

THE UNIVERSITY OF CALGARY

BUTYL ACETATE SYSTEM

by

NORMAN L. ARRISON

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

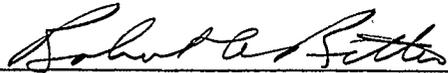
CALGARY, ALBERTA

JUNE 1972

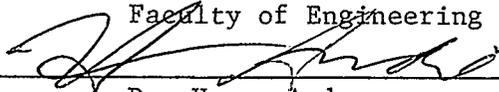
© N. L. Arrison 1972

THE UNIVERSITY OF CALGARY
FACULTY OF GRADUATE STUDIES

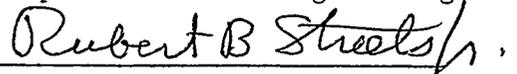
The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Butyl Acetate System", submitted by Norman L. Arrison, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.



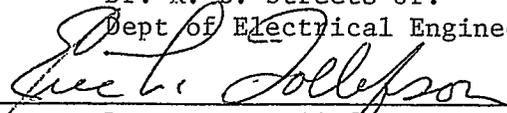
Supervisor: Dr. R. A. Ritter
Faculty of Engineering



Dr. H. Andre
Dept of Chemical Engineering



Dr. R. B. Streets Jr.
Dept of Electrical Engineering



Dr. E. L. Tollefson
Dept of Chemical Engineering



External Examiner: Dr. F. D. Otto
Dept of Chemical Engineering
University of Alberta

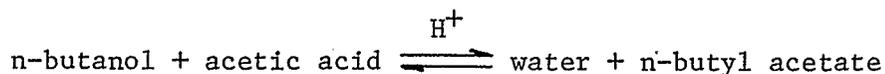
June 23, 1972

Date

ABSTRACT

The production of n-butyl acetate by esterification in a reaction distillation column is investigated by the use of an experimental pilot plant column. In order to properly examine and simulate the pilot plant column on the hybrid computer, vapor-liquid equilibrium data and kinetics data are gathered. To obtain the necessary vapor-liquid equilibrium data, two approaches are used. First a new vapor-liquid equilibrium still is designed capable of handling reaction and two liquid phase systems. The still is then used to collect experimental data on the two ternary systems (water, acetic acid, butanol) and (acetic acid, butanol, butyl acetate). The second approach to obtain vapor-liquid equilibrium data is to investigate the possibility of predicting the data with two new activity coefficient correlations strongly recommended in the literature. Unfortunately, the results are mainly negative.

Kinetics data for the esterification reaction



is collected from still studies and from runs on the pilot plant column at steady state. The data is used to develop a kinetics rate equation with a wider range than is presently available in the literature.

With the vapor-liquid equilibrium correlations and the kinetics rate equations the esterification column is successfully simulated on the hybrid computer. The information obtained illustrates how four times the n-butyl acetate can be produced from a distillation column as compared to that which would be produced by operating the

same column in previously studied ranges. However, the experimental studies show that to obtain the higher production, fouling problems occur; and the separation system must be more sophisticated for the product stream.

ACKNOWLEDGEMENTS

The author expresses his appreciation to the following persons and organizations for their assistance in this work:

Dr. R. A. Ritter for his advice, encouragement, and helpful criticism;

Mr. D. G. Turnbull for his aid and assistance during construction and design of the esterification column;

Dr. F. P. Stainthorp for his supervision and detailed criticism during the experimental work on the esterification column;

Mr. J. McRae for assistance on the hybrid computer; and to

The National Research Council of Canada and the G. A. Gaherty Memorial Foundation for their financial assistance.

DEDICATED TO MY WIFE
FLORENCE

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	x
LIST OF FIGURES	xiv
Chapter	
1. INTRODUCTION	1.01
2. LITERATURE REVIEW	2.01
2.1 Literature Review Outline	2.01
2.2 Vapor-Liquid Equilibrium Studies	2.01
2.3 Esterification Column Studies	2.05
2.4 Simulation of Esterification Columns	2.06
3. VAPOR-LIQUID EQUILIBRIUM STUDIES	3.01
3.1 Vapor-Liquid Equilibrium Studies Outline	3.01
3.2 Description of Vapor-Liquid Equilibrium Still and Related Apparatus	3.01
3.3 Procedure for Operating Vapor-Liquid Equilibrium Still	3.05
3.4 Vapor-Liquid Equilibrium Data Taken from Still	3.07
3.5 Discussion and Conclusions of Vapor-Liquid Equilibrium Experimental Data Gathering	3.19
3.6 Binary and Ternary Activity Coefficient Curve Fitting	3.24
3.7 Analysis of Binary Activity Coefficient Curve Fitting	3.25
3.7.1 Binary Curve Fitting Results for Acetic Acid and Water	3.26
3.7.2 Binary Curve Fitting Results for Water and Butanol	3.26

Chapter		Page
3.7.3	Binary Curve Fitting Results for Water and Butyl acetate	3.27
3.7.4	Binary Curve Fitting Results for Acetic Acid and Butanol	3.28
3.7.5	Binary Curve Fitting Results for Acetic Acid and Butyl acetate	3.28
3.7.6	Binary Curve Fitting Results for Butanol and Butyl acetate	3.28
3.7.7	Discussion and Conclusions of Binary Activity Coefficient Curve Fitting	3.29
3.8	Analysis of Ternary Activity Coefficient Curves	3.30
3.8.1	Results of Curve Fitting the Data for the Water, Acetic Acid, and Butanol Ternary System	3.31
3.8.2	Results of Curve Fitting the Data for the Acetic Acid, Butanol, and Butyl acetate Ternary System	3.35
3.8.3	Results of Curve Fitting the Data for the Water, Butanol, and Butyl acetate Ternary System	3.39
3.9	Discussion and Conclusions of Ternary Activity Coefficient Curve Fitting	3.44
4.	EXPERIMENTAL PILOT PLANT ESTERIFICATION COLUMN DESCRIPTION OPERATION, AND DATA GATHERING	4.01
4.1	Experimental Esterification Column Description, Operation, and Data Gathering Outline	4.01
4.2	Description of Esterification Column and Procedure of Operation	4.01
4.2.1	Description of Esterification Column	4.02
4.2.2	Experimental Procedure for the Esterification Column	4.09
4.3	Analysis of Data Gathered from the Esterification Column	4.11

Chapter	Page
4.3.1 Steady State Data of the Esterification Column	4.11
4.3.1.1 Effect of Catalyst Concentration on Column Operation	4.14
4.3.1.2 Effect of Boil-up Rate on Column Operation	4.19
4.3.1.3 Effect of Feed Rate on the Column	4.21
4.3.1.4 Effect of Feed Ratio on the Column	4.23
4.3.2 Mass Balance of Esterification Column	4.24
4.3.3 Heat Balance on Esterification Column	4.27
4.3.4 Kinetics Calculations from Steady State Esterification Data	4.29
4.3.5 Transient Data from the Esterification Column	4.37
4.3.5.1 Catalyst Step Change	4.38
4.3.5.2 Steam Step Change	4.42
4.3.5.3 Feed Flow-Rate Step Change	4.48
4.3.5.4 Feed Composition Step Change	4.52
4.4 Discussion of Steady State and Transient Experimental Behaviour of the Esterification Column	4.61
5. HYBRID MODEL OF ESTERIFICATION COLUMN	5.01
5.1 Hybrid Model of Esterification Column Outlines	5.01
5.2 General Description of the Column and the System Data Used	5.01
5.3 Mathematical Model of the Esterification Column	5.07
5.4 Hybrid Computer Solution of Simulation Equations	5.15
5.4.1 Contribution by the 680 Analog Computer to the Solution of the Mathematical Model	5.15

Chapter	Page
5.4.2 Contribution by the 680 Digital Logic Computer to the Solution of the Mathematical Model	5.19
5.4.3 Contribution by the 640 Digital Computer to the Solution of the Mathematical Model . .	5.19
5.5 Results of the Hybrid Computer Simulation . .	5.23
5.5.1 Simulated Catalyst Step Change	5.23
5.5.2 Simulated Boil-up Step Change	5.25
5.5.3 Simulated Flow Rate Step Change	5.26
5.5.4 Simulated Acetic Acid Concentration Change in the Column Feed	5.27
5.6 Summary and Conclusions to the Simulation Studies	5.29
6. SUMMARY AND CONCLUSIONS	6.01
BIBLIOGRAPHY	6.07
APPENDICES	A0.0
1. Description of Computer Programs	A1.01
2. Tables Giving Margules, Renon, Wilson and Van Laar Fits to Experimental Data	A2.01
3. Experimental Vapor-Liquid Equilibrium Data	A3.01
4. Esterification Column Experimental Data	A4.01
5. Statistical Terms	A5.01
6. Filter Description	A6.01
7. Esterification Column Transient Data	A7.01

LIST OF TABLES

Table	Page
3.81 Margules-Ternary Water-Acetic Acid-Butanol	3.32
3.82 Margules-Ternary Acetic Acid-Butanol-Butyl acetate .	3.37
3.83 Margules-Ternary Water-Butanol-Butyl acetate	3.40
3.84 Margules-Ternary Water-Butanol-Butyl acetate	3.41
A2.11 Water-Acetic Acid System	A2.01
A2.12 Water-Butanol System	A2.02
A2.13 Water-Butyl acetate System	A2.03
A2.14 Acetic Acid-Butanol System	A2.04
A2.15 Acetic Acid-Butyl acetate System	A2.05
A2.16 Butanol-Butyl acetate System	A2.06
A2.31 Renon-Ternary Water-Acetic Acid-Butanol	A2.07
A2.32 Renon-Ternary Water-Acetic Acid-Butanol	A2.08
A2.33 Renon-Ternary Water-Acetic Acid-Butanol	A2.09
A2.34 Wilson-Ternary Water-Acetic Acid-Butanol	A2.10
A2.35 Wilson-Ternary Water-Acetic Acid-Butanol	A2.11
A2.36 Renon-Ternary Acetic Acid-Butanol-Butyl acetate . .	A2.12
A2.37 Renon-Ternary Acetic Acid-Butanol-Butyl acetate . .	A2.13
A2.38 Renon-Ternary Acetic Acid-Butanol-Butyl acetate . .	A2.14
A2.39 Wilson-Ternary Acetic Acid-Butanol-Butyl acetate . .	A2.15
A2.40 Wilson-Ternary Acetic Acid-Butanol-Butyl acetate . .	A2.16
A2.41 Renon-Ternary Water-Butanol-Butyl acetate	A2.17
A2.42 Renon-Ternary Water-Butanol-Butyl acetate	A2.18
A2.43 Renon-Ternary Water-Butanol-Butyl acetate	A2.19

Table	Page
A2.44	Wilson-Ternary Water-Butanol-Butyl acetate A2.20
A2.45	Wilson-Ternary Water-Butanol-Butyl acetate A2.21
A2.46	Wilson-Ternary Water-Butanol-Butyl acetate A2.22
A3.11	Experimental Data for Ternary Vapor-Liquid Equili- brium System Acetic Acid, Butanol, and Butyl acetate A3.01
A3.12	Experimental Data for Ternary Vapor-Liquid Equili- brium System Water, Acetic Acid, and Butanol A3.02
A3.21	Predicted Ternary Vapor Composition Using Margules Equation A3.03
A3.22	Predicted Ternary Vapor Composition Using Margules Equation A3.04
A3.23	Vapor Composition in Mole Fraction Giving Only the First Two Concentrations for the Ternary Water, Butanol and Butyl acetate A3.05
A3.31	Binary Data for n-Butanol and n-Butyl acetate A3.06
A3.32	Binary Data for Acetic Acid and Butanol A3.07
A3.33	Binary Data for Acetic Acid and n-Butyl acetate A3.08
A3.34	Binary Data for Acetic Acid and Water A3.09
A4.11	Weight Percent Composition of Reboiler at Steady State A4.01
A4.12	Weight Percent Composition of Feed Plate at Steady State A4.02
A4.13	Weight Percent Composition of Oil Layer in Decanter at Steady State A4.03

Table	Page	
A4.21	Temperature of Esterification Column Plate at Steady State in Degrees Centigrade	A4.04
A4.22	Column D/P, Reflux Rate, Cooling Water Rate, and Cooling Water Temperature Change	A4.05
A4.31	Steady State Mass Balance in Grams	A4.06
A4.32	Steady State Mass Balance in Moles	A4.07
A4.33	Steady State Heat Balance on Esterification Column .	A4.08
A4.34	Steady State Heat Transfer Coefficient and Temperature Difference	A4.09
A4.41	Composition of Esterification Plates at Steady State in Weight Percent	A4.10
A4.42	Composition of Esterification Plates at Steady State in Weight Percent	A4.11
A4.43	Composition of Esterification Plates at Steady State in Weight Percent	A4.12
A4.44	Composition of Esterification Plates at Steady State in Weight Percent	A4.13
A4.45	Composition of Esterification Plates at Steady State in Weight Percent	A4.14
A4.46	Composition of Esterification Plates at Steady State in Weight Percent	A4.15
A7.1	Transient for Catalyst Step Change in Reboiler . . .	A7.01
A7.2	Transient for Catalyst Step Change on Feedtray . . .	A7.02
A7.3	Transient for Steam Step In Reboiler	A7.03

Table		Page
A7.4	Transient for Steam Step on Feedtray	A7.04
A7.5	Transient for Flow-rate Step Change in Reboiler .	A7.05
A7.6	Transient for Flow-rate Step Change on Feedtray .	A7.06
A7.7	Transient for Acetic Acid Feed Concentration Step Change in Reboiler	A7.07
A7.8	Transient for Acetic Acid Feed Concentration Step Change on Feedtray	A7.08

LIST OF FIGURES

Figure		Page
3.1	Schematic of Vapor-Liquid Equilibrium Still	3.02
3.2	Schematic of Thermocouple Circuit Used to Obtain Temperatures From Vapor-Liquid Equilibrium Still	3.04
3.3	Butanol and Butyl acetate Binary	3.08
3.4	Acetic Acid and Butanol Binary	3.08
3.5	Acetic Acid and Butyl acetate Binary	3.10
3.6	Water and Acetic Acid Binary	3.12
3.7	Water and Acetic Acid Binary	3.13
3.8	Water and Acetic Acid Binary	3.14
3.81	Ternary Vapor-Liquid Equilibrium Diagram For Acetic Acid, Butanol, and Butyl acetate	3.16
3.82	Ternary Vapor-Liquid Equilibrium Diagram For Water, Acetic Acid, and Butanol	3.18
3.83	Ternary Vapor-Liquid Data by Brunjes and Furnas (4)	3.20
3.91	Ternary Data Calculated by Margules Activity Coefficient Equations	3.34
3.92	Ternary Data Calculated by Margules Activity Coefficient Equations	3.38
3.93	Ternary Data Calculated by Margules Activity Coefficient Equations	3.43
4.1	Schematic of Pilot Plant Esterification Column	4.03
4.10	Esterification Column Legend	4.04
4.11	Steady State Composition of Reboiler	4.12
4.12	Steady State Composition of Feedtray	4.13

Figure	Page	
4.21	Steady State Concentration of Sulphuric Acid in Reaction Zone	4.15
4.22	Steady State Steam Feed Rate	4.15
4.23	Steady State Feed Rate to Feedtray	4.16
4.24	Steady State Concentration of Acetic Acid in Feed . . .	4.16
4.31	Steady State Temperature Throughout Column for Run No. 6	4.30
4.32	Steady State Temperature Throughout Column for Run No. 8	4.30
4.33	Steady State Temperature Throughout Column for Run No. 23	4.31
4.34	Steady State Temperature Throughout Column for Run No. 29	4.31
4.41	Component Composition Through Column at Steady State for Run No. 6	4.33
4.42	Component Composition Through Column at Steady State for Run No. 8	4.33
4.43	Component Composition Through Column at Steady State for Run No. 23	4.34
4.44	Component Composition Through Column at Steady State for Run No. 29	4.34
4.45	Reaction Rate Constant 'k' as a Function of the Sulfuric Acid Concentration in a Mixture of Butanol, Acetic Acid, and Butyl acetate for Equation 4.34 . . .	4.36

Figure		Page
4.51	Acetic Acid Transient for Catalyst Step Change in Reboiler	4.39
4.52	Butanol Transient for Catalyst Step Change in Reboiler	4.39
4.53	Butyl acetate Transient for Catalyst Step Change in Reboiler	4.39
4.54	Water Transient for Catalyst Step Change on Feedtray	4.40
4.55	Acetic Acid Transient for Catalyst Step Change on Feedtray	4.40
4.56	Butanol Transient for Catalyst Step Change on Feedtray	4.40
4.57	Butyl acetate Transient for Catalyst Step Change on Feedtray	4.41
4.58	Temperature Transient for Catalyst Step Change in Reboiler	4.41
4.59	Temperature Transient for Catalyst Step Change on Tray 10	4.41
4.61	Acetic Acid Transient for Steam Step Change in Reboiler	4.43
4.62	Butanol Transient for Steam Step Change in Reboiler	4.43
4.63	Butyl acetate Transient for Steam Step Change in Reboiler	4.44
4.64	Water Transient for Steam Step Change on Feedtray .	4.44
4.65	Acetic Acid Transient for Steam Step Change on Feedtray	4.44

Figure		Page
4.66	Butanol Transient For Steam Step Change on Feedtray	4.45
4.67	Butyl acetate Transient for Steam Step Change on Feedtray	4.45
4.68	Temperature Transient for Steam Step Change in Reboiler	4.46
4.69	Temperature Transient for Steam Step Change on Tray 10	4.46
4.71	Acetic Acid Transient for Flow-rate Step Change in Reboiler	4.49
4.72	Butanol Transient for Flow-rate Step Change in Reboiler	4.49
4.73	Butyl acetate Transient for Flow-rate Step Change in Reboiler	4.49
4.74	Water Transient for Flow-rate Step Change on Feedtray	4.50
4.75	Acetic Acid Transient for Flow-rate Step Change on Feedtray	4.50
4.76	Butanol Transient for Flow-rate Step Change on Feedtray	4.50
4.77	Butyl acetate Transient for Flow-rate Step Change on Feedtray	4.51
4.79	Temperature Transient for Flow-rate Step Change on Tray 10	4.51
4.80	Water Transient for Acetic Acid Feed Concentration Step Change in Reboiler	4.53
4.81	Acetic Acid Transient for Acetic Acid Feed Concentration Step Change in Reboiler	4.53

Figure	Page	
4.82	Butanol Transient for Acetic Acid Feed Concentration Step Change in Reboiler	4.54
4.83	Butyl acetate Transient for Acetic Acid Feed Concentration Step Change in Reboiler	4.55
4.84	Water Transient for Acetic Acid Feed Concentration Step Change on Feedtray	4.56
4.85	Acetic Acid Transient for Acetic Acid Feed Concentration Step Change on Feedtray	4.56
4.86	Butanol Transient for Acetic Acid Feed Concentration Step Change on Feedtray	4.57
4.87	Butyl acetate Transient for Acetic Acid Feed Concentration Step Change on Reboiler	4.57
4.88	Temperature Transient for Acetic Acid Feed Concentration Step Change in Reboiler	4.58
4.89	Temperature Transient for Acetic Acid Feed Concentration Step Change on Tray 10	4.58
5.21	Mole Fraction of Water in the Vapor as a Function of the Mole Fraction of Water in the Liquid	5.04
5.22	Mole Fraction of Acetic Acid in the Vapor as a Function of the Mole Fraction of Acetic Acid in the Liquid	5.05
5.23	Mole Fraction of Butyl acetate in the Vapor as a Function of the Mole Fraction of Butyl acetate in the Liquid	5.06
5.31	Schematic of One Generalized Tray of the Esterification Column	5.10

Figure		Page
5.32	Schematic of Linear Equations Describing Two-Phase Liquid Region for the Water, Butanol, and Butyl acetate Ternary System	5.14
5.41	Analog Flow Chart of Hybrid Simulation	5.17
5.42	Legend of Analog Flow Chart of Hybrid Simulation . .	5.18
5.43	Digital Logic Flow Chart of Hybrid Simulation . . .	5.20
5.44	Flow Chart of Monitor Program of Hybrid Simulation .	5.21

CHAPTER 1 INTRODUCTION

1.1 Introduction to n-Butyl acetate Esterification Studies

In research, the quest for knowledge on one topic often necessitates the examination of related subjects. The information brought forth on the related areas is sometimes as important as that of the initial objective of the study. This study on the esterification of butyl acetate* by the use of a reaction distillation column, is such an investigation.

The initial purpose of the investigation is to study the manufacture of butyl acetate from butanol** and acetic acid. The reason for studying the process is to explore the possibility of better production methods for greater capital return and to know the behaviour of the process so that it can be properly incorporated into a large integrated plant operation. A proper examination of any system is achieved through a close study by actual experimentation and then a simulation to verify that the forces thought to be controlling are, in actual fact, the dominant ones. Thus this work examines the esterification of butyl acetate directly by building a pilot plant esterification column and operating it to obtain steady-state and transient data; then the pilot plant column is simulated on a hybrid computer. The initial designing, building, and operation of the pilot plant esterification column is accomplished by using data by Leyes and Othmer (19). Because the range of the investigation is extended beyond

*The term 'butyl acetate' throughout this work will mean n-butyl acetate.

**The term 'butanol' throughout this work will mean n-butanol.

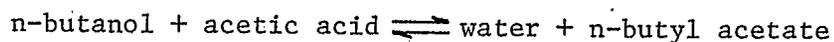
that done by Leyes and Othmer, simulation studies cannot be carried out on the hybrid computer to match experimental ranges until vapor-liquid equilibrium information and kinetics equations are obtained for the wider ranges. Hence, the study is expanded to include an investigation into vapor-liquid equilibrium data and the creation of a new and broader kinetic equation. Both are independent studies but provide information necessary for a proper simulation and, hence, examination of the manufacture of butyl acetate.

Vapor-liquid equilibrium data are the first basic information obtained. The attempt to establish the required correlations followed two paths. First, a newly designed vapor-liquid equilibrium still is erected which has a fast enough transient to equilibrium to reach steady state before the effects of reaction become large. The vapor-liquid equilibrium still is also designed to handle two-phase liquid systems. Using the still, vapor-liquid equilibrium data are collected on the four binary systems (butanol, butyl acetate), (butanol, acetic acid), (butyl acetate, acetic acid), and (water, acetic acid) and on the two ternary systems (water, acetic acid, butanol) and (acetic acid, butanol, butyl acetate). The second approach examines two new predictive methods in the literature, by Renon (29) and Wilson (16), for calculating ternary and quaternary data from binary data. Since the Margules (12) and Van Laar (12) equations are well known, the predictive and curve fitting ability of the Renon and Wilson equations are compared to them for the systems involved in this study.

The literature (7); (16), (27), (29) presently predicts that the Renon equation should out-perform others in immiscible systems

while the Wilson equation should show its strength in miscible systems. To least-squares curve fit the Renon and Wilson equations, it is found necessary to use complex regression routines (22). Although the Margules equation is shown to be best from a curve-fitting point of view, all four equations prove of little use for prediction in the systems studied in this investigation. As a result of the failure of the above equations to predict data with reasonable precision, the data required for the quaternary system are obtained by using the ternary system which is the closest approximation on a given tray. Since the simulated data from the esterification column agree reasonably well with the experimental data, the indications are that the above approach worked.

Using the vapor-liquid equilibrium data obtained from the still and from the literature, kinetics data for the reversible reaction



are calculated by a steady state model from pilot plant esterification column data. The information is combined with kinetics data obtained from the still to produce a rate equation applicable to a wide composition range. The kinetics rate equations, calculated from the pilot plant and still data by a digital computer, are modified for the dynamic model on the hybrid computer so that the hybrid simulation and experimental results are forced to agree at steady state.

The information obtained above is used in the hybrid model. The physical property correlations provided to the hybrid computer model and the assumptions made in developing the model are such that fairly close simulations of the experimental results are produced. In

producing the results, a number of important lessons are learned on the use of hybrid computers as a computational tool.

The topics discussed above can be separated into three categories under the general headings of vapor-liquid equilibrium studies, experimental pilot plant esterification column studies, and hybrid simulation studies. Hence, this work is separated into three sections. The first section discusses the new vapor-liquid equilibrium still and data obtained from it along with the testing of the Margules, Renon, Wilson, and Van Laar equations for curve fitting and prediction purposes. The second section presents the pilot plant esterification column with the data obtained from it and the kinetics rate equation. The third section states the equations, assumptions, and approximations used to simulate the pilot plant esterification column and analyzes the results of the simulation on the hybrid computer.

CHAPTER 2 LITERATURE REVIEW

2.1 Literature Review Outline

Three parts make up the following literature review. The first covers the design of vapor-liquid equilibrium stills, the gathering of data, and the curve fitting of the experimental data. The second section examines the literature regarding continuous esterification columns. The third discussion concerns the literature related to the application of hybrid computer techniques in the simulation of esterification columns.

2.2 Vapor-Liquid Equilibrium Studies

Hála et al. (12) is the handbook of those working in the field of vapor-liquid equilibrium studies. The book covers the theory well, giving a detailed literature review along with developments of equations and numerous practical examples. Because the book was published in 1967, it does not have all the latest expressions for the excess Gibbs energy, such as the Renon equation; however, it covers all earlier ones. Hála et al do an excellent job of cataloguing and critically examining all vapor-liquid equilibrium equipment that has been used in studies published. Their suggested methods are of superb assistance; and if not used, they at least alert one to possible experimental error. The book also has a summary (up to 1967) of what Hála et al believe to be all the systems studied for their vapor-liquid equilibrium relationships. The book's greatest fault lies in some of the facts it accepts at face value from the literature.

One paper referenced by Hála et al is theirs (11). The paper gives experimental data on the ternary system water, butanol, and butyl acetate. The experimental data of the paper err on the composition of the binary azeotrope between butanol and butyl acetate. Hála et al give the azeotrope composition to be 0.2 and 0.8 mole fraction butanol and butyl acetate respectively when it should be 0.7 butanol and 0.3 butyl acetate as given by Brunjes and Furnas (5). Hence the binary azeotropes' composition is in error 0.5 mole fraction. After presenting experimental data, the paper (11) goes on to fit the experimental activity coefficients to the Margules equation. Because Hála et al use the binary Margules coefficients from Reference 26, they employ only one experimental point from the ternary system to calculate the Margules equations for the ternary activity coefficients. In this particular case, this turns out to be a misleading procedure. The second and third activity coefficients are fairly precise but the first one (for water) is in error enough to cause a third of the ternary diagram to be in error by 0.3 mole fraction or more. Hence the paper has an experimental error and a procedure for calculating activity coefficient curves which is faulty for immiscible ternary systems. Experimental data for the above system are given correctly by References (4), (5), (18), and (26).

Hirata and Hirose (13), (14) present all the experimental data necessary to completely describe the ternary system water, acetic acid, and butyl acetate. Where it is possible to check, the data agree with other authors (10), (24), (26). Data related to two ternaries encountered in the present study could not be found in the

literature; they are: water, acetic acid, and butanol; and acetic acid, butanol, and butyl acetate. The quaternary system needed for this study, namely water, acetic acid, butanol, and butyl acetate, is missing from the literature.

