX^i_n}{dt} = \frac{1}{H_n} \left\{ F_n (X^i_n - X^i) + V_{n+1} (Y^i_{n+1} - X^i_n) + \frac{L}{n} (X^i_n - X^i) - (V_n + D_n)(Y^i_n - X^i_n) \right\} \quad (25b)
\]

\[
\frac{dX^i_{N+1}}{dt} = \frac{1}{H_{N+1}} \left\{ F_{N+1} (X^i_{N+1} - X^i) + \frac{L}{N} (X^i_{N+1} - X^i) \right\} \quad (25c)
\]

\[
\frac{dM_{N+1}}{dt} = F_{N+1} + L - V_{N+1} - D_{L_{N+1}} - D_{v_{N+1}} \quad (25d)
\]

The above system of differential equations can be solved numerically provided all the liquid molar holdups, the liquid flows, the vapor flows, and the vapor composition can be calculated simultaneously at any time.
3.4.1.3 Difference equations for the vapor and the liquid flow

In practice, the feed flows and the flows of side-product streams are all defined according to certain operating policies, like the reflux ratio, so that they can have fixed values or they can be related to the vapor and the liquid flows. Therefore, the system of equations, (25), has only two profiles which have not been determined, namely the vapor flows and the liquid flows.

The vapor and the liquid flows can be calculated simultaneously through a simple system of difference equations which can be derived by the concept of the backward derivative technique. First of all, all of the L.H.S. of the heat balance equations, equation (7) to equation (9), are simplified into their individual derivatives. Then the derivatives of the temperatures and the the liquid enthalpies are substituted by their corresponding approximations, while the derivatives of the liquid holdups are retained for the next substitutions. This results in the following intermediate equations.

\[
\frac{d}{dt} \left( h_o h_o + C_p o (T_o - T_R) \right) = h_o \frac{dH_o}{dt} + H_o \delta h_o + C_p o \delta T_o \tag{26}
\]

\[
\frac{d}{dt} \left( h_n h_n + C_p n (T_n - T_R) \right) = h_n \frac{dH_n}{dt} + H_n \delta h_n + C_p n \delta T_n \tag{27}
\]
The next step is to equate equation (7), equation (8), and equation (9) with equations (26), equation (27), and equation (28) respectively. Following this, the derivatives of the liquid holdups of the resulting equations are each substituted by the R.H.S of the corresponding overall material balance equations, equations (1), (3), and (5) respectively. This results in the following subsystem of difference equations.

\[
\frac{d}{dt}\left[N_{n+1}h_{n+1} + C_{P_{n+1}}(T_{n+1} - T_{R})\right] = h_{n+1} \frac{dM_{n+1}}{dt} + N_{n+1} \delta h_{n+1} + C_{P_{n+1}} \delta T_{n+1} \tag{28}
\]

\[
F_0(h_0 - h_o) + V_i(h_i - h_o) - D_v(h_o - h_i) - M_0 \delta h_o - C_{P_0} \delta T_0 - Q_o - Q_c = 0 \tag{29a}
\]

\[
F_n(h_n - h_n) + V_{n+1}(h_{n+1} - h_n) + L_{n-1}(h_{n-1} - h_n) - (V_n + D_v)(h_n - h_n) - N_1 \delta h_n - C_{P_1} \delta T_n - Q_n = 0 \tag{29b}
\]

\[
F_{n+1}(h_{FN+1} - h_{N+1}) - (V_{N+1} + D_{VN+1})(h_{N+1} - h_{N+1}) + L_n(h_n - h_{N+1}) - N_{n+1} \delta h_{n+1} - C_{P_{n+1}} \delta T_{n+1} - Q_{n+1} + Q_B = 0 \tag{29c}
\]

This subsystem of difference equation, equation (29) is not yet complete because both the vapour flows and the liquid
flows profiles are still present in the L.H.S. of the equation. Furthermore, there appear other quantities involved in the equation, namely the stage temperatures, the vapor enthalpies, the liquid enthalpies, the liquid molar holdups, and the heat flows. However, these quantities are independent of both the vapor and the liquid flows, and therefore they can be calculated in advance through separate routines.

There are four alternative methods available to complete the above equation (25) associated with the four alternative models of the holdup dynamics which have been previously discussed.

1) **Using the constant molar holdup model**

In this model, the derivative of the liquid molar holdup is equal to zero according to equation (18). It applies to all stages, except for the reboiler holdup. The application of this model to the overall material balance equations, equation (1) and (3), will give the following equations

\[ F_o + V_i - L_o - D_{lo} - D_{vo} = 0 \]  \hspace{1cm} (30a)

\[ F_n + V_{n+1} + L_{n-1} - V_n - L_n - D_{vn} - D_{ln} = 0 \]  \hspace{1cm} (30b)

2) **Using the constant volume holdup model**

By contrast, the derivative of the liquid molar holdups in
this model are not equal to zero but are equated to their backward derivative approximations. As a result of this the overall material balance equations can be transformed into the following equations.

\[ F_0 + V_1 - L_0 - D_{lo} - D_{vo} - \delta M_0 = 0 \]  
(31a)

\[ F_n + V_{n+1} + L_{n-1} - V_n - L_n - D_{vn} - D_{tn} - \delta M_t = 0 \]  
(31b)

3) Using the hydraulic time constant model

Here, the liquid flow profile constitutes another subsystem of differential equations which has to be solved simultaneously with the modified system of deferential equations, equation (25), in the previous discussion. This strategy makes the above subsystem of difference equation, equation (30), complete in itself. Whereas the constituent of the modified differential equation is added with the overall material balance equations, equations (1) and (3), and the differential equations of the liquid flows. The latter can be derived directly by substituting the L.H.S. of equation (20) with the R.H.S. of the corresponding overall material balance equation.

\[ \frac{dL_0}{dt} = \frac{1}{\tau_n} \left\{ F_0 + V_1 - L_0 - D_{lo} - D_{vo} \right\} \]  
(32a)

\[ \frac{dL_n}{dt} = \frac{1}{\tau_n} \left\{ F_n + V_{n+1} + L_{n-1} - V_n - L_n - D_{vn} - D_{tn} \right\} \]  
(32b)
4) **Using the simplified tray dynamic model**

In this case, the liquid flow profile can be calculated by solving the equation of the simplified tray dynamic model, equation (21).

\[
L_n = \left\{ \frac{G_n - L \beta}{A_n W_{e}} \right\}^{3/2}
\]

(33)

Since the liquid molar holdups are not constant, the constituent of the modified differential equation of the D.A.E. system is added by the overall material balance equations (1) and (2).

### 3.4.1.4 Bubble-point calculation

As has been stated above, the subsystem of difference equations (29), is complete if the temperature profiles, the liquid enthalpies, the vapor compositions, the vapor enthalpies and the liquid molar volumes are known. These unknowns can be solved successively beginning from the calculation of the temperature profiles.

The temperature profile can be calculated by solving the algebraic equation of vapor liquid equilibria, equation (12), known as the bubble-point calculation. The method of solution adopted in this analysis is the Newton-Raphson method which
can be explained in general as follows.

First of all, the above equation (12) is reformulated as a function of $T_n$.

$$E_n(T_n, \mathbf{x}_n) = \sum_{i=1}^{NC} K_n^i(\mathbf{x}_n, T_n) x_i^n - 1 = 0 \quad (34)$$

The temperature $T_n$ can then be calculated iteratively by using the following formula.

$$T_{n \text{ new}} = T_{n \text{ old}} - \frac{E(T_n)_{\text{ old}}}{\left( \frac{\partial E}{\partial T_n} \right)_{\text{old}}} \quad (35)$$

3.4.1.5 Algorithms of the backward derivative technique

For the purpose of performing the integration of the above modified system of differential equation by a numerical integrator routine, certain subroutines to calculate the R.H.S. of the system of differential equations are needed. The following are several examples of such algorithms which can be used as a guide to construct the required subroutines. The algorithms are based on the assumed operating policy where the overhead vapor flow, $V_1$, is held constant and the side-product streams and the possible feed streams are specified.
1) Algorithm for the constant molar holdup model

Step 1
Perform the bubble-point calculation, using equations (34) and (35) to determine the temperature profile, $T_n$, based on the current value of the liquid composition profile, $X_n^i$, at time $t_n$ and the constant pressure profile, $p_n$. The iteration can start from either the previously stored value of $T_n$ or a certain fixed value.

Step 2
Calculate the vapor composition profile, $Y_n^k$, using equations (10) and (13). The calculation can be performed easily if it starts from the bottom to the top.

Step 3
Calculate the vapor enthalpies $H_n$ and the liquid enthalpies, $h_n$, by using equation (14) and equation (15) respectively.

Step 4
Calculate the backward derivatives, $\delta_T^n$ and $\delta_h^n$, by using equation (23) and (24) respectively. The calculations are each based on the current values at time $t$ and the previously stored values at time $t_o$.

Step 5
Calculate the heat loss profile, $Q_n$, by using equation (17).
Step 6
Calculate the liquid flow, $L_o$, and the condenser heat flow, $Q_c$, based on the specified overhead vapor flow, $V_1$. This can be performed by using equation (29a) and equation (30a).

Step 7
Calculate the vapor flow profile, $V_{n+1}$, and the liquid flow profile, $L_{n-1}$, starting from stage number 1 to stage number N. This can be done by using equation (29b) for $V_{n+1}$ and equation (30b) for $L_n$ successively for each stage.

Step 8
Calculate the heat flow supplied to the reboiler, $Q_r$, using equation (29c).

Step 9
Calculate the R.H.S of the modified system of differential equations using equation (25a) to (25d).

2) Algorithm for the constant volume holdup model

Step 1 and 2
The same as the constant molar holdup model.

Step 3
Calculate the vapor enthalpies, $H_n$, the liquid enthalpies, $h_n$, and the liquid molar volume, $\varphi_n$, by using equation (14), equation (15), and equation (16) respectively. Then calculate
the liquid molar holdup profile, \( M_n \), based on the calculated liquid molar volume.

**Step 4**

Calculate the backward derivatives, \( \delta_t M_n \), \( \delta_t T_n \), and \( \delta_t h_n \), by using equation (22), equation (23), and equation (24) respectively. The calculation are each based on the current values at time \( t \) and the previously stored value at time \( t_0 \).

**Step 5**

The same as the constant molar holdup model.

**Step 6**

Calculate the liquid flow, \( L_0 \), and the condenser heat flow, \( Q_c \), based on the constant overhead vapor flow, \( V_1 \). This can be performed by using equation (29a) and equation (31a).

**Step 7**

Calculate the vapor flow profile, \( V_{n+1} \), and the liquid flow profile \( L_n \) starting from stage number 1 to stage number \( N \). This can be done by using equation (29b) for \( V_{n+1} \) and equation (31b) for \( L_n \) successively for each stage.

**Step 8 and 9**

The same as the constant molar holdup model.
3) Algorithm for the hydraulic time constant model

Step 1 to 5
The same as the constant molar holdup model.

Step 6
Calculate the condenser heat flow \( Q_c \) based on the constant overhead vapor flow \( V_i \). This can be performed by using equation (29a).

Step 7
Calculate the vapor flow profile, \( V_{n+1} \), by using equation (29b) from stage number 1 to stage number \( N \).

Step 8
The same as the constant molar holdup model.

Step 9
Calculate the R.H.S. of the modified system of differential equations using equations (1), (3), (5), (25a) to (25d), and (32a) to (32b).

4) Algorithm for the simplified tray dynamic model

Step 1 and 2
The same as the constant molar holdup model.
Step 3
Calculate the vapor enthalpies, $H_n$, the liquid enthalpies, $h_n$, and the liquid molar volume, $\phi_n$, by using equation (14), equation (15), and equation (16) respectively. Then calculate the liquid molar holdup profile, $M_n$, based on the calculated liquid molar volume.

Step 4 and 5
The same as the constant molar holdup model.

Step 6
Calculate the liquid flow, $L_0$, and the condenser heat flow, $Q_c$, based on the constant overhead vapor flow, $V_0$. This can be performed by using equation (29a) and equation (33).

Step 7
Calculate the vapor flow profile, $V_{n+1}$, and the liquid flow profile, $L_n$, starting from stage number 1 to stage number N. This can be done by using equation (29b) for $V_{n+1}$ and equation (33) for $L_n$ successively for each stage.

Step 8
The same as the constant molar holdup model.

Step 9
Calculate the R.H.S. of the modified system of differential equations using equations (1), (3), (5), and (25a) to (25d).
3.4.2 Analytical Derivative Technique

From the above discussion of the backward derivative technique, it is clear that the computational time is affected by the calculation of the temperature profile whose trajectory with time is related by the implicit equation of the vapor-liquid equilibria. The backward derivative technique solves the implicit equation by the Newton-Raphson technique which is an iterative method and therefore demands several function evaluations.

The analytical derivative technique developed here adopts another way of relating the trajectory of the temperature profile with time, namely transforming the implicit equation of the vapor-liquid equilibria into its differential form. This technique makes the calculation of the trajectory of the temperature profile less iterative than the backward derivative technique at the cost of calculating several analytical derivatives.

3.4.2.1 Differential equation of the vapor-liquid equilibria

The implicit equation of the vapor-liquid equilibria as formulated by equation (34) can be transformed into its differential equation. This can be done by treating the R.H.S. of the equation as a function of the temperature, $T_n$, and the composition, $X_n^L$, which is possible due to the above primary assumption of the constant pressure profile.
Since both the temperature and the composition profiles change with time, then equation (36) can be differentiated to give the desired differential equation.

\[
\frac{dE_n}{dt} = \frac{\partial E_n}{\partial T_n} \frac{dT_n}{dt} + \sum_{i=1}^{NC} \frac{\partial E_n}{\partial x_n^i} \frac{dx_n^i}{dt} = 0 \tag{37}
\]

3.4.2.2 Formulation of several analytical derivatives

The above differential equation of the vapor-liquid equilibria, equation (37), provides a basic formulation of relating the analytical derivative of the temperature profile with the derivatives of the composition profile. The basic formulation can be derived by introducing the temperature gradient in the composition space, \( T_{xn}^i \)

\[
T_{xn}^i = - \frac{\begin{bmatrix} \frac{\partial E_n}{\partial x_n^i} \\ \frac{\partial E_n}{\partial T_n} \end{bmatrix}}{\begin{bmatrix} \frac{\partial x_n^i}{\partial x_n^i} \\ \frac{\partial x_n^i}{\partial T_n} \end{bmatrix}} \tag{38}
\]

so that equation (37) can be modified to form the following relationship.
\[ \frac{dT_n}{dt} = \sum_{i=1}^{NC} T_{xn} \frac{dX^i_n}{dt} \]  

Equation (39) can in turn help to formulate the analytical derivatives of the liquid enthalpy and the liquid molar volume. The primary assumption of the constant pressure profile also makes it possible to treat both the liquid enthalpy and the liquid molar volume each as a function of the temperature \( T_n \), and the composition, \( X^i_n \), so that they can be differentiated thus:

\[
\frac{dh_n}{dt} = \frac{\partial h_n}{\partial T_n} \frac{dT_n}{dt} + \sum_{i=1}^{NC} \frac{\partial h_n}{\partial X^i_n} \frac{dX^i_n}{dt} 
\]  

(40)

\[
\frac{d\rho_n}{dt} = \frac{\partial \rho_n}{\partial T_n} \frac{dT_n}{dt} + \sum_{i=1}^{NC} \frac{\partial \rho_n}{\partial X^i_n} \frac{dX^i_n}{dt} 
\]  

(41)

By substituting equation (39) to equations (40) and (41), the analytical derivatives of the liquid enthalpy and the liquid molar volume can be expressed in a form similar to equation (39).

\[
\frac{dh_n}{dt} = \sum_{i=1}^{NC} h^i_{xn} \frac{dX^i_n}{dt} 
\]  

(42)
where the gradients of the liquid enthalpy, \( h_{\text{xn}}^i \), and the liquid molar volume, \( \varphi_{\text{xn}}^i \), in the composition space are given respectively by

\[
\begin{align*}
\frac{\partial h_{\text{xn}}^i}{\partial x_n} &= \frac{\partial h_{\text{xn}}^i}{\partial T_{\text{xn}}} + T_{\text{xn}}^i \frac{\partial h_{\text{xn}}^i}{\partial T_{\text{n}}} \\
\frac{\partial \varphi_{\text{xn}}^i}{\partial x_n} &= \frac{\partial \varphi_{\text{xn}}^i}{\partial T_{\text{xn}}} + T_{\text{xn}}^i \frac{\partial \varphi_{\text{xn}}^i}{\partial T_{\text{n}}}
\end{align*}
\]  

(44)

(45)

3.4.2.3 Modified differential equation of the D.A.E. system

For the analytical derivative technique, the constituents of the modified differential equation of the D.A.E. system basically consist of: the overall material balance equations (1), (3), (5); the differential equations of the liquid compositions, (25a) to (25c); and the differential equation of the temperature profile. For the sake of clarification, the modified differential equation can be shown as follows

\[
\frac{dN_o}{dt} = F_o + V_s - L_o - D_{lo} - D_{vo}
\]

(46a)
\[
\frac{dX^n_i}{dt} = \frac{1}{H_n} \left\{ F_n (X^n_i - X^n_0) + V_n (Y_n^i - X^n_i) - D_{vn} (Y_n^i - X^n_i) \right\} \quad (46b)
\]

\[
\frac{dT^n_i}{dt} = \sum_{i=1}^{NG} T^n_i \frac{dX^n_i}{dt} \quad (46c)
\]

\[
\frac{dM^n}{dt} = F_n + V_{n+1} + L_{n+1} - V_n - L_n - D_{vn} - D_{ln} \quad (46d)
\]

\[
\frac{dX^n_i}{dt} = \frac{1}{H_n} \left\{ F_n (X^n_i - X^n_0) + V_{n+1} (Y_{n+1}^i - X^n_i)
+ L_{n+1} (X^n_i - X^n_n) - (V_n + D_{vn}) (Y^n_i - X^n_i) \right\} \quad (46e)
\]

\[
\frac{dT^n_i}{dt} = \sum_{i=1}^{NG} T^n_i \frac{dX^n_i}{dt} \quad (46f)
\]

\[
\frac{dM_{n+1}}{dt} = F_{n+1} + L_n - V_{n+1} - D_{ln+1} - D_{vn+1} \quad (46g)
\]

\[
\frac{dX^n_{n+1}}{dt} = \frac{1}{H_{n+1}} \left\{ F_{n+1} (X^n_{n+1} - X^n_{n+1}) + L_n (X^n_i - X^n_{n+1})
- (V_{n+1} + D_{vn+1}) (Y^n_{n+1} - X^n_{n+1}) \right\} \quad (46h)
\]
Similar to the case of the modified differential equation for the backward derivative technique, there are three profiles which have to be available simultaneously at any time in order to solve equation (46) numerically. Those profiles are the vapor flows, the liquid flows, and the vapor compositions.