Hála et al (12) have very little criticism of the Othmer-Gilmont-Conti still for vapor-liquid equilibrium studies. Since they are not interested in the time to reach steady state (approximately 1 hour), it is suitable for their work. If the time to equilibrium can be no more than one minute, then the Othmer-Gilmont-Conti still cannot be used. If reaction is present in the system, it is vitally important to cut the time to reach equilibrium to a minimum. The only still that Hála et al (12) discuss with a short time constant is the Cathala dynamic still. The Cathala dynamic still is a flow still in which one component enters as a vapor and the other as a heated liquid. The two continuous streams are mixed and flashed in a chamber. The still's accuracy depends on the precision that the flow rates of the incoming vapor and liquid streams are measured with and on the efficiency of the flash separation.

Rius et al (30) proposed a combination flow and distillation still with a time constant of 30 seconds. The still operates by mixing the two reacting liquids and then super heating them before they are flashed in a chamber. The liquid is analyzed along with the condensed vapor. A question arises here as to the existence of equilibrium between the vapor and liquid phases. Since it is difficult to know, this apparatus can be improved upon. No other still in the literature except that of Rius et al is able to decrease the

time required for the study of reacting systems.

The Wohl expansion for the excess free enthalpy is explained in an excellent fashion by Hála et al (12). They show the direct relationship of the Wohl equation to the Scatchard, Van Laar, Margules, and Symmetrical equations. The Benedict, White, Li-Coull, Yu-Coull, Redlich-Kister, Black and Wilson equations are also discussed very briefly. The Wilson equation does not get the attention from Hála et al that it is at present getting in current literature. The Wilson equation has shown great ability to curve fit accurately the activity coefficients of many miscible systems. Its ability as a predictive equation for possible ternary and quaternary systems is also promising according to References (16) and (27). These two references use the Wilson equation on approximately 250 systems; it easily represents the data better than all other equations it is compared with in all tests. Hence, like all other equations when initially introduced in the literature, the Wilson equation shows great success. It remains for workers to show its weakness as they have for all other equations.

The Renon or NRTL equation is put forth by References (1), (7), and (29) as the equation which will work when the Wilson equation fails to fit or predict the data. Renon gives convincing arguments for his equation; however, it has yet to be tested extensively by anyone; or if it has, the results have not yet been published. The Renon equation is designed primarily for immiscible systems and contains a random constant* which is selected at various values depending on the

*The term 'random constant' in this study refers to the constant which Renon and Prausnitz (29) used to measure the degree of nonrandomness in liquid mixtures.

type of attraction between liquid molecules. Only practical testing will determine if the Renon equation is one of great practical importance, or just another in the long line of attempts to properly describe vapor-liquid equilibrium phenomena.

2.3 Esterification Column Studies

Leyes and Othmer (20) describe a study done on a small laboratory esterification column with a packed rectifying column for removing water. The study is carefully documented and gives all details necessary for a complete analysis of the laboratory column that is used to make butyl acetate from acetic acid and butanol. The greatest weakness in the data presented is the vapor-liquid equilibrium data for the quaternary system. Because of the need for simplicity, they assumed the concentration of a component in the vapor is only dependent on its own concentration in the liquid. Since they assumed the other components have no effect on a given component's concentration in the vapor, their data are badly scattered. Considering the assumption made, however, the behaviour of the curves for water, acetic acid, and butyl acetate is amazingly good.

Leyes and Othmer put forth a procedure for designing reacting distillation columns. The method in practice is of little use, however, because in almost any system with reaction, one has a multicomponent vapor-liquid equilibrium system with reaction and there is little likelihood that the necessary relationships needed for design will be available. Hence, a study to obtain the necessary vapor-liquid equilibrium data must be made or one must make his own small laboratory model

and test the total system completely. Since the latter suggestion is probably safer and easier, no one will bother collecting vapor-liquid equilibrium data for design.

Leyes and Othmer (19) conducted a batch study on the kinetics of the esterification reaction to obtain information for the verification of their reaction column design. The study is very well done over the range it covers. As a result, Leyes and Othmer developed a reaction rate equation which showed the effects of temperature and catalyst as well as the concentration of acetic acid and butanol on the reaction. Because the rate equation becomes meaningless if one goes slightly beyond the range covered by Leyes and Othmer (19) (negative values are produced), the equations can be greatly improved upon. The form of the Leyes and Othmer equation is also lacking in that it depends primarily on the concentration of acetic acid; whereas, kinetics theory would predict that both butanol and acetic acid should control the rate of reaction equally.

The work of Marek (21) is merely intended to inform workers on how to design a reaction distillation column when the kinetics and vapor-liquid equilibrium information are available. Since vapor-liquid equilibrium data is almost totally nonexistent for reacting systems, it is highly doubtful if anyone will ever use the work presented by Marek.

2.4 Simulation of Esterification Columns

Recently T. J. Williams (38) did an extensive literature review concerning all the latest work published on dynamic column

modeling. This review followed an early one (37). In his latest critique, he only comments on the unsteady state models; whereas, in the earlier study he examined what, in his opinion, was the best model of the time. The reason Williams only comments in his latest summary is because he feels nothing new has been contributed recently to the science of modeling distillation columns. Because general models such as those in Holland's textbook (15) cover every possible facet of a column, Williams is correct. However, the correlations of the physical data necessary to make the models work are missing or in need of improving in all cases.

Because the esterification column is just a column with chemical reaction, Williams' comments also hold true for it. Ruszkoy and Mitchell (31) point this out vividly. Their paper theoretically describes an esterification column assuming only that vapor hold-up and the downcomer time constants may be neglected and that perfect mixing occurs throughout the column. Hence, the model is a very complete one. Because Ruszkoy and Mitchell did not even attempt to run their hybrid model, the question of why arises. The reason is basically practical. First, in the literature there is no system in which all the basic physical data, such as reaction rates and vapor-liquid equilibrium correlations, are available. Secondly, the model has a few impractical approaches in it which make it difficult, if not impossible, to operate. Hence, the model which is complete and proper, theoretically, fails because of the practical lack of physical correlations and the errors made by the programmer in adapting the model for solution on the hybrid computer. Therefore, formulating the

problem is no longer a difficult task for any type of column; rather, the problem is one of ease of solution and of obtaining the necessary correlations for the dynamic models. Ruszkoy and Mitchell (31) were attempting to demonstrate why a hybrid computer was the most practical for the purposes of simulating an esterification column. Their arguments are persuasive. Since they did not actually verify them, there is no way of knowing whether they were correct or not.

Leyes and Othmer (20) and Marek (21) have proposed hand calculation techniques for simulating a steady state esterification column. Because the models described by the two works are simplified versions of Holland's textbook models previously discussed, they suffer from the same weaknesses. Hence, a physical information shortage and calculation problems make the models useless until research is done on any given system. Thus as with the unsteady state models, the problems can be defined but the numerical values and correlations are missing.

Coble (6) has compared the hybrid computer with the analog computer, the digital computer using CSMP, the digital computer using PACTOLUS, and the digital computer using standard FORTRAN techniques. His conclusions are that the analog is the fastest machine but requires a great deal of equipment. The Hybrid is slower than the analog but faster than the digital and doesn't require the large amount of equipment that the analog computer needs. However, the hybrid uses by far the greatest amount of programmer man hours. The three digital techniques are similar in results in that they are quick to program but require a great deal of digital computer time for obtaining a solution. All methods were about equal in precision. Hence, Coble

recommends the hybrid computer when a given problem must be solved quickly a great many times. In all other cases, except where a man-machine relationship is desired and the analog is suggested, Coble recommends the digital computer.

3.1 Vapor-Liquid Equilibrium Studies Outline

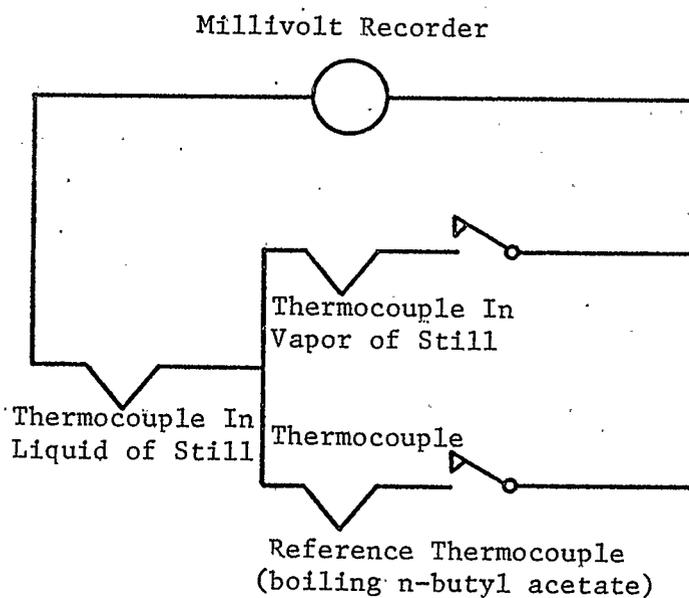
A description of the vapor-liquid equilibrium still designed for this study is given along with directions on its use. Data gathered from the still are then presented. The Margules, Renon, Van Laar, and Wilson equations are tested for their ability to correlate and predict six binary and three ternary systems. Errors in curve fitting are displayed through the use of diagrams and statistics.

3.2 Description of Vapor-Liquid Equilibrium Still and Related Apparatus

The still used to produce the vapor-liquid equilibrium samples is shown in Figure 3.1. It holds a maximum of 1200 cc of fluid. Three thermocouples play a vital function in the operation of the still and are shown in Figure 3.1 as T1, T2, and T3. T3 is a hot reference of pure butyl acetate to which T1 is compared to obtain the temperature of the boiling liquid. (A hot reference is used so that the milli-volt range can be expanded for greater sensitivity.) T1 and T2 are compared, after the last of the sample has been injected at E2, to see when the still reaches equilibrium. Figure 3.2 illustrates the electrical connections for T1, T2, and T3. E2 and E4 are tapered glass Luer fittings to which injection syringes can be coupled to add components or remove vapor samples respectively. The valves E3 connected to the syringe fittings are three-way dog-leg valves. This ensures that the valves are always purged. A third glass valve (E5 on Figure 3.1) is at the bottom of the still and it has a fine bore. This straight-

VAPOR-LIQUID EQUILIBRIUM STILL LEGEND

E1	Vapor inlet (sloped 45 degrees) and liquid collector
E2	Tapered glass Luer fitting for injecting liquid
E3	Dog-leg valves
E4	Tapered glass Luer fitting for removing liquid
E5	Valve for removing liquid sample
S1	Cooling water inlet to condenser
S2	Cooling water outlet from condenser
S3	Heating mantle for n-butyl acetate container
S4	Water or oil filled manometer
S5	Aluminum heater for still
T1	Thermocouple to measure liquid temperature
T2	Thermocouple to measure vapor temperature
T3	Thermocouple to measure reference temperature



Schematic of Thermocouple Circuit Used To Obtain
Temperatures From Vapor-Liquid Equilibrium Still
Figure 3.2

through valve is used to gather liquid samples. The sloping (45°) trough to catch the liquid that runs down the condenser walls has a hole (E1 in Figure 3.1) in it to allow the vapor entrance to the condenser. The condenser pressure is controlled by an air regulator (P on Figure 3.1) and the pressure is monitored on manometer S4 of Figure 3.1. The heater (S5 on Figure 3.1) is shown by the cross-hatching and is controlled by a standard variac. Maximum power is 1000 watts. The heating jacket about the hot reference, shown as S3 in Figure 3.1, has its own variac for ease of control. The shaded area in Figure 3.1 designates vacuum insulation; hence, the need for the bellows to allow the glass to expand and contract.

The gas chromatograph used to analyse the samples is a Varian Aerograph (Series 1700) with a Varian Aerograph recorder (Model 20). The separation column is a Porapak Q, 80 to 100 mesh, in a 0.125 in. teflon tube 6 ft long. The helium flow is 136 milliliters per minute, the temperature of the column is 215°C , and the sample size is 2.0 microliters.

If the sample is composed of two liquid layers when removed from the still, it is put on dry ice to cool. Once cooled the sample is shaken to form an emulsion so that a true representative sample can be obtained. All chemicals dealt with met A.C.S. standards.

3.3 Procedure for Operating Vapor-Liquid Equilibrium Still

The still equipment is washed internally with the chemicals to be studied. Program (1) of Appendix A1 is consulted for the most efficient way to add chemicals during the study to save both time and

chemicals. If no chemical reaction can occur, all the chemicals are added. Heating then begins. However, if reaction can occur, the chemicals that will not react together and that account for the greatest heat capacity are first added to the still. These are brought to a boil and then the other reacting component is injected at E2 on Figure 3.1. Heating proceeds until equilibrium is established as in the case when no reacting material is present. Equilibrium exists when T2 and T1 have equivalent temperatures. With reacting components, steady state occurred in 15 to 60 seconds. The temperature of the vapor and liquid phases in equilibrium is then taken by comparing T1 and T3. A liquid sample is withdrawn at E5. A vapor sample is removed using a dry ice cooled injection syringe at E4 on Figure 3.1. The equilibrium temperatures at T2 and T1 are checked as is the liquid temperature T2 by comparison again with T3. The pressure on the system is set and checked throughout the above procedure.

The syringe and sample bottles used to collect the samples of vapor and liquid from the still are all pre-cooled on dry ice as mentioned previously. This cools the solution removed and helps stop any loss of volatile components. If immiscible layers of liquid occur, the solution is cooled on dry ice until shaking provides a stable enough emulsion to obtain a truly representative sample.

Once a proper two-microliter sample is obtained, it is injected into the Varian gas chromatograph under the conditions previously stated in Section 3.2. Each sample from the still that goes into the gas chromatograph for analysis is accompanied by three calibration samples of the same approximate composition. Once the

integral strokes* are counted from all the gas chromatograph analyses, the values for each component in each sample are fed to Program (2) of Appendix A1 which totally converts the integral stroke values into normalized weight percent and mole fraction values.

3.4 Vapor-liquid Equilibrium Data Taken from Still

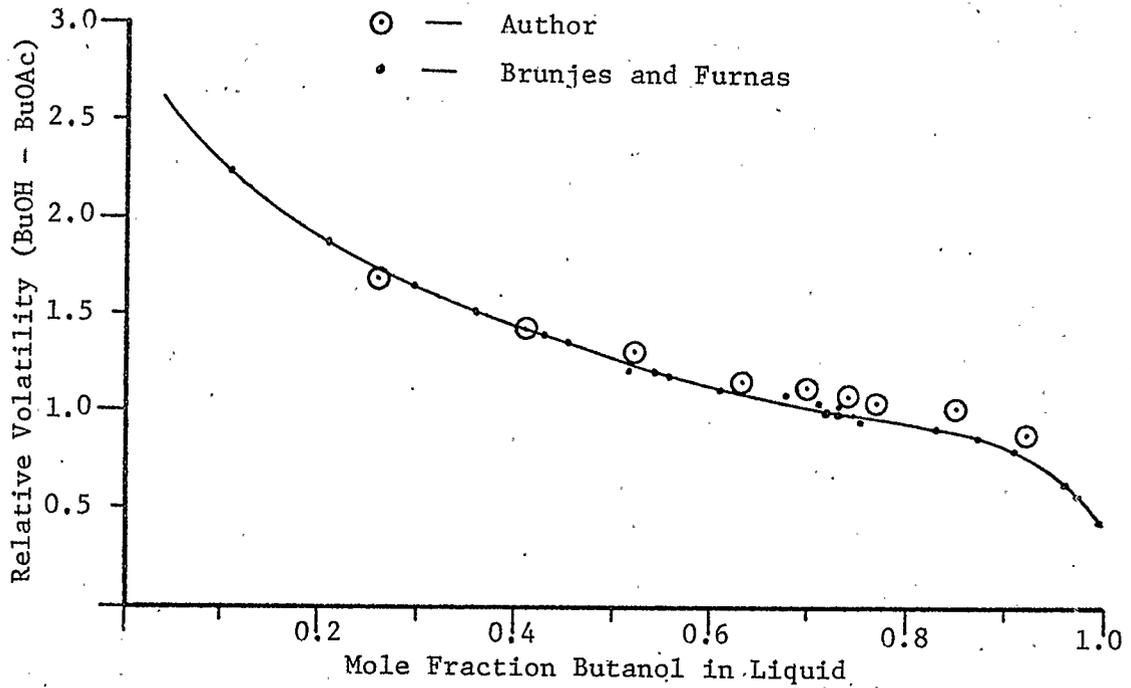
Six sets of vapor-liquid equilibrium data were taken using the still described in Section 3.2 . Four of those gathered were the binaries butanol and butyl acetate, acetic acid and butanol, acetic acid and butyl acetate, and acetic acid and water. (The data are given numerically in Tables A3.31, A3.32, A3.33 and A3.34 respectively.)

Two studied were the ternary systems acetic acid, butanol, and butyl acetate, and water, butanol, and acetic acid. (Tables A3.11 and A3.12 present this data.)

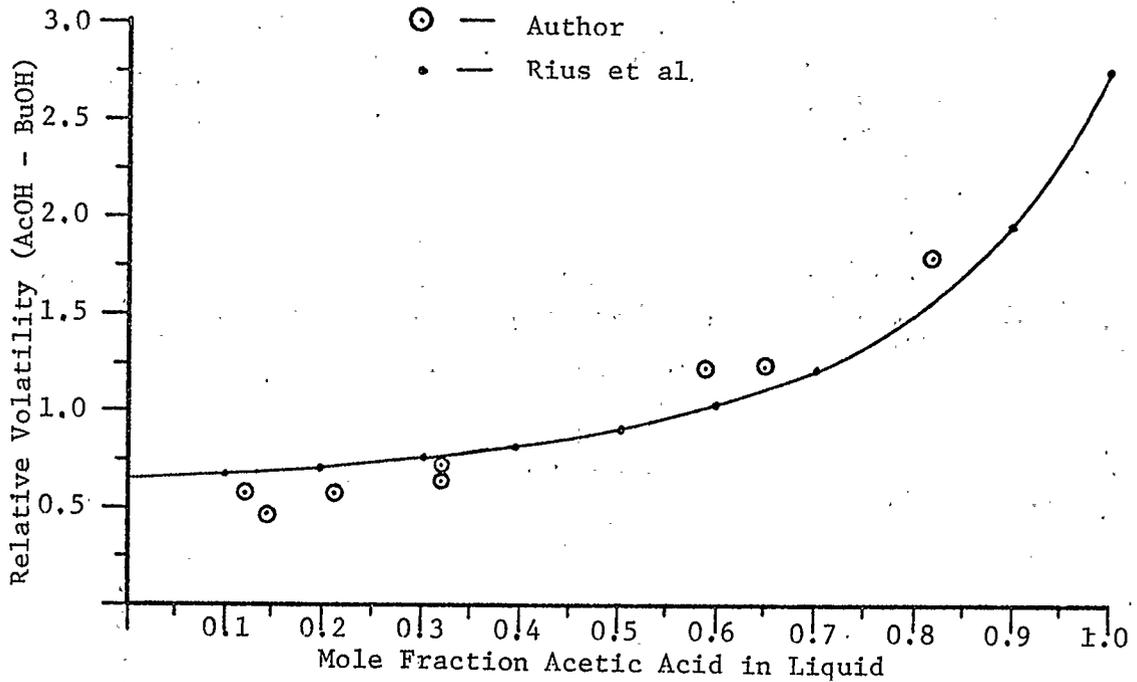
The four binaries have been examined by other workers; hence, they are used to verify the still design. Because the two ternary investigations are original work, they cannot be compared directly to previous work. As a result, a third ternary, water, butanol, and butyl acetate, investigated by Brunjes and Furnas (4), is examined as an aid in judging the quality of the work in this study.

For the binary butanol and butyl acetate, the relative volatilities of this study are shown compared to the values from the work of Brunjes and Furnas (5) in Figure 3.3 . (Relative volatility is compared because of its sensitivity to the smallest differences in

*The term 'integral stroke' refers to one unit of area under the curve produced by the gas chromatograph. The unit of area has different values depending on the scale being used.



Butanol and Butyl acetate Binary
Figure 3.3



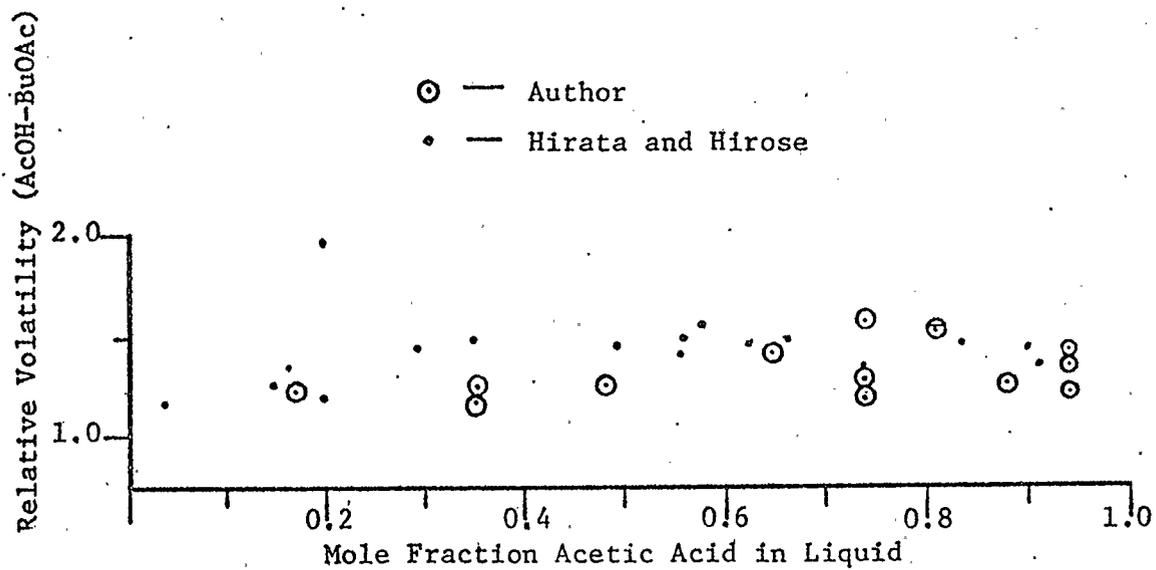
Acetic Acid and Butanol Binary
Figure 3.4

experimental data.) Note that the author's data indicate an azeotrope at a concentration of 0.8 to 0.85 mole fraction butanol. Hence, the data of Brunjes and Furnas differs in the position of the azeotrope by 0.1 mole fraction from the present work. Since the curves are flat in the area of the azeotrope, the error is not large. Note how the relative volatility data of the present work tend to produce a flatter gradient than the work by Brunjes and Furnas. Both data sets line up very well. The information from this study is unsmoothed. Whether Brunjes and Furnas smoothed their data or not is unknown.

The binary acetic acid and butanol has its relative volatility values found in this study compared to those found by Rius et al (30) in Figure 3.4. Both sets of data indicate the azeotrope position as 0.57 mole fraction butanol. Note that in this case, the author's data produce a slightly steeper gradient than that which results from the work of Rius et al. Rius et al stated that they smoothed the data they presented in their paper. The data of this study has again been left in its raw form.

The binary acetic acid and butyl acetate has its relative volatility values found in this study compared to those of Hirata and Hirose (13) in Figure 3.5. In this case, it is obvious that neither set of data has been smoothed. A dashed line indicates the approximate slope of the author's data while a solid line depicts roughly the slope produced by the data of Hirata and Hirose. The work done by Hirata and Hirose definitely indicates a steeper gradient than that of the present work.

Because the binary acetic acid and water has been studied extensively by a great number of investigators, it is examined in a

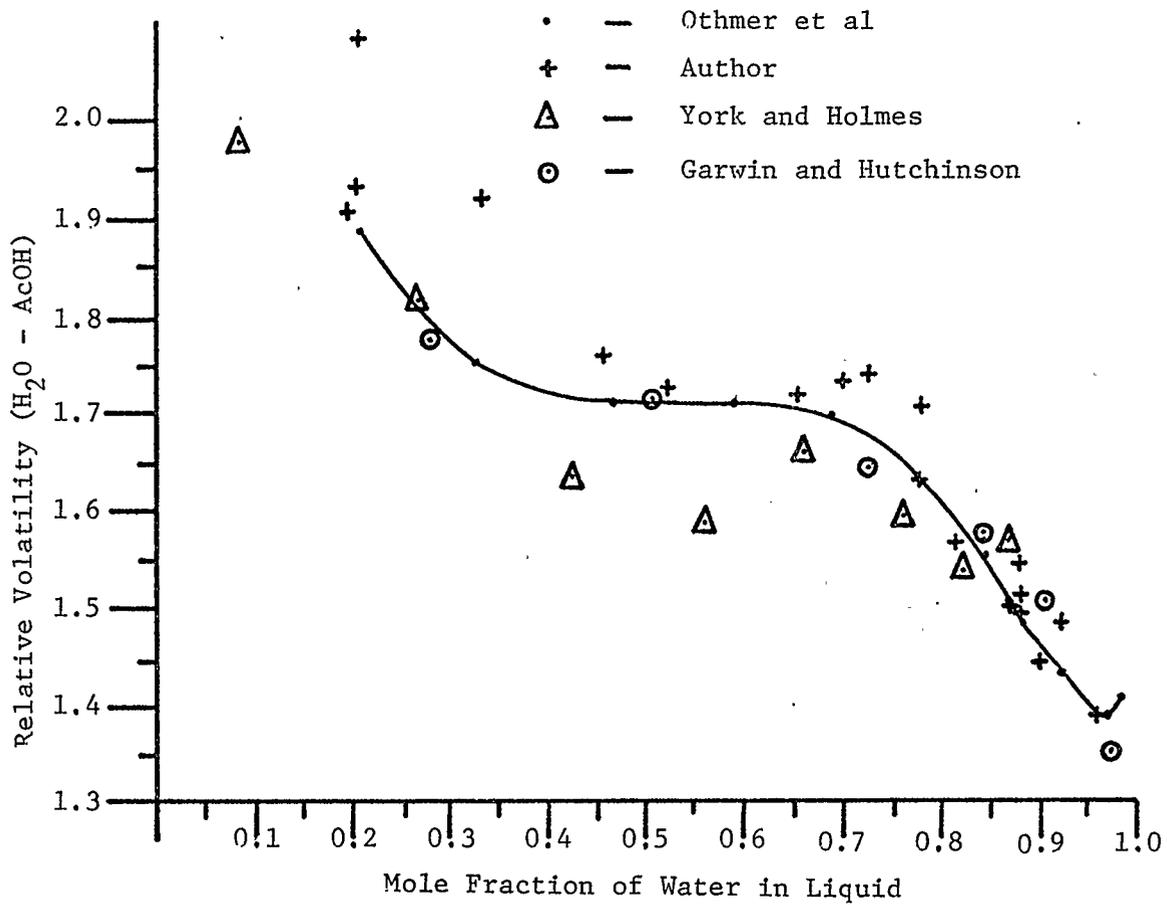


Acetic Acid and Butyl acetate Binary
Figure 3.5

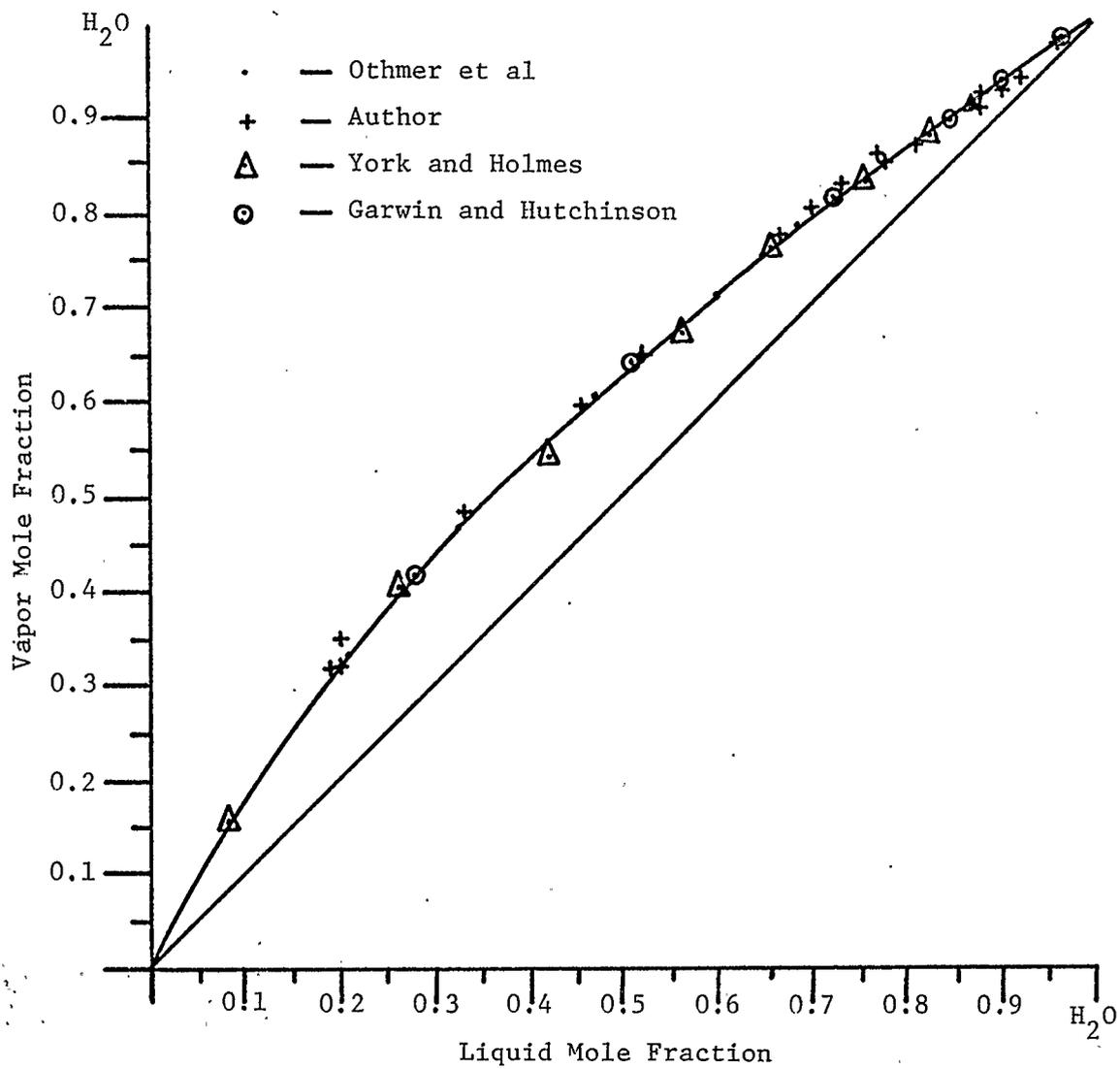
number of ways. This is done primarily to help the reader judge the quality of data taken from the still. Since plotting relative volatility values shows clearly even small differences in data, the data of this work and that by Garwin and Hutchinson (9), Othmer et al (25) and York and Holmes (38) are shown for comparison on Figure 3.6. The results by Othmer et al are the presently accepted correct values in the literature. As shown in Figure 3.6, the relative volatility curve from the data of Garwin and Hutchinson agrees well with that of Othmer et al. The relative volatility values from the data by York and Holmes are low compared to those of Othmer et al while the values produced by this study are slightly higher. The scatter of values in Figure 3.6 is about the same for York and Holmes' values and those of this study.

Figure 3.8 illustrates the acetic acid activity coefficients produced by the data from all four studies mentioned above. The activity coefficient values, from a mole fraction of 0.2 to 0.5, are higher according to the data of Garwin and Hutchinson and York and Holmes. The results of this study produce lower values but do not have the 'oscillation' effect of the Othmer et al data. The scatter in the data of York and Holmes appears worse than that occurring in the author's data in Figure 3.8. The data of Othmer et al lines up perfectly as does that of Garwin and Hutchinson. To illustrate how close in agreement all the data are, a McCabe-Thiele diagram (Figure 3.7) is shown with the data of all four studies. Figure 3.7 demonstrates clearly that for practical purposes the data of all studies are the same. The actual composition and temperature values for all data points found in this study are presented in Table A3.34.

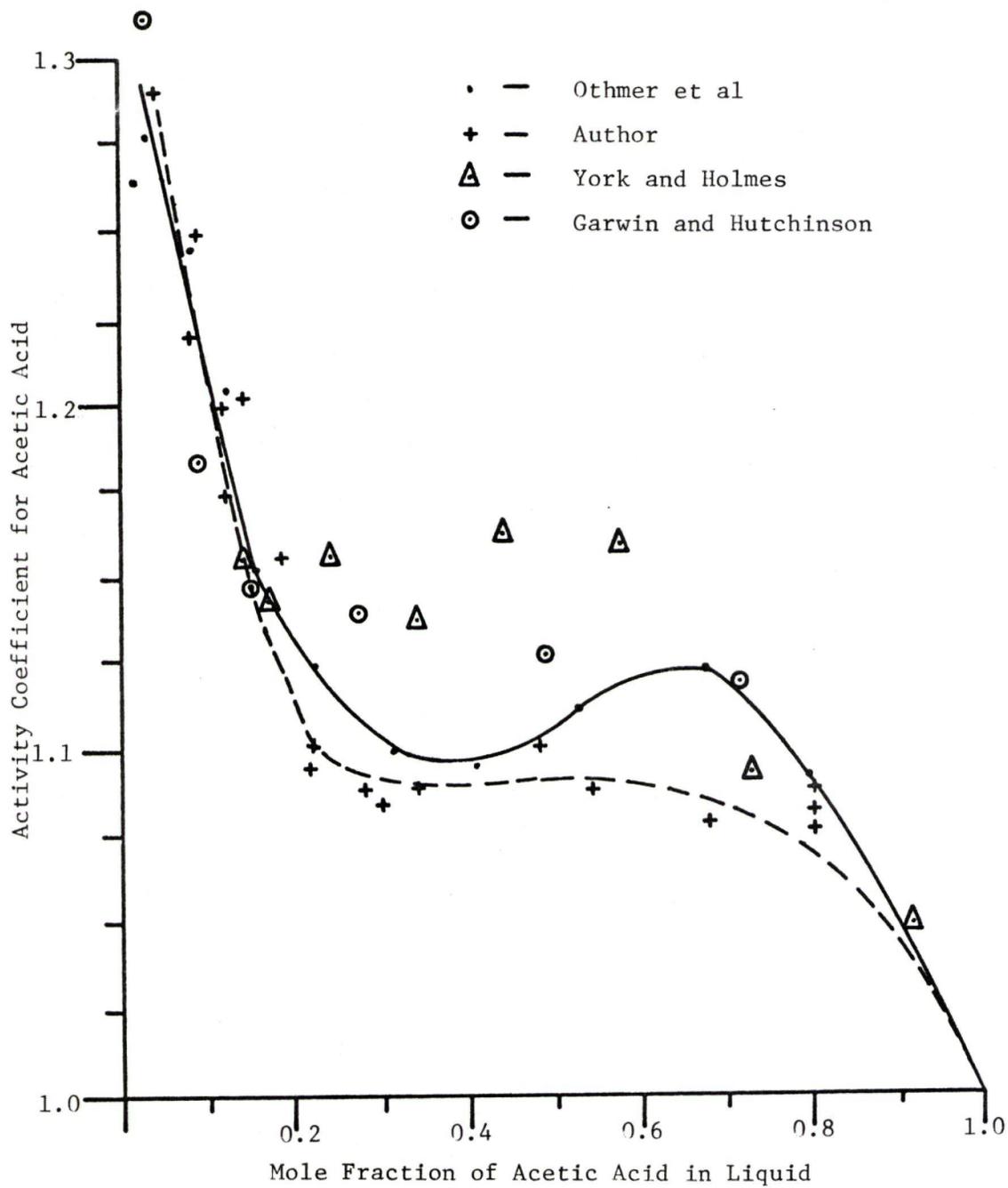
The ternary system acetic acid, butanol, and butyl acetate



Water and Acetic Acid Binary
Figure 3.6



Water and Acetic Acid Binary
Figure 3.7

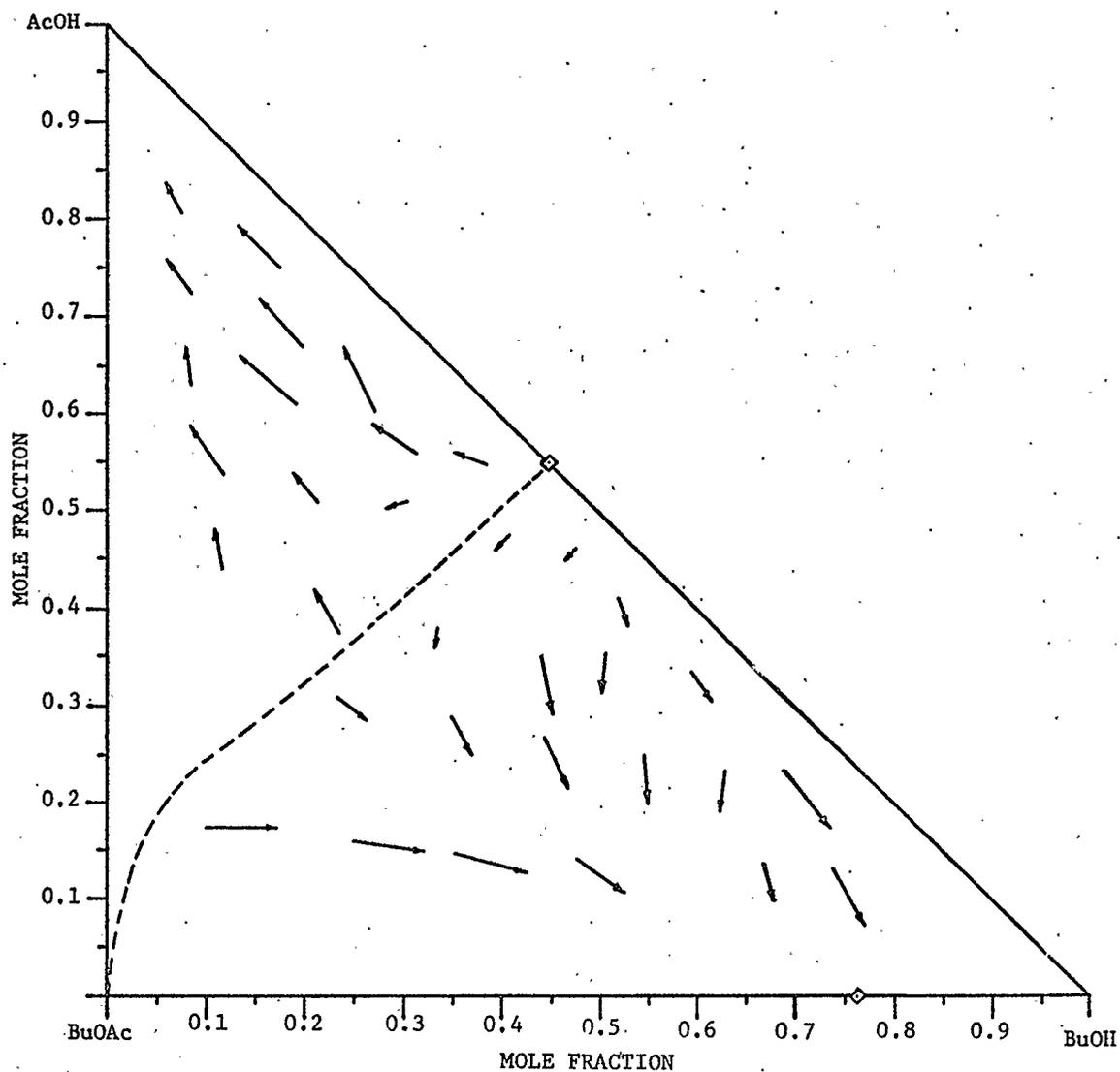


Water and Acetic Acid Binary
 Figure 3.8

is shown in Figure 3.81. The pressure on the system is one atmosphere. (The arrow heads in Figure 3.81 represent the vapor composition that is in equilibrium with the liquid composition at the arrow tail. The vapor and liquid equilibrium compositions of a given arrow have the same temperature. The arrow heads point in the direction of a decreasing temperature on the diagram.) Note that the system has a ridge which starts at the negative azeotrope* between acetic acid and butanol and goes across the diagram, in Figure 3.81, ending at the pure butyl acetate corner. The arrows, as a group, point away from the ridge and on one side bend towards pure acetic acid while on the other side the arrows bend toward the positive azeotrope between butanol and butyl acetate. The actual numerical values of the vapor-liquid equilibrium results shown in Figure 3.81 are given in Table A3.11 of Appendix 3.0.

Since the mole fractions in Table A3.11 do not add up to 1.0, it is apparent that reaction occurred. (The difference between the sum of the mole fractions and one represents the water mole fraction formed by reaction.) In the majority of the vapor-liquid equilibrium points obtained, the water mole fraction was kept well below 0.005 mole fraction in the liquid and at about 0.01 mole fraction in the vapor. In some cases, the mole fraction of water in the vapor jumped from 0.01 to 0.025. Since the effect of water is to carry butanol and butyl acetate in the ternary azeotrope, the concentrations

*The term 'negative azeotrope' means an azeotrope that boils at a higher temperature than the components making up the solution.

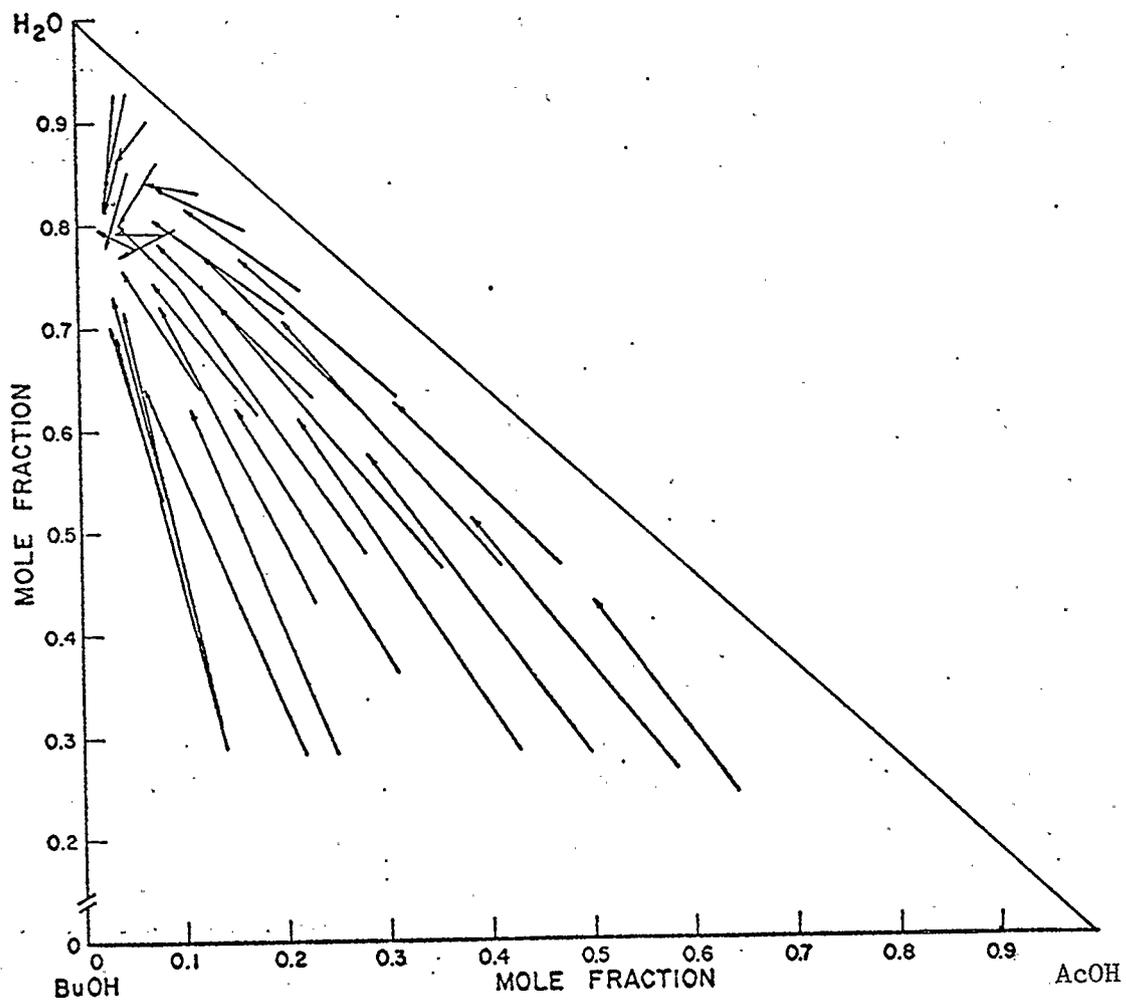


Ternary Vapor-Liquid Equilibrium Diagram
For Acetic Acid, Butanol, and Butyl Acetate (1 Atmosphere Pressure)
Figure 3.81

of butanol and butyl acetate are probably slightly too high in relation to acetic acid in the vapor for the vapor-liquid equilibrium data collected. Since the data were taken in 15 to 60 seconds in all cases, the data are probably more practical than it would be if no water due to reaction was present. This is because the speed of the reaction is such that in very few practical cases can the components be distilled without the reaction occurring as evidenced in this study. The effect of water on the temperature is unknown; however, the temperature is certain to be lower than it would be if no water were present; and over a period of about 6 minutes the temperature drops approximately 3.0°C when working with the still due to water which is produced by the reaction.

The water, acetic acid, and butanol ternary system, at one atmosphere pressure, is shown in Figure 3.82. (Again the arrow head composition is the vapor in equilibrium with a given liquid tail composition.) The high point in Figure 3.82 is the negative azeotrope between butanol and acetic acid. The low point is the positive azeotrope of water and butanol. Because no other azeotrope is present, no ridge or trough is formed and all the arrows point down the temperature gradient to the low boiling water-butanol azeotrope. The data presented in Figure 3.82 are given numerically in Table A3.12 of Appendix 3.0.

Since the values in Table A3.12 add up to nearly 1.0 in all cases for both the liquid and the vapor, it is apparent that very little reaction took place before the vapor-liquid equilibrium data were obtained. (Any difference from 1.0 represents butyl acetate formed by



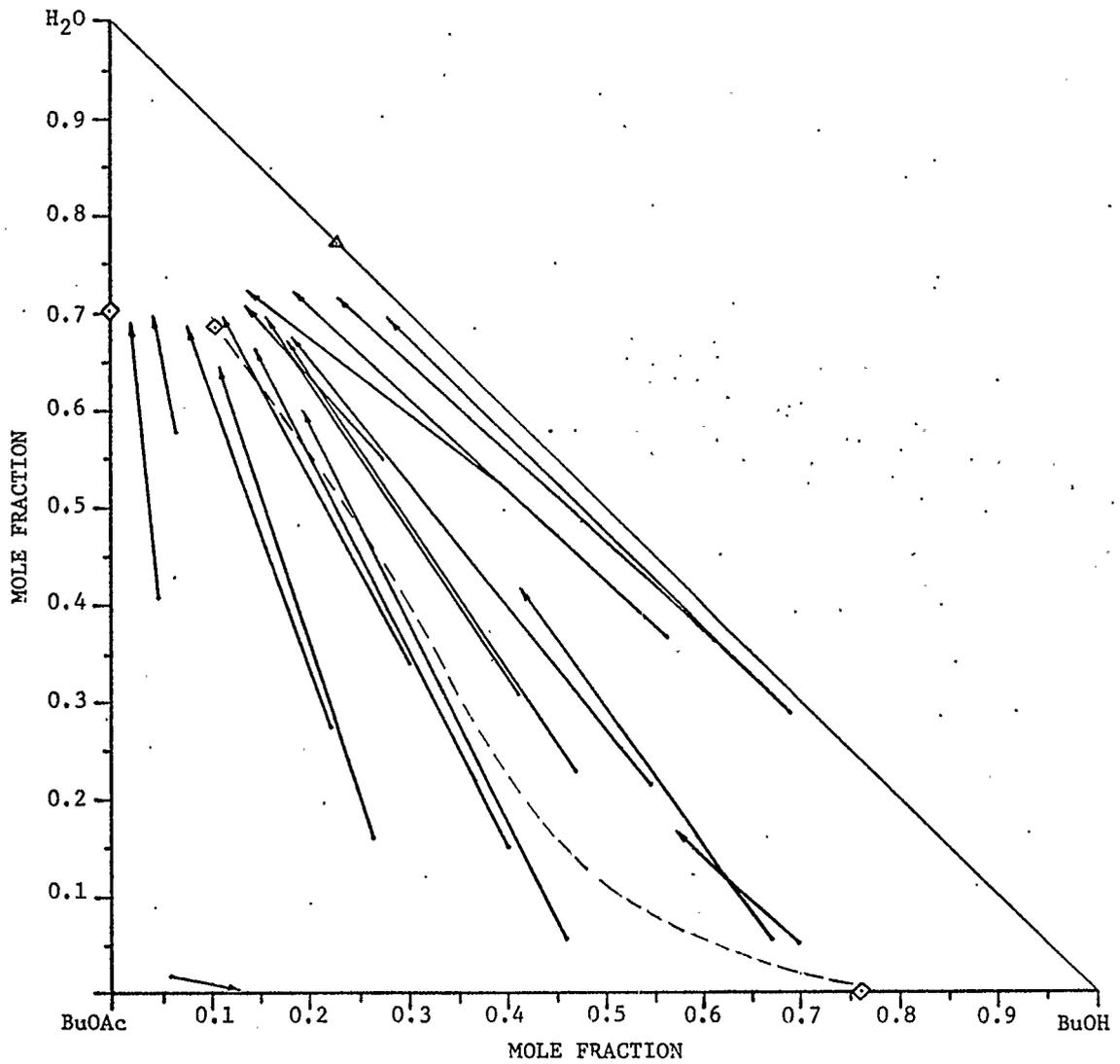
Ternary Vapor-Liquid Equilibrium Diagram For Water, Acetic Acid, and Butanol
 (1 Atmosphere Pressure)
 Figure 3.82

reaction.) In all cases the butyl acetate remained under 0.005 mole fraction in the vapor where it would concentrate if reaction occurred because of the water-butyl acetate azeotrope. The effect of trace amounts of butyl acetate on the temperature is unknown. However, over a period of approximately 6 minutes, the still temperature would drop approximately 2.0°C because of butyl acetate formed by esterification.

The ternary data, of Brunjes and Furnas (4), for the system water, butanol, and butyl acetate are shown in Figure 3.83. Since the data of Brunjes and Furnas are unsmoothed, they are shown here for the sake of comparison with the data gathered in this work. Note how most of the arrows in Figure 3.83 point down the temperature gradient to the two strongly positive azeotropes of (water and butanol) and (water and butyl acetate). In the pure butyl acetate corner one of the arrows points towards the positive butanol and butyl acetate azeotrope. The data also indicates a trough running from the positive butanol plus butyl acetate azeotrope to the positive ternary azeotrope between the water plus butanol and the water plus butyl acetate azeotropes. Some of the arrows cross in Figure 3.83 indicating that an inconsistency or error in analysis has occurred in the study.

3.5 Discussion and Conclusions of Vapor-Liquid Equilibrium Experimental Data Gathering

The data collected in this study for the binaries butanol plus butyl acetate and acetic acid plus butyl acetate both produce flatter gradient relative volatility curves than the data gathered by previous workers. The opposite is true for the binaries acetic acid plus butanol



Ternary Vapor-Liquid Equilibrium Data By Brunjes and Furnas (4)
Figure 3.83

and acetic acid plus water. Since the actual values of the relative volatility are in fair agreement with each other for a given binary system, the split in slopes indicates that the quality of data collected in this study is probably about the same as that of the data gathered by the other sets of workers. Because Figure 3.8 shows that the extensive number of acetic acid and water data points are in practical agreement with the data collected by three sets of international workers, the still and analytical method of this study has to be judged proper for practical work. Whether or not the differences, shown in Figure 3.7, between the data from the still and the data from the work of others are the result of an error in this study or by others using different stills cannot as yet be resolved. The relatively small difference in the highly sensitive activity coefficient is an academic problem which can only be decided after many tests and counter checks. Hence, whether or not this still is better for highly precise work than others is unknown. The still's quick response, for reactive systems, and the ability to handle two-phase systems, by using a syringe, should make it a popular still for many practical investigations.

The innovation of using a syringe to remove a small and representative sample of liquid from the condensate return line proves successful as shown by the consistent data. The use of dry ice for emulsifying both liquid and vapor two-phase samples, also, is successful in helping obtain a representative sample to inject into the gas chromatograph for analysis. This was proven by test injections into the gas chromatograph of various samples from a sample bottle with an emulsified two-phase suspension.

The ternary data for the system acetic acid, butanol, and butyl acetate shows the ridge expected between the butyl acetate and the negative azeotrope. (Both boil at a higher temperature than other compositions on the diagram.) The arrows point down the temperature gradient properly; however, there are a few data sets, represented by arrows, on both sides of the ridge which may have an analysis error as their direction and length are not in agreement with the rest of the diagram. Since chemical reaction occurred to a small degree while obtaining the vapor-liquid equilibrium data, the direction of the arrows could have been affected by water, produced by the reaction, carrying butanol and butyl acetate into the vapor. The faster reaction rate in the acetic acid, butanol, and butyl acetate ternary as compared to the water, acetic acid, and butanol ternary shows that the reaction does not occur as fast if water is present in abundance. The slowing effect of water could possibly be due to immiscible layers forming or the dissociation of acetic acid. The vapor-liquid equilibrium data for the system definitely is not perfect because a bit of reaction did occur; however because the reaction that did occur happened in 15 to 60 seconds, it is unlikely that a practical situation will need better data since the time the components are together will probably also match or exceed the above amount of time. Even if there is no reaction in a system where the components are instantly mixed and flashed, the difference in the vapor composition values from those in this study will not be more than ± 0.03 mole fraction. The evidence (assuming linearity) for the above statement is that when a second sample is taken from the still one minute after the first sample, there is no case where any of the mole fraction values of the components change more than ± 0.03 m.f.