3.4.2.4 Difference equations of the vapor and the liquid flows

To derive the difference equations of the vapor and the liquid flows, all of the L.H.S. of the heat balance equations, (7) to (9), are differentiated into their individual derivatives as in the backward derivative technique. However, the derivatives of the temperatures and the liquid enthalpies are then substituted by their corresponding analytical derivative formulas instead of their backward derivative approximations. The results of this treatment are

\[
\frac{dT_{N+1}}{dt} = \sum_{i=1}^{NG} T_i^{N+1} \frac{dX_i}{dt} \quad (46)
\]

\[
\frac{d\left(H_o h_o + C_{po} (T_o - T_R)\right)}{dt} = H_o \sum_{i=1}^{NC} \left( h_{i0} + \frac{C_{po}}{H_o} T_{i0} \right) \frac{dX_i}{dt} + h_o \frac{dH_o}{dt} \quad (47)
\]
\[
\frac{d}{dt} \left( N_n h_n + C_{Pn} (T_n - T_R) \right) = N_n \sum_{i=1}^{\text{NC}} \left( h_{x_n}^i + \frac{C_{Pn}}{N_n} T_{x_n}^i \right) \frac{dX^i_n}{dt} + h_n \frac{dM_n}{dt}
\]

(48)

\[
\frac{d}{dt} \left( N_{n+1} h_{n+1} + C_{Pn+1} (T_{n+1} - T_R) \right) = h_{n+1} \frac{dM_{n+1}}{dt} + N_{n+1} \sum_{i=1}^{\text{NC}} \left( h_{x_{n+1}}^i + \frac{C_{Pn+1}}{N_{n+1}} T_{x_{n+1}}^i \right) \frac{dX^i_{n+1}}{dt}
\]

(49)

Following this, the desired difference equations can be established by substituting equations (1), (7), (25a) into equation (47), equations (3), (8), (25b) into equation (48), equations (5), (9), (25c) into equation (49).

For the condenser-accumulator subsystem the difference equations are

\[
aF_1 + bV_1 - cD_v_o - Q_o - Q_c = 0
\]

(50a)

where

\[
a = h_{F_o} - h_o - \sum_{i=1}^{\text{NC}} \left( h_{x_o}^i + \frac{C_{P_o}}{N_o} T_{x_o}^i \right) (X_{F_o}^i - X_o^i)
\]

(50b)
\[ b = H_1 - h_0 - \sum_{i=1}^{NC} (h_{x0}^i + \frac{C_{Po}}{H_o} T_{x0}^i)(Y_1^i - X_c^i) \] (50c)

\[ c = H_0 - h_0 - \sum_{i=1}^{NC} (h_{x0}^i + \frac{C_{Po}}{H_o} T_{x0}^i)(Y_0^i - X_0^i) \] (50d)

The difference equations for the tray number n subsystem are as follows

\[ \alpha V_{n+1} - b(V_n + D_n) + cL_{n-1} + dF_n - Q_n = 0 \] (50e)

where

\[ \alpha = H_{n+1} - h_n - \sum_{i=1}^{NC} (h_{xn}^i + \frac{C_{Pn}}{H_n} T_{xn}^i)(Y_{n+1}^i - X_{n}^i) \] (50f)

\[ b = H_n - h_n - \sum_{i=1}^{NC} (h_{xn}^i + \frac{C_{Pn}}{H_n} T_{xn}^i)(Y_n^i - X_n^i) \] (50g)

\[ c = H_{n-1} - h_n - \sum_{i=1}^{NC} (h_{xn}^i + \frac{C_{Pn}}{H_n} T_{xn}^i)(X_{n-1}^i - X_n^i) \] (50h)

\[ d = H_{F_n} - h_n - \sum_{i=1}^{NC} (h_{xn}^i + \frac{C_{Pn}}{H_n} T_{xn}^i)(X_{F_n}^i - X_n^i) \] (50i)
And for the difference equations for the reboiler subsystem are as follows

\[ \alpha F_{N+1} + \beta L_N - \sigma (V_{N+1} + D_{N+1}) + Q_{N+1} - Q_B = 0 \]  

where

\[ \alpha = h_{FN+1} - h_{N+1} - \sum_{i=1}^{NC} \left( h_{iN+1} + \frac{C_{iN+1}}{H_{N+1}} T_{iN+1} \right) \left( x_i^{N+1} - x_i^{N+1} \right) \]

\[ \beta = h_{N+1} - h_{N+1} - \sum_{i=1}^{NC} \left( h_{iN+1} + \frac{C_{iN+1}}{H_{N+1}} T_{iN+1} \right) \left( x_i^N - x_i^{N+1} \right) \]

\[ \sigma = H_{N+1} - h_{N+1} - \sum_{i=1}^{NC} \left( h_{iN+1} + \frac{C_{iN+1}}{H_{N+1}} T_{iN+1} \right) \left( y_i^{N+1} - x_i^{N+1} \right) \]

Similar to the case of the backward derivative technique, there are four methods to complete the above equation (50).

1) Using the constant molar holdup model

In this model, the L.H.S. of the overall material balance equations, (46a) and (46d), are equal to zero, so that they can be taken out from the modified system of differential equation, equations (46). By equating the R.H.S. of equations (46a) and (46d) to zero, there result two corresponding subsystems of difference equation necessary for completing the
above equations (50). These subsystems of difference equation are the same as the above equations (30a) and (30b).

2) Using the constant volume holdup model

First of all, the above equation of constant volume holdup model, equation (19), is modified by transforming into its individual derivatives. The derivative of the liquid molar volumes, \( \phi_n \), is then substituted by the R.H.S. of equation (43). This treatment applies for the condenser-accumulator subsystem and the tray number \( n \) subsystem so that

\[
\begin{align*}
M_o & \sum_{i=1}^{NC} \phi_{xo}^i \frac{dX_c^i}{dt} + \phi_o \frac{dM_o}{dt} = 0 \quad (51a) \\
M_n & \sum_{i=1}^{NC} \phi_{xn}^i \frac{dX_n^i}{dt} + \phi_n \frac{dM_n}{dt} = 0 \quad (51b)
\end{align*}
\]

The next step is to substitute the overall material balance equations, (46a) and (46d), and the the modified component balance equations, (46b) and (46e), into equations (51a) and (51b) respectively.

For the condenser-accumulator subsystem, this treatment results in the following equations.
\[ aV_1 + bF_0 - cD_{vo} - L_0 - D_{lo} = 0 \] 

(52a)

where

\[ a = 1 + \sum_{i=1}^{\text{NC}} \frac{\varphi_{x0}^i}{\varphi_0} (Y_{i1}^i - X_{i0}^i) \] 

(52b)

\[ b = 1 + \sum_{i=1}^{\text{NC}} \frac{\varphi_{x0}^i}{\varphi_0} (X_{i1}^i - X_{i0}^i) \] 

(52c)

\[ c = 1 + \sum_{i=1}^{\text{NC}} \frac{\varphi_{x0}^i}{\varphi_0} (Y_{i2}^i - X_{i0}^i) \] 

(52d)

And for the tray number \( n \) subsystem, the equations are

\[ aV_{n+1} + bL_{n-1} - cF_n - d(V_n + D_n) - L_n + D_{ln} = 0 \] 

(52e)

where

\[ a = 1 + \sum_{i=1}^{\text{NC}} \frac{\varphi_{xn}^i}{\varphi_n} (Y_{i,n+1}^i - X_{i,n}^i) \] 

(52f)

\[ b = 1 + \sum_{i=1}^{\text{NC}} \frac{\varphi_{xn}^i}{\varphi_n} (X_{i,n}^i - X_{i,n-1}^i) \] 

(52g)
\[ c = 1 + \sum_{i=1}^{\text{NC}} \frac{\phi_{x_n}^i}{\phi_n^i} (X_n^i - X_n^i) \quad (52h) \]

\[ d = 1 + \sum_{i=1}^{\text{NC}} \frac{\phi_{x_n}^i}{\phi_n^i} (Y_n^i - X_n^i) \quad (52i) \]

3) Using the hydraulic time constant model

The treatment for using the hydraulic time constant is the same as the case of the backward derivative technique where the liquid flow profile is expressed by another system of differential equation. The latter has been formulated by the above equations (32a) and (32b).

4) Using the simplified tray dynamic model

Similar to the case of the backward derivative technique, the liquid flow profile can be directly calculated from equation (33). However, this case applies if the available tray dynamic model, like the above equation (21), can be explicitly inverted. For the case where the explicit inversion is impossible, it is recommended to transformed the tray dynamic model into its differential equations. The following treatment is made by assuming the tray dynamic model, equation (21), as an implicit equation in \( L_n \).

First of all, equation (21) is differentiated with respect to time into its individual derivatives of the liquid molar
holdup, $M_n$, the liquid molar volume, $\varphi_n$, and the liquid flow, $L_n$. The derivative of the liquid flow can then be explicitly isolated as follows.

For the condenser-accumulator subsystem

$$\frac{dL_o}{dt} = \frac{1.5L_o \varphi_o}{A_s W_c} \left\{ \frac{d\varphi_o}{dt} + \frac{dM_o}{dt} \right\} \quad (53a)$$

and for the tray number $n$ subsystem

$$\frac{dL_n}{dt} = \frac{1.5L_n \varphi_n}{A_s W_c} \left\{ \frac{d\varphi_n}{dt} + \frac{dM_n}{dt} \right\} \quad (53b)$$

Following this, the individual derivatives of the liquid molar holdups and the liquid molar volume are eliminated by substituting equations (43), (46a), (46b) into equation (53a) and equations (43), (46d), (46e) into equation (53b). After rearranging the equations, there results the following formulae.

For the condenser-accumulator subsystem

$$\frac{dL_o}{dt} = \frac{1.5L_o \varphi_o}{A_s W_c} \left\{ aV_o + bF_o - cD_v - L_o - D_{lo} \right\} \quad (54a)$$
where \( a, b, \) and \( c \) have the same formulation as the above equations (52b), (52c), and (52d) respectively. And for the tray number \( n \) subsystem

\[
\frac{dL_n}{dt} = \frac{1.5L_n V_n}{\Delta \rho \overline{W_c}} \left\{ \alpha V_{n+1} + bL_{n-1} + cF_n - d(V_n + D_{vn}) - L_n - D_{vn} \right\}
\]

(54b)

where \( a, b, c, \) and \( d \) have the same formulation as the above equations (52f), (52g), (52h), and (52i) respectively.

3.4.2.5 Algorithms of The Analytical Derivative Technique

The following algorithms are based on the same operating policy as for the backward derivative technique previously discussed, where the overhead vapor flow, \( V_s \), is held constant and any side-product streams and the possible feed streams are specified.

1) Algorithm for the constant molar holdup model

Step 1
Calculate the vapor composition profile, \( V_n \), using equations (10) and (13). The calculation can be performed easily if it works from the bottom to the top.
Step 2
Calculate the vapor enthalpies, \( H_n \), and the liquid enthalpies, \( h_n \), using equation (14) and equation (15) respectively.

Step 3
Calculate the gradients in composition space of the temperature profiles, \( T_{xn}^i \), and the liquid enthalpy profile, \( h_{xn}^i \), using equations (38) and (44) respectively.

Step 4
Calculate the heat loss profile, \( Q_n \), using equation (17).

Step 5
Calculate the liquid flow, \( L_o \), and the condenser heat flow, \( Q_c \), based on the specified overhead vapor flow, \( V_4 \). This can be performed by using equations (30a) and (50a) to (50d).

Step 6
Calculate the vapor flow profile, \( V_{n+1} \), and the liquid flow profile, \( L_{n-1} \), starting from stage number 1. This can be done by using equations (50e) to (50i) for \( V_{n+1} \) and equation (30b) for \( L_n \) successively for each stage.

Step 7
Calculate the heat flow supplied to the reboiler, \( Q_b \), using equations (50j) to (50m).
Calculate the R.H.S of the modified system of differential equations using equations (46b), (46c), (46e), (46f), (46h) and (46i).

2) Algorithm for the constant volume holdup model

Step 1 and 2
The same as the constant molar holdup model.

Step 3
Calculate the gradients in composition space of the temperature profiles, $T_{mn}$, the liquid enthalpy profile, $h_{mn}^l$, and the liquid molar volume, $\phi_{mn}^l$, using equations (38), (44) and (45) respectively.

Step 4
Calculate the heat loss profile, $Q_n$, using equation (17).

Step 5
Calculate the liquid flow, $L_o$, and the condenser heat flow, $Q_c$, based on the specified overhead vapor flow, $V_t$. This can be performed by using equations (50a) to (50d) and (52a) to (52d).

Step 6
Calculate the vapor flow profile, $V_{n+1}$, and the liquid flow profile, $L_{n-1}$, starting from stage number 1. This can be done
by using equations (50e) to (50i) for $V_{n+1}$ and equations (52e) to (52i) for $L_n$ successively for each stage.

**Step 7**
The same as the constant molar holdup model.

**Step 8**
Calculate the R.H.S. of the modified system of differential equation, using equations (48a) to (46i).

3) Algorithm for the hydraulic time constant model

**Step 1 to 4**
The same as the constant molar holdup model.

**Step 5**
Calculate the condenser heat flow, $Q_c$, based on the specified overhead vapor flow, $V_A$, by using equations (50a) to (50d).

**Step 6**
Calculate the vapor flow profile, $V_{n+1}$, by using equations (50e) to (50i) from stage number 1 to stage number $N$.

**Step 7**
The same as the constant molar holdup model.

**Step 8**
Calculate the R.H.S of the modified system of differential
4) Algorithm for the simplified tray dynamic model

Step 1 and 2
The same as the constant molar holdup model.

Step 3
Calculate the gradients in composition space of the temperature profiles, $T_{xn}^i$, the liquid enthalpy profile, $h_{xn}^i$, and the liquid molar volume, $\phi_{xn}^i$, using equations (38), (44) and (45) respectively.

Step 4
Calculate the heat loss profile, $Q_n$, by using equation (17).

Step 5
Calculate the condenser heat flow, $Q_c$, based on the specified overhead vapor flow, $V_i$, by using equations (50a) to (50d).

Step 6
Calculate the vapor flow profile, $V_{n+1}$, by using equations (50e) to (50i) from stage number 1 to stage number N.

Step 7
The same as the constant molar holdup model.
Step 6
Calculate the R.H.S. of the modified system of differential equations, using equations (46a) to (46i), (54a) and (54b). The last two equations (54a) and (54b) involve the calculation of coefficients \(a\), \(b\), \(c\), and \(d\) which use equations (52f), (52g), (52h), and (52i) respectively.

3.5 Results and discussion

3.5.1 Comparison of results obtained by the two techniques

For the purpose of validating the proposed analytical derivative technique and the possibility of extending the backward derivative technique to simulate a start-up process, a case study with the constant volume holdup model is treated using the two techniques. The start-up procedure adopted is the one proposed by Luyben (1971), where the equilibrium composition in all the trays, the reboiler, and the accumulator holdup are initially the same.