The ternary system water, acetic acid, and butanol in Figure 3.82 shows no troughs or ridges as expected. The data are of a high quality as most of the arrows point in the expected directions. Close to the positive water plus butanol azeotrope, a few errors in the data occur as evidenced by the crossing arrows. The differences in the data about the positive azeotrope are probably due to the flat temperature profile in that region of the data values; the flat temperature profile makes it more difficult to tell when equilibrium is reached by the still apparatus since a lack of equilibrium produces only a very small temperature difference between the liquid and vapor temperatures. Because chemical reaction can cause the vapor to have increased amounts of water and butanol due to the butyl acetate which forms and because the reaction rate changes for different data sets due to concentration changes, the fact that the data sets all tend to line up properly indicates that the reaction did not have a strong effect on the vapor-liquid equilibrium data. The weak effect of the esterification reaction on the vapor-liquid equilibrium data is also demonstrated by the fact that the butyl acetate in the vapor never exceeds 0.005 mole fraction where it concentrates if produced. The data for the water, acetic acid, and butanol ternary are more consistent than that produced by Brunjes and Furnas (4) because it has only one region in which inconsistencies occur whereas the data by Brunjes and Furnas has two regions in which inconsistencies occur. Thus the vapor-liquid equilibrium data for the water, acetic acid, and butanol ternary, displayed in Table A3.12, are consistent ternary data and by being good data indicate that the still has the capability to handle a reaction system with immiscible components.

3.6 Binary and Ternary Activity Coefficient Curve Fitting

A great deal of effort has been exerted over the years in an attempt to find a vapor-liquid equilibrium activity coefficient equation which can be of use in predicting the vapor-liquid equilibrium relationships of ternary and quaternary systems from binary relationships. There has been some success but prediction techniques cannot be trusted until proven. Since the amount of work required to gather enough experimental information to completely describe the quaternary water, acetic acid, butanol, and butyl acetate is so large as to be almost prohibitive, an investigation into possibly predicting the data is made in this study. Two new equations in the literature by Renon (29) and Wilson (16) are used. So that a measurement of the ability of the Wilson and Renon equations for predicting and curve fitting can be made, they are compared to the Margules (12) and Van Laar (12) equations which are well known.

To test the prediction power of the Margules, Renon, Wilson, and Van Laar equations, they are first curve fit, by least-squares criteria, to the six binary systems making up the quaternary system. The four activity coefficient equations are then least-squares fit to three ternary systems. A check is then made to see if the constants in the binary activity coefficient equations can be used properly in the ternary equations. In this study there is a lack of correlation between the binary and ternary equation constants. Hence the binary activity coefficient equations cannot be used to predict the ternary equations and, therefore, not the quaternary equation.

Since the attempt to predict the ternary and quaternary data

failed, this study primarily discusses the least-squares curve fitting of the binary and ternary activity coefficient equations mentioned above. An analysis is given of the results of least-squares curve fitting the four activity coefficient equations to the six binary data sets making up the quaternary system mentioned above. This is followed by a second analysis of the least-squares curve fitting of the data sets from the three ternary systems (water, acetic acid, butanol), (acetic acid, butanol, butyl acetate), and (water, butanol, butyl acetate).

3.7 Analysis of Binary Activity Coefficient Curve Fitting

Each of the six sections that follow discusses the fit of the four activity coefficient equations by Margules, Renon, Wilson, and Van Laar to the data of a binary system. The equations are given in Appendix A1.0 under Programs (4), (5), (6), and (7). (The Renon equation is examined for its ability to fit the binary data with random constants of 0.2, 0.3, and 0.47. Hence, three tests are completed for the Renon equation on each set of binary data.) Marquardt's (22) regression routine is used to least-squares fit all equations to the experimental data. Each binary activity coefficient is fit independently to the data for each equation. Therefore, there are two sets of constants for each equation for each binary data set. A summary of the constants for all four binary activity coefficient equations to fit the six binary data sets is given in Tables A2.11, A2.12, A2.13, A2.14, A2.15, and A2.16 along with two statistical statements (variance of estimate and correlation coefficient) on the fit of each

equation to the binary data set.

3.7.1 Binary Curve Fitting Results for Acetic Acid and Water

Table A2.11 lists the coefficient values for the four binary equations of Programs (4), (5), (6), and (7) to fit the experimental data of acetic acid and water. The Wilson equation provides the closest fit statistically for the activity coefficient of water with the Margules equation and the Renon equation with a 0.2 random constant running a close second and third respectively. The Van Laar equation fits the data of the acetic acid activity coefficient the best, statistically, with the Margules equation being the second best. The constants within the Margules equation are close to each other in value for both activity coefficients, whereas all the other equations have a large spread in the constant values for the two different activity coefficient fittings. All equations are fit to obtain the least-squares error according to the procedure outline in the explanation of Program (3) to the data of Othmer et al.

3.7.2 Binary Curve Fitting Results for Water and Butanol

The four equations being tested for their curve fitting ability are shown in Table A2.12 for the binary system of water and butanol. In this test, the Renon equations with random constant values of 0.3 and 0.47 fit the experimental data with the smallest error for the two activity coefficients. The poorest fit for both activity coefficients is provided by the Wilson equation. The constants given by Hála et al (12) to fit the Margules equation to the water-butanol

system have been tested along with the lowest least-squares values produced by Program (3). The values 0.61 and 1.34 given by Hála et al do not produce a tight fit. The results of Program (3) produce a close fit to the data but the constants required for the two activity coefficients differ. The Margules equation, however, again has the two sets of constants that are closest in relation to each other for fitting both activity coefficients. The data of Smith and Bonner (34) are used for the curve fitting.

3.7.3 Binary Curve Fitting Results for Water and Butyl acetate

The four binary activity coefficient equations' constants and measurement of statistical fit, from curve fitting the water and butyl acetate binary data, are illustrated in Table A2.13. Because Hála et al (12) provided the Margules constants 2.01 and 0.81 for the water and butyl acetate system, they are tested along with the constants that have the lowest least-squares for the Margules equation when the equation is fit to the data by Program (3). Note that the variance of estimate created by the constants used by Hála et al is one to two orders of magnitude larger than any other fit, hence, showing that the constants produce a poor fit. The Renon equation provides the tightest fit for the first activity coefficient. The Van Laar equation follows the experimental data of butyl acetate the best to properly describe the second activity coefficient the closest. The Margules equation gives excellent results for this data set while the performance of the Wilson equation is weak. Hirata and Hirose (13) data are used for the curve fitting.

3.7.4 Binary Curve Fitting Results for Acetic Acid and Butanol

The binary curve fitting results of the four equations to the experimental data of Rius et al (30) are illustrated in Table A2.14 . Because the data presented by Rius et al is smoothed, all the equations represent the activity coefficient values very accurately as is evident from the low variance of estimate and correlation coefficient of nearly one for all four equations.

3.7.5 Binary Curve Fitting Results for Acetic Acid and Butyl acetate

Hirata and Hirose (13) data has its statistical fit to the four binary activity coefficient equations being tested shown in Table A2.15 . The Van Laar is the equation which is least able to fit the experimental data in this case as is evident from its higher variance of estimate and lower correlation coefficient. The Margules equation proves the most adequate for this binary by fitting both activity coefficients closely. The two sets of constants required for the Margules equation differ substantially. The Renon equation produces a tight fit without as large a relative difference in constant values for the equation.

3.7.6 Binary Curve Fitting Results for Butanol and Butyl acetate

Brunjes and Furnas (5) binary data for the system butanol and butyl acetate are illustrated fit to the four binary activity equations in Table A2.16 . Hála et al provided the set of Margules constants 0.22 and 0.24 for the butanol and butyl acetate binary. The constants given by Hála et al create a variance of estimate one order of magnitude

bigger than any of the other equation fits, hence, showing that their constants cause the Margules equation not to represent the data as accurately as the constants found in this study. All four binary activity coefficient equations fit the experimental data about equally in this case with the constants produced by Program (3) and the fit is a close one.

3.7.7 Discussion and Conclusions of Binary Activity Coefficient Curve Fitting

Since the purpose of this study is to represent the experimental data as accurately as possible, the equations were fit separately to each of the two activity coefficients in each binary rather than make a compromise in the fit to obtain only one set of constants. If a compromise equation with one set of constants is desired, it can easily be calculated from the binary activity coefficient equations mentioned above.

The binary data, by the five internationally known workers, are fit quite accurately by the Margules equation in all cases studied. The other equations are sometimes a little better than the Margules equation but they all have cases when they are much poorer in their ability to represent the experimental data. The Renon equation does not perform best or second best as often as the Margules equation; however, it does fit the immiscible systems well as expected. The Van Laar equation shows its weakness in the miscible acetic acid and butyl acetate system while the Wilson equation performs poorly in the miscible water and butyl acetate binary. (Since the binary activity coefficient equations represent the experimental data, none of the experimental

data that the equations were fit to has been presented.) Because of the tight fit of the Margules equation, its international acceptance, and the fact that it does not use temperature (calculation time is saved if temperature is not in the equation), it is the equation recommended to represent all of the above experimental data.

3.8 Analysis of Ternary Activity Coefficient Curves

Each of the three sections that follow discuss the fit of the three activity coefficient equations by Margules, Renon and Wilson to the data of a ternary system. The equations are presented in Appendix A1.0 under the discussion of Programs (8), (9) and (10). The ternary Van Laar equation is dropped from consideration because Marquardt's (22) regression routine, which is used to least-squares fit the equations, is not able to properly fit the equation to the experimental activity coefficient data. (The Renon equation is examined for its ability to fit each set of ternary data with random constants of 0.2, 0.3 and 0.47. Hence, three tests are completed for the Renon equation on each set of ternary data.) Each of the three activity coefficients in each ternary system are fit independently by least-squares criteria, hence, producing three independent sets of constants. A compromise least-square fit for each equation in each ternary system is also completed, hence, producing a fourth set of constants that give the best least-squares fit for all three activity coefficients of each equation over the complete ternary data set. Since individually fitting each activity coefficient for each equation describes the experimental data the most accurately, the compromise fit, using one

set of constants, is carried out primarily to see if the Margules, Renon, and Wilson equations can describe the experimental data with one set of constants. For all three ternary systems investigated, one set of constants, for any of the equations, is not enough to properly represent the experimental data. Even when three sets of constants (one set per activity coefficient) for each equation are used, regions of the vapor-liquid equilibrium activity coefficient data are badly represented. The detailed discussion of each equation's fit to the data of the three ternary systems now follows.

3.8.1 Results of Curve Fitting the Data for the Water, Acetic Acid, and Butanol Ternary System

The constants required to fit the Margules equation of Program (8) to the ternary water, acetic acid, and butanol are shown in Table 3.81 along with stated values on the resulting correlation coefficients and variance of estimates. At the top of Table 3.81, three sets of constants are shown for the Margules equation. This means that the activity coefficient for water, acetic acid, and butanol are all fit optimally, by least-squares criteria, by Program (3) to the Margules equation to obtain the constants shown. The fit obtained by the Margules equation to the ternary data is better than that obtained by the Renon or Wilson equations. Because the fit of the Margules equation is the tightest, calculated vapor compositions values are produced using it and they are given in Table A3.21 for comparison to the experimental values in Table A3.11 (Liquid compositions and temperatures are kept the same.). Any error in the fit of

TABLE 3.81

MARGULES

Ternary Water(1) - Acetic-acid(2) - Butanol(3)

Margules Equation (3 sets of constants)

		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	-0.802546	-0.8295	-8.14875
	2)	-0.506958	0.662589	1.29469
	3)	4.49555	-0.482253	0.433185
	4)	2.78186	5.83771	2.96689
	5)	3.21135	-5.0251	-2.25514
	6)	-6.91615	-0.97	-4.21703
	7)	2.4112	-7.087	0.54412
Correlation Coefficient* of Logs		0.99902	0.97232	0.99949
Correlation Coefficient of Arithmetic Values		0.91193	0.95265	0.95471
Variance of Estimate* of Logs		0.00295	0.07178	0.01333
Variance of Estimate of Arithmetic Values		0.00167	0.00114	0.00037

Margules Equation (1 set of constants)

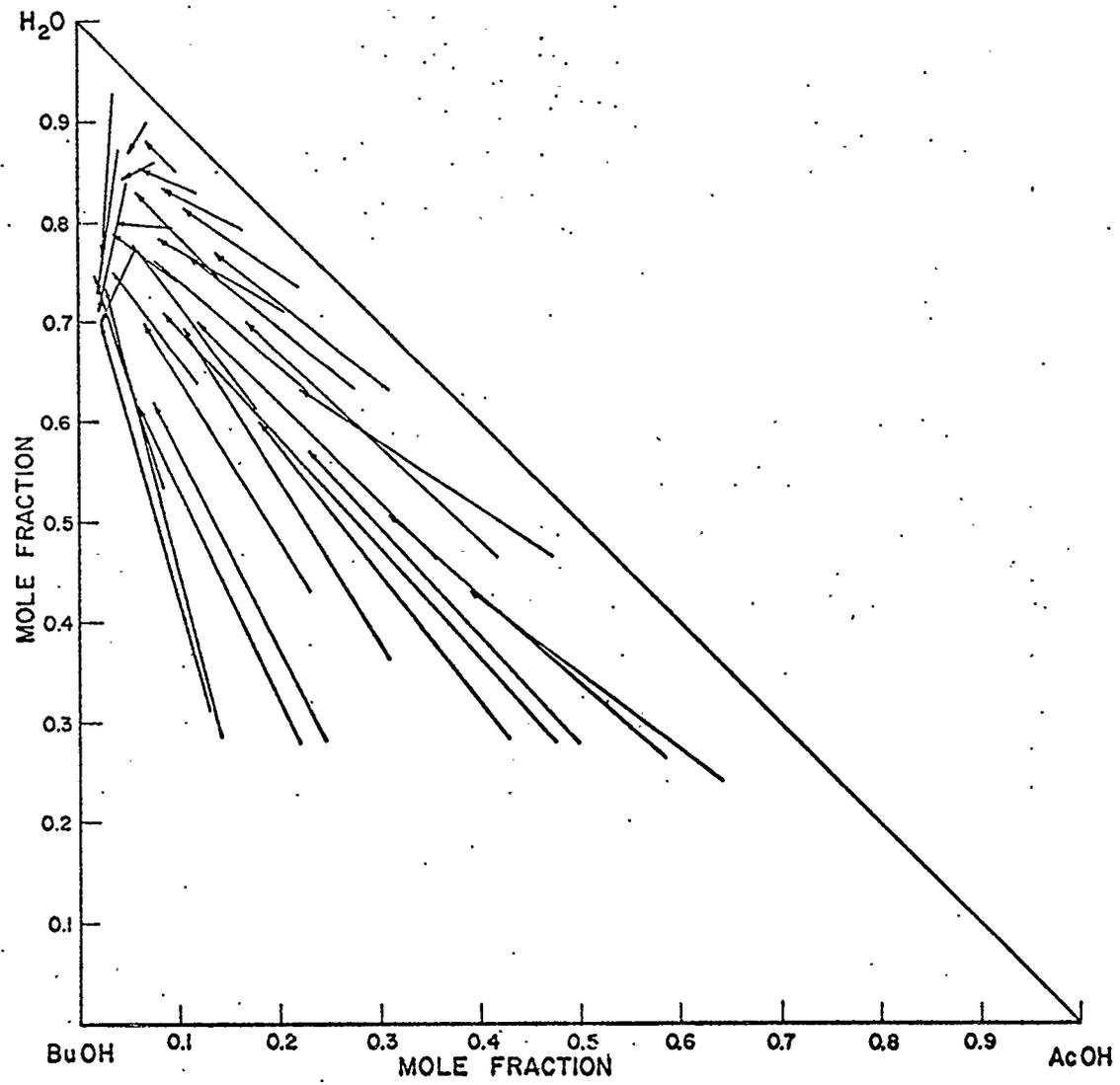
		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	-3.11	same	same
	2)	1.65229		
	3)	-0.433924		
	4)	2.21474		
	5)	-0.173063		
	6)	-0.0740857		
	7)	-0.0624587		
Correlation Coefficient of Logs		0.98966	0.94345	0.99469
Correlation Coefficient of Arithmetic Values		0.61389	0.87764	0.66904
Variance of Estimate of Logs		0.03110	0.14453	0.13929
Variance of Estimate of Arithmetic Values		0.01371	0.00285	0.00232

*See Appendix 5

the Margules equation is all concentrated in the vapor composition shown in Table A3.11 . Figure 3.91 illustrates the calculated vapor compositions (the liquid compositions are the same as Figure 3.82) produced by the Margules equation with a set of constants for each activity coefficient. If the Margules equation fit the experimental data perfectly, Figures 3.91 and 3.82 would be identical. The Margules equation is inaccurate when the water concentration is high and the acetic acid concentration low, and when the acetic acid concentration is high and the butanol concentration is low. The vapor composition most in error in Figure 3.91 is that with a liquid composition of 0.776, 0.056, and 0.167 mole fraction water, acetic acid, and butanol respectively.

A fit of the Margules equation to all three activity coefficients using only one set of constants is also shown in Table 3.81 . Here the best least-squares fit to all three activity coefficients (the cycling principle is applied to the constants) is required of the seven constants in the Margules equation. Because one set of constants is used instead of three, the variance of estimate of the error in the first and third activity coefficients increases an order of magnitude and on the second it doubles. The correlation coefficients decrease significantly with one set of constants. Hence the compromise of using only seven constants instead of twenty-one greatly increases the error in the Margules fit of the experimental data.

Tables A2.31, A2.32, and A2.33 give the constant values to fit the Renon equation of Program (9) to the experimental data with the random constant values of 0.2, 0.3, and 0.47 respectively. Again the individually fit activity coefficient equation values approximate



Ternary Data Calculated By Margules Activity Coefficient Equations
Figure 3.91

those obtained experimentally more closely by an order of magnitude in the variance of estimate of the error than the compromise fit using only one set of constants. The Renon equation fits the data of the water, acetic acid, and butanol ternary best when it is applied with a random constant of 0.47 as shown in Table A2.33 . Because all of the fits by the Renon equations are not as tight as the Margules equation fit presented in Table 3.81, their calculated activity coefficient values have not been displayed or the vapor composition values produced from the activity coefficient values.

Tables A2.34 and A2.35 illustrate the constant values necessary to fit the Wilson equation of Program (10) to the activity coefficients of the ternary water, acetic acid, and butanol. All the various sets of constants for the Wilson equation provide a very bad fit. The fact that the coefficients provided for the first activity coefficient give better results for the second activity coefficient than those selected by Program (3) shows that Program (3) is not always able to optimize properly. The problem of getting stuck in secondary minimum modular pockets when searching for the constants with the least-squares value proved a continual problem in this study for all equations; but the Wilson equation constants were affected most often. The results in Table A2.34 illustrate the problem clearly for the ternary system water, acetic acid, and butanol.

3.8.2 Results of Curve Fitting the Data for the Acetic Acid, Butanol, and Butyl acetate Ternary System

The constants required to fit the Margules equation of

Program (8) to the ternary acetic acid, butanol, and butyl acetate are shown in Table 3.82 with the correlation coefficients and the variance of estimates. A ternary graph of the resulting calculated vapor composition values from the Margules equation using twenty-one coefficients is shown in Figure 3.92. Comparing Figure 3.92 to Figure 3.81, a judgment can be made on the correctness of the Margules equation fit in any area of the ternary diagram since the two figures should be the same because the liquid composition, temperatures, and pressure are the same. As a whole the results are good except for close to the high temperature ridge and near the positive azeotrope between butanol and butyl acetate. The calculated vapor compositions that should match the experimental vapor compositions in Table A3.12, if the Margules equation fit were perfect, are shown in Table A3.22. Because the liquid compositions and the temperature are kept constant in the test of the fit, all the error is shown in the vapor composition. The vapor composition that is in error the greatest amount, using the Margules calculated values, is that with a liquid composition of 0.6036, 0.27553, and 0.11665 mole fraction acetic acid, butanol, and butyl acetate respectively. The single set of constants shown in Table 3.82 provides an excellent fit. Very little improvement is obtained for the Margules equation, with fourteen extra constants, in the correlation coefficient or the variance of estimate.

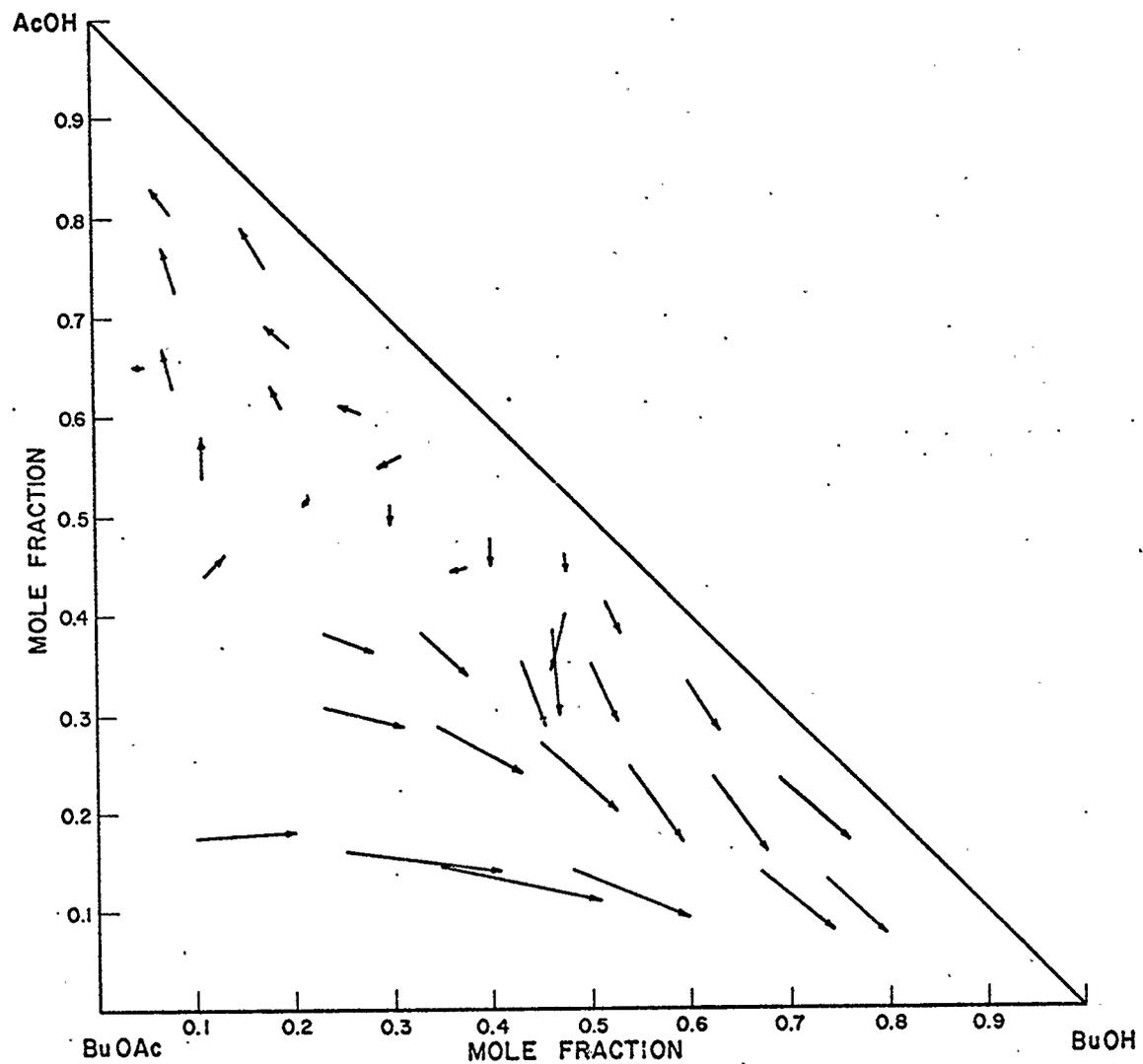
The Renon equation constants produced by Programs (9) and (3) for random constants of 0.2, 0.3, and 0.47 are shown in Tables A2.36, A2.37, and A2.38 for the ternary data of acetic acid, butanol, and butyl acetate. All three versions of the Renon equation fit the

TABLE 3,82

MARGULES

TERNARY ACETIC-ACID(2) - BUTANOL(3) - BUTYL ACETATE(4)

Margules Equation (3 constant sets)				
		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	-0.742757	-0.641605	1.54079
	2)	-0.254176	-0.110711	1.75949
	3)	-0.102617	-1.73497	0.219395
	4)	0.131459	-0.0088113	-0.0551248
	5)	0.647462	1.04672	1.33423
	6)	2.25714	0.836	0.0531426
	7)	0.701109	1.71655	-2.29267
Correlation Coefficient of Logs		0.99619	0.98964	0.99353
Correlation Coefficient of Arithmetic Values		0.99370	0.97573	0.99201
Variance of Estimate of Logs		0.00913	0.02458	0.01555
Variance of Estimate of Arithmetic Values		0.00064	0.00219	0.00034
Margules Equation (1 constant set)				
		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	-1.23158		
	2)	-0.686434		
	3)	-0.0840378		
	4)	0.470267	same	same
	5)	1.01299		
	6)	0.284		
	7)	0.386323		
Correlation Coefficient of Logs		0.99469	0.98978	0.98353
Correlation Coefficient of Arithmetic Values		0.99136	0.97665	0.97418
Variance of Estimate of Logs		0.01274	0.02425	0.03939
Variance of Estimate of Arithmetic Values		0.00088	0.00211	0.00109



Ternary Data Calculated By Margules Activity Coefficient Equations
 Figure 3.92

miscible system well. The Renon equation produces a slightly tighter fit on the second (butanol) activity coefficient than the Margules equation for all random constant values. The Renon equation provides almost exactly the same fit when it uses only 6 constants as when the Margules equation applies 7 constants.

The Wilson equation constants produced by Programs (10) and (3) are displayed in Tables A2.39 and A2.40 to fit the ternary data of the acetic acid, butanol, and butyl acetate system. The Wilson equation provides a tight fit to the data but one slightly inferior to that of either the Margules or Renon equations. Table A2.39 indicates that the least-squares optimization program has definitely become caught in a secondary module in the search for the best constants to least-squares fit the equation because the constants given to fit the second activity coefficient (when 18 constants are used) are not the best possible. Therefore the optimization program stopped before the true minimum value for the least-squares fit occurred. The Wilson equation, like the Margules and Renon equations, shows a strong ability to fit the miscible system with only one set of constants.

3.8.3. Results of Curve Fitting the Data for the Water, Butanol, and Butyl acetate Ternary System

The constants used to fit the Margules equation of Program (8) to the ternary water, butanol, and butyl acetate are shown in Tables 3.83 and 3.84. The constants shown in Table 3.83 are those produced by this study using Program (3) whereas those of Table 3.84 are those of Hála et al (12). When the twenty-one constants shown at the top of

TABLE 3.83
MARGULES
TERNARY WATER(1) - BUTANOL(3) - BUTYL ACETATE(4)

Margules Equation(3 sets of constants)				
		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	- 1.76036	0.948796	0.206828
	2)	3.87914	0.55345	0.547858
	3)	- 4.7047	7.14209	2.70603
	4)	3.44448	2.28104	1.09069
	5)	2.51448	0.85684	-0.347986
	6)	7.97423	0.3	-1.25712
	7)	-21.11063	-2.51163	-3.17095
Correlation Coefficient of Logs		0.99892	0.99527	0.98049
Correaation Coefficient of Arithmetic Values		0.80302	0.97125	0.95552
Variance of Estimate of Logs		0.03545	0.01234	0.17890
Variance of Estimate of Arithmetic Values		0.00898	0.00062	0.00184
Margules Equation (1 set of constants)				
		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	1.92629		
	2)	3.8765		
	3)	0.605434	same	same
	4)	2.7725		
	5)	-4.42051		
	6)	0.00383825		
	7)	-4.29825		
Correlation Coefficient of Logs		0.96380	0.73701	0.87701
Correlation Coefficient of Arithmetic Values		-4.73398	0.75412	0.65056
Variance of Estimate of Logs		1.16965	0.59818	1.06911
Variance of Estimate of Arithmetic Values		0.59229	0.00473	0.01222

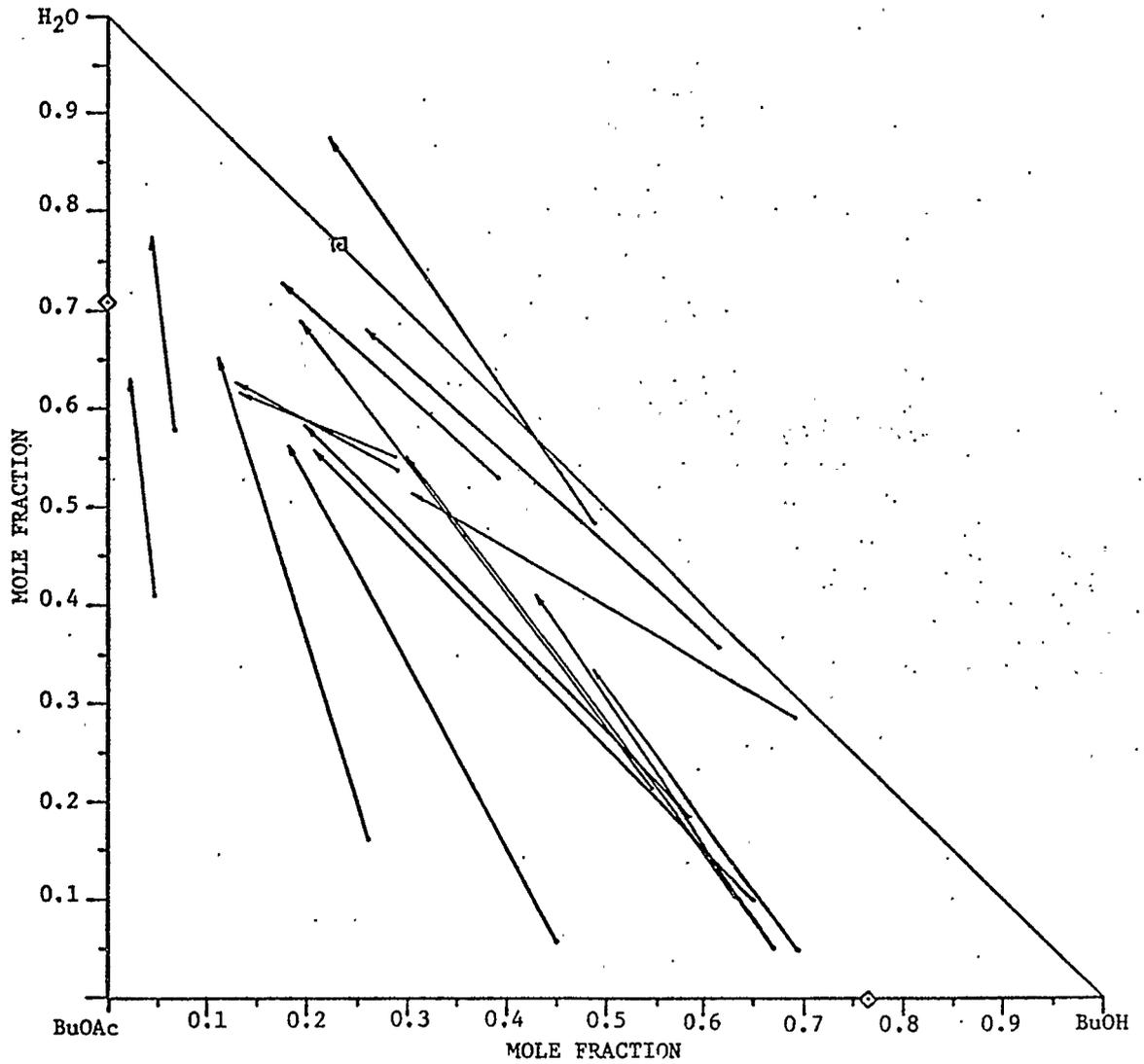
TABLE 3.84
MARGULES
TERNARY WATER(1) - BUTANOL(3) - BUTYL ACETATE(4)

Margules Equation (Hala et al's one set of constants)

		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	0.61		
	2)	1.34		
	3)	2.01	same	same
	4)	0.81		
	5)	0.22		
	6)	0.24		
	7)	1.1		
Correlation Coefficient of Logs		0.96280	0.98871	0.95682
Correlation Coefficient of Arithmetic Values		-1.87770	0.95085	0.94907
Variance of Estimate of Logs		1.20126	0.02938	0.39127
Variance of Estimate of Arithmetic Values		0.11448	0.00105	0.00208

Table 3.83 are used a relatively tight fit to the activity coefficient data occurs. The results of the fit are shown in the ternary diagram of Figure 3.93 and should be compared to Figure 3.83 which displays the experimental data. The fit is weak in the regions of low butyl acetate and near the two strongly positive azeotropes. It is apparent from Figure 3.93 that if the Margules equation is to be used, it must be taylored for the region of interest. Because the fit provided by seven constants is much worse than that by twenty-one, it is obvious that over a large portion of the ternary system seven constants would produce highly erroneous results. A single set of constants can be taylored for a given region in the ternary. The experimental vapor compositions given by Brunjes and Furnas (4) are shown compared to the calculated vapor compositions in Table A3.23 resulting from the use of the twenty-one Margules constants found by this study and the seven constants of Hála et al (12).

The Renon equation of Program (9), with the three different random constants, has the constants chosen by Program (3) for the ternary water, butanol, and butyl acetate displayed in Tables A2.41, A2.42, and A2.43. In all cases, the fit provided by the Renon equation using eighteen constants is worse than that obtained with twenty-one constants in the Margules equation. The Renon equation does fit the data better than the Margules equation if six constants for the Renon equation are compared with seven constants for the Margules equation. Thus the Renon equation might be able to represent a larger region of the ternary correctly with six constants than the Margules equation could with seven. The crude fit provided by the Renon equation with 18



Ternary Data Calculated By Margules Activity Coefficient Equations
Figure 3.93

constants is not accurate enough to represent the whole ternary data set.

The results of the least-square curve fitting for the Wilson equation of Program (10) are shown in Tables A2.44, A2.45, and A2.46. By the low correlation coefficients and the high variance of estimates, the evidence indicates that the Wilson equation fits the ternary data set for water, butanol, and butyl acetate worse than even the Renon equation. All three sets of the individual activity coefficients, for each component, are illustrated as a single set, for all components, to again illustrate that the least-squares optimization program is not able to always find the absolute minimum fit for an equation to the data set. The Wilson equation fits the ternary water, butanol, and butyl acetate very badly.

Because the ternary Van Laar equation produced a low quality least-squares fit to the experimental data of all three ternaries, its fit was dropped from the above discussion. Some of the activity coefficients were represented fairly well by the Van Laar equation but in no case was a total ternary system even approximately represented by the equation. Hence, it was omitted from consideration.

3.9 Discussion and Conclusions of Ternary Activity Coefficient Curve Fitting

Many problems occurred while least-squares fitting the ternary experimental data with Programs (3), (8), (9), and (10). The first problem occurred because the binary constants of the Renon and Wilson equations put the ternary equations' activity coefficient

values out so badly, in many cases, that the optimization Program (3) could not recover. Hence arbitrary starting values were chosen by the author to overcome the problem. The second problem was that of having Program (3) caught in a secondary minimum least-squares value rather than the minimum. With all the equations except the Wilson equation, this could be overcome by switching Program (3) to a Taylor series approximation method of finding the optimum. In the case of the Wilson equation, new starting points for the curve fitting procedure had to be used as well as the Taylor series approach. Because of the secondary minima, there is no way of knowing if the fits obtained for the different equations are the best possible. Since the uncertainty cannot be overcome, it can only be said that the fits given are the best found by giving approximately equal effort and computer time to all the equations' fit.

The Margules equation provides the most accurate fit of the experimental data in two ternaries and in the third runs a close second. Because the Margules equation is simple, is the easiest to fit, is very well known, and does not use temperature, it is the equation recommended for use by the evidence of this study. Since temperature is not used in the equation, calculation time with the Margules equation would be greatly reduced compared to any of the other equations.

The Renon equation showed ability to fit the miscible ternary better than any of the other equations. However, the Renon equation is more difficult to curve fit and incorporates temperature within its expressions. The variable temperature being in the equation means that the Renon equation must be in the iteration loop to make the

vapor mole fractions add up to one. This means a great deal more calculation using the Renon equation as compared to the Margules equation. Also, if a computer is used, the calculations of exponential expressions require a great deal of time in most computers. Hence a slight edge in one area of fitting experimental data is not enough to recommend the use of the Renon equation. There is little evidence that the random constants give the Renon equation the flexibility first hoped for in the literature. The author was forced to abandon the procedure for random constant applications recommended by Renon and Prausnitz (29) in order to obtain a respectable fit. Because the various random constants did affect the performance of the Renon equation, however, it is apparent that the equation might produce much better results if constants other than 0.2, 0.3 and 0.47 were used. This would represent a whole new study, however, and the author did not investigate it.

The Wilson equation of Program (10) performed poorly in all three of the ternary systems. Thus the optimism expressed by Holmes and Van Winkle (16) is not justified by the results of this study. Because the Wilson equation has the disadvantages, compared to the Margules equation, of complexity and the use of exponentials and temperature, it cannot at any time be suggested for ternary systems on the evidence of this study.

One unknown feature which could have seriously affected the performance of the Renon, Wilson, and Van Laar ternary equations in the two ternary systems with reaction is the inaccuracy in temperature. The temperature was measured correctly but because the small amount of

water or butyl acetate in either of the two ternary systems could have changed the temperature, the three equations mentioned may have failed due to the experimental values being in error. However, because all three equations also failed in the non-reacting system of water, butanol, and butyl acetate, the temperature inaccuracies are definitely proven not to be the only reason the Renon, Wilson, and Van Laar equations fail. Hence, if the equations did fail due to experimental temperature errors, then such a high sensitivity to temperature fluctuations might be another practical reason for using the Margules equation rather than the other three equations.

Since the binary constants previously found cannot, in any way be said to be able to predict the ternary constants for the Margules, Renon, and Wilson equations, it automatically follows that any attempt to predict quaternary data from ternary constants would be fruitless. From the experience of this study, the most accurate way to predict ternary data from binary data is to linearly curve fit the three binary diagrams on the boundaries of the ternary across the surface of the ternary diagram. By the above statements it is obvious very little reliable prediction can be achieved.

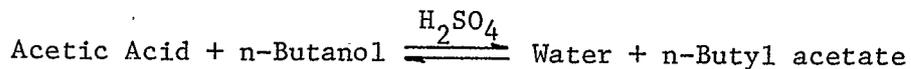
CHAPTER 4 EXPERIMENTAL PILOT PLANT ESTERIFICATION COLUMN
DESCRIPTION, OPERATION, AND DATA GATHERING

4.1 Experimental Esterification Column Description, Operation, and
Data Gathering Outline

The pilot plant esterification column used to continuously produce butyl acetate from butanol and acetic acid is described. Details of the operating procedure and the methods used to obtain both steady-state and transient data are discussed. The data from the column are analyzed for the steady-state conditions of composition, temperature, mass balance, and heat balance. Kinetics rate equations are developed from steady-state information from the column and previous vapor-liquid equilibrium studies. Transient changes in composition and temperature are examined.

4.2 Description of Esterification Column and Procedure of Operation

Basically the esterification column is a 10-tray distillation column with a reboiler, total condenser, and a decanter. The column is fed butanol and acetic acid along with a small amount of sulphuric acid catalyst. The butanol and acetic acid react to form water and butyl acetate according to the reversible reaction;



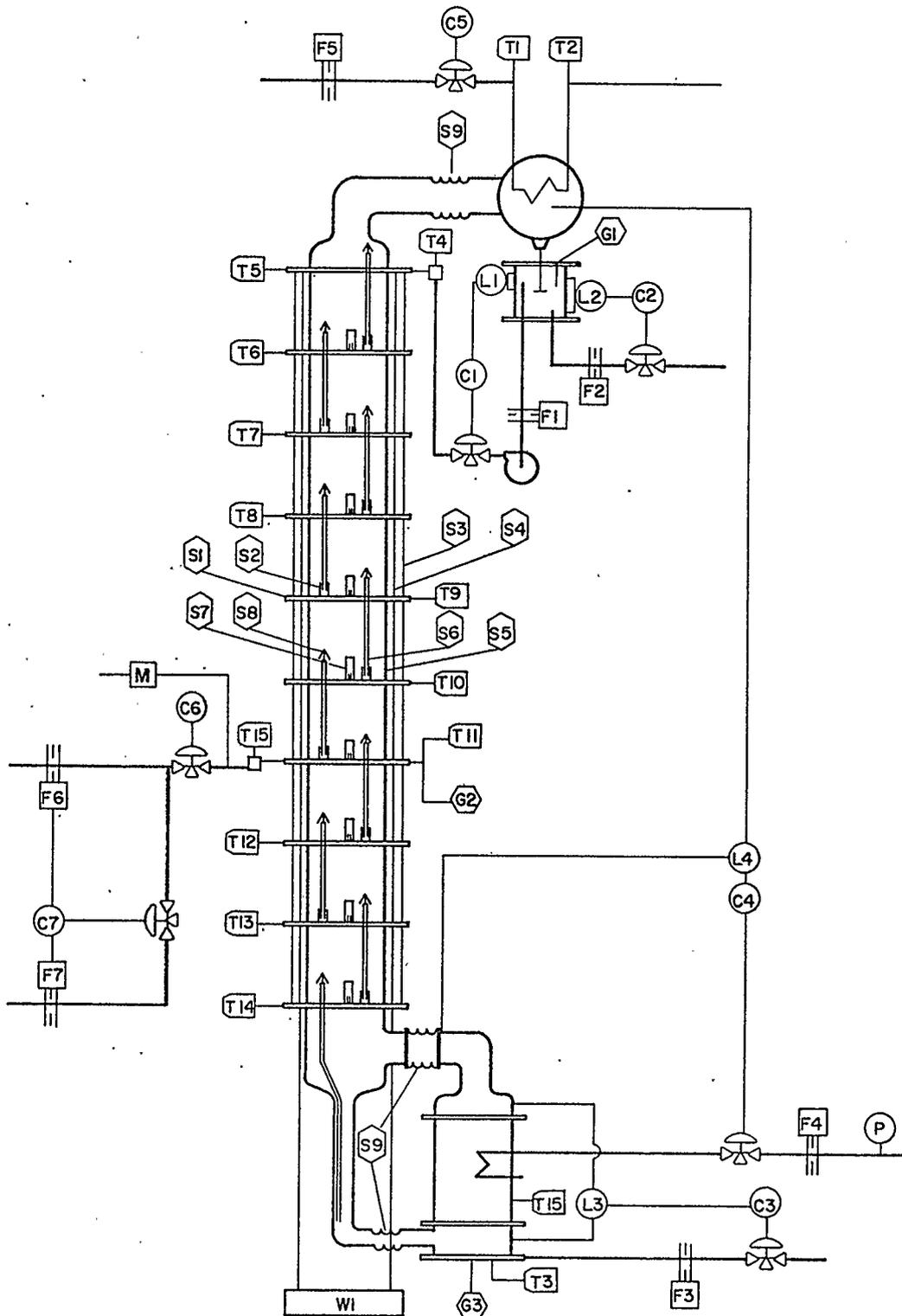
The reaction takes place on the feedtray (Number 4) and lower trays including the reboiler; and it is forced to the right by concentrating water in the top six trays and separating it from butanol and

butyl acetate in the decanter. The water is removed from the decanter as overhead product and the butanol and butyl acetate are refluxed as drying agents. The butyl acetate product is removed as a bottoms product from the reboiler along with the excess butanol and catalyst. (The pilot plant experimental column is now described in detail.)

A drawing of the esterification column is shown in Figure 4.1. Figure 4.10 gives the meaning of the symbols used in Figure 4.1. None of the equipment represented by tags in Figure 4.1 (differential pressure cells, thermocouples, recorders, controllers) or any other equipment (titration equipment, weight scales) used during the operation of the esterification column has been illustrated. (Should any questions arise on the details of the supporting equipment to the esterification column that are not contained in this study, they may be obtained from the Hybrid Computer Laboratory at the University of Calgary.)

4.2.1 Description of Esterification Column

The drawing of the esterification column in Figure 4.1 shows a column with ten trays, a reboiler, and condenser. The condenser discharges its effluent into a decanter. The top oil layer of the decanter flows back into the column as reflux and the bottom water layer is taken off as overhead product. The reflux flow is measured by flow recorder F1 and the overhead product by F2. The rate of cooling water to the condenser is measured by flow recorder F5. The copper-constantan thermocouples T1 and T2 give the temperature of the incoming and outgoing cooling water to the condenser respectively. A teflon bellows, S9, allows the column a slight amount of independent movement from the



Schematic Of Pilot Plant Esterification Column
Figure 4.1

ESTERIFICATION COLUMN LEGEND

(Figure 4.10)

⊙ C1	Reset-proportional controller for interface
⊙ C2	Reset-proportional controller for decanter liquid-level
⊙ C3	Reset-proportional controller for reboiler liquid-level
⊙ C4	Reset-proportional controller for steam
⊙ C5	Reset-proportional controller for cooling water
⊙ C6	Reset-proportional controller for feed-rate
⊙ C7	Reset-proportional controller for feed ratio
⊠ F1	Flow recorder for reflux
⊠ F2	Flow recorder for overhead product
⊠ F3	Flow recorder for bottoms product
⊠ F4	Flow recorder for steam
⊠ F5	Flow recorder for cooling water
⊠ F6	Flow recorder for butanol feed
⊠ F7	Flow recorder for acetic acid feed
⊙ G1	Beckman chromatograph analyzing decanter oil layer
⊙ G2	Beckman chromatograph analyzing feed tray composition
⊙ G3	Beckman chromatograph analyzing reboiler composition
⊙ L1	Liquid level recorder and transmitter for interface level
⊙ L2	Liquid level recorder and transmitter for decanter level
⊙ L3	Liquid level recorder and transmitter for reboiler level
⊙ L4	Differential pressure recorder and transmitter for column
⊠ M	Metering pump for sulphuric and acetic acid mixture
⊙ P	Pressure gauge on steam feed line

ESTERIFICATION COLUMN LEGEND (contd)

S1	Stainless steel plate 3/4" thick and 15" diameter
S2	Cup to stop vapor going up downcomer
S3	Plexiglass insulation
S4	Plexiglass insulation
S5	Glass cylinder made by QVF (9" diameter and 9" high)
S6	Downcomer tube (3/4" diameter)
S7	Bubble cap
S8	Shield to stop splashing of liquid into downcomer
S9	Teflon bellows so column is free to move vertically
T1	Temperature of inlet cooling water
T2	Temperature of outlet cooling water
T3	Temperature of reboiler
T4	Temperature of reflux about to go onto tray
T5	Temperature of tray 10
T6	Temperature of Tray 9
T7	Temperature of Tray 8
T8	Temperature of Tray 7
T9	Temperature of Tray 6
T10	Temperature of Tray 5
T11	Temperature of Tray 4
T12	Temperature of Tray 3
T13	Temperature of Tray 2
T14	Temperature of Tray 1
T15	Temperature of steam chest
W1	Recorder on column weight

condenser. A pump is used to force the oil from the decanter back onto the top tray. The proportional-reset controllers C1 and C2 are used to keep the holdup in the decanter constant.

The stainless steel (Type 316) plates of the column are separated by nominal 9-inch diameter QVF glass that is 9 inches high. Two sets of 1/8-inch 'O' rings provide seals between the plates and the glass. The glass is indicated by S5 on the fifth tray. The glass is insulated with two cylinders of clear plexiglass indicated by S3 and S4 on the sixth tray. The sixth tray is identified as S1. Each tray has a downcomer indicated by S6, a bubble cap S7, a vapor trap S2 and a cap on a downcomer indicated by S8 to stop splash into the downcomer. There are five bubble caps on each tray and each tray is 14.5 inches in diameter and 3/4 of an inch thick. Three holes are drilled in the side of each tray and after the holes have penetrated 3 to 4 inches they turn 90 degrees to make contact with the liquid on the tray surface. A copper-constantan thermocouple occupies one hole, transmitting continuously the liquid temperature; the tray thermocouples are designated by the tags T5 to T14. The other two holes drilled into the tray are used to add or remove liquid from the tray surface.

The acetic acid feed comes from two glass tanks so no interruption in flow need occur when a tank is emptied during a run; the acetic acid passes through flowmeter F7. The butanol feed comes from two storage tanks, again so no interruption in flow need occur, and it passes through flowmeter F6. The acetic acid and butanol feed streams are forced out of the storage tanks through the use of air

pressure and they are mixed as they pass through the valve tied to controller C6. After the butanol and acetic acid streams are mixed, a metering pump then injects a predetermined amount of acetic acid and sulphuric acid mixed to a 10 to 1 weight percent ratio respectively. The temperature of the stream is taken by a thermocouple marked T15 as the solution flows onto the feedtray. Once on the feedtray, the liquid has its temperature recorded by the thermocouple marked T11.

The downcomer on the bottom tray of the column goes well down into the reboiler as illustrated in Figure 4.1. This is done to prevent vapor locks. The reboiler is a shell and tube stainless steel (Type 316) unit with nominal 9-inch diameter QVF glass fittings attached to each end. Two teflon bellows marked by S9 in Figure 4.1 allow the column a small amount of free movement from the QVF glass fittings attached to the reboiler, hence, allowing the column a small amount of independent movement so it can be properly weighed. The steam coming into the shell side of the reboiler is measured with flow recorder F4 and the pressure of the steam is obtained from the gauge marked P. Flow recorder F3 keeps a measurement record of the fluid discharged from the reboiler by the valve controlled by the proportional-reset controller C3. The temperature of the liquid in the reboiler is recorded by the thermocouple marked T3 while the temperature of the steam on the shell side is recorded by T15. The steam flow to the reboiler is controlled by the proportional-reset controller C4 which uses the pressure difference across the column to control the steam.

The column is held vertical by oiled roller bearings that touch the first and sixth trays. The total column weight is supported

on a bellows filled with water marked as W1 in Figure 4.1 . The static weight of the esterification column is balanced by a column of water in a tube that is attached to the opposite side at a differential pressure cell. The sensitive differential pressure cell is then used to pick up any changes in weight occurring in the esterification column. The weighing system for the column is accurate to within 40 grams.

Three gas chromatographs that provide an analysis on liquid every three minutes are used with the esterification column and are marked as G1, G2, and G3 on Figure 4.1 . G1 is used to analyze the composition of the decanter oil layer. The composition of the liquid of the feed tray is analyzed by G2. The large holdup of liquid in the reboiler is analyzed by G3. The three continuous gas chromatographs are permanent and record the composition only at the positions mentioned. The gas chromatographs are made by Beckman Inc. and have a 620 programmer and a D series analyzer.

By using the manual Varian gas chromatograph mentioned in Section 3.2 of the vapor-liquid equilibrium studies, it is possible to completely analyze all the trays in the esterification column at steady state. The Varian gas chromatograph required three hours to do a complete analysis on all parts of the esterification column.

The control valves used on the column are made by Precision Control Inc. and all controllers and differential pressure cells are produced by Foxboro Ltd.

4.2.2 Experimental Procedure for the Esterification Column

Because accuracy of measurement is desired, the first step in starting the esterification column is the calibration of all instruments. All copper-constantan thermocouples are calibrated against a standardized mercury thermometer. The flow recorders are calibrated with the fluid they are to measure. The liquid level and differential pressure cells are checked with static columns of water. The gas chromatographs are compared with known weight percent samples. Records are filed so that second checks on all calibrations can be compared after or during experimental data gathering runs. Checks and practice titrations are carried out on samples of butanol, butyl acetate, water, acetic acid, and sulphuric acid using 0.5 molar sodium hydroxide (phenolphthalein is used as the indicator).

Once calibration is complete, the utility systems of steam, air, sewer, cooling water, and electricity are checked for any malfunction that could cause a shut down within the next nine days. If everything is in proper working order, the acetic acid and butanol feed tanks are loaded and air pressure is applied to start liquid into the empty esterification column. As the butanol and acetic acid start to flow onto the feedtray, the metering pump is started; it injects the correct measured amount of catalyst into the acetic acid and butanol feed stream from the 10:1 (weight percent) acetic acid and sulphuric acid mixture, respectively. The catalyst mixture is contained in a small plastic gallon jar. Nothing is then done until the liquid rises to a height that extends through the shell and tube reboiler. Since this is the height the liquid in the reboiler should be kept at, the

steam is turned on to provide a rate of boiling so that the level in the reboiler is kept constant. After the steam has been on for about two hours, the upper trays and the decanter will all contain liquid of the proper composition and depth. The reflux pump is started. The cooling water flow rate to the condenser is set at a reasonable level to provide a 15 degree temperature change as it passes through the condenser. The bottoms and overhead product streams have their flows initiated and the column is then left alone until steady state has been achieved.

The esterification column takes 8 to 10 hours to reach steady state conditions after being totally drained of all chemicals. Since the time to start the column is quite long, the column is not shut down until all studies required have been completed. Once steady state is obtained, samples are removed from all trays for analysis in the Varian gas chromatograph; the column is then stepped to the new conditions for which the transient and steady state information is desired. As the column is stepped from one set of operating conditions to another, the automatic electronic and pneumatic recorders log all the information on temperature, flow, and composition. The esterification column is operated over the full range of feed ratios, feed flow rates, catalyst flow rates, and steam boil-up rates that is considered practical.