Important aspects to be examined are:

1) Start-up problem with the backward derivative techniques

The integration of the constant volume holdup model with the Luyben's (1971) start-up procedure treated by the analytical derivative technique presents no difficulty in the implementation of its algorithm, whereas the treatment of the

© Details of the test data are given in Appendix 2a and column details in Appendix 2b.
integration by the backward derivative technique poses an ambiguous problem in its algorithm. This problem arises in initialising the approximate derivatives as formulated by equations (22) to (24). In the previous study by Distefano (1968a), this problem does not appear because all the approximate derivatives are inherently zero due to the nature of their solutions which start from the steady state total reflux conditions. However, for a problem with a general start-up policy, which does not start from the steady state total reflux conditions, the approximate derivatives are finite. There is no method available to estimate the initial values of the approximate derivatives.

In this study, the initial values of the approximate derivatives are all initialized to zero. There is no reason for not choosing other initial values. It is believed that convergence to steady-state total reflux conditions will be achieved regardless of the different choice of the initial values. The only possible differences are the start-up times to achieve the steady-state total reflux conditions.

However, the results of integration by both techniques as shown by Figure 1 reveal that steady-state total reflux conditions, indicated by the composition of the first component, achieved by the two techniques occur almost exactly at the same time and the same values. Slight differences of the two curves appear only at the first few time steps from the initial start-up. These differences are however not very
Operating Time

Figure 1 The backward derivative technique (a) versus the analytical derivative technique (b) in the start-up region.
2) The validity of the analytical derivative technique

The treatment of the constant volume model using the backward derivative technique by Distefano (1968a) was adopted by Stewart (1973) who confirmed the results by experimentation. Although their treatment only started from the steady state total reflux conditions, it is reasonable to use the results from the backward derivative technique to validate the analytical derivative technique, at least after the steady-state total reflux condition has been attained.

Figure 2 shows that the results of integrations by the two techniques agree well for the whole operation. Therefore, the analytical derivative technique can be said to be undoubtedly satisfied.

3) The computation times

The integrations of the constant volume holdup model by the two techniques were carried out using the same computer. It was found that the computation times for the two techniques were approximately the same. This fact probably can be explained by the trade off between eliminating the solution of the non-linear bubble point equations in the backward derivative technique and calculating the gradients and coefficients in the analytical derivative techniques.
Figure 2 The backward derivative technique versus the analytical derivative technique in the start-up and the topping region.
3.5.2 The influence of holdup models

First of all, let the constant molar holdup model, the constant volume holdup model, the hydraulic time constant model and the simplified tray dynamic model be model 1, model 2, model 3 and model 4 respectively. In the topping period, Figure 3 shows that after the start-up period there are two groups of curves representing the compositions of the first component calculated by the four models. The first group represents the compositions of models 1 and 2. At a particular time, the composition of model 1 is slightly lower than that of model 2 differs by less than 2%. The second group represents the compositions of models 3 and 4 which are approximately 7% lower than those of the first group. The composition of model 3 is slightly lower than that of model 4.

Figure 4 shows that in the start-up period models 3 and 4 approach steady state more rapidly than models 1 and 2. Close to the end of start-up period, the two groups converge and spread into another two groups in Figure 4. The new first group represents model 1 and model 3 and the second group represents model 2 and model 4. The compositions of the new first group are slightly higher than those of the new second groups, being less than 0.1% at the end of the start-up period. The start-up times of the new first group are slightly lower than those of the new second group.
Figure 3 Comparison of the four holdup models in the start-up region.
Operating Time

Figure 4 Comparison of the four holdup models in the start-up and the topping region.
3.5.3 Variable flow versus updated flow integration

There is a temptation to improve the computation time by letting the liquid flow and the vapor flow be constant during each time step and be updated at the end of the time step after the integration for the next time step. This method will be called the updated flow integration in order to distinguish it from the normal method which will be called the variable flow integration.

The results of integration reveal that the updated flow integration can improve the computation time by a factor of three. However, Figures 5 and 6 show that the results of the integrations are very different. In the start-up period, as shown by Figure 5, the results of the updated flow integration show a severe instability compared with the variable flow integration. The compositions and the corresponding start-up times of the two methods do not agree well. This cannot be accepted for practical purposes. Figure 6 shows the results of integration by the two methods in the topping period. In the beginning, the result of the updated flow integration is lower than that of the variable flow integration. Then both curves cross each other at certain time. Therefore, it is clear the two results of integration are not compatible in any respect.
**Operating Time**

Figure 5 Variable flowrate integration versus Updated flowrate integration in the start-up region.
Figure 6 Variable flowrate integration versus Updated flowrate integration in the start-up and the topping region.
3.6 Conclusion

Some important conclusions which can be drawn from the above discussions of multi-component batch distillation modelling are:

1) rigorous models of multi-component batch distillation which include heat balances and the Luyben's (1971) start-up procedure have been analysed,

2) the proposed analytical derivative technique has successfully solved the integration of the rigorous models,

3) the backward derivative technique can be extended to solve the integration of the rigorous models by initialising all the approximate derivatives to zero,

4) the performance of the analytical derivative technique and the backward derivative techniques are comparable,

5) the updated flow integration can improve the computation time but leads to gross inaccuracies.
4. Optimisation of Ternary System with Recycle Slop

4.1 Introduction

This chapter is devoted to studying the optimisation of a ternary system with recycle slop. In this study, a ternary system is defined as a system which has only three components, namely the light component, the medium component, and the heavy component. The definition might not sound realistic in practice, because it neglects the presence of possible minor impurities. However, it will avoid distracting discussions due to various alternative treatments of the impurities.

Ideally, there are three products which can be produced from the charge of a ternary system. Each product contains mainly one of the three components. However, unless required purities are very low, it is inevitable for a single batch cycle of a ternary distillation that at least one slop will be produced as well as the desired products. This slop can be separated further to produce additions to the desired products. The capability of a single batch still to produce various products is an interesting aspect to be analysed. This leads to the idea of recycling the slop to the batch still at various times. As a result of this, there exists a series of successive batch processes resembling a continuous process. There are many possible ways of recycling the slop. Therefore, the choice of a single batch still to achieve the desired products leads to the creation of alternative pseudo
continuous flowsheets, which will be called modes of operation.

In this analysis, the composition of a charge which will be fractionated is assumed to be more or less equal proportions of the constituents. It is assumed there is constant availability of the charge with the same composition and at the same price level. The three products are each valuable if they satisfy the specified product purities. The demand is assumed unlimited, so that there is an impetus to produce continuously the three main products.

Optimisation is aimed at achieving a maximum profit which is gained from the sales of the three products minus the operating cost and the charge or raw material costs. The operating cost is assumed to be predominantly the heating and the cooling costs. The profit, which is the objective function of the maximisation, is computed only with difficulty as it is function of a large number of variables. In this study the constant molar holdup model of batch distillation already discussed in the last chapter is used to relate some of the constraint equations of the state variables. The mode of operation is treated as an integer decision variable. The main policy which will be discussed is the optimum reflux ratio for each mode of operation.

* See Appendix 2 for details.
4.2 Simulation of a simple ternary distillation

A simple batch-cycle of ternary distillation comprises the start-up period, the first product topping period, the first slopping period, the second product period, the second slopping or the third product period, and the cleaning or charging period. For the purpose of analysing the behaviour of the system in each period, a simulation using the constant molar holdup model is carried out to provide data for the illustration.

4.2.1 Preparation for Luyben's start-up procedure

Luyben's (1971) start-up procedure begins with the assumption of initial conditions where the compositions and the flow profiles have been already established. The compositions in all subsystem are the same and the temperatures are at the equilibrium boiling point condition. The flow profiles are at the total reflux condition. This theoretical initial condition can be used for practical purposes. One possible way of doing it is by preheating the charge to its boiling point in the reboiler and followed by pumping some of the charge to the reflux accumulator so that all the accumulator holdup and the tray holdups can be filled with liquid of the same composition and temperature. At the same time the condenser is turned on to condense the vapor arising from the reboiler, and hence the start-up begins.
It is impossible to calculate exactly how much time and energy are required to prepare the Luyben's start-up period due to many uncertainties involved, particularly if the cleaning and charging process is done manually. The easiest way to deal with the preparation time is to assign it a constant value based on experience.

The energy used to preheat the charge can be easily calculated provided the temperature of the charge is given, while the mechanical energy for cleaning and charging can be set to a constant value.

4.2.2 Stopping criterion for the start-up period

During the start-up period at the total reflux condition all the composition profiles, $X_n$, the flow profiles, $V_n$ and $L_n$, and the temperature profile, $T_n$, are moving asymptotically toward a steady-state total reflux conditions. In order to monitor the course of the process, it is necessary to choose one variable as indicator. There are many possible candidates which can be proposed. In this study, the composition $X_c$ is chosen as the indicator variable. This choice is implementable in practice if there is a rapid composition analyser available.

Theoretically, the steady-state total reflux condition will be achieved at indefinite time, but there is no compelling reason to end the start-up process at any particular time,
provided the desired first product purity has been reached. However, if the first product purity is far lower than the theoretical steady-state value, there will be a redundant period of separation process and a danger of topping poor product composition. One way of dealing with this problem is by letting the start-up time vary and be lower bounded by the minimum value where the first product purity has been achieved.

The other way adopted in this study is to approximate the steady-state total reflux condition to some practical degree of accuracy. Theoretically, the derivative of $X^t$ with respect to time is zero at the steady state-total reflux condition. In practice, this condition can be approximated by comparing the last two results of the composition analyser. The decision can be made by setting a tolerance as the criterion. In the computer simulation, this criterion can be implemented straightforwardly by comparing the last two values of $X^t$ at every integration step. This method demands a smaller time step for accuracy, but it can be done in one integration process. Mathematically, the stopping criterion for the start-up process can be expressed by

$$X^t(t_o) - X^t(t_o - \delta t) \leq \varepsilon \quad (1)$$

Heat consumption by the reboliler and the heat rejected by the
Figure 1a: The backward derivative technique (a) versus the analytical derivative technique (b) in the start-up region.
Figure 1b The instantaneous composition of the liquid in the accumulator versus operating time.
Operating Time

Figure 1: Comparison of short-cut models of Diwekar and of Gumay with Luyben’s semi-rigorous model for a binary distillation.

162
condenser during the start-up period can be expressed respectively by

\[ q_{BO} = \int_{0}^{t_o} Q_B \, dt \]  

\[ q_{CO} = \int_{0}^{t_o} Q_C \, dt \]

4.2.3 Stopping criterion for the first product

Depending upon the composition of the charge and the number of stages of the column, the steady state composition of the light component at the end of the start-up period can be either less than or greater than the specified first product purity. If the steady state composition of the light component is less than the specified first product purity, no first product can be withdrawn from the column. The process can be continued directly to the second slopping step.

Otherwise, the process enters the beginning of the first topping period. Liquid is withdrawn continuously from the accumulator holdup and is separated into two parts, namely the first product and the reflux. The reflux is returned to the column, while the first product is directed into the first product container.
In this study, the overhead vapor flow, $V_1$, is assumed constant and overhead product is withdrawn from the accumulator. The amount of the reflux flow divided by the overhead product flow is called the reflux ratio, $R$, which is a control variable. The reflux ratio can be made constant or variable with respect to time during the topping or slopping process.

The amount of the first product, $P_1$, collected at any time during the topping period can be expressed by

$$P_1 = \int_{t_0}^{t_1} \frac{V_1}{R + 1} \, dt$$

While the amount of heating and cooling required are given respectively by

$$q_{h1} = \int_{t_0}^{t_1} Q_h \, dt$$

$$q_{c1} = \int_{t_0}^{t_1} Q_c \, dt$$

The cumulative composition of the light component in the first product container can be expressed by
Since the first topping period begins from the steady state total reflux condition, it is expected that the composition of the light component in the accumulator as shown by Figure 1 is gradually dropping and so is the cumulative composition of the light component in the first product container.

The first topping period has to be stopped when the cumulative composition of the light component drops to the specified first product purity. In practice, this criterion will be difficult to implement unless a continuous report from the composition analyser is available and integrated. The same problem appears in the computer simulation, because this criterion will involve a one dimensional direct search technique which demands several evaluations of a function which can only be evaluated at significant cost in computation effort.

To overcome this problem, a similar technique to the case of the stopping criterion for the start-up period is adopted. Here, the cumulative composition of the light component is examined at every integration step. The decision is made when the cumulative composition appears to be lower than or equal to the specified first product purity. This criterion can be stated symbolically by

\[
X_{P_1}^t = \frac{1}{P_1} \int_{t_0}^{t_1} \frac{V X_{P_0}^t}{R + 1} \, dt
\]

(7)
Operating Time

Figure 1 The instantaneous composition of the liquid in the accumulator versus operating time.
4.2.4 Stopping criterion for the first slop

At the end of the first topping period, there is normally a considerable amount of the light component in the accumulator, whereas the composition of the medium component in the vapor reaching the condenser is still lower than the specified second product purity. Therefore, it is necessary to purge the undesired part of the product which is called the first slop to the first slop container.

The amount of the first slop collected during the first slopping period and its cumulative composition can be expressed respectively by

\[ S_1 = \int_{t_1}^{t_2} \frac{V_1}{E + 1} \, dt \]  
\[ X_{S_1}^i = \frac{1}{S_1} \int_{t_1}^{t_2} \frac{V_1 X_1^i}{E + 1} \, dt \]

And the amount of heating and cooling required are given respectively by
As shown by Figure 1, it is expected that during the first stopping period, the composition of the light component in the accumulator is reduced and the corresponding composition of the medium component increases until it finally reaches its maximum value. A similar problem to the stopping criterion of the start-up period arises, namely when the first slopping process should be ended. For the sake of consistency, the stopping criterion for the first slop can handled by a similar technique. The composition of the medium component in the accumulator is examined at the end of each integration step. The decision can be made when the composition of the medium component starts to drop. This criterion can be stated symbolically by

\[ X_0^Z(t_2) \geq X_0^Z(t_2 - \delta t) \]  

4.2.5 Stopping criterion of the second product

After the first slopping period ends, the composition of the medium component in the accumulator has to be examined to see
whether it is lower or higher than the specified second product purity. If it appears to be lower, there will be no second product which must be withdrawn from the column and the process can be continued to the next step. However if it turns out to be greater, the process enters the second topping period.

The amount of the second product collected in the second product container and the corresponding composition of the medium component can be expressed respectively by

\[ P_2 = \int_{t_2}^{t_1} \frac{V_1}{R + 1} \, dt \quad (9) \]

\[ X_{P2}^z = \frac{1}{P_2} \int_{t_2}^{t_1} \frac{V_1 X_o^z}{R + 1} \, dt \quad (10) \]

And the amount of heating and cooling are given respectively by

\[ q_{BS} = \int_{t_2}^{t_1} Q_B \, dt \quad (11) \]

\[ q_{CS} = \int_{t_2}^{t_1} Q_C \, dt \quad (12) \]

The stopping criterion of the second product can be derived in a similar fashion to the first product;
4.2.6 Stopping criterion for the second slopping

Whether a second slop is necessary depends on whether the specified third purity has already been achieved at the end of the second product period. In this study, the third product is taken by combining all holdups in the column. The amount of the third product and the corresponding composition of the heavy component can be expressed respectively by

\[ P_g = \sum_{n=0}^{N+1} H_n \]

\[ X_{p3}^{g} = \frac{1}{P_g} \sum_{n=0}^{N+1} H_n X_n^{s} \]

During the process, the cumulative composition of the heavy component as expressed by equation (15) is gradually increased. To detect the end of the second topping period, it is necessary to examine whether the specified third product purity has been achieved. The stopping criterion can be stated by

\[ X_{p3}(t_g) \geq X_{p3}^{*} \]
If the specified third product purity has been achieved at the end of the second product period, there will be no second slop, and the process can enter the cleaning and recharging step. If it has not been achieved, the process enters the second slopping period.

The amount of the second slop and its cumulative compositions in the second slop container are expressed respectively by

\[ S_2 = \int_{t_2}^{t_4} \frac{V_1}{R + 1} \, dt \]  
\[ X_{sz}^i = \frac{1}{S_2} \int_{t_2}^{t_4} \frac{V_1 X_0^i}{R + 1} \, dt \]

The amount of heating and cooling required during the second slopping period can be expressed respectively by

\[ q_{b4} = \int_{t_3}^{t_4} Q_b \, dt \]  
\[ q_{c4} = \int_{t_3}^{t_4} Q_c \, dt \]

During the second topping period, the stopping criterion expressed by equation (16) above, is applied at the end of each integration step, giving
This theoretical criterion is easily applied in the computer simulation but it is difficult to implement in practice unless there is access to all compositions of the liquid holdups during the process or an accurate overall material balance has been carried out.

4.2.7 Pseudo continuous representation

For the sake of clarification, it is proposed to illustrate the above operation steps of a simple ternary distillation as a pseudo continuous operation. Each operation step can be represented by a box with arrows of input and output streams. The input streams should be numbered corresponding to the operation step assigned to the box.
Figure 2 Simple Ternary System

A : Cleaning and charging / preparation.
B : Start-up.
C : First topping.
D : First slopping.
E : Second topping.
F : Second slopping.

Figure 2 shows a pseudo continuous flow sheet which represents the pseudo continuous operation of the above simple ternary distillation.

4.2.8 Typical results of a simple ternary distillation

Typical results from the simulation of a simple ternary distillation are as follow.
1) Material balance

Initial Charge to the Reboiler: \( F = 505. \text{ kmol} \)

Initial Charge Composition:
\[
\begin{align*}
X_F^1 &= 0.40 \\
X_F^2 &= 0.35 \\
X_F^3 &= 0.25
\end{align*}
\]

First Product Collected: \( P_1 = 194. \text{ kmol} \)

First Product Composition:
\[
\begin{align*}
X_{P1}^1 &= 0.950 \\
X_{P1}^2 &= 5.003587 \times 10^{-2} \\
X_{P1}^3 &= 6.147970 \times 10^{-5}
\end{align*}
\]

First Slop Collected: \( S_1 = 112. \text{ kmol} \)

First Slop Composition:
\[
\begin{align*}
X_{S1}^1 &= 0.159 \\
X_{S1}^2 &= 0.835 \\
X_{S1}^3 &= 5.595531 \times 10^{-3}
\end{align*}
\]

Second Product Collected: \( P_2 = 45. \text{ kmol} \)

Second Product Composition:
\[
\begin{align*}
X_{P2}^1 &= 3.32990 \times 10^{-3} \\
X_{P2}^2 &= 0.950 \\
X_{P2}^3 &= 4.676932 \times 10^{-2}
\end{align*}
\]

Second Slop Collected: \( S_2 = 41. \text{ kmol} \)

Second Slop Composition:
\[
\begin{align*}
X_{S2}^1 &= 1.734089 \times 10^{-4} \\
X_{S2}^2 &= 0.610 \\
X_{S2}^3 &= 0.390
\end{align*}
\]

Third Product Collected: \( P_3 = 113. \text{ kmol} \)

Third Product Composition:
\[
\begin{align*}
X_{P3}^1 &= 1.898421 \times 10^{-6} \\
X_{P3}^2 &= 4.996258 \times 10^{-2} \\
X_{P3}^3 &= 0.950
\end{align*}
\]
2) Time and energy consumption

<table>
<thead>
<tr>
<th>Description</th>
<th>Time</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning and charging time</td>
<td>$\theta_A$</td>
<td>$q_{DA} = q_{CA}$</td>
</tr>
<tr>
<td>Start-up time</td>
<td>$\theta_B$</td>
<td>$q_{BO} = 1.362389E+06$ kcal</td>
</tr>
<tr>
<td>First topping time</td>
<td>$\theta_C$</td>
<td>$q_{CO} = 1.354574E+06$ kcal</td>
</tr>
<tr>
<td>First slopping time</td>
<td>$\theta_D$</td>
<td>$q_{D1} = 6.393609E+06$ kcal</td>
</tr>
<tr>
<td>Second topping time</td>
<td>$\theta_E$</td>
<td>$q_{C1} = 6.524924E+06$ kcal</td>
</tr>
<tr>
<td>Second slopping time</td>
<td>$\theta_F$</td>
<td>$q_{B2} = 4.060152E+06$ kcal</td>
</tr>
<tr>
<td>Second topping heating</td>
<td>$\theta_{B3}$</td>
<td>$q_{B2} = 4.111932E+06$ kcal</td>
</tr>
<tr>
<td>Second topping cooling</td>
<td>$\theta_{B4}$</td>
<td>$q_{B3} = 1.638979E+06$ kcal</td>
</tr>
<tr>
<td>Second slopping heating</td>
<td>$\theta_{B4}$</td>
<td>$q_{C3} = 1.659554E+06$ kcal</td>
</tr>
<tr>
<td>Second slopping cooling</td>
<td>$\theta_{C4}$</td>
<td>$q_{B4} = 1.588673E+06$ kcal</td>
</tr>
<tr>
<td>Cleaning and charging energy</td>
<td>$\theta_A$</td>
<td>$q_{DA} = q_{CA}$</td>
</tr>
<tr>
<td>Start-up heating</td>
<td>$\theta_B$</td>
<td>$q_{BO} = 1.362389E+06$ kcal</td>
</tr>
<tr>
<td>Start-up cooling</td>
<td>$\theta_B$</td>
<td>$q_{BO} = 1.362389E+06$ kcal</td>
</tr>
<tr>
<td>First topping heating</td>
<td>$\theta_C$</td>
<td>$q_{C1} = 6.393609E+06$ kcal</td>
</tr>
<tr>
<td>First topping cooling</td>
<td>$\theta_C$</td>
<td>$q_{C1} = 6.524924E+06$ kcal</td>
</tr>
<tr>
<td>First slopping heating</td>
<td>$\theta_D$</td>
<td>$q_{D2} = 4.060152E+06$ kcal</td>
</tr>
<tr>
<td>First slopping cooling</td>
<td>$\theta_D$</td>
<td>$q_{D2} = 4.111932E+06$ kcal</td>
</tr>
<tr>
<td>Second topping heating</td>
<td>$\theta_E$</td>
<td>$q_{B3} = 1.638979E+06$ kcal</td>
</tr>
<tr>
<td>Second topping cooling</td>
<td>$\theta_E$</td>
<td>$q_{B3} = 1.659554E+06$ kcal</td>
</tr>
<tr>
<td>Second slopping heating</td>
<td>$\theta_F$</td>
<td>$q_{C4} = 1.588673E+06$ kcal</td>
</tr>
<tr>
<td>Second slopping cooling</td>
<td>$\theta_F$</td>
<td>$q_{C4} = 1.606411E+06$ kcal</td>
</tr>
</tbody>
</table>

4.3. Simulation of a ternary distillation with slop recycle

The above results of a simple ternary distillation reveal that there are considerable amounts of the first and second slop which can be reprocessed or recycled in the next batch cycle. Luyben (1988) suggested that there are three methods of treating the slops, one of which has been reported. These include 1) using the first slop cut to fill up the reflux drum (and perhaps the column) prior to the start-up under total reflux conditions in the next batch cycle; 2) charging fresh feed to the still pot and feeding the slop cuts into the column at an appropriate tray and appropriate time during the
course of the next batch; and 3) saving up a number of slop cuts and doing binary batch distillations on each of the slop cuts, when an adequate still charge has accumulated.

In this study, these three methods will be used to develop alternative modes of operation for slop recycle.

4.3.1 Development of the first method

The first method of slop recycle is based on the idea that the two slops, instead of only the first slop as considered by Luyben (1988), are recycled to the column during the preparation for the start-up period. If the total charge to the column is kept constant, the new fresh charge required for the cycle is less than the simple method with no slop recycle. The required fresh charge can be expressed by

\[ C_f = \sum_{n=0}^{N+1} M_n - S_1 - S_2 \quad (21) \]

The first method of slop recycle is illustrated in Figure 3. There are many ways of implementing this method. Some of these are treated in this study and can be described by the following modes of operation.

1) Mode of operation 1

The two slops are combined together with the new fresh charge
to fill the accumulator, the trays and the reboiler. The initial compositions in each holdup in the column are all the same, namely

\[ x^i_{n0} = \frac{C X^i_f + S X^i_1 + S X^i_2}{C_f + S_1 + S_2} \]  

(22)

2) Mode of operation 2

Some of the first slop is used to fill the accumulator and the trays, and the rest of it is combined with the fresh charge and the second slop to fill the reboiler. The initial compositions in the accumulator and the trays are

\[ x^i_{n0} = x^i_{e1} \]  

(23)

and in the reboiler

\[ x^i_{(N+1)0} = \frac{C X^i_f + S X^i_2 + (H_{N+1} - C_f - S_2)x^i_{e1}}{H_{N+1}} \]  

(24)

3) Mode of operation 3

Both slops are first combined. The combined slops are used to fill the accumulator and the trays and the rest are used to fill the reboiler together with the fresh charge. The initial compositions in the accumulator and the trays are
and in the reboiler

\[ X^{i}_{n0} = \frac{S_t X^{i}_{1} + S_z X^{i}_{2}}{S_t + S_z} \]  \hspace{1cm} (25)

\[ X^{i}_{N+1,0} = \frac{C_t X^{i}_{1} + (H_{N+1} - C_f)X^{i}_{n0}}{H_{N+1}} \]  \hspace{1cm} (26)

Figure 3 The first method of slop recycle

A : Cleaning and charging / preparation.
B : Start-up.
C : First topping.
D : First slopping.
E : Second topping.
F : Second slopping.

4.3.2 Development of the second method

In the second method, either one or both slops are fed to the column at appropriate plates, at appropriate times and for appropriate durations. Several modes of operation resulting from this idea are as follow:

\[ \text{Figure 3 The first method of slop recycle} \]

A : Cleaning and charging / preparation.
B : Start-up.
C : First topping.
D : First slopping.
E : Second topping.
F : Second slopping.

4.3.2 Development of the second method
1) Mode of operation 4

The second slop is combined with the new fresh charge to fill the accumulator and the trays, any surplus going to the reboiler together with fresh charge. The first slop is fed to the column at an appropriate plate and appropriate time and duration. This mode of operation is illustrated in Figure 4. The required fresh charge and the rate of slop injection for this mode of operation are respectively

\[ C_f = \sum_{n=0}^{N+1} N_n - S_2 \]  

(27)

\[ F_n = \frac{S_t}{t_o - t_f} \]  

(28)

The initial compositions of each holdup are the same, given by

\[ x_{no}^i = \frac{C_f x_f^i + S_2 x_2^i}{C_f + S_2} \]  

(29)
Figure 4 Mode of operation 4

A: Cleaning and charging / preparation.
B: Start-up.
C: First topping.
D: First slopping.
E: Second topping.
F: Second slopping.

2) Mode of operation 5

This mode of operation is illustrated by Figure 5. The column is filled only with the new fresh charge at the beginning of the new batch cycle, so that the required fresh charge is

\[ C_f = \sum_{n=0}^{N+1} M_n \]  

(30)

While each slop is fed to the column at an appropriate plate, time, and duration. The constant rate of slop injection for the first slop is given by
and for the second slop

\[ F_{n2} = \frac{S_2}{t_s - t_f} \]  

(32)

Figure 5 Mode of operation 5

A : Cleaning and charging / preparation.
B : Start-up.
C : First topping.
D : First slopping.
E : Second topping.
F : Second slopping.

3) Mode of operation 6

This mode of operation is illustrated in Figure 6. The column is filled only with the new fresh charge at the beginning of the new batch cycle. Both slops are combined together and fed
to the column at an appropriate plate, time, and duration. The amount of the combined slop and its composition can be expressed respectively by

\[ S_m = S_1 + S_2 \quad (33) \]

\[ \frac{X_i}{S_m} = \frac{S_1 X_i^1 + S_2 X_i^2}{S_1 + S_2} \quad (34) \]

and the constant rate of injection for the combined slop is given by

\[ F_n = \frac{S_m}{t_a - t_f} \quad (35) \]
4) Mode of operation 7

This mode of operation is similar to Mode of operation 6, except that the combined slop is distributed to several plates at appropriate time and duration. If the combined slop is evenly distributed to $N_s$ plates, the constant rate of injection for each chosen plate can be expressed by

$$F_n = \frac{S_m}{(t_{S_j} - t_{f_j})N_s}$$

$$j = 1, 2, 3, \ldots, N_s$$

$$n = n_1, n_2, n_3, \ldots, n_{N_s}$$
5) Mode of operation 8

This mode of operation is a modification of mode of operation 4, where the first slop is distributed to several plates at appropriate time and duration. If the first slop is distributed with the same quantity to each of \( N_s \) chosen plates, the constant rate of injection can be defined by

\[
F_n = \frac{S_i}{(t_s - t_f)N_s}
\]  

(37)

4.3.3 Development of the third method

In this study, only one mode of operation is developed from the third method of slop recycle. That is mode of operation 9 illustrated in Figure 7. There are two possible types of cycle which can occur in this mode of operation, namely the long cycle and the short cycle. If the amount of the first slop available is greater than the required minimum level, the long cycle is executed. On the other hand, if the available first slop is lower than the required minimum level, the short cycle is executed. The required minimum level adopted in this study is defined by

\[
S_{i\min} = 0.1 M_{N+1} + \sum_{n=0}^{N} M_n
\]  

(38)
1) Long cycle operation

In the long cycle, the first slop is further treated as a binary distillation which consists of the preparation period, the start up period, and the slopping period. It is expected that the binary distillation will give an additional second product which results from the summation of all the holdups at the end of the slopping period. The third slop which is collected during the slopping period of the binary system is combined with the second slop and the new fresh charge to start the new cycle.
The required fresh charge to begin a new cycle can be expressed by

\[ C_f = \sum_{n=0}^{N+1} M_n - S_2 - S_3 \]  

(39)

And the initial compositions in each holdups is given by
The initial compositions of each holdup for the binary distillation are the same as the composition of the available first slop which is either a direct slop first from the current long cycle or accumulated first slop from the previous short cycles.

A stopping criterion for the start-up period of the binary distillation similar to the previous one of the simple ternary system can be defined as

\[
X^i_0(t_s) - X^i_0(t_s - \Delta t) \leq \varepsilon \tag{41}
\]

The amount of heating and cooling required during the binary start-up period can be calculated respectively by

\[
q_{BS} = \int_{t_4}^{t_5} Q_B \, dt \tag{42}
\]

\[
q_{CS} = \int_{t_4}^{t_5} Q_C \, dt \tag{43}
\]
The amount and the composition of the third slop during the third slopping period of the binary distillation can be expressed respectively by

\[ S_z = \int_{t_5}^{t_6} \frac{V_i}{R + 1} \, dt \]  

\[ X_{Sz}^i = \frac{1}{S_z} \int_{t_5}^{t_6} \frac{V_i X_0^i}{R + 1} \, dt \]  

At the same time, the amount of the fourth product and its composition can be expressed by

\[ P_4 = \sum_{n=0}^{N+1} N_n \]  

\[ X_{P4}^i = \frac{1}{P_4} \sum_{n=0}^{N+1} N_n X_n^i \]  

The stopping criterion for the slopping period of the binary is similar to that of the second slopping period for the simple ternary system, namely.

\[ X_{P4}^2(t_5) \geq X_{P2}^* \]  

124
The amount of heating and cooling during the third slopping period can be expressed by

\[ q_{hc} = \int_{t_b}^{t_c} Q_b \, dt \tag{50} \]

\[ q_{co} = \int_{t_b}^{t_c} Q_c \, dt \tag{51} \]

2) Short cycle operation

In the short cycle operation the first slop and the second slop are each saved in their containers waiting for the additional first and second slop from the next cycle. Therefore, the initial charge following a short cycle is always the same fresh charge. And the column operates as a simple ternary system.

4.3.4 Simulation results and discussions

The simulations of the above modes of operation are carried out based on the same basic data as that of the previous simple ternary system. Therefore, the results from each mode of operation can be compared to a common base point.
There are many results from the simulations which can be reported, such as the quantities produced per cycle of the first product, the second product, the first slop, and the second slop. The graphs of each of these five quantities versus cycle number are shown respectively in Figures 6 to 12. Each Figure consists of nine graphs corresponding to the nine modes of operation. These nine modes represent variations of the three methods of handling the recycle slops, namely modes of operation 1 to 3 from the first method, modes 4 to 8 from the second method, and mode 9 from the third method. Some features worthy of note in the results of simulation are:

1) Steady state properties

Each of the five quantities referred to above initially changes with respect to cycle number and finally converges to a steady state value after about six batches. It means that, for relatively long term operation, the ternary batch distillation with slop recycle can be regarded as quasi-continuous operation. As a result of this, optimisation analysis of the ternary system with slop recycle can be treated in similar way to analysing a continuous operation.

2) Variances due to modes of operation

There exist significant differences between the five quantities resulting from the three methods of slop handling compared to the simple ternary distillation without slop
Figure 8 Comparison of the first products.
Figure 9 Comparison of the second products.
Figure 10 Comparison of the third products.
Figure 11 Comparison of the first slopes.
Figure 12 Comparison of the second slopes.
recycle. Therefore, there are grounds for trying to distinguish them on the basis of an appropriate objective function.

Among the first methods of slop handling which are represented by modes of operation 1 to 3, it appears that only relatively small differences occur. However, for the second methods (4 to 8), the differences are more pronounced. From the single representative of the third method, mode of operation 9, it appears that for simulations chosen here only the long cycle operation is executed.

3) Accumulated slops

It appears from Figures 11 and 12 that the amount of the first slop for each mode of operation is always greater than that from a simple ternary system, whereas the amount of the second slop for each mode of operation decreases.