Calibration checks are done periodically on the gas chromatographs and on the overhead and bottoms product flow meters. The quantity of sulphuric acid catalyst injected is checked by titrating the bottoms product from the esterification column. All other

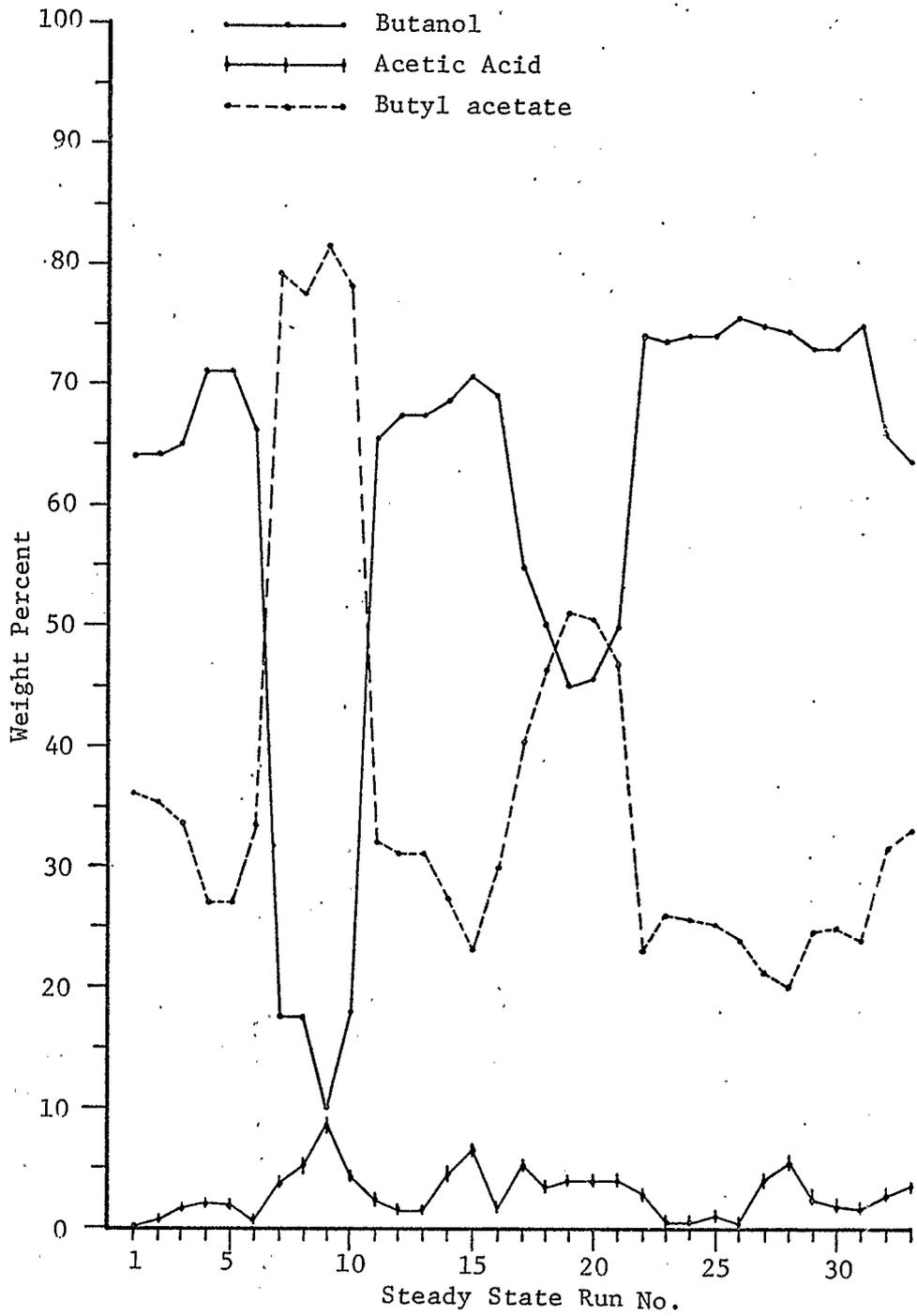
instruments are checked when the esterification column is shut down.

4.3 Analysis of Data Gathered from the Esterification Column

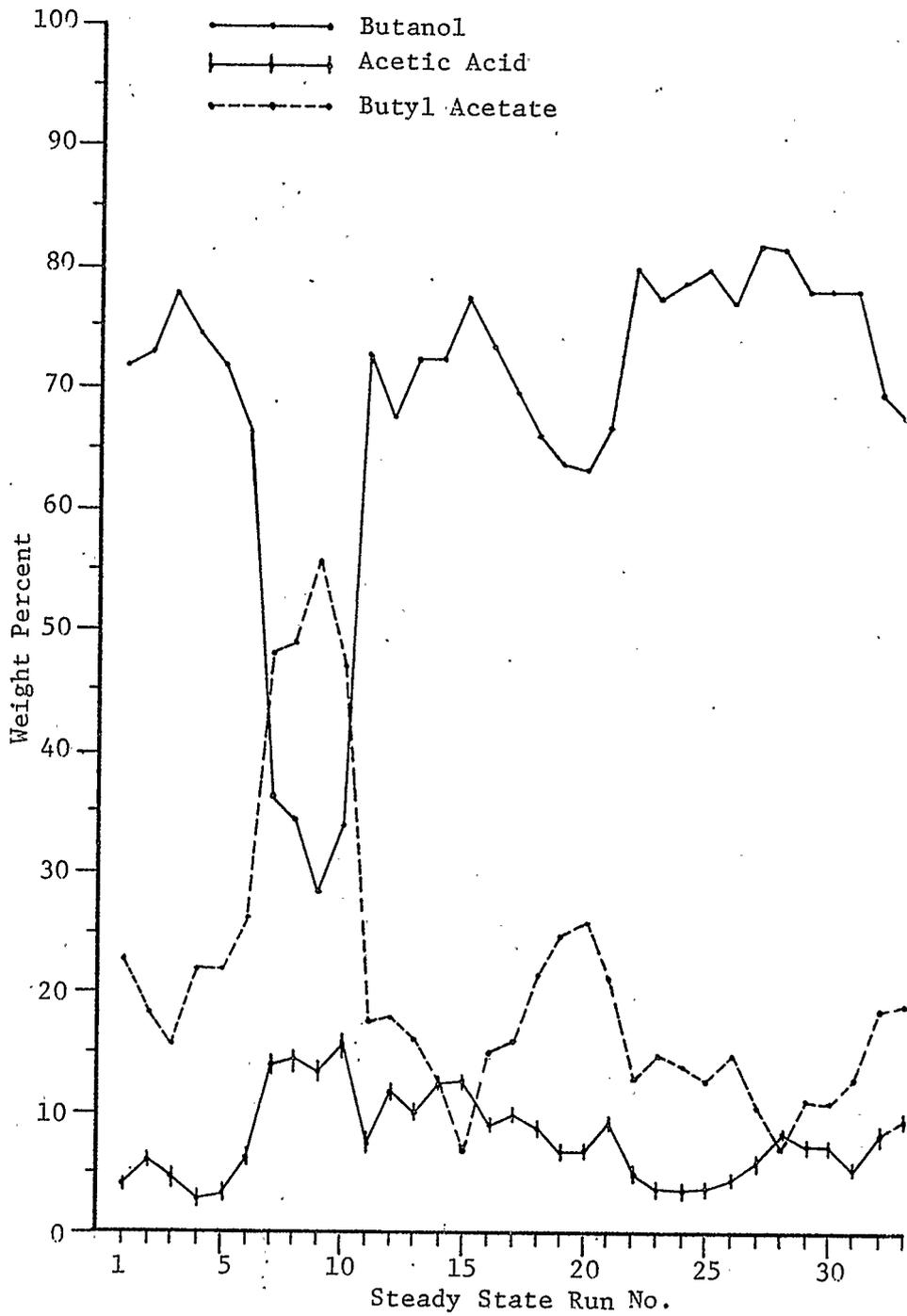
Since the purpose of the esterification column is to produce as large an amount of pure butyl acetate as possible, the four independent variables, catalyst (sulphuric acid) concentration, boil-up or reflux rate, feed flow rate, and feed ratio are judged as to their ability to help accomplish the objective. Hence, the four independent variables mentioned are examined for their effect on the esterification column at various steady-state levels. Once the independent variables have been analyzed, an examination of the mass and heat balances points out the precision of the experimental data. Following the discussion on the mass and heat balances, steady-state data and a steady-state model of the esterification column are used to obtain kinetic rate information for the esterification reaction for five levels of catalyst concentration. After the kinetics discussion, four experimental transient responses on the esterification column are illustrated and analyzed. The discussion and conclusion section on the experimental esterification column gives the operating conditions recommended by this study for the column.

4.3.1 Steady-state Data of the Esterification Column

Figures 4.11 and 4.12 show the steady-state composition of the reboiler and feedtray for all thirty-three runs carried out on the esterification column. The same data are given numerically, along with the steady-state condition of the decanter oil composition, in



Steady State Composition of Reboiler
Figure 4.11



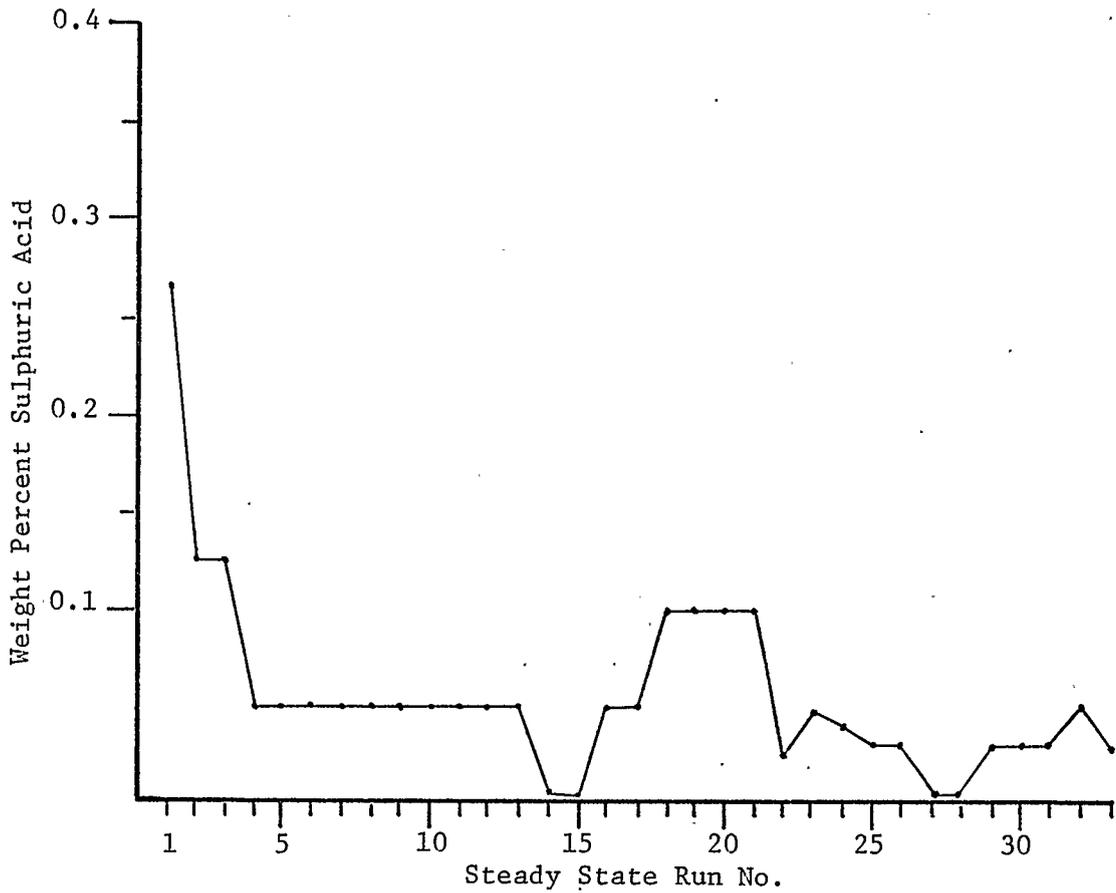
Steady State Composition of Feedtray
Figure 4.12

Tables A4.11, A4.12 and A4.13 . The steady-state temperatures, which are only important as an indicator on the amount of water present, are shown in Table A4.32 . The heat balance for all runs at steady state is displayed in Table A4.21 . The heat balance table is accompanied by Table A4.34 giving the product of the heat transfer film coefficient and the area, (hA), for the column and the average temperature between the liquid in the column and the surrounding ambient temperature for all runs. Figure 4.23 displays the feed rate to the esterification column for all thirty-three steady states. Figure 4.22 states the amount of steam fed to the reboiler for the thirty-three conditions tested at steady state on the esterification column. The weight percent of acetic acid and sulphuric acid catalyst in the feed at steady state is given by Figures 4.24 and 4.21 respectively for all runs. Since the above figures and tables make possible the analysis of the esterification column, and since the reboiler composition is the product composition, the catalyst concentration, the boil-up rate, the feed rate and the feed composition ratio are all judged for their effect on the reboiler composition along with any desirable or undesirable secondary features created by a given operation of the column.

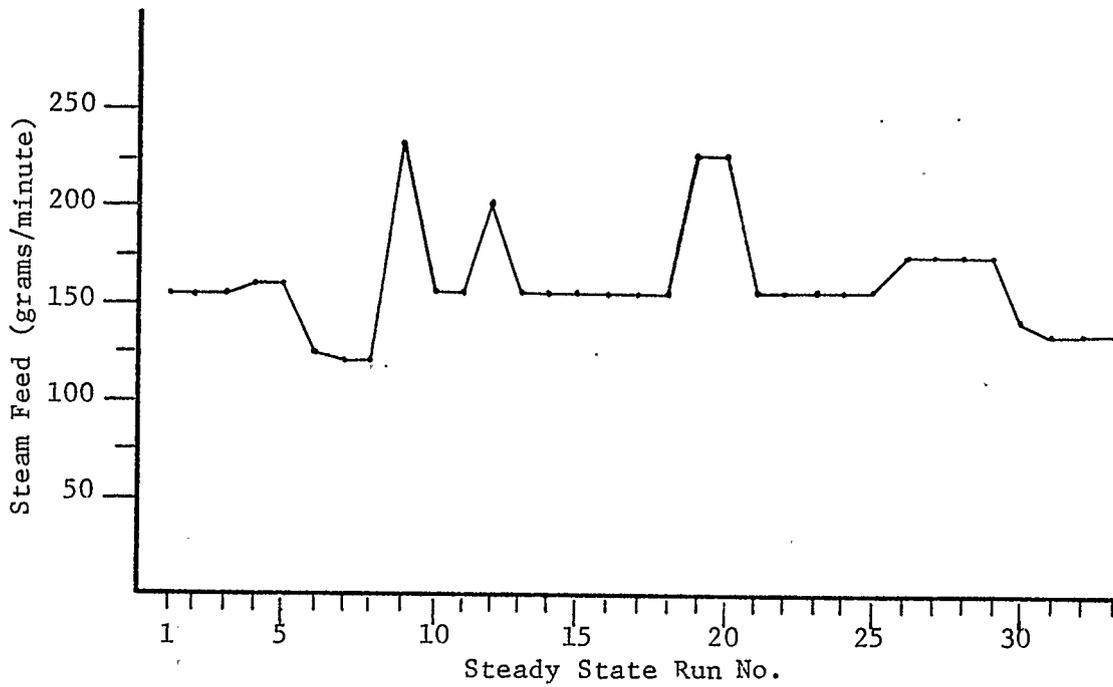
4.3.1.1 Effect of Catalyst Concentration on Column Operation

To illustrate the effects of catalyst, Runs 1, 2, 13, 14, 15, 17, and 18 will be examined using Figure 4.21 which states the catalyst concentration, and Figures 4.11 and 4.12 which give the composition of the reboiler and feed plate respectively.

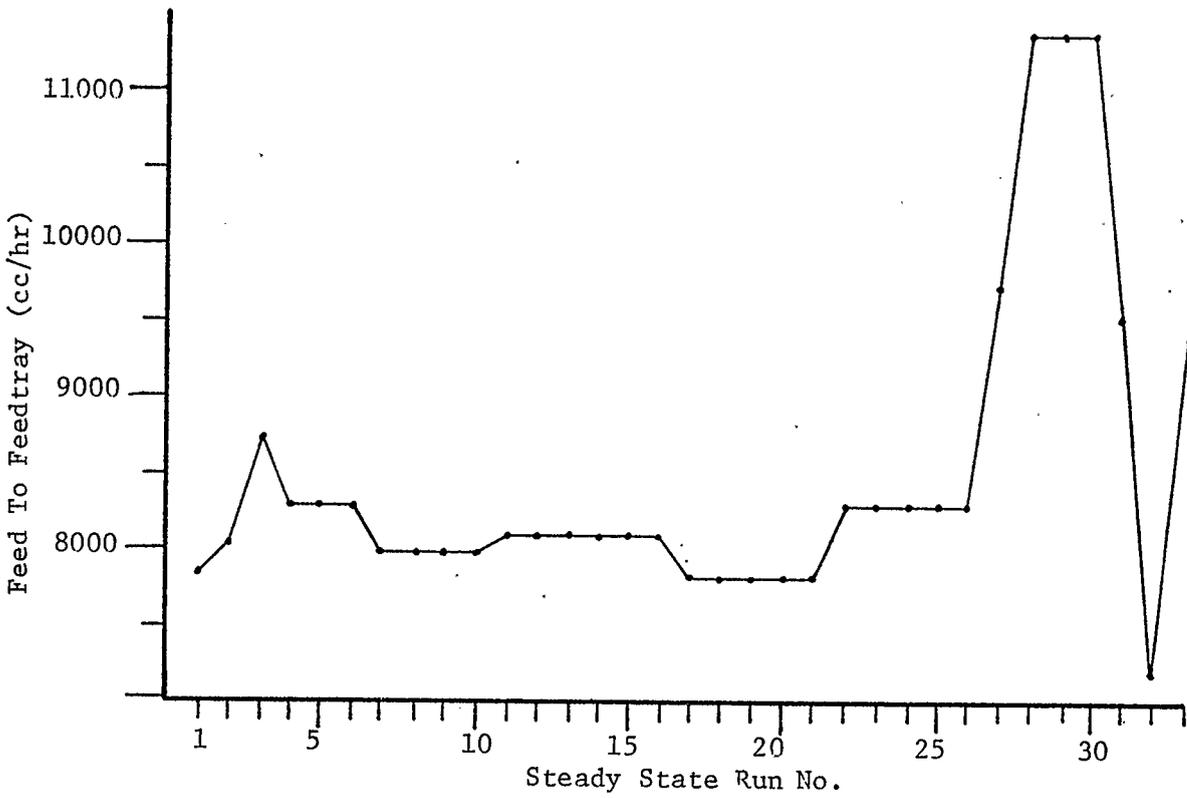
A 55 percent decrease in catalyst concentration is carried



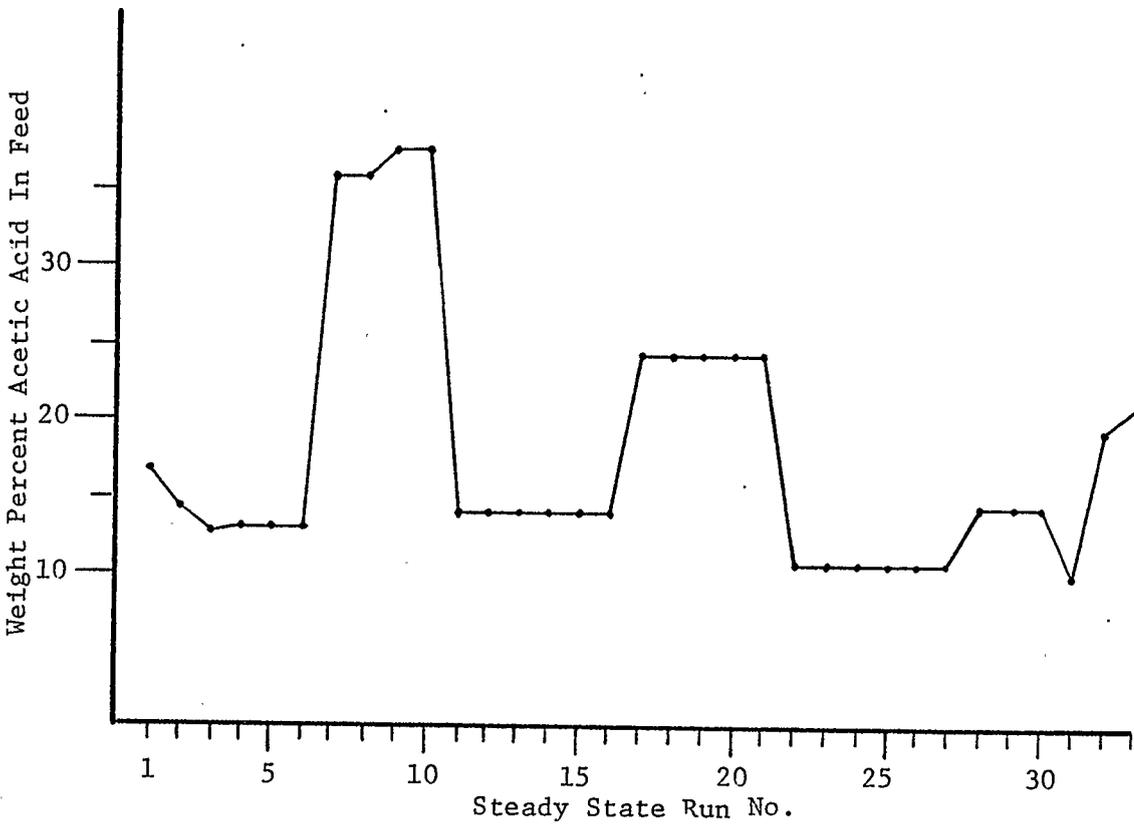
Steady State Concentration of Sulphuric Acid in Reaction Zone
Figure 4.21



Steady State Steam Feed Rate
Figure 4.22



Steady State Feed Rate To Feedtray
Figure 4.23



Steady State Concentration Of Acetic Acid In Feed
Figure 4.24

out between Runs Number 1 and 2 at steady state. Figures 4.11 and 4.12 show a small decrease in butyl acetate and a small increase in acetic acid concentration. The change in the reboiler or product composition is very slight for all components. Since the decrease in the corrosive and polymer inducing sulphuric acid is dramatic in the bottoms product and the other components are only affected slightly, the evidence suggests that a catalyst increase from 0.125 to 0.29 weight percent has little positive effect on the esterification reaction. (As will be shown below, small amounts of catalyst have a strong effect on the speed of the esterification reaction, but as the catalyst concentration increases its effectiveness drops. Figure 4.45 shows the parabolic relationship of the rate constant, k , of Equation 4.3.4 and the catalyst concentration.) The small amount of extra acetic acid resulting in the bottoms product stream due to the sulphuric acid cut would be removed in the downstream separation equipment by the esterification reaction because the acetic acid concentration (below 1.0 percent) is low enough. Hence, there is no reason to operate with a catalyst concentration above 0.125 weight percent.

The difference between Runs Number 13 and 14 is caused by a cut in the catalyst concentration in the feed from 0.5 percent to 0.05 percent. Since the decrease in catalyst causes the butyl acetate to drop four percent and that of acetic acid and butanol to rise three and one, respectively, in the reboiler, the change from Run 13 conditions to those of 14 demonstrates the large effect of a small amount of catalyst in speeding the esterification reaction to the right.

The change in conditions from Runs Number 14 to 15 illustrates

the importance of a small amount of catalyst even more dramatically. The only change in feed conditions from Runs 14 to 15 is a decrease in the catalyst concentration in the incoming feed from 0.005 to 0.003 . The change causes the butyl acetate concentration in the reboiler to drop another four percent and the acetic acid and butanol to rise as shown in Figure 4.11 . The same dramatic effects are shown on the feed plate results of Figure 4.12 . Hence, the evidence shows that small amounts of catalyst have a strong effect but as the catalyst concentration increases the effect it has decreases.

Since the only change to the input manipulated variables on the column from Runs 17 to 18 is to increase the catalyst fed in, from 0.05 percent to 0.10 percent, the change illustrates again the weakening effect of the catalyst at high concentrations. The butyl acetate concentration increases 6.0% and that of the acetic acid and butanol decreases 1.5% and 4.5% respectively. Thus the change on the butyl acetate is nearly the same as that caused by the catalyst adjustment from 0.05% to 0.03%.

The concentration at which the sulphuric acid catalyst should be set is not a decision which can be made only on the basis of the speed of reaction. As evidenced by the change from Runs 1 to 2, an increase in high catalyst concentration tends to speed the esterification reaction slightly while the catalyst dramatically increases the rate of corrosion and tar production. Hence, the amount of catalyst must be determined by the conditions which can be tolerated, with regard to corrosion and tar production under the conditions of operation of the column. If the speed of production is very important,

then a high level of catalyst should be used and the fouling and loss of chemical through tar production should be accepted. A low level of catalyst should be used if the equipment and chemicals are to be spared. While operating the esterification column, the tar production within the column produced no problems in the fouling of the $\frac{1}{4}$ -inch bottoms product line until a concentration of over 0.125% catalyst occurred. At catalyst concentrations over 0.125%, the outlet and analysis lines gathered salts and polymer which at times caused a complete stoppage of flow.

4.3.1.2 Effect of Boil-up Rate on Column Operation

The effect of steam rate (boil-up rate) is ascertained by examining Runs 5, 6, 8, 9, 10, 11, 12, 18, 19, 20, 21, 25, 26, 29 and 30. Figure 4.22 illustrates the steam feed rate to the column during all 33 runs. The butanol concentration throughout the esterification column is 14 to 20 times higher than the acetic acid concentration for Runs 5 and 6 for which there is a steam feed rate difference. Because of the steam feed rate decreases from Runs 5 to 6 the butanol and acetic acid concentration in the reboiler is lowered and butyl-acetate is increased as shown in Figure 4.11. Hence, a low level of steam boil-up is desirable when there is a high concentration of butanol. The steam rate should be no more than enough to remove water so that steam is saved and the reaction rate enhanced.

When the acetic acid concentration on the feed plate reaches 14 weight percent as shown in Figure 4.12 for Runs 7 to 10, a different result occurs with a steam change. The increase in steam (Runs 8 to 9)

tends to 'wash' the less volatile acetic acid down the column, increasing the butyl acetate concentration and decreasing the butanol concentration because of esterification. When the steam is decreased (Runs 9 to 10), the acetic acid and butyl acetate concentrations in the reboiler decrease while that of butanol increases. Hence, at high acetic acid concentrations on the feedtray, butanol and butyl acetate concentrations are affected in the opposite manner to that which occurs when the acetic acid percentage is low throughout the column.

The butanol and acetic acid negative azeotrope explains the behaviour of the column at low acetic acid concentrations. Lower boil-up means less butanol and acetic acid 'wash' down the column. At the high feedtray concentrations of acetic acid the column's behaviour is explained by both kinetics and vapor-liquid equilibrium forces. Initially the negative azeotrope 'washes' down both acetic acid and butanol. The acetic acid and butanol react to form butyl acetate. As the butyl acetate concentration increases by reaction, the positive azeotrope of butyl acetate and butanol carries the butanol back up the column. Hence the direction of movement of butanol and butyl acetate in the column are reversed by the esterification reaction and the increasing concentration of the positive butanol and butyl acetate azeotrope. The other runs mentioned confirm the above observations and explanations.