For modes of operation 1 to 3, the first slop increases by a factor of 2 and the second slop decreases by the same factor. For mode of operation 4 to 8, the first slop increases by factor of 3 to 4 and the second slop decreases by factor of 1.6 to 1.8. For mode of operation 9, only slight changes to the first and the second slop are noticed.
4.4 Objective function

In this study, two types of objective function are introduced for the purpose of comparison, namely capacity and profit. It is necessary to ensure that the two objective functions are so defined that they can be used to compare each of the above-mentioned modes of operation. For this purpose, only the long cycle operation of mode of operation 9 will be analysed together with the other eight modes of operation. The definitions of the two objective functions are as follows.

4.4.1 Capacity

According to Luyben's (1988) definition, the capacity of a ternary distillation is defined by the total amounts of the three products per cycle time. For modes of operation 1 to 8, the capacity can be expressed by

\[ C = \frac{P_1 + P_2 + P_3}{t_{\text{cycle}}} \]  \hspace{1cm} (52)

where the total cycle time, \( t_{\text{cycle}} \), is the summation of operating time in each operation steps, \( \theta_i \), so that

\[ t_{\text{cycle}} = \sum_{i=1}^{F} \theta_i \]  \hspace{1cm} (53)
For the long cycle operation of mode of operation 9, the capacity is defined by

\[ C = \frac{P_1 + P_2 + P_3 + P_4}{t_{cycle}} \]  

(54)

where the cycle time is expressed by

\[ t_{cycle} = \sum_{i=A}^{I} \theta_i \]  

(55)

4.4.2 Profit

In this study the profit is defined by the sales of the three products minus the cost of the fresh charge, the cost of heating, and the cost of cooling per cycle time.

The sales of the three products can be calculated by summing up the multiplication of each product, \( P_i \), with its unit price, \( C_{pi} \). For modes of operation 1 to 8, the sales can be expressed by

\[ C1 = \sum_{i=1}^{3} P_i C_{pi} \]  

(56)

and for mode of operation 9
\[ C_1 = \sum_{i=1}^{a} P_i C_{pi} + P_4 C_{p2} \]  

The cost of the fresh charge in each case can be calculated by multiplying the amount of the fresh charge required, \( C_f \), by its unit price, \( C_{pf} \), so that

\[ C_2 = C_f C_{pf} \]  

The cost of heating is calculated by multiplying the total amount of heat during the operation, \( q_{Htot} \), by its unit price, \( C_{qH} \).

\[ C_3 = q_{Htot} C_{qH} \]  

where for modes operation 1 to 8

\[ q_{Htot} = q_{BA} + \sum_{i=0}^{4} q_{Bi} \]  

and for mode of operation 9

\[ q_{Htot} = q_{BA} + q_{BG} + \sum_{i=0}^{6} q_{Bi} \]  

The cost of cooling can be calculated in a similar fashion to
the cost of heating, so that.

\[ C_4 = q_{C_{tol}} C_q \]  \hspace{1cm} (62)

where for modes operation 1 to 8

\[ q_{C_{tol}} = q_{CA} + \sum_{i=0}^{\Delta} q_{Ci} \]  \hspace{1cm} (63)

and for modes of operation 9

\[ q_{C_{tol}} = q_{CA} + q_{CG} + \sum_{i=0}^{\Delta} q_{Ci} \]  \hspace{1cm} (64)

Finally, the profit can be calculated with the help of the above expressions as

\[ P = \frac{C_1 - C_2 - C_3 - C_4}{t_{cycle}} \]  \hspace{1cm} (65)

4.5 Direct search with respect to modes of operation

It is important to note that the modes of operation examined in this study do not represent all possible modes of operation which can be possibly created from the ternary distillation with slop recycle. This fact poses a limitation of this
search where the highest or the lowest value of an objective function observed is not necessarily the absolute maximum or minimum obtainable.

Despite this limitation, this study yields some interesting information about the behaviour of the capacity and the profit with respect to the method of handling slop recycle. Figure 13 shows that the steady-state capacity for each mode of operation is lower than the simple ternary system. On the other hand, Figure 14 shows the steady-state profit of each mode of operation is greater than the simple ternary system. This contrast arises because Luyben's (1988) definition of the capacity does not recognise the advantage of the recycle slops which reduce the required fresh charge. Therefore, capacity is not a suitable criterion to use for maximisation problem in this study.

The improvements to the profit by the modes operation 1 to 3, which represent the first method of handling slop recycle, after the steady-state value is achieved are approximately the same, namely about 37% with respect to the simple ternary system. It means that there are no significant differences in the length of the start-up periods which are expected to be different due to the three modes of operation.

Modes of operation 4 to 8 which represent the second method of handling recycle slops shows more diverse improvements to the profits. They are respectively 62%, 59%, 63%, 90%, and 69%.
Figure 13 Comparison of Capacities.
Figure 14 comparison of Profits.
with respect to the simple ternary system. Broadly, it can be stated that the second method of handling slop recycle is about twice as efficient as the first method.

The great improvement to the profit found in this study is due to mode of operation 9 which represents the third method of handling slop recycle. The improvement is 146% with respect to the simple ternary system. The superiority of the third method of handling slop recycle over the second method probably arises because the third method takes shorter cycle times than the second method.

Note that, in Figure 14, the profits of modes 1 to 8 each coincides at cycle number 1, whereas the profit of mode 9 separates itself. This is because, at the first cycle number, modes of operation 1 to 8 perform the same series of operational steps as the simple ternary system which is used as the basic mode of operation for profit comparison. On the other hand, mode of operation 9 has to perform additional operation steps to complete its first cycle.

4.6 Direct search with respect to the reflux ratio

The choice of the reflux ratio plays an important role in the distillation processes. For a batch distillation, the higher the reflux ratio the higher the product purity and the longer the cycle time. Therefore, there is an impetus to investigate
the maximization of the profit with respect to the reflux ratio which represents a trade off between the improvement to the amount of product per cycle and the extension of the cycle time. There are many ways of setting the reflux ratio. In this study, the reflux ratio is set to a constant value, \( R \), and the same for each operation step.

Since the above results of simulation suggest that each of the nine modes of operation converges to quasi steady-state operation after about six batches, an objective function was defined based on the system quantities at cycle number 7. As result of this, the cycle number can be removed from the analysis. The investigation of the profit with respect to the mode of operation and the reflux ratio can be analysed in the same fashion as the analysis in the previous section.

Figure 15 shows the plots of the profit, after the steady-state value is approximately achieved at cycle number 7, versus the reflux ratio for the nine modes of operation. It is shown that for each mode of operation the steady-state profit indicates the existence of a maximum value with respect to constant reflux ratio.

Modes of operation 1 to 3 show almost flat curves with the optimal reflux ratio around 2.3. Modes of operation 4 to 8 show more diverse curves with optimal reflux ratio ranging from 3.1 to 3.5. Mode of operation 9 also shows a rather flat curve with optimal reflux ratio around 2.9.
Figure 15 Profit versus Reflux Ratio.
From the curves in Figure 15, it can be surmised that if the maximum profit is to be determined, an appropriate choice of mode of operation is more important than an optimal choice of reflux ratio. This is because the magnitude of improvement due to the mode of operation is much greater than due to the reflux ratio. By using this rule with only nine modes of operation available in this study, the optimal mode of operation is due to mode of operation 9 with the optimal reflux ratio around 2.9 which results in 152% improvement to the profit with respect to the simple ternary system, compared to 146% from the previous improvements due to the same mode of operation with an arbitrary reflux ratio of 3.5.

4.7 The effect of the number of plates

The effect of varying the number of plates, N, on the product purity is roughly equivalent to varying the reflux ratio, namely the higher the number of plate means the higher product purity. Therefore, if the capital costs is not taken into account, the profit increases as the number of plates increases. It would be more realistic to incorporate an element of capital charges in to the objective function. This would require an estimate of the fraction of the plant's life which is spent idle and the issue is side-stepped in this study. This is satisfactory when always comparing with a base case.
Figure 16 Profits versus Reflux Ratio for mode of operation 9 for varying number of stages from 9 to 13.
The effect of varying the number of plates is illustrated by Figure 16 which shows the plots of the profit for mode of operation 9 versus the reflux ratio for the number of plates 9 to 13. Figure 16 also shows that the optimal reflux ratio reduces as the number of plates increases.

4.8 Conclusion

From the above study, it appears that the methods of handling the recycle slops suggested by Luyben (1988) result in various degrees of improvement with respect to the simple ternary distillation. The profit seems to be a suitable criterion for analysing the maximisation problem in this study. The choice of mode of operation has a far more profound influence on economic efficiency than the choice of the reflux ratio.
5. Derivation Of New Short-cut Model

5.1 Introduction

This chapter deals with derivation of a new short-cut model for multi component batch distillation. The new short-cut model has the capability of approximating the instantaneous composition of the liquid in the accumulator by explicit expressions which can be easily solved without using a non-linear equation solver. In addition, the model requires minimal data, namely the number of stages, \( N \), the reflux ratio, \( R \), the relative volatility, \( \alpha_i \), and the composition of the liquid in the reboiler, \( X^i_n \).

From the collection of short-cut models currently available, only that of Chao Kwang-Chu (1954) is an explicit model. But the Chao Kwang-Chu (1954) model requires one more datum than other models such as Diwekar and Madhavan's (1986) model. This is because Chao Kwang-Chu (1954) uses the vapor liquid equilibrium constant, \( K_i \), instead of the relative volatility, \( \alpha_i \), used by Diwekar and Madhavan (1986). In this study, the derivation the new short-cut model which refines that of Chao Kwang-chu is discussed fully.

5.2 The concept of Normalisation Factor

The most explicit and easiest method of relating the mole fractions of liquid in the accumulator, \( X^i_p \), and liquid in the
reboiler, $X_B^i$, is by direct proportionality using factor $Z^i$. However, there are constraints which have to be satisfied, namely that the calculated $X_D^i$ must be between zero and unity, and that the summation of $X_D^i$ has to be unity. The application of a normalisation factor is designed to satisfy these two constraints. For this purpose, a suitable form of the new short-cut model is

$$X_D^i = \frac{Z^i X_B^i}{\sum_{i=1}^{NC} Z^i X_B^i}$$  \hspace{1cm} (1)$$

Factor $Z^i$ is called the normalisation factor. A further requirement for equation (1) to be an ideal short-cut model is that the expression of $Z^i$ is an explicit function of the number of stages, $N$, the reflux ratio, $R$, the relative volatilities, $\alpha$, and the composition of the liquid in the reboiler, $X_B^i$. So, each normalisation factor $Z^i$ has to be of the form

$$Z^i = Z^i(N, R, \alpha, X_B^i)$$  \hspace{1cm} (2)$$
5.3 Derivation of the normalisation factor formula

5.3.1 Assumptions

The explicit formula of the normalisation factor in equation (2) is derived from the material balance equations of a multi-component batch distillation by using some simplifications. The common simplifications are based on the following assumptions: 1) negligible tray and accumulator holdups, 2) constant relative volatility with respect to composition, temperature and stage number, 3) molar flowrates constant from tray to tray and 4) no feed and side-product streams.

In this study, the column is divided into stages which are numbered from the top of the column. The accumulator is numbered zero and the reboiler numbered N.

5.3.2 Simplified material balance equations

Based on the above assumption of flat flow profiles, both the vapor flow, \( V \), and the liquid flow, \( L \), are constant with respect to stage number, \( n \). If \( D \) is the flow of distillate withdrawn from the accumulator, the overall material balance in each stage except the reboiler can be expressed in terms of net flow equation

\[
V - L = D
\]
And the corresponding material balance for each component is expressed by

\[ V Y_{n+1}^i - L X_n^i = D X_0^i \]  

(4)

where \( X_c^i \) is the composition in the zero holdup accumulator.

If the reflux ratio, \( R \), is defined by

\[ R = \frac{L}{D} \]  

(5)

equation (4) can be modified to be

\[ Y_{n+1}^i = \frac{R X_n^i}{R + 1} + \frac{x_0^i}{R + 1} \]  

(6)

which is known as the operating line.

5.3.3 Simplified vapor liquid equilibria

The vapor liquid equilibria in each stage can be approximated by using the assumption of constant relative volatility expressed by
Equation (7) can be linearised by introducing an adjustable factor, \( \theta \), the reciprocal of the denominator which will be discussed later. The linearised form of the vapor liquid equilibria is expressed by

\[
y_{n}^{i} = \theta a_{i} x_{n}^{i}
\]  

5.3.4 Generalised concept of normalisation factor

For the sake of easy discussion, the short-cut model expressed by equation (1) is generalised to relate the composition at the accumulator to that any stage \( n \) with the equations of material balance and vapor liquid equilibria. The generalised form is expressed by

\[
x_{0}^{i} = \frac{z_{n}^{i} x_{n}^{i}}{\sum_{i=1}^{N_{C}} z_{n}^{i} x_{n}^{i}}
\]  

If the denominator of equation (9) is written as \( \phi_{n} \), so that

\[
\phi_{n} = \sum_{i=1}^{N_{C}} z_{n}^{i} x_{n}^{i}
\]
then equation (9) becomes

\[ X_n^i = \frac{\phi_n X_0^i}{Z_n^i} \]  

(11)

Summing mole fraction \( X_n^i \) in equation (11) to unity results in the following relationship

\[ \sum_{i=1}^{\text{NG}} X_n^i = \phi_n \sum_{i=1}^{\text{NG}} \frac{X_0^i}{Z_n^i} = 1 \]  

(12)

or

\[ \phi_n = \frac{1}{\sum_{i=1}^{\text{NG}} \frac{X_0^i}{Z_n^i}} \]  

(13)

The substitution of equation (13) into equation (11) results in the inverted form of equation (9), namely

\[ X_n^i = \left\{ \frac{X_0^i}{Z_n^i} \right\} \frac{1}{\sum_{i=1}^{\text{NG}} \left\{ \frac{X_0^i}{Z_n^i} \right\}} \]  

(14)

This expression relating mole fraction in stage \( n \) explicitly with mole fraction in stage zero can be expressed in another
way by introducing an inverse normalisation factor $\tilde{W}_n^i$ as in equation (11):

$$\tilde{W}_n^i = \frac{X_n^i}{\tau_n^i} = \frac{\phi_n}{\tau_n^i}$$ (15)

5.3.5 Difference equation of inverse normalisation factor

Combination of the above equations (6) and (8) results in a difference equation in mole fraction, $\tau_n^i$:

$$\Theta_\alpha X_n^i = \frac{R X_n^i}{R + 1} + \frac{X_o^i}{R + 1}$$ (16)

This equation can be simplified by introducing a modified reflux ratio $u$ defined by

$$u = \frac{R}{R + 1}$$ (17)

so that equation (16) becomes

$$\Theta_\alpha X_{n+1}^i - u X_n^i - (1-u)X_o^i = 0$$ (18)

Now the inverse normalisation factor $\tilde{W}_n^i$ can be introduced by dividing equation (18) by $X_o^i$ which results in a difference equation as follows
\[ \theta \alpha_i \psi_{i, n+1}^i - u \psi_{i, n}^i - (1 - u) = 0 \]  \hspace{1cm} (19)

Equation (19) can be solved analytically by using initial condition

\[ \psi_{i, 0}^i = 1 \]  \hspace{1cm} (20)

The analytical solution of equation (19) is expressed by

\[ \psi_{i, n}^i = \frac{1 - u + (\theta \alpha_i - 1) \left\{ \frac{u}{\theta \alpha_i} \right\}^n}{\theta \alpha_i - 1} \]  \hspace{1cm} (21)

Eliminating \( \psi_{i, n}^i \) between equation (15) and (21) gives

\[ Z_{i, n} = \frac{\phi_n (\theta \alpha_i - u)}{1 - u + (\theta \alpha_i - 1) \left\{ \frac{u}{\theta \alpha_i} \right\}^n} \]  \hspace{1cm} (22)

It is interesting to note that factor \( \phi_n \) in equation (22) is immaterial in this argument as equation (22) is only used in conjunction with equation (9). Therefore, factor \( \phi_n \) in
equation (22) can be omitted, so that $Z_n^i$ may be written

$$Z_n^i = \frac{(\theta \alpha_i - u)}{1 - u + (\theta \alpha_i - 1)} \left( \frac{u}{\theta \alpha_i} \right)^n$$

(23)

The particular overall normalisation factor $Z^i$ can now be found by setting stage number $n$ as $N$ which is the stage number of the reboiler having liquid composition $X^i_N$. Therefore, the normalisation factor $Z^i$ is

$$Z^i = \frac{(\theta \alpha_i - u)}{1 - u + (\theta \alpha_i - 1)} \left( \frac{u}{\theta \alpha_i} \right)^N$$

(24)

5.3.6 The optimal choice of the adjustable factor

First of all, the adjustable factor, $\theta$, in equation (24) will be determined with the relative volatility of the heaviest component is set to unity. Since the new short-cut model is an approximate solution of the the semi-rigorous model described by simultaneous difference equations (6) and (7), the best values of $\theta$ should give a minimum error with respect to the exact solution of the semi-rigorous model.
The exact solution of the semi-rigorous model for calculating the mole fractions $X^i_D$ given the mole fraction $X^i_x$ is difficult to perform. On the other hand, the inverse problem for calculating the mole fractions $X^i_x$ given the mole fraction $X^i_D$ can be easily performed using the following recurrent formula derived from the semi-rigorous model.

$$X^i_{n+1} = \frac{\left\{ \frac{R X^i_n + X^i_o}{\alpha_i} \right\}}{\sum_{j=1}^{NC} \left\{ \frac{R X^j_n + X^j_o}{\alpha_j} \right\}} \quad (25)$$

$n = 0, 1, 2, \ldots N-1$

$X^i_o = X^i_D$

Given the values of $X^i_x$, the approximate values of $X^i_D$ can be calculated by using the new short-cut model with a chosen value of $\theta$. By using these values of $X^i_x$, the corresponding values of the mole fraction of the liquid in the reboiler, $X^i_N$, can be calculated using equation (25). If $\theta$ is rightly chosen the values of $X^i_N$ should be close to the given values of $X^i_D$. The deviation between these two quantities is measured as a function of $\theta$ by an error which can be expressed by

$$E(\theta) = \sum_{i=1}^{NC} 100 \text{ABS} \left( X^i_D - X^i_N \right) \quad (26)$$
The best value of $\theta$ can be obtained by minimizing the error function given by equation (26) using a direct search technique. Except for a binary system, the minimum error is not zero. This is because the new short-cut model, like the other short-cut models, uses only one instead of NC-1 adjustable factor. Therefore, there is an inherent limitation of the new short-cut model, namely the calculated $X^*_D$ can never be exactly the same as that calculated by the semi-rigorous model.

A more realistic value of $\theta$ can be obtained by using the above technique of minimizing error, if equation (25) is replaced by a more rigorous model. An even more realistic estimate of $\theta$ can be obtained if a large set of data for $X^*_b$ and $X^*_D$ from experiments is available representative of the type of system to be modelled.

5.3.7 Modelling of the adjustable factor $\theta$

The above method of choosing optimal values of $\theta$ requires a one dimensional search which will make the new short-cut model no more efficient than the other short-cut models. However, by using the above method, a large set of the best values of $\theta$ for various values of $X^*_b$, $\alpha$, $u$, $N$, and the number of components, NC, can be generated. This set of data can be used to construct a model for calculating $\theta$ by using a suitable regression technique.
Considering equations (7) and (8), it is convenient to combine $X^i_n$, $\alpha_i$, and $N_c$ into a single quantity $\omega$ which can be expressed by

$$\omega = \frac{1}{\sum_{i=1}^{NC} \alpha_i X^i_n}$$

(27)

Using this definition, the general formula for approximating $\Theta$ can be expressed by

$$\Theta = \Theta(\omega, u, N, N_c, \alpha^t)$$

(28)

For a particular of study, a more specific model for estimating $\Theta$ may be made by fixing some of the arguments in equation (28). In the study of optimal reflux profile, for example, the number of plates $N$, the number of component $N_c$, and the relative volatilities of the components are fixed, so that $\Theta$ is only a function of $u$ and $\omega$. An example of this model is

$$\Theta = \alpha_0 + \alpha_1 u + \alpha_2 u^2 + \alpha_3 \omega + \alpha_4 \omega^2 + \alpha_5 u \omega$$

(29)

where $\alpha_0$ to $\alpha_5$ are coefficients to be determined by a linear regression technique. Examples of the coefficients for particular situations are given in Table 1.
Table 1. Coefficients model \( \theta \)

<table>
<thead>
<tr>
<th>( N )</th>
<th>( 4 )</th>
<th>( 8 )</th>
<th>( 10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_c )</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>( (2.,1.) )</td>
<td>( (4.,3.,2.,1.) )</td>
<td>( (4.,3.,2.,1.) )</td>
</tr>
<tr>
<td>( \alpha_0 )</td>
<td>0.72338584</td>
<td>-0.01228663</td>
<td>-0.01535444</td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>-0.11503630</td>
<td>0.07270333</td>
<td>0.06896224</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>-1.14720236</td>
<td>0.69873842</td>
<td>0.69778393</td>
</tr>
<tr>
<td>( \alpha_3 )</td>
<td>1.55239881</td>
<td>1.17957346</td>
<td>1.18932356</td>
</tr>
<tr>
<td>( \alpha_4 )</td>
<td>-0.29609809</td>
<td>-1.58343047</td>
<td>-1.58401045</td>
</tr>
<tr>
<td>C.O.D.</td>
<td>0.9918</td>
<td>0.9974</td>
<td>0.9973</td>
</tr>
</tbody>
</table>

(1) (2) (3)

The first column in Table 1 applies to a particular condition of a binary system which had been used in optimisation studies by Murty (1980) et al. and by Diwekar (1987) et al. The second and the third column in Table 1 are particular conditions of a quaternary system used by Diwekar (1987) et al. as an extended case of their optimisation study. The last row of Table 1 shows that the coefficients of determination (C.O.D.) for the linear regressions of \( \theta \) by using equation (29) are each close to unity, hence equation (29) is a good formula for the specific model of estimating \( \theta \) referred to above.

5.4 Validation of the new short-cut model

To check the validity of the new short-cut model, three types of investigation were carried out, namely; extreme conditions,
comparative simulation, and comparative optimisation. The latter will be discussed in the next chapter.

5.4.1 Extreme conditions

If a batch distillation column is regarded as an instantaneous stripping section of a continuous distillation, there are two extreme conditions commonly considered, namely minimum number of plates and minimum reflux ratio. In this study, only the condition of minimum number of plates will be discussed.

The condition of minimum number of plates is that the reflux ratio, \( R \), is infinity or the modified reflux ratio, \( u \), is equal to unity. By using equation (24), the normalisation factor, \( Z_i \), is found to be

\[
Z_i = \left( \theta \alpha_i \right)^N
\]  

(30)

If two key-components are considered as the light key, \( l_k \), and the heavy key, \( h_k \), mole fractions of the key-components in the accumulator, \( X_{D}^{l_k} \) and \( X_{D}^{h_k} \), can be related to the mole fractions of the key components in the reboiler, \( X_{B}^{l_k} \) and \( X_{B}^{h_k} \), by using equation (1). The ratio of the two mole fraction is found to be

\[
\frac{X_{D}^{l_k}}{X_{D}^{h_k}} = \left( \frac{\alpha_{l_k}}{\alpha_{h_k}} \right)^N \frac{X_{D}^{l_k}}{X_{D}^{h_k}}
\]  

(31)
If $N$ in equation (31) is called $N_{\text{min}}$, and the ratio of light-key's relative volatility to heavy-key's relative volatility is called $\alpha_{\text{lh}}$, then the minimum number of plates can be expressed by

$$N_{\text{min}} = \frac{\ln \left( \frac{x_D^{\text{lk}}}{x_D^{\text{hk}}} \frac{x_D^{\text{lk}}}{x_D^{\text{lk}}} \right)}{\ln \alpha_{\text{lh}}}$$  \hspace{1cm} (32)

Equations (31) and (32) are the same as that found by Fenske (1932).

5.4.2 Comparative simulation

For the purpose of comparison, the general differential equations of batch distillation using short-cut models, equations (1) to (3) in Chapter 2 Section 2.1.4 are employed. The performance of the new short-cut model is compared to that of Diwekar and Madhavan's (1986) model which is described by equations (14) to (19) in the same Chapter 2 Section 2.1.4. For the purpose of validation, it is ideal to compare the performances of the two short-cut models with that of the semi-rigorous model without holdup. This is because each short-cut model is essentially an approximate solution of the semi-rigorous model without holdup described by the above equations (6) and (7) in this chapter. However, because the semi-rigorous model is difficult to solve, it is wise to use
the semi-rigorous model of Luyben (1971) described in Chapter 2 Section 2.1.3 which is easy to integrate. For this purpose, the tray holdups are each set as small as possible in order to approximate the semi-rigorous model without holdups.

In this study, two systems are analysed, namely the four-stage binary system with relative volatilities \((2.,1.)\) and the ten-stage quaternary system with relative volatilities \((4.,3.,2.,1.)\). The coefficients of model \(\theta\) for both systems are already given in Table 1, section 5.3.7.

For the purpose of comparison for the binary system, the vapor flow is set to 110 moles per hour and the amount of charge is set to 116.1 moles with the initial composition equal to \((0.5,0.5)\). For the quaternary system, the vapor flow is also set 110 mole per hour and the amount of initial charge is set to 200 moles with the initial composition equal to \((0.25,0.25,0.25,0.25)\).

The results of simulation for the above binary system and quaternary system are presented in Figures 1 and 2 respectively. From the graphs in Figures 1 and 2, it appears that the performance of the new short-cut model is consistently closer to the semi-rigorous model of Luyben (1971) than Diwekar and Nadhavan’s (1986).
Operating Time

Figure 1 Comparison of short-cut models of Diwekar and of Gumay with Luyben's semi-rigorous model for a binary distillation.
Figure 2 Comparison of short-cut models of Diwekar and of Gumay with Luyben's semi-rigorous model for a quaternary distillation.
Further comparison is made by calculating the amount of the first distillate collected during one hour operating time for given charge compositions and product purities. The vapor flow and the amount of initial charges for both the binary system and the quaternary system are kept the same as the previous simulation. The results of calculations are presented in Table 2.

### Table 2. The amount of distillate

<table>
<thead>
<tr>
<th>Case No.</th>
<th>N</th>
<th>Nc</th>
<th>X_p</th>
<th>DIWEKAR</th>
<th>LUYBEN</th>
<th>GUHAY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>2</td>
<td>0.95</td>
<td>20.081</td>
<td>26.314</td>
<td>25.910</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>2</td>
<td>0.93</td>
<td>12.300</td>
<td>16.289</td>
<td>16.415</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>4</td>
<td>0.90</td>
<td>20.429</td>
<td>7.426</td>
<td>6.932</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>4</td>
<td>0.90</td>
<td>24.714</td>
<td>0.411</td>
<td>1.017</td>
</tr>
</tbody>
</table>

The figures of column 5 in Table 2 are quoted from the results reported by Diwekar (1987) et al. From the results shown in Table 2, it is seen that the performance of the new short-cut model is consistently closer to that of Luyben (1971) model than is that of Diwekar and Madhavan (1986).

### 5.5 Conclusion

An explicit short-cut model for estimating the instantaneous overhead compositions of a multi-component batch still has been successfully derived. The model is shown to be capable of simulating the operation of multi-component batch distillation with acceptable accuracy.
6. Optimal Reflux Profile

6.1 Introduction

This chapter deals with the application of variational calculus to obtaining an optimal trajectory of the reflux ratio. The applicability of the proposed new short-cut model, described in the previous chapter, in solving the variational problem is demonstrated in detail. Results of the optimisation problem performed here are compared with those of Murty et al. (1979) and Diwekar et al. (1987).

6.2 Theory of variational method for optimal reflux profile

6.2.1 Variational operator

For ease of discussion of the variational method for determination of optimal reflux profile, it is convenient to introduce here some primary concepts of the variational operator, $\delta$, with respect to a function of time, $X(t)$. The operation, $\delta X$, is called the variation of $X$ which, at a particular time $t$, has either zero value or an infinitesimal non-zero value according to the following condition.

$$\delta X = \begin{cases} 
\text{zero, if } X \text{ is a stationary function or value} \\
\text{non-zero, if } X \text{ is non-stationary function or value}
\end{cases}$$
A function \( X \) is called stationary function if it is assigned to a specified function of time. If \( X \) has a specified value at a particular time, it is said to have a stationary value at that particular time.

The property of the variational operator is comparable to the derivative operator, \( d/dt \). A compound operator, \( \delta d/dt \), satisfies the commutative laws.

\[
\delta X = \frac{d \delta X}{dt} \quad (1)
\]

The variation of a compound function satisfies the same laws as does the derivative operator.

\[
\delta f(X) = \frac{\partial f}{\partial X} \delta X \quad (2)
\]

Also the variation of an integral function satisfies the first Hopital laws

\[
\delta \int_0^T f(X) \, dt = f(X(T)) \delta T + \int_0^T \delta X \frac{\partial f}{\partial X} \, dt \quad (3)
\]

6.2.2 Dynamic equation of state for batch distillation

Batch distillation dynamics can be described by a general dynamic equation of state relating the trajectory of the modified reflux ratio, \( u \), the reboiler holdup, \( X^o \), and the multi-component mole fractions in the reboiler, \( X^i \)
\[
\frac{dX^i}{dt} = f^i(u, X^0, X^1, X^2, \ldots X^{NC})
\]

\[i = 0, 1, 2, \ldots NC\]

\[\delta X^i(0) = 0\]

where

\[f^0 = -(1-u)V\]

\[f^i = (1-u)V(X^i_d - X^i)/X^0\]

\[i = 1, 2, \ldots NC\]

Since the new short-model will be employed, \(X^i_d\) in equation (6) can be written as

\[X^i_d = X^i_d(u, X^1, X^2, \ldots X^{NC})\]

### 6.2.3 Objective function and isoperimetric constraint

In order to compare results with those of Murty et al. (1980) and Diwekar et al. (1987), the objective function used in this study is the amount of distillate which is the first product collected, \(P\), during a specified operating time, \(T\).
Equation (8) can be written in the form of a differential equation by introducing a new state function $X^p$.

\[
\frac{dX^p}{dt} = g(u) = (1-u)V
\]

$X^p(0) = 0$

If the vapor flow, $V$, is held constant during the specified operating time, $T$, the amount of distillate collected, $P$, as expressed by equation (8) depends only on the trajectory of the modified reflux ratio, $u(t)$. Therefore, the optimisation is required only with respect to the trajectory of the modified reflux ratio. According to Murty et al. (1980) and Diwekar et al. (1987), the type of optimisation problem involved is a maximisation problem which can be stated by

\[
\text{Maximum } \left\{ P = X^p(T) \right\}_{u(t)}
\]

The purity of the first product which is indicated by the mean mole fraction of the first component is specified. This results in an isoperimetric constraint which can be expressed

\[
\int_0^T (1-u) V (X^a_p - X^s_p) \, dt = 0
\]
The equal sign, =, in equation (11) is more practical than the unequal sign, ≥. This is because if the unequal sign, ≥, is used, it means that there is always still an amount of distillate which can be further collected until the mean mole fraction the first component drops to the specified value.

Equation (11) can also be written in a form of differential equation by introducing another state new function $X_c$ such that

$$\frac{dX_c}{dt} = c(u, X_1, X_2, \ldots, X_{N_c}) = (1-u)V(X_D - X_P)$$

$$\delta X_c(0) = 0 \quad \text{and} \quad \delta X_c(T) = 0$$

6.2.4 Augmented objective function and Hamiltonian

The maximum distillate problem expressed in equation (10) is subject to the dynamic equations of state, equations (4) and (9), and the isoperimetric constraint, equation (12). These constraints can be removed by introducing an augmented objective function, $I$. This is done by using a set of adjoint functions, $q^i$, $q^p$, and $q^c$, which correspond to $X_i$, $X_p$, and $X_c$ respectively. The augmented objective function, $I$, is then expressed by
\[
I = X^P(T) + \int_0^T \left[ q^P(g - X^P) + q^c(c - X^c) + \sum_{i=0}^{NC} q^i(f^i - X^i) \right] dt \quad (13)
\]

Equation (13) can be simplified further by introducing Hamiltonian of the system which is defined by

\[
H = q^P g + q^c c + \sum_{i=0}^{NC} q^i f^i \\
= (1-u)V\left\{ q^P + q^c(X^A_D - X^A_P) \right\} - q^o(1-u)V + \sum_{i=1}^{NG} q^i(1-u)V(X^i - X^i_D) / X^o \quad (14)
\]

so that

\[
I = X^P(T) + \int_0^T \left[ H - q^P \dot{X}^P - q^c \dot{X}^c - \sum_{i=0}^{NC} q^i \dot{X}^i \right] dt \quad (15)
\]

From equations (4), (9), (12), and (14), it is found that the partial derivatives of Hamiltonian with respect to each adjoint function satisfy the following canonical equations of the first kind.

\[
\frac{\partial H}{\partial q^P} = \dot{X}^P \quad (16)
\]
6.2.5 Stationary condition

As implied by equation (10), the objective function \( P \) is a function of the trajectory \( u(t) \). This means that any variation \( \delta u \) from trajectory \( u(t) \) results in a variation \( \delta P \) which will increase or decrease the amount of distillate \( P \). A trajectory \( u(t) \) is called optimal if it is so adjusted that it brings the amount of distillate \( P \) into a stationary state which can be maximum or minimum. The stationary state of \( P \) is achieved if the variation \( \delta P \) is zero. However, this condition is not sufficient because the constraint equation have not yet been taken into account.

Since the augmented objective function, \( I \), is numerically the same as the objective function, \( P \), if all the constraints are satisfied, the complete stationary condition for the objective function with constraint is that \( \delta I \) is zero.