As with the catalyst feedrate, the best steam feedrate depends on the demands placed on the column. If the column is operated so that the acetic acid concentration is low throughout, then the boil-up rate of the esterification should be no more than that required to remove the water formed by reaction. However, if the acetic acid

concentration is high on the feedtray, then the question becomes one that is tied into demands for amount and quality of product. If the steam is increased with a high concentration of acetic acid on the feedtray, then both the acetic acid and butyl acetate are increased in the bottoms product. Whether or not the increase in acetic acid can be tolerated to increase the butyl acetate is a question which would depend on the quality of the separating equipment and the demand for butyl acetate.

4.3.1.3 Effect of Feed Rate on the Column

The effect of feed rate on the esterification column is ascertained by examining Runs 27, 28, 30, 31 and 32. The flow rate onto the feedtray at steady state is shown in Figure 4.23 for all 33 runs. Two changes are made on the operating conditions of the column from Runs 27 to 28. The feed flow rate is changed from 9650 cc/hr to 11350 cc/hr, and the ratio of acetic acid to butanol in the feed is changed from 10.67 to 14.25. (An increase in feed flow rate causes the residence time the chemicals are in the column to decrease.) The flow rate change is the more prominent. Since the butyl acetate drops from 21.0 to 20.0% (Figure 4.11), and the acetic acid rises from 6.0 to 8.5% in the reboiler (Figure 4.11), the ratio of the incoming feed cannot be the dominating factor. As will be shown later, in Section 4.3.1.4, an increase in the acetic acid to butanol ratio alone causes both the acetic acid and butyl acetate concentration in the reboiler to rise; hence, the decrease in butyl acetate from Runs 27 to 28 is due to the increased flow rate. The butyl acetate would have dropped in concentration even further if the ratio of acetic acid to

butanol had not been increased. Figure 4.12 above shows that the feedtray responds the same way as the reboiler, indicating as back-up evidence, the lack of residence time for the esterification reaction to occur.

The change in flow rate from Runs 30 to 31 is accompanied, as above, with a ratio change. The flow cutback from 11350 cc/hr to 9560 cc/hr and ratio of acetic acid from 13.5% to 10.0% causes a slight decrease in both acetic acid and butyl acetate in the reboiler as illustrated in Figure 4.11. The same decrease in acetic acid ratio without an accompanying cut in flow rate would have caused two or three times the percentage drop in butyl acetate concentration. The reason the acetic acid did not drop more in the reboiler is because of the new distribution in the column which lowers the concentration of acetic acid on the feedtray and, hence, slows the reaction down. Thus, an approximate 10% change in feed rate is again seen to have a very definite effect on the column's performance. The change in column conditions from Runs 31 to 32 results in the same effects as found for the change from 30 to 31.

The above observations on the effect of flow rate show that no absolute statement can be made on what the best flow rate is for the column feed. Rather than indicate any particular level of flow rate as the optimum, the evidence shows that the drop in butyl acetate concentration does not match the rise in through-put. This is shown later to be true because of the form of the kinetics equation where the rate of reaction is found to be a function of the product of the acetic acid and butanol concentration. Hence, if large quantities of

butyl acetate are demanded and the separation system downstream of the column can handle contaminated product, then the column should have a high feed rate. However, if a high quality product with a low percentage of acetic acid and butanol is desired, then the column should be operated at the flow rate to produce the desired product. Thus the flow rate that produces the optimum operating conditions depends entirely on external constraints imposed upon the operation of the total system.

4.3.1.4 Effect of Feed Ratio on the Column

The weight percent of acetic acid in the feed for all 33 runs is illustrated in Figure 4.24 . The runs which demonstrate the effect of the feed ratio of acetic acid to butanol on the esterification column are 6, 7, 10, 11, 16, 17, 21 and 22. The acetic acid to butanol change made in going from Runs 6 to 7 has a powerful effect on the column as evidenced by Figures 4.11 and 4.12 . The butyl acetate in the reboiler of Run 7 is 46.0% higher than that of Run 6 and the butanol concentration falls 50.0% . The undesirable feature is that the acetic acid concentration rises 3.0% to 4.0% in the reboiler. (The feedtray changes are illustrated in Figure 4.12 .) Hence, the change from the conditions of Run 6 to those of 7 shows that increasing the acetic acid concentration in the feed increases the butyl acetate in the reboiler. Thus the evidence of the change from 6 to 7 shows that an approximate 1.0% increase in acetic acid in the feed increases the bottoms product butyl acetate concentration by 2.0% and at the same time slightly increases the contamination by

acetic acid. The acetic acid in the reboiler tends to increase approximately by 1/5 the amount it is increased in the feed to the column. (The 1/5 value is obtained by averaging the results from all the above-mentioned runs.)

When the concentration of acetic acid is cut in the feed, as occurred between Runs 10 and 11, the butyl acetate drops the amount expected as illustrated in Figure 4.11. If the other runs mentioned above are examined, the results already mentioned will be confirmed. Thus the acetic acid to butanol ratio has a very strong effect on the butyl acetate concentration in the bottoms product. However, to have a high butyl acetate concentration, a higher level of acetic acid must also be tolerated.

The proper feed ratio for the column is a function of the quantity of butyl acetate desired and the level of acetic acid that is tolerable in the bottoms product. Hence, the concentration of acetic acid in the feed must be set by the tolerance of downstream equipment to acetic acid and the demand for butyl acetate.

4.3.2 Mass Balance on Esterification Column

The overall mass balance on the esterification column is given in gms/hr (Table A4.31) and in moles/hr (Table A4.32). The total amount of each chemical fed in at steady state along with the quantity removed is stated for all 33 runs. Since the weight and number of moles in and out of the esterification column should match, but donot, the error in the mass balance is stated. A positive error means more chemical is measured going into the column than is measured

leaving the column. The stated percentate error is based on the mass weight or moles injected into the column.

Because the moles of water do not match the moles of butyl acetate produced from the column, it is apparent that either the water or butyl acetate measurement is in error. The moles of water produced should match the moles of acetic acid that disappear due to the reaction. However, the number of moles of water is at times 50% to 70% in error based on the incoming acetic acid. The low exit water flow rate values measured from the column force almost all the mass balance readings into a positive error as illustrated in Table A4.31 and Table A4.32 .

The mole balance in the column shows that the measurements on the quantity of butanol leaving the column are low and the measurements for the amount of butyl acetate are high. The butanol and butyl acetate flow rates could be correct, however, and instead it may possibly be that the acetic readings are high; however, a high acetic acid reading is not as likely as the butanol and butyl acetate flow rates being in error. The reason the acetic acid flow measurement is not as likely to have caused the calculated balance to be out between butanol and butyl acetate is because many runs, such as Run 31, cannot be corrected anywhere near the correct balance for butanol and butyl acetate by adjusting acetic acid because there is not a high enough flow rate of acetic acid. Hence, the butanol and butyl acetate flow rates measured are definitely in error. The exact amount the flows are in error is impossible to determine because not only is the error in the measured quantity of outgoing components not known exactly but

neither is that of the incoming streams.

The incoming butanol and acetic acid streams are calibrated carefully and should have an error of flow measurement under $\pm 1.0\%$. The flow measurement out of the column has three variables that could affect the precision of measurement. First there is the above-mentioned problem of the precision of the calibrated instrument. Second, because the outgoing fluid changed density, this could have affected flow measurements along with some fouling problems that occurred. Third, because the exact precision of the gas chromatographs at a given time varied from a precise $\pm 1.0\%$ to a rough $\pm 10.0\%$, there is no way of knowing for certain what the exact accuracy of analysis is for all components in the outgoing streams.

The overhead water stream is analyzed properly but in this case, a flow meter is working at the limit of its ability to properly function. Hence, because the outgoing water flow is so small, the precision obtained from the flow meter is unknown and by the results of the mass balance, it does not look as if it is good. The runs where the precision of the water measurement seems better are those where the water output is measured in a graduated cylinder over the entire duration of the run. The large capacity in the decanter affected the water balance because when small amounts of water were produced the controller was not sensitive enough to have obtained steady state when the rest of the column reached it. The controller's sensing device in the decanter was the cause of the trouble. If it was made sensitive enough, it oscillated with the noise and when the noise was eliminated it did not respond properly.

4.3.3 Heat Balance on Esterification Column

The heat balance is displayed in Table A4.33 for all 33 runs. The reflux flow rate back into the column from the decanter is shown in Table A4.22 along with the cooling water flow rate and the temperature change occurring in the cooling water on passing through the condenser. The steady state temperatures for all 33 runs for the reboiler, Tray 2, Tray 4, Tray 8, and Tray 10 are illustrated in Table A4.21 . The average product of the heat transfer film coefficient and the area, (hA), of the column is shown in Table A4.34 accompanied by the average difference between the temperature of the inside of the column and the ambient air.

The run with the highest heat loss is Run 15 with a loss of 51.79% (Table A4.33). However, it is doubtful if the loss is actually as high as 51.79% . Since the temperature difference for the cooling water during Run 15 (Table A4.22) is 10.6 degrees and since the closest any temperature could be read is ± 1.0 degrees centigrade with high precision, a 20.0% error could be due to a lack of accurate temperature recording. Because the error should average out over the 33 runs, it is much more profitable to talk about average heat losses. Since the temperature of the column remained almost constant for all of the runs, practically speaking (Table A4.34), the heat loss should have been about the same for all runs except for the small amounts carried out by the different product flow rates. The average calculated heat loss is 1481.75 K-cal/hr from the column which represents a 33.41% loss if the steam rate is 155 gms/min and the average product of the heat transfer film coefficient and the area, (hA), is 17.04 K-cal/(hr⁰C).

Since the composition of the reflux is such that it has an average latent heat of 170 cal/gm; it can be seen from Table A4.22 that the heat removal required to produce the reflux is in agreement with the measured quantity of heat removed by the cooling water. (Depending on the reflux ratio, only about 2.0 to 8.0% of the heat removed in the condenser is used to condense the water overhead product.)

The heat loss from the esterification column could have been improved if more extensive insulating on the column had been done. However, a 33.41% heat loss is tolerable. If more temperature recorders had been available, a more sensitive temperature span could have been applied eliminating much of the error in measurement that did occur. Since the quantity of heat removed to condense the reflux stream is in good agreement (within the error allowed) with the measured quantity of heat removed by the cooling water, it is apparent that the heat balance is well within the error limits that result because of the sensitivity of the instruments used.

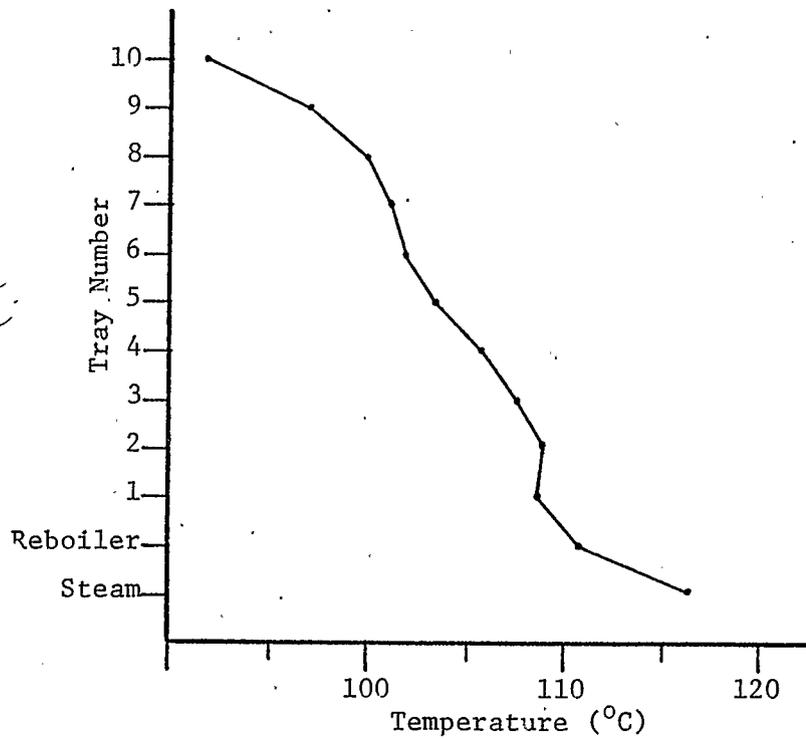
Since the reflux rate fluctuated from 1.5 times the feed rate (Run 2) to 4.0 times the feed rate (Run 18), the temperatures in Table A4.21 are in close agreement. The reason the temperatures are so close is that the temperature depends primarily on the amount of water present. Since even a boil-up rate that gives a reflux 1.5 times that of the feed rate is enough to remove most of the water the temperature remains fairly constant. The high temperatures caused by the high boil-up rate would have been affected by increased pressure in the reboiler as well as extra drying, as evidenced by Run 9 and the increased pressure differential across the column. The higher pressure

would have increased the temperature without any change in water composition or any other composition change in the column. Also, because the latent heat of vaporization for acetic acid is about 0.6 of that of water, the Clausius-Clapeyron equation predicts that acetic acid is twice as sensitive to pressure changes as the other three components. Hence, at high boil-up rates, the extra pressure on the lower trays, where acetic acid is concentrated, should have a stronger effect on the temperature than an increase in pressure on the top trays where there is little acetic acid.

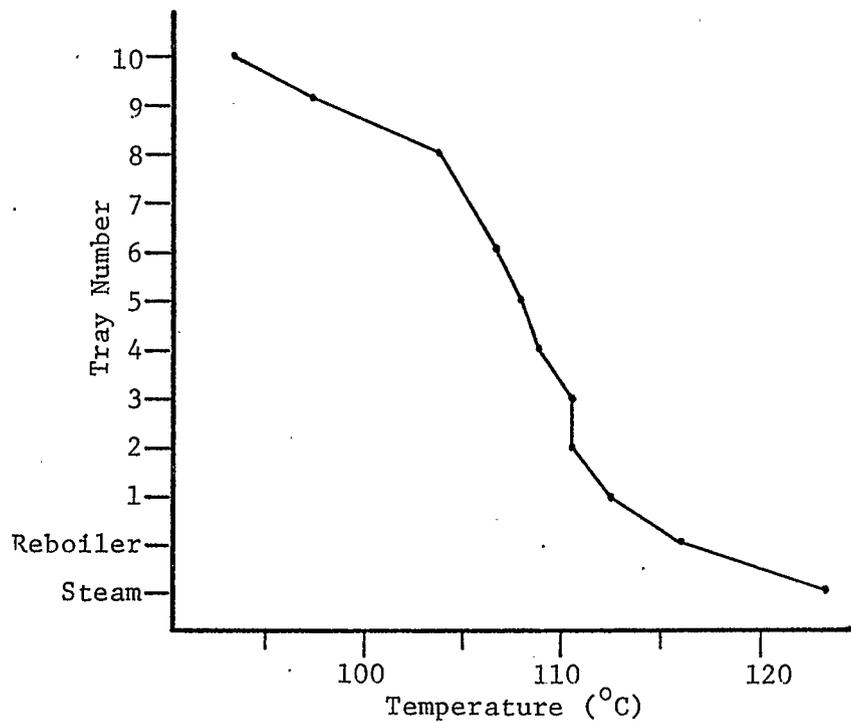
4.3.4 Kinetics Calculations from Steady-state Esterification Data

To calculate the rate of esterification in the column, complete composition profiles at steady state are needed. The composition profiles for 16 runs are presented in Tables A4.41 to A4.46 . The temperature profile that accompanies the above composition profiles may be obtained by noting the run the composition profile was taken on and then going to Table A4.21 and obtaining the corresponding temperatures that match the stated tray number.

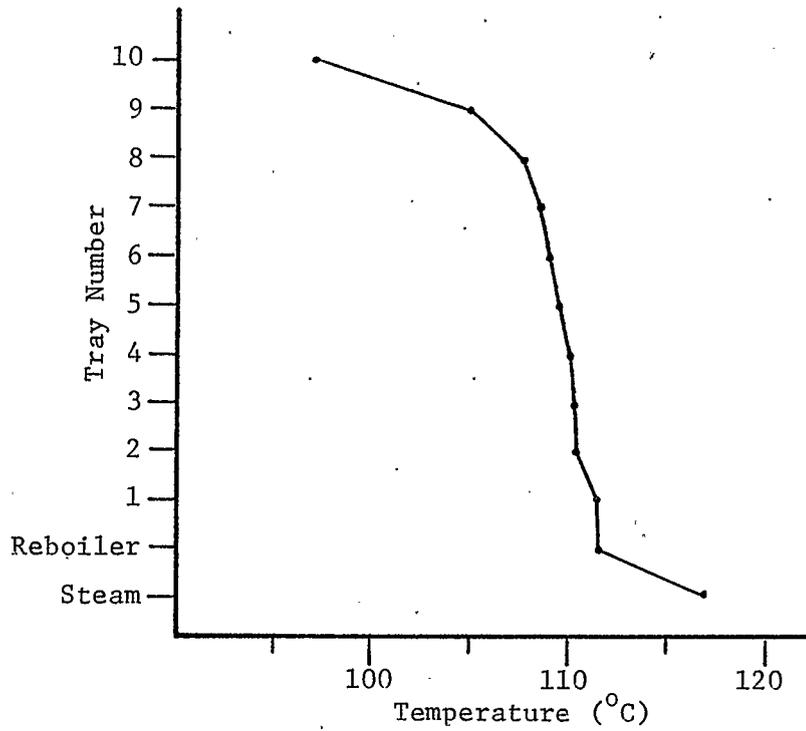
Four temperature profiles through the esterification column are illustrated in Figures 4.31, 4.32, 4.33 and 4.34 . Figure 4.31 shows a temperature profile at a low steam rate (Run 6). Figure 4.32 shows a temperature profile at a high acetic acid feed rate (Run 8). The temperature is primarily governed by the amount of water present in the liquid. When the temperature reaches 95.0°C , there is approximately 1.5 weight % water in the liquid of the column. As mentioned previously, trays with large percentages of acetic acid, under



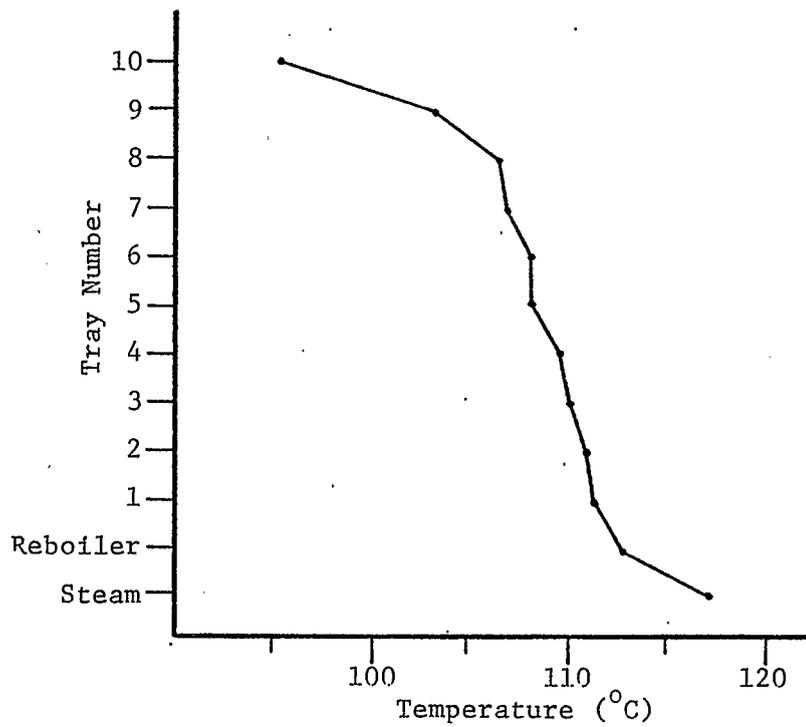
Steady State Temperature Throughout
Column For Run No. 6
Figure 4.31



Steady State Temperature Throughout
Column For Run No. 8
Figure 4.32



Steady State Temperature Throughout
Column For Run No. 23
Figure 4.33

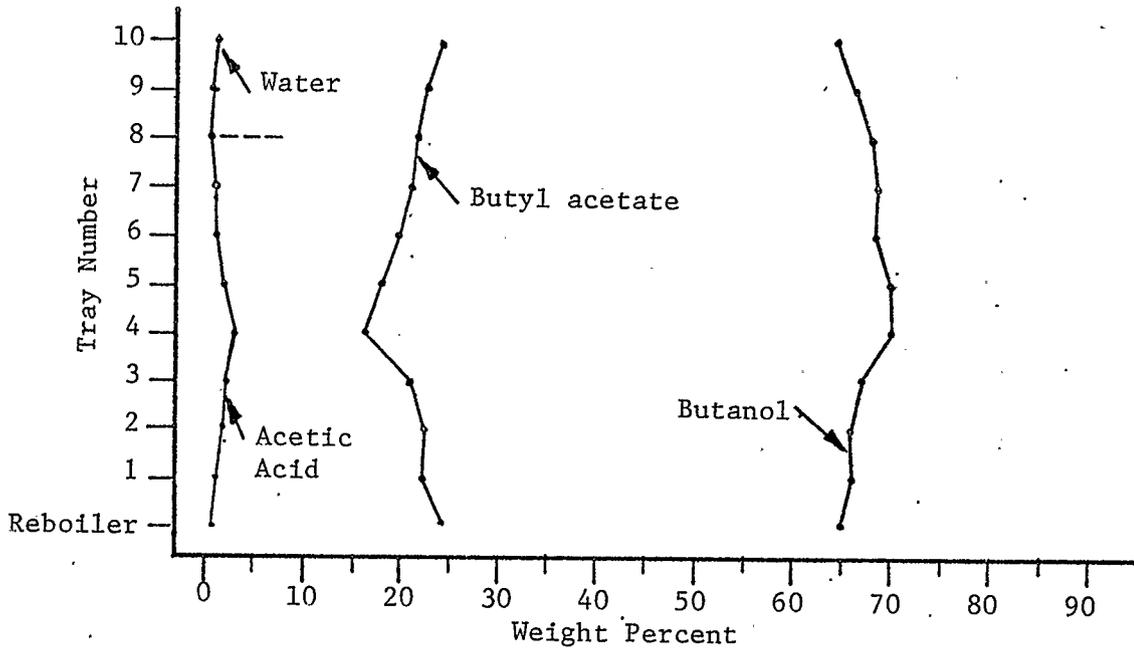


Steady State Temperature Throughout
Column For Run No. 29
Figure 4.34

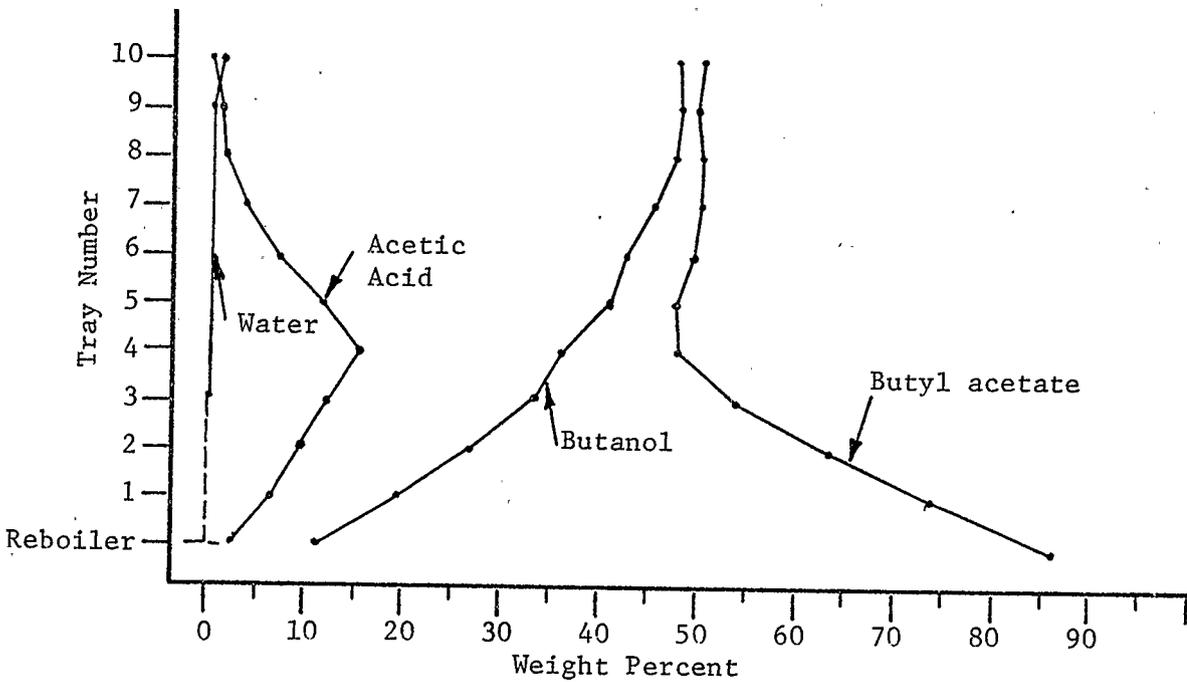
pressure, could also have affected the temperature, to a degree unknown, as well as the water percentage. The temperature profile of Figure 4.33 (Run 23) is typical for moderate steam rates and low acetic acid percentages in the feed. Figure 4.34 (Run 29) represents the temperature profile for the column at a high feed rate.

As mentioned above the water content of the liquid in the column can only be estimated by the temperature. The acetic acid, butanol, and butyl acetate profiles are shown in Figures 4.41, 4.42, 4.43, and 4.44 for Runs 6, 8, 23 and 29 respectively. (The water composition is shown for the top trays.) Figure 4.41 (Run 6) represents the composition through the column at a low boil-up rate and a low percentage of acetic acid in the feed. Figure 4.42 illustrates the profile when the acetic acid is high in the feed (Run 8). Figure 4.43 and 4.44 represent the typical runs made on the column with average boil-up rates, average acetic acid feed rates and average catalyst concentration. Figure 4.44 (Run 29) is for a much higher than average flow rate; hence, the higher acetic acid concentration on the lower trays as compared to Run 23.