The variation \( \delta I \) can be obtained by applying the variational operator \( \delta \) to equation (15) by employing some primary concepts previously expressed in equations (1) to (3) and by

\[
\frac{\partial H}{\partial q^c} = \dot{x}^c 
\]

(17)

\[
\frac{\partial H}{\partial q^t} = \dot{x}^t
\]

(18)
integrating by parts to establish the necessary relations to be met by \( u(t) \). Some simplifications can be made by taking the canonical equations (16) to (18) into account and by taking into consideration that all initial values of the state functions, \( X^p(0), X^c(0), \) and \( X^i(0) \) are stationary. Rosenbrock and Storey (1966) used a closely similar approach. The simplified form of \( \delta I \) is

\[
\delta I = \left\{ 1 - q^P(T) \right\} \delta X^p(T) + q^c(T) \delta X^c(T) + q^i(T) \delta X^i(T) + \\
\int_0^T \left( \frac{\partial H}{\partial X^p} + q^P \right) \delta X^p + \left( \frac{\partial H}{\partial X^c} + q^c \right) \delta X^c + \\
\frac{\partial H}{\partial u} \delta u + \sum_{i=0}^{NC} \left( \frac{\partial H}{\partial X^i} + q^i \right) \delta X^i \, dt \tag{19}
\]

The first condition for \( \delta I \) to be zero is that the integrand in equation (19) has to be zero. If each state variable is not stationary during the process, each term in braces of the integrand has to be zero. This results in the second kind of canonical equations

\[
\frac{\partial H}{\partial X^p} = -q^P \tag{20}
\]

\[
\frac{\partial H}{\partial X^c} = -q^c \tag{21}
\]
\[ \frac{\partial H}{\partial x_i} = -q^i \]  

(22)

The other term in the integrand which has to be zero is

\[ \frac{\partial H}{\partial u} \delta u = 0 \]  

(23)

The second condition for \( \delta I \) to be zero is that each term outside the integration in equation (19) has to be zero. This results in the following equations

\[ \left\{ 1 - q^p(T) \right\} \delta x^p(T) = 0 \]  

(24)

\[ q^c(T) \delta x^c(T) = 0 \]  

(25)

\[ q^i(T) \delta x^i(T) = 0 \]  

(26)

The treatment of the second kind of canonical equations (20) to (22) results in a set of differential equations of the adjoint function. Equations (24) to (26) give the final values which have to be satisfied by the differential equations of the adjoint functions.

The combination of equations (22) and (26) gives
\[
\frac{dq^0}{dt} = \sum_{i=1}^{NC} q^i (1-u) V (X^i - X^i_d) / (X^0)^2 \quad (27)
\]

\[q^0(T) = 0\]

\[
\frac{dq^i}{dt} = -q^i (1-u) V \frac{\partial X^i_d}{\partial X^i} - \sum_{i=1}^{NC} \frac{q^j (1-u) V}{X^0} \left\{ \frac{\partial X^j}{\partial X^i} - \frac{\partial X^j}{\partial X^i} \right\} \quad (28)
\]

\[q^i(T) = 0\]

Since the Hamiltonian is not a function of \(X^c\), the derivative of the Hamiltonian with respect to \(X^c\) is zero. This results in the adjoint function \(q^c\) being a constant which is called the Lagrange multiplier \(\lambda\). As a result of this, the combination of equations (21) and (25) gives

\[
\frac{dq^c}{dt} = 0 \quad (29)
\]

\[q^c(T) = \lambda\]

The Lagrange multiplier \(\lambda\) has to be adjusted to satisfy equation (25), namely until the specified product purity is achieved.

The Hamiltonian is also not a function of \(X^p\). Therefore, the derivative of Hamiltonian with respect to \(X^p\) is zero. This causes \(q^p\) to be a constant. In order to satisfy equation (24), this constant has to be unity. As a result of this, the
combinations of equation (20) and (24) is as follows

$$\frac{dq^P}{dt} = 0$$
$$q^P(T) = 1$$

The treatment of equation (23) results in the optimal trajectory of the modified reflux ratio. If \( u \) is not stationary during the process, the optimal trajectory of the modified reflux ratio is

$$u(t) = \text{Root of } \left\{ \frac{\partial H}{\partial u} = 0 \right\}$$

where

$$\frac{\partial H}{\partial u} = q^c V \left\{ (1-u) \frac{\partial X_i^D}{\partial u} - X_i^D + X_p^* \right\} + (q^o - 1) V - \sum_{i=1}^{NG} \frac{q^i V}{X^o} \left\{ (1-u) \frac{\partial X_i^i}{\partial u} + X_i^i - X_i^D \right\}$$

There is an inherent constraint which has to be satisfied by the modified reflux ratio, namely

$$0 \leq u \leq 1$$

This constraint can be accommodated by employing Pontryagin's (1962) continuous maximum principle which was refined by
The principle is that the optimal \( u \) is the one which makes the Hamiltonian maximum. This principle can be implemented in this problem. The first step is to find \( u \) from equations (31) and (32) followed by calculating the Hamiltonian. This value of the Hamiltonian is then compared with the values of the Hamiltonian at the two extremes of \( u \) in equation (33). The other method is by using a direct search technique for maximising the Hamiltonian with respect to \( u \).

However, according the results reported by Hurty (1980) et al. and Diwekar (1987) et al., the values of the optimal trajectory \( u \) are always within the interval \( 0 < u < 1 \). Therefore, the two extremes of \( u \), 0 and 1, may be treated only for optional checking.

6.2.6 Solution by Gradient Method in Function Space

From the above discussion of the stationary conditions, the overall solution to the problem of variational optimisation resolves into a system of two-point boundary value problems in the state functions, \( X^p, X^c, X^i \) and their corresponding adjoint functions, \( q^p, q^c, q^i \). While \( q^p \) is fixed to be unity, \( q^c \) plays the role of the Lagrange multiplier which has to be adjusted to make \( X^c \) zero.

The above two-point boundary value problem can be solved by an iterative method. This is done by integrating numerically the
differential equations (4), (9), and (12) with respect to time forwardly from 0 to T. For this purpose, the trajectory of the modified reflux ratio $u$ has to be initialised and stored. Each value of the state functions and the modified reflux ratio is stored at every time step. By using these stored values, the differential equations (27) and (28) are integrated backwardly with respect to time from T to 0. During this backward integration, the trajectory of the modified reflux ratio is corrected by a technique called the gradient method in function space which can be formulated by

$$u_{\text{new}} = u_{\text{old}} + \epsilon \frac{\partial H}{\partial u} \quad (34)$$

where $\epsilon$ is a small value which according to Diwekar (1988) should be carefully chosen to ensure the convergence of the iteration. The whole iterative scheme is ended if the corrected trajectory of the modified reflux ratio is roughly constant.

The trajectory of the Hamiltonian which corresponds to the convergent trajectory of the modified reflux ratio should be constant with respect to time. However, to satisfy the constraint equation (33), the trajectory of the Hamiltonian has to be checked at every time step against its two extreme values in order to choose the correct optimal trajectory of the modified reflux ratio.
6.2.7 Improvement to the gradient method in function space

The inconvenience of the gradient method in function space as expressed by equation (34) is the need for careful choice of the constant \( \varepsilon \). This is a somewhat haphazard process for the inexperienced.

To overcome the above problem, a Newton-Raphson like method can be used. The idea comes from the fact that the optimal trajectory is the solution of equation (31) which at every time step can be regarded as a non-linear equation in \( u \). By using this technique the constant \( \varepsilon \) can be automatically calculated by the following expression.

\[
\varepsilon = -\frac{1}{\frac{\partial^2 H}{\partial u^2}}
\]

where

\[
\frac{\partial^2 H}{\partial u^2} = q^c V \left\{ (1-u) \frac{\partial^2 \chi^i_D}{\partial u^2} - 2 \frac{\partial \chi^i_D}{\partial u} \right\} - \sum_{i=1}^{NC} \frac{q^i V}{\chi^0} \left\{ (1-u) \frac{\partial^2 \chi^i_D}{\partial u^2} - 2 \frac{\partial \chi^i_D}{\partial u} \right\}
\]

6.2.8 Application of the new short-cut model

From the above analysis, it appears that the differential equations of the adjoint function, equations (27) and (28),
requires a matrix of the first derivatives of $X^i$ with respect to $X^i$. The solution by using the gradient method in function space, equation (34), requires the first derivatives of $X^i_d$ with respect to $u$. While the proposed improvement of gradient method in function space, equation (35), requires the second derivatives of $X^i_d$ with respect to $u$.

If the current implicit short-cut models, such as that of Diwekar and Madhavan (1986) and Domenech and Enjalbert (1978), are used, the exact values of above mentioned derivatives will be very difficult to calculate. This is because the inherent difficulty of the implicit short-cut models which require many iterative calculations in their formula.

The superiority of the new short-cut over the current implicit short-cut models is in its explicitness. All of the required derivatives mentioned above can be calculated analytically by using the explicit formula developed in Appendix 1.

6.2.9 Algorithm of the gradient method in function space

The following algorithm can be used as a guide for implementing the above techniques of solving the variational problem for optimal reflux trajectory. The algorithm requires a one dimensional direct search routine for solving the non-linear equation in the Lagrange multiplier, $\lambda$, for example the golden-section search routine.
Step 1
Initialise the trajectory of the modified reflux ratio \( u \) and store it. The most convenient estimate is a trajectory of constant value.

Step 2
Guess the range of values for searching the Lagrange multiplier, \( \lambda \). There is no clue available for estimating the magnitude of the values. Once a realistic range has been established the golden-section search routine is an appropriate technique for finding the value of \( \lambda \).

Step 3
If the gradient method in function space is used, guess the small value of \( \varepsilon \). Use a positive small value.

Step 4
Initialise all the state functions \( X^P \) and \( X^C \) to zero, and \( X^i \) to the specified initial values of the still charge.

Step 5
Integrate forwardly step by step the differential equations of the state functions, equations (4), (9) and (12), from time zero to \( T \), by using the stored values of the trajectory \( u \). Store each trajectory of the state functions at every time step.
Integrate backwardly step by step the differential equations of the adjoint function, equations (27) and (28), from time $T$ to zero, by employing the stored values of the trajectory $u$ and $X^i$. The integrand of equations (27) and (28) can be calculated with the help of the first derivative formula of $X^i_D$ with respect to $X^i_D$ which for the new short-cut model are available in Appendix 1.

At the end of each integration step, calculate the Hamiltonian and its partial derivatives with respect to $u$, by using equations (14) and (32) and store them. This can be done by employing the formula of the partial derivatives of $X^i_D$ with respect to $u$ in Appendix 1.

Update the trajectory of $u$, by using the gradient method in function space, equation (34), or by using the improved gradient method in function space, equation (35).

Step 7
Check whether the trajectory of the first derivative of Hamiltonian with respect to $u$ is already converged to zero within the desired accuracy.

If not converged, the iteration goes to either step 3 for necessary change of $\varepsilon$ or to directly to step 4 if the old $\varepsilon$ is considered suitable.
If converged, go to step 8 or, for optional checking, calculate the values of the Hamiltonian at a particular time step as a function of \( u \) within the interval \( 0 \leq u \leq 1 \).

**Step 8**
Check whether the state function \( X^c \) is already converged to zero within the desired accuracy.

If not converged, the calculation either returns to step 2, following the golden-section search routine for a new \( \lambda \), or to step 1 to change the range of searching \( \lambda \).

If converged, the iterations are terminated and the results reported.

### 6.3 Case study

In this study, two particular systems are analysed, namely a binary system and a quaternary system.

#### 6.3.1 Binary system

Murty (1980) *et al.* studied the maximum distillate problem of a binary system whose components have the relative volatilities 2. and 1. in a four-stage batch still. The vapor flow, \( V \), was set to 110 moles per hour and the operating time, \( T \), to one hour. They used the distillate rate, \( D \), as the decision trajectory and a semi-rigorous model without holdups,
equations (6) and (7) in the previous chapter, for estimating the instantaneous overhead compositions. Table 1 shows the seven different input conditions of their case-study which were analysed with the variations in the amount of charge, the composition, and the product purity.

Table 1. Input conditions for binary system

<table>
<thead>
<tr>
<th>Case No.</th>
<th>$X^0(0)$</th>
<th>$X^*(0)$</th>
<th>$X^*_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>116.1</td>
<td>0.750</td>
<td>0.950</td>
</tr>
<tr>
<td>2</td>
<td>74.3</td>
<td>0.420</td>
<td>0.900</td>
</tr>
<tr>
<td>3</td>
<td>116.1</td>
<td>0.580</td>
<td>0.930</td>
</tr>
<tr>
<td>4</td>
<td>116.1</td>
<td>0.487</td>
<td>0.930</td>
</tr>
<tr>
<td>5</td>
<td>74.3</td>
<td>0.715</td>
<td>0.950</td>
</tr>
<tr>
<td>6</td>
<td>116.1</td>
<td>0.715</td>
<td>0.930</td>
</tr>
<tr>
<td>7</td>
<td>116.1</td>
<td>0.715</td>
<td>0.900</td>
</tr>
</tbody>
</table>

Diwekar (1987) et al. used the same binary system with the same input conditions and compared the results of their study to that of Hurty (1980) et al. They employed the Diwekar and Madhavan (1988) short-cut model and used the reflux ratio $R$ as the decision trajectory.

For the purpose of comparison in this study, the same binary system with the same input conditions as in Table 1 are also analysed here by using the new short-cut model using the modified reflux ratio $u$, as the decision trajectory. The coefficients of $\theta$ for this binary system are as in Table 1. in the chapter 5. Comparative results from this study with those
of Hurty and Diwekar are shown in Table 2.

Table 2. Comparative results for binary system

<table>
<thead>
<tr>
<th>Case No.</th>
<th>(R) DIWEKAR</th>
<th>(D) HURTY</th>
<th>(U) GUNAY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ</td>
<td>P</td>
<td>λ</td>
</tr>
<tr>
<td>1</td>
<td>29.36</td>
<td>20.290</td>
<td>27.15</td>
</tr>
<tr>
<td>2</td>
<td>50.11</td>
<td>4.731</td>
<td>42.69</td>
</tr>
<tr>
<td>4</td>
<td>131.36</td>
<td>3.170</td>
<td>102.93</td>
</tr>
<tr>
<td>5</td>
<td>29.24</td>
<td>18.238</td>
<td>25.76</td>
</tr>
<tr>
<td>6</td>
<td>15.30</td>
<td>30.240</td>
<td>13.06</td>
</tr>
<tr>
<td>7</td>
<td>8.74</td>
<td>37.261</td>
<td>10.40</td>
</tr>
</tbody>
</table>

From the figures in Table 2, it appears that the results predicted by the new short-cut model are consistently closer to those predicted by Hurty (1980) et al. than are the results predicted by Diwekar (1987) et al.

6.3.2 Quaternary system

Diwekar (1987) et al. tried to extend their study to the case of a quaternary system. The input conditions which they used are shown in Table 3. Two cases were analysed, namely for N equal to 8 and 10. Both cases use the same vapor flow, V, equal to 110 mole per hour and the same amount of initial charge equal to 200 moles. The common operating time for both
cases is set to one hour.

Table 3. Input conditions for quaternary system

<table>
<thead>
<tr>
<th>Component</th>
<th>composition $X_i(0)$</th>
<th>Relative volatility $\alpha_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
<td>4.</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>3.</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>2.</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1.</td>
</tr>
</tbody>
</table>

In this comparative study, the same quaternary system with the same input conditions is analysed again using the new short-cut model. For the two cases with $N$ equal to 8 and 10, the coefficients of model $\Theta$ are given in Table 1 of the chapter 5. The comparative results of this study and that of Diwekar (1987) are shown in Table 4.

Table 4. Comparative results for quaternary system

<table>
<thead>
<tr>
<th>No.</th>
<th>$N$</th>
<th>$\lambda$</th>
<th>$P$</th>
<th>$\lambda$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>285.12</td>
<td>25.5420</td>
<td>167.93</td>
<td>1.0179</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>15.32</td>
<td>20.4387</td>
<td>17.01</td>
<td>6.9351</td>
</tr>
</tbody>
</table>

From the figures in Table 4, it appears that the results of the new short-cut model are entirely different from those of Diwekar (1987). There seems to be an anomaly in the case of
Diwekar's results where the maximum distillate for N equal to 8 is greater than for N equal to 10. According to the figures in Table 2 in the previous chapter, the tests by Luyben (1971) model using the same input conditions and very small tray holdups indicate that distillate collected by using a constant reflux operation are 0.411 and 7.426 respectively for N equal to 8 and 10. Since the results of a constant reflux operation and an optimal reflux operation are close to each other, it is believed that the results obtained by the new short-cut model are better than those of Diwekar.

6.4 Conclusions

The theory of the variational method for solving the problem of optimal reflux profile for multi-component batch distillation by using short-cut models has been discussed.

The explicitness of the new short-cut model makes it possible to implement the Newton-Raphson like method for improving the performance the gradient method in function space, conferring considerable advantages in speed of computation.

The results of comparative case studies show that the predictive performance of the new short-cut model is better than that of Diwekar (1987) et al. as well as the computational performance referred to above.
7. SUGGESTION for FUTURE WORK

The above analytical derivative technique may be used to solve other models of unsteady-state processes which involve systems of differential-algebraic equations. Such processes are, for example, packed-tower distillation, other operation of a boiler or evaporator with holdup.

Problems in simulation and optimisation of batch distillation with slop recycle may be extended to the following situations:

1) Extension of the number of components or products. This will increase the number of operational steps in each mode of operation.

2) Treatment of possible impurities in the system. This may necessitate an increase in the number of operational steps compared with a separation which does not consider the treatment of impurities. The need for extra operational steps depends on the concentration, the relative volatilities and the number of components.

3) Selective products. This situation is analogous to the treatment of possible impurities, where the number of saleable or valuable products is lower than the number of major components in the system.
4) Integrated system. In this situation a batch distillation is part of an integrated system. A simple integrated system of batch processes which could be interesting is the one comprising a slow batch reaction and a batch distillation.

For the short-cut model, the general expression of the adjustable factor, \( \theta \), could be completed in an explicit form, including the consideration of the percentage holdups. The possible derivation of normalisation factor for the system having multiple feed streams may also be of interest for simulating batch distillations with slop recycle.
Appendix 1

Derivation of Partial Derivatives required by the Newton-Raphson like method.

1. Gumay short-cut model

Step A: \[ \omega = \frac{1}{\sum_{i=1}^{NC} \alpha_i x_i} \]

Step B: \[ \theta = \Theta(N, u, \omega) \]

Step C (repeat i = 1, NC):

\[ Z^i = \frac{\theta \alpha_i - u}{1 - u + (\theta \alpha_i - 1) \left( \frac{u}{\theta \alpha_i} \right)^N} \]

Step D (repeat i = 1, NC):

\[ X^i_D = \frac{\sum_{i=1}^{NC} Z^i x^i_D}{\sum_{i=1}^{NC} x^i_D} \]
2. The derivatives of $x^i_d$ with respect to $u$

Steps E to L are repeated in sequence for $i = 1, N_C$.

Step E: \[ P = N \left( \frac{\partial \alpha_i}{\partial \alpha_i} - 1 \right) \left( \frac{u}{\partial \alpha_i} \right)^{N-1} \]

Step F: \[ Q = \alpha_i \left( 1 - N \left( \frac{\partial \alpha_i - 1}{\partial \alpha_i} \right) \right) \left( \frac{u}{\partial \alpha_i} \right)^N \]

Step G: \[ A = -1 + P + Q \frac{\partial \theta}{\partial u} \]

Step H: \[ \frac{\partial \ln Z^i}{\partial u} = \left\{ \frac{\alpha_i \frac{\partial \theta}{\partial u} - 1 - A Z^i}{\partial \alpha_i - u} \right\} \]

Step I: \[ \frac{\partial P}{\partial u} = P \left\{ \frac{N - 1}{u} + \left( \frac{\alpha_i}{\partial \alpha_i - 1} - \frac{N}{\theta} \right) \frac{\partial \theta}{\partial u} \right\} \]

Step J: \[ \frac{\partial Q}{\partial u} = Q \left\{ \frac{N}{u} - \left( \frac{N + 1 - (N - 1)\partial \alpha_i}{N - (N - 1)\partial \alpha_i} \right) \frac{N}{\theta} \frac{\partial \theta}{\partial u} \right\} \]

Step K: \[ \frac{\partial A}{\partial u} = \frac{\partial P}{\partial u} + \frac{\partial Q}{\partial u} \frac{\partial \theta}{\partial u} + Q \frac{\partial^2 \theta}{\partial u^2} \]

Step L: \[ \frac{\partial^2 \ln Z^i}{\partial u^2} = \left\{ 1 - A Z^i - \alpha_i \frac{\partial \ln Z^i}{\partial u} - Z^i \frac{\partial A}{\partial u} + \alpha_i \frac{\partial^2 \theta}{\partial u^2} \right\} \left( \frac{\partial \alpha_i - u}{\partial \alpha_i} \right) \]

Steps M and N are repeated in sequence $i = 1, N_C$. 

190
Step N: \[
\frac{\partial^2 X_D^i}{\partial u^2} = \frac{1}{X_D^i} \left( \frac{\partial X_D^i}{\partial u} \right)^2 + X_D^i \frac{\partial^2 \ln Z^i}{\partial u^2} - X_D^i \sum_{j=1}^{NC} \frac{\partial X_D^j}{\partial u} \frac{\partial \ln Z^j}{\partial u} + X_D^i \frac{\partial^2 \ln Z^i}{\partial u^2}
\]

3. The derivatives of \( X_D^j \) with respect to \( X_D^i \)

Step 0 (repeat \( i = 1, NC \)): \[
\frac{\partial \theta}{\partial X_D^i} = - \alpha_i \frac{\partial \theta}{\partial \omega} \omega^2
\]

Step P is repeated \( j = 1, NC \):
Step P: repeat steps Q, R and S in sequence \( i = 1, NC \).

Step Q: \[
B = \alpha_i \left\{ 1 - N \left( \frac{\theta \alpha_j - 1}{\theta \alpha_j} \right) \right\} \left( \frac{u}{\theta \alpha_i} \right)^N
\]

Step R: \[
\frac{\partial \ln Z^j}{\partial \theta} = \frac{\alpha_j - B Z^j}{\theta \alpha_j - u}
\]

Step S: \[
\frac{\partial \ln Z^j}{\partial X_D^i} = \frac{\partial \ln Z^j}{\partial \theta} \frac{\partial \theta}{\partial X_D^i}
\]

Step T is repeated \( j = 1, NC \)
Step T (repeat \( i = 1, NC \)): 191


\[
\frac{\partial X^j_b}{\partial X^i_c} = \frac{X^j_b}{X^i_c} \left\{ \frac{\partial X^j_b}{\partial X^i_c} \right\} + \frac{X^i_b}{X^i_c} \frac{\partial \ln Z^j}{\partial X^i_c} \right\} - \\
X^j_b \sum_{k=1}^{NC} \frac{X^k_b}{X^i_c} \left\{ \frac{\partial X^k_b}{\partial X^i_c} \right\} + \frac{X^i_b}{X^i_c} \frac{\partial \ln Z^k}{\partial X^i_c} \right\}
\]

Appendix 2a

A benzene(1)-toluene(2)-xylene(3) mixture of composition, 
\[X_1 = 0.40 \quad X_2 = 0.35 \quad X_3 = 0.25,\]
was used as the examples in cases of the rigorous method. It was taken to be at its boiling point. Enthalpy, heat capacity and density data were taken from C. L. Yaws, "Physical Properties", McGraw-Hill Publishing Co., 1977. Antoine's coefficients were taken from F. J. Zuiderweg, "Recommended Test Mixtures for Distillation Columns", C. Baldwin Ltd., 1966.

Appendix 2b

Number of trays = 10.
Heat loss per tray = 66 kJ /hr °K.
Heat capacity of equipment per tray = 0.42 kJ / °K.
Murphree tray efficiency in each tray = 0.9.
Boil-up rate = 600 kmol / hr.
Reflux Ratio = 3.5.
Product purity = 0.95.
Raw material cost = £ 5.00 /kmol.
First product price = £ 10.00 /kmol.
Second product price = £ 15.00 /kmol.
Third product price = £ 12.50 /kmol.
Cooling cost = £ 0.24 / GJ.
Heating cost = £ 1.02 / GJ.
BIBLIOGRAPHY


Rosenbrock, H. H. and C. Storey, (1966), 'Computational
Techniques for Chemical Engineers', Pergamon Press Ltd., London.


**NOMENCLATURE**

\( a \) to \( d \) - coefficients of difference equations.

\( a_t \) to \( a_s \) - coefficients of model \( \Theta \).

\( A_s \) - cross sectional area of the column.

\( b \) - Domenech-Enjalbert's adjustable parameter.

\( B \) - reboiler molar liquid holdup.

\( B_0 \) - initial value of the reboiler molar liquid holdup.

\( C \) - total amount of products per cycle time.

\( C_1 \) - total sale of the products in a single cycle.

\( C_2 \) - total cost of the fresh charge in a single cycle.

\( C_3 \) - total cost of heating process in a single cycle.

\( C_4 \) - total cost of cooling process in a single cycle.

\( C_i \) - Diwekar-Madhavan's adjustable factor.

\( C_f \) - the molar amount of fresh charge.

\( C_{Pn} \) - heat capacity of the equipment in stage \( n \).

\( C_{pi} \) - price per mole of the \( i \)th product.

\( C_{pf} \) - price per mole of the fresh charge.

\( C_{qH} \) - unit cost of heating process.

\( C_{qC} \) - unit cost of cooling process.

\( D \) - top product molar flow.

\( D_{ln} \) - liquid side product molar flow from stage \( n \).

\( D_{vn} \) - vapor side product molar flow from stage \( n \).

\( E \) - total absolute fractional composition error.

\( E_n \) - the equilibrium function in stage \( n \).

\( F \) - initial molar charge to the reboiler.

\( F_n \) - molar feed flow into stage \( n \).

\( G_n \) - liquid volume holdup in stage \( n \).

\( h_n \) - liquid molar enthalpy in stage \( n \).
\( h_{xn} \) - molar enthalpy gradient in composition space at stage n.

\( h_{Fn} \) - liquid molar enthalpy associated with \( F_n \).

\( H \) - the Hamiltonian function.

\( H^n \) - vapor molar enthalpy in stage n.

\( i \) - component i.

\( k^i \) - Chao Kwang Chu's proportionality factor for component i.

\( K^i_a \) - average equilibrium constant for component i.

\( K^r_a \) - average equilibrium constant for the reference component r.

\( K^r_b \) - reboiler equilibrium constant for the reference component r.

\( K^n_i \) - equilibrium constant for component i in stage n.

\( K^n_r \) - equilibrium constant for the reference component in stage n.

\( L \) - liquid molar flow.

\( L^n \) - liquid molar flow to stage n.

\( L_w \) - the weir height.

\( N^n \) - liquid molar holdup in stage n.

\( n \) - stage number, from zero to \( N + 1 \).

\( N \) - number of plates or stages.

\( N_{\text{min}} \) - the minimum number of plates.

\( N_C \) - number of components.

\( N_S \) - the number of distributed slops.

\( P \) - profit per cycle time.

\( P_1 \) - the molar amount of the first product.

\( P_2 \) - the molar amount of the second product.

\( P_3 \) - the molar amount of the third product.

\( P_4 \) - the amount of the fourth product.
$P_n$ - absolute pressure in stage $n$.

$Q_C$ - condenser heat flow.

$Q_n$ - heat loss flow from stage $n$.

$Q_B$ - reboiler heat flow.

$q_{BA}$ - heat consumption during charging period.

$q_{GA}$ - heat rejected during charging period.

$q_{DO}$ - heat consumption during the start-up period.

$q_{GO}$ - heat rejected during the start-up period.

$q_{D1}$ - heat consumption during the first topping period.

$q_{G1}$ - heat rejected during the first topping period.

$q_{S2}$ - heat consumption during the first slopping period.

$q_{C2}$ - heat rejected during the first slopping period.

$q_{D3}$ - heat consumption during the second topping.

$q_{G3}$ - heat rejected during the second topping.

$q_{B4}$ - heat consumption during the second slopping.

$q_{G4}$ - heat rejected during the second slopping.

$q_{B5}$ - heat consumed during the second start-up period.

$q_{G5}$ - heat rejected during the second start-up period.

$q_{B6}$ - heat consumed during the third slopping period.

$q_{G6}$ - heat rejected during the third slopping period.

$q_{B tot}$ - total heat consumption.

$q_{C tot}$ - total heat rejected.

$q^i$ - adjoint function associated with $X^i$.

$q^B$ - adjoint function associated with $B$.

$q^i$ - adjoint function associated with $X^i_B$.

$r$ - reference component.

$R$ - the reflux ratio.

$R_{min}$ - the minimum reflux ratio.
$R_{\text{max}}$ - upper bound of the reflux ratio search.

$S_1$ - the amount of the first slop.

$S_{1\text{min}}$ - the minimum of $S_1$ for the long cycle operation.

$S_2$ - the amount of the second slop.

$S_3$ - the amount of the third slop.

$S_m$ - the amount of the combined slop.

$S_i^F$ - Brown and Souders' absorption factor for component $i$.

$t$ - operating time.

$t_c$ - preparation time (binary system).

$t_E$ - the end time of start-up process (binary system).

$t_f$ - the final time (binary system).

$t_{F_1}$ - the end time of the topping process (binary).

$t_o$ - the end time of the start-up process.

$t_{s_1}$ - the end time of the first topping process.

$t_{s_2}$ - the end time of the first slopping process.

$t_{s_3}$ - the end time of the second topping process.

$t_{s_4}$ - the end time of the second slopping process.

$t_{s_5}$ - the end time of the second start-up process.

$t_s$ - the initial time of feeding a slop.

$t_{f_1}$ - the end time of feeding a slop.

$t_{a_j}$ - the $t_o$ for the distributed slop at plate $j$.

$t_{f_j}$ - the $t_f$ for the distributed slop at plate $j$.

$t_{\text{cycle}}$ - total cycle time.

$T$ - the final time in maximum distillate problem.

$T_n$ - equilibrium temperature at stage $n$.

$T_{x_i}^T$ - temperature gradient in composition space.
\( u \) – modified reflux ratio.
\((UA)_n\) – heat transfer factor in stage \( n \).
\( V \) – molar vapor flow.
\( V_n \) – molar vapor flow from stage \( n \).
\( \dot{W}_c \) – the weir constant.
\( \dot{W}_i^n \) – the inverse normalisation factor for component \( i \).
\( X \) – parameter in Gilliland’s correlation.
\( X_i^n \) – state function.
\( X_{\text{lb}}^i \) – reboiler liquid mole fraction for component \( i \).
\( X_{\text{lt}}^i \) – \( X_i^n \) at time \( t \).
\( X_i^D \) – instantaneous overhead mole fraction of component \( i \).
\( \overline{X}_D^i \) – mole fraction of component \( 1 \) in the top product.
\( X_{\text{p1}}^* \) – specified value of \( \overline{X}_D^i \).
\( X_{\text{p1}}^i \) – liquid mole fraction for component \( i \) in stage \( n \).
\( X_{\text{n0}}^i \) – the initial value of \( X_i^n \).
\( \overline{X}_n^i \) – vector liquid mole fraction in stage \( n \).
\( X_{\text{p1}}^i \) – average mole fraction of component \( 1 \) for the first product.
\( X_{\text{p1}}^* \) – specified value of \( X_{\text{p1}}^i \).
\( X_{\text{p2}}^i \) – average mole fraction of component \( 2 \) for the second product.
\( X_{\text{p2}}^* \) – specified value of \( X_{\text{p2}}^i \).
\( X_{\text{p3}}^i \) – average mole fraction of component \( 3 \) in the third product.
\( X_{\text{p3}}^* \) – specified value of \( X_{\text{p3}}^i \).
\( X_{\text{p4}}^i \) – average mole fraction of component \( 4 \) in the fourth product.
\( X_{\text{s1}}^i \) – average mole fraction of component \( i \) in the first slope.
\( X_{\text{s2}}^i \) – average mole fraction of component \( i \) in the second slope.
- average mole fraction of component $i$ in the third slop.
- average mole fraction of component $i$ in the combined slop.
- parameter in Gilliland's correlation.
- vapor mole fraction for component $i$ in stage $n$.
- vector vapor mole fraction in stage $n$.
- equilibrium vapor mole frac. corresponding to $Y^i_n$.
- the normalisation factor for component $i$.
- the generalised normalisation factor for component $i$.
- relative volatility of component $i$.
- relative volatility vector.
- the relative volatility of the heavy key component.
- the ratio of $\alpha^i_k$ over $\alpha^i_h$.
- the relative volatility of the light key component.
- variational operator.
- the approximate time-derivative of $h^i_n$.
- the approximate time-derivative of $H^i_n$.
- the approximate time-derivative of $T^i_n$.
- a small time integration step.
- small real number.
- Murphree tray efficiency of tray $n$ for component $i$.
- Gumay's adjustable factor.
- preparation time.
- start-up time.
- first topping time.
- first slopping time.
- second topping time.
\( \theta_f \) - second slopping time.

\( \theta_g \) - preparation time a long cycle operation.

\( \lambda \) - the Lagrange multiplier.

\( \rho_L \) - liquid molar density.

\( \rho_n \) - liquid molal density at stage n.

\( \rho_v \) - vapor molal density.

\( \tau_n \) - the hydraulic time constant.

\( \phi_n \) - liquid molal volume at stage n.

\( \phi_{xn} \) - liquid molal volume gradient in composition space.

\( \omega \) - Gumay's dimensionless group.