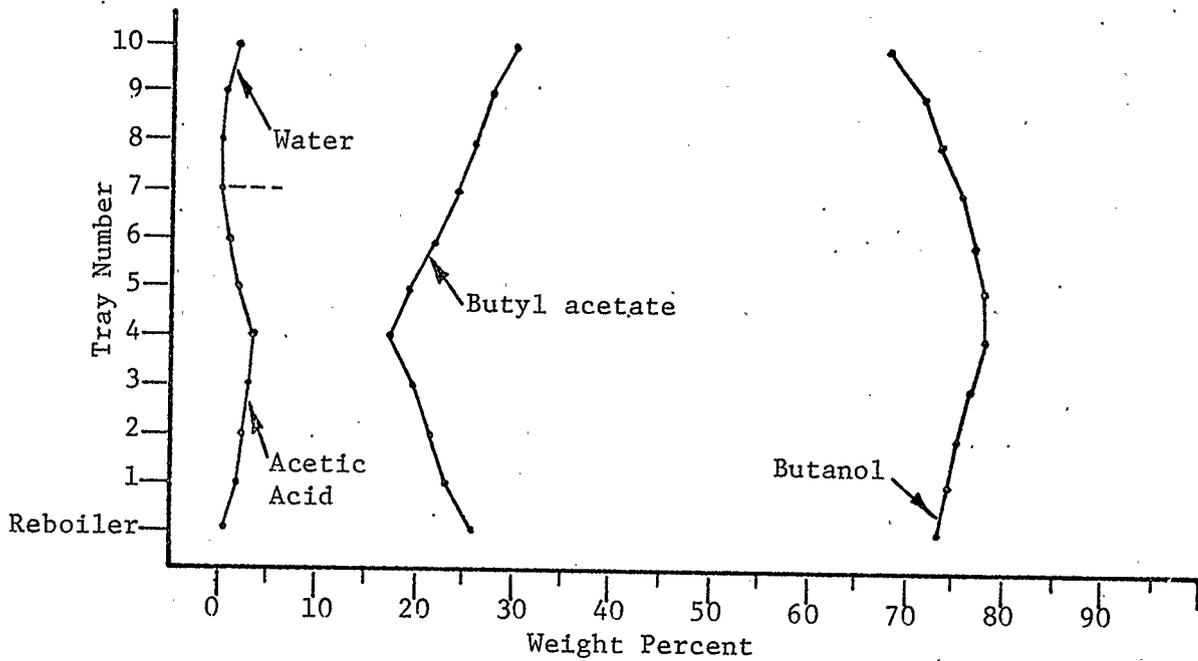
Using all the composition profiles given in Tables A4.41 to 4.46 and the feed and discharge steady-state rates for the esterification column, it is possible to calculate the rate of esterification at different sulphuric acid (catalyst) concentrations. Program 16 (Appendix 1) is used. Program 16 needs all the profile composition information, plus the feed and discharge rates, plus vapor-liquid equilibrium data which is taken from Leyes and Othmer (19) and Section 3 of this study. Thus with all other variables known, it is possible



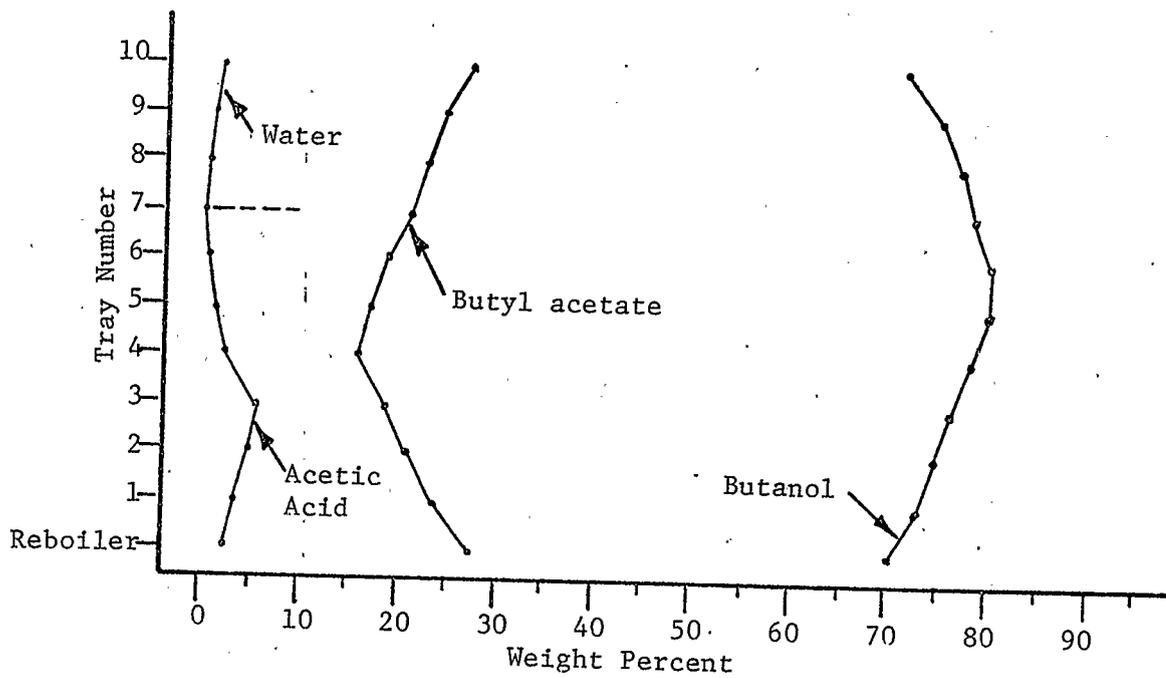
Component Composition Through Column At Steady State For Run No. 6
Figure 4.41



Component Composition Through Column At Steady State For Run No. 8
Figure 4.42



Component Composition Through Column At Steady State For Run No. 23
Figure 4.43



Component Composition Through Column At Steady State For Run No. 29
Figure 4.44

to calculate the reaction rate occurring on each tray.

Once the rates of reaction are known they are correlated. An attempt is made to use the equation put forth by Leyes and Othmer (20); however, success with their equation proves limited. Hence, an equation of the following form is used which is closer to what reaction kinetic theory would predict.

$$r = k (X_{\text{AcOH}} X_{\text{BuOH}})^2 \quad (4.34)$$

r = rate of reaction (moles/(hr.cc))

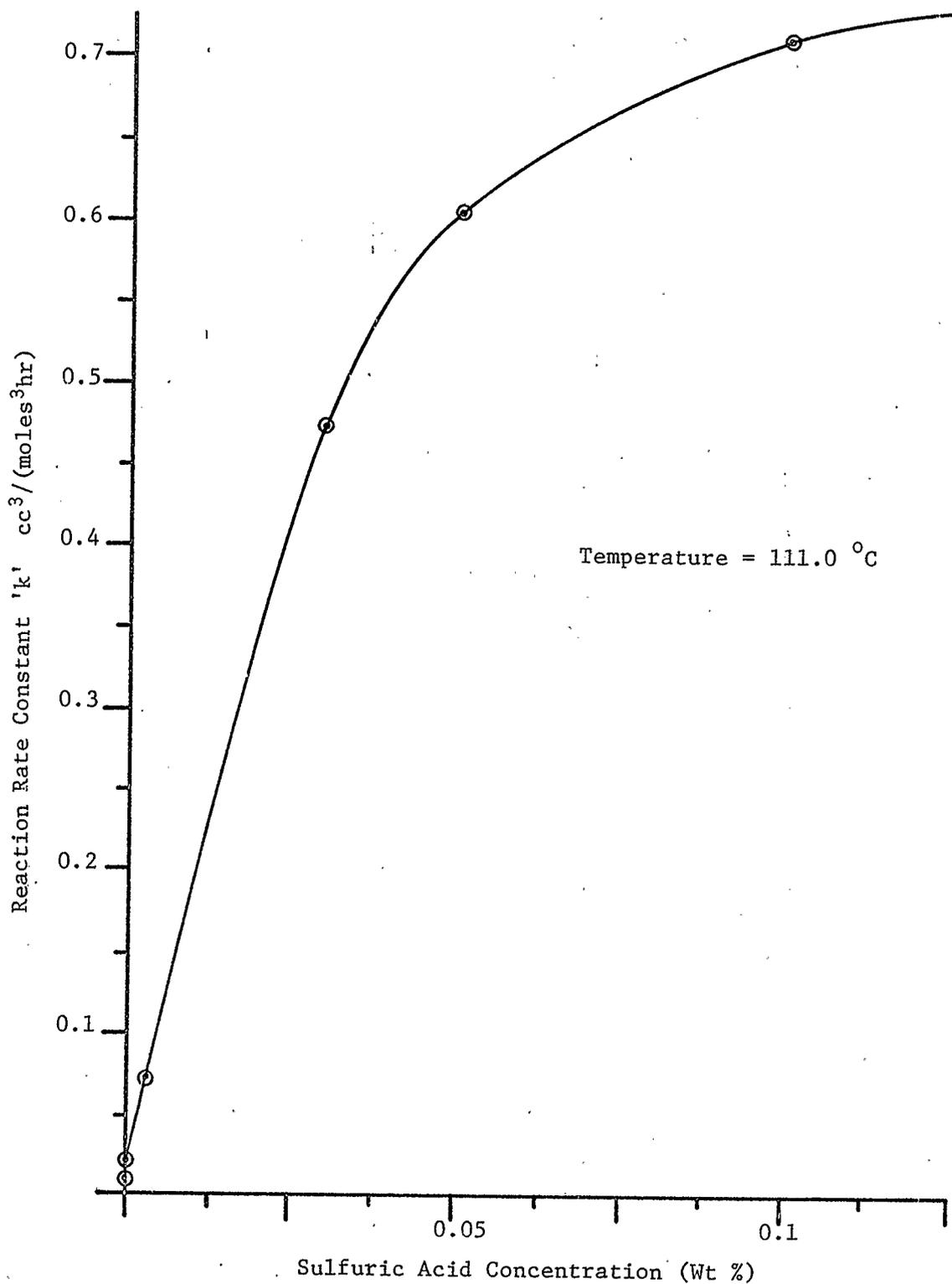
k = reaction constant (cc³/moles³ hr)

X_{AcOH} = moles acetic acid/cc (moles/cc)

X_{BuOH} = moles butanol/cc (moles/cc)

The value of k is 0.714, 0.603, 0.474, 0.0692, 0.0204 and 0.01 for catalyst concentrations of 0.1, 0.05, 0.03, 0.003, 0.00 and 0.00 weight percent respectively (Figure 4.45). The two different values for zero catalyst are obtained from the vapor-liquid equilibrium studies. The 0.0204 constant is from work on the ternary acetic acid, butanol, and butyl acetate and the 0.01 constant is from studies on the ternary system water, acetic acid, and butanol.

To calculate the rate of reaction from the esterification column, the vapor-liquid equilibrium data of Leyes and Othmer (19) and of Section 3 of this study is used. The results are scattered badly; however, the slope obtained is near two in all cases when r is plotted versus $X_{\text{AcOH}} X_{\text{BuOH}}$ on a log-log plot. To obtain the value of the constant, (k), presented here, simulation studies are



Reaction Rate Constant 'k' as a Function of the Sulfuric Acid Concentration in a Mixture of Butanol, Acetic Acid, and Butyl acetate for Equation 4.34

Figure 4.45

done (see Section 5). During the simulation studies the vapor-liquid equilibrium data of Leyes and Othmer (19) and Section 3 is again used. To make the end points in the simulation studies agree, the k values of the kinetics equation are adjusted to force agreement. Hence, rather than use a least squares fit or a fit by judgment on the log-log plot, the final value of k is decided so as to make the simulation studies done on the column agree with what happened experimentally. The scatter of the kinetics data is such that the calculated rate constants, (k), can be shifted $\pm 20.0\%$. Since the vapor-liquid equilibrium data of Leyes and Othmer varies $\pm 20.0\%$ and the approximations made using the data of Section 3 are of the same order of precision, the rate constants fluctuation is probably due to the vapor-liquid equilibrium data.

Because of the way the above rate constants are calculated, the author does not put the rate equation forward as being correct for kinetics studies. Rather, the constants chosen are those that make the simulation studies' results agree with those obtained from the experimental column. Hence, what the correct values of the k for the above catalyst concentrations is cannot be stated from the results of this study.

4.3.5 Transient Data from the Esterification Column

Four open loop transient responses for the esterification column are illustrated by Figures 4.51 to 4.89 (Tables A7.1 to A7.8). The four changes investigated are a step change in catalyst, a step change in boil-up rate, a step change in feed rate, and a step change

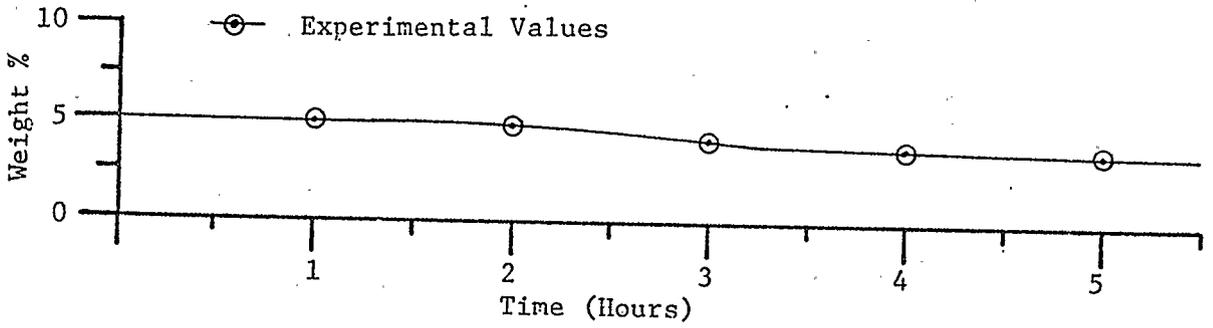
in the weight percent of acetic acid in the feed. In each case, the transient response for the various component concentration changes is given for both the reboiler and the feedtray. The transient response of the reboiler temperature and the temperature of Tray 10 is given. Tray 10 is chosen rather than the feedtray because it is the one that has the largest water concentration changes, and hence, the largest temperature changes. The dashed lines on Figures 4.51 to 4.89 represent the results of simulation studies and are discussed in Section 5.

4.3.5.1 Catalyst Step Change

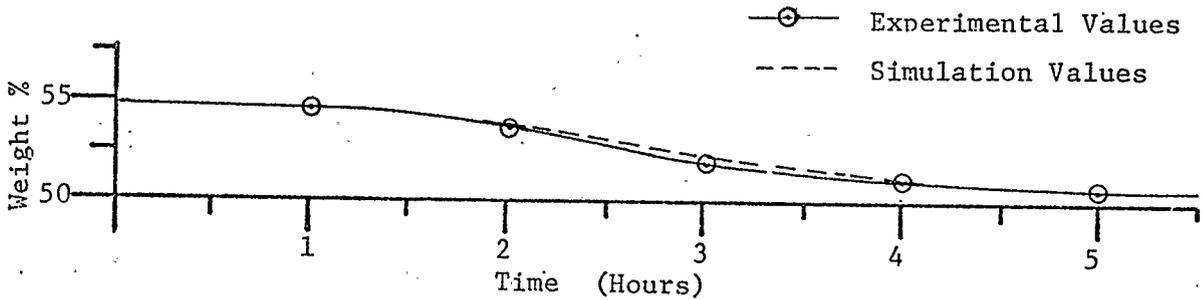
The transient change in the esterification column illustrated by Figures 4.51 to 4.59 (Tables A7.1 and A7.2) is that brought about by increasing the catalyst concentration from 0.05 weight percent to 0.1 weight percent. The steady-state conditions that exist at the start and end of the transient are those represented by Runs 17 and 18, respectively, in Figures 4.11 to 4.24 and Tables A4.11 to A4.34 .

The effect on the reboiler composition as a function of time when the catalyst concentration is doubled at the steady-state conditions of Run 17 is shown in Figures 4.51 to 4.53 . Table A4.11 states that the water concentration remains constant in the reboiler for the catalyst step. Figures 4.51 to 4.53 demonstrate the long dead time in the reboiler before any effect is felt. This is due to the time required to 'flush' the higher catalyst concentration through the column to the reboiler.

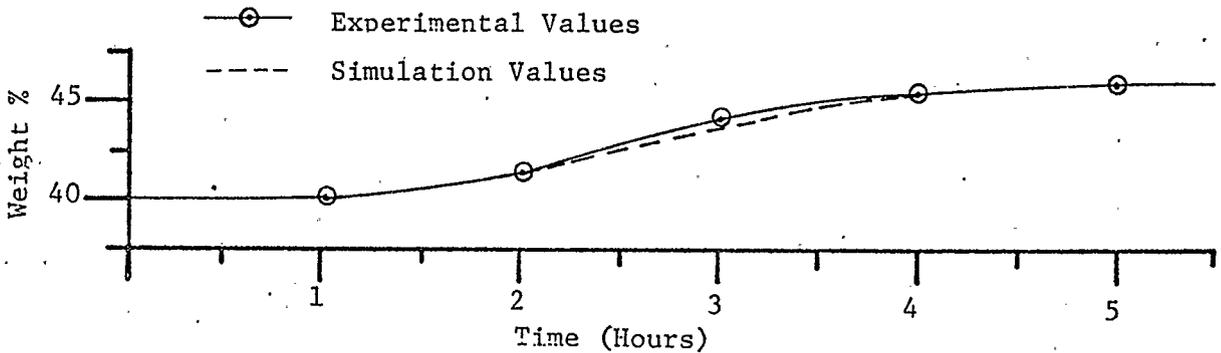
Figures 4.54 to 4.57 illustrate the changes that occur on the feedtray after the catalyst is stepped up in concentration. The



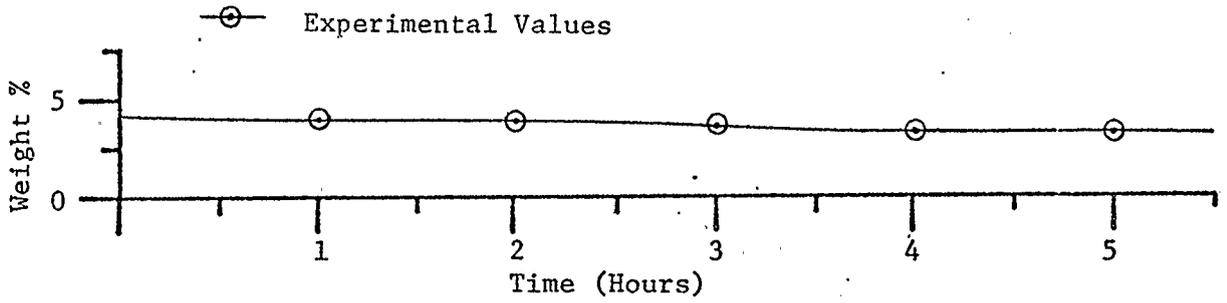
Acetic Acid Transient For Catalyst Step Change in Reboiler
Figure 4.51



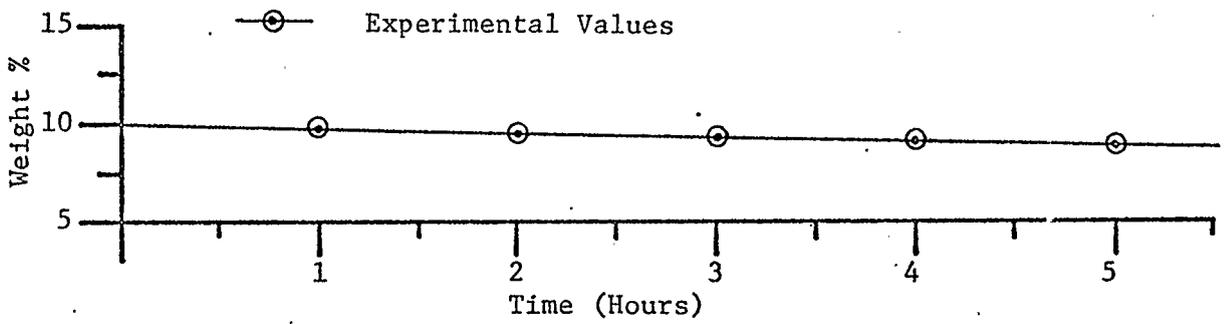
Butanol Transient For Catalyst Step Change in Reboiler
Figure 4.52



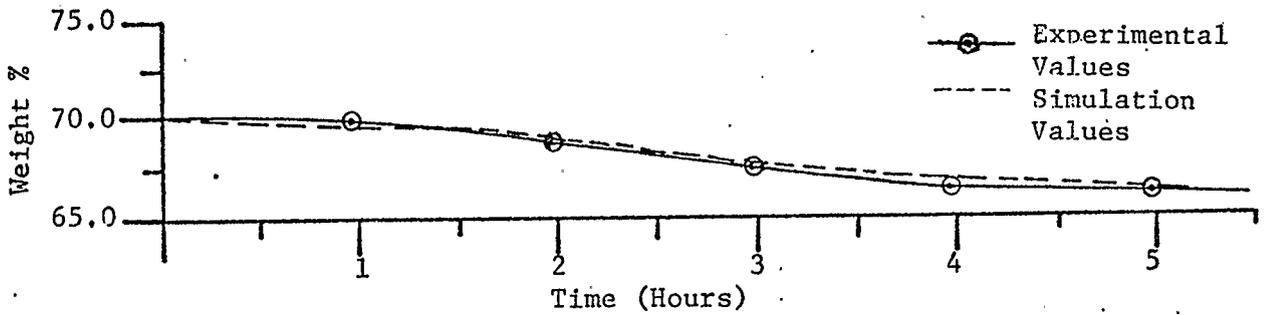
Butyl acetate Transient For Catalyst Step Change in Reboiler
Figure 4.53



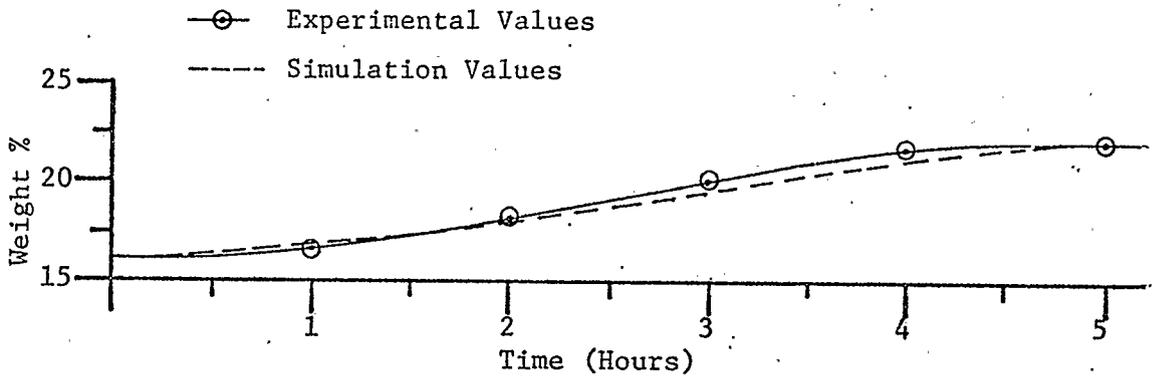
Water Transient For Catalyst Step Change on Feedtray
Figure 4.54



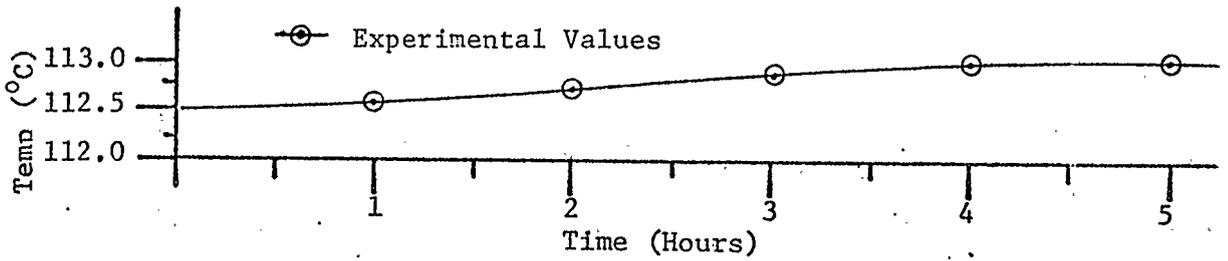
Acetic Acid Transient For Catalyst Step Change on Feedtray
Figure 4.55



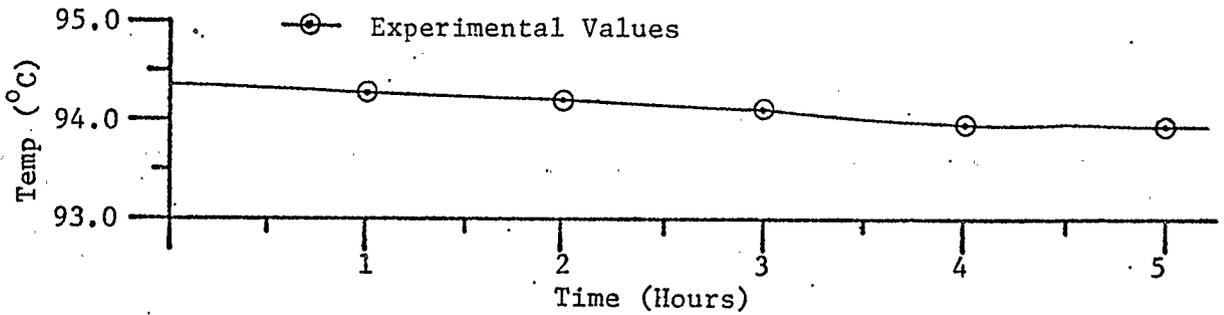
Butanol Transient For Catalyst Step Change on Feedtray
Figure 4.56



Butyl acetate Transient For Catalyst Step Change on Feedtray
 Figure 4.57



Temperature Transient For Catalyst Step Change in Reboiler
 Figure 4.58



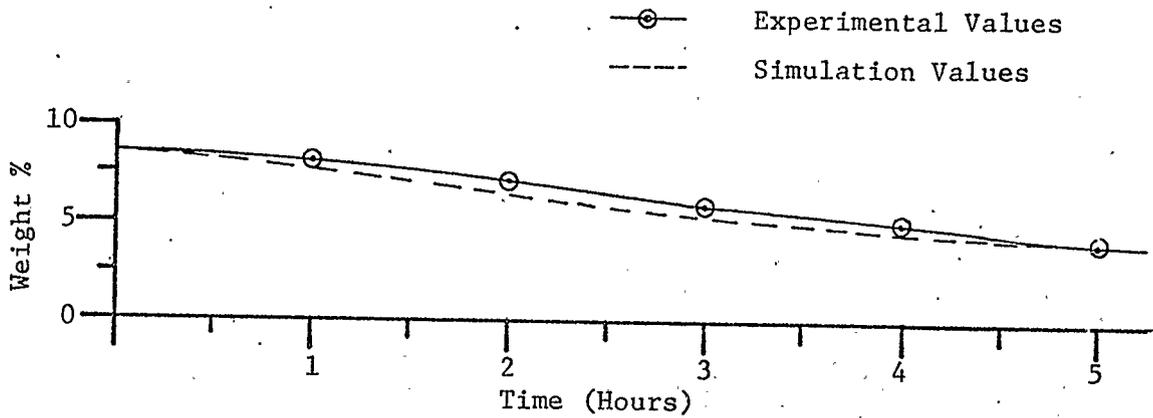
Temperature Transient For Catalyst Step Change on Tray 10
 Figure 4.59

feedtray displays a very pronounced deadtime for all four components. The speed of the response on the feedtray should theoretically be instant if the tray is a first order system because that is the tray on which the catalyst step change is introduced to the column. The fact that the feedtray response is like that of a multi-order system shows that the non-linear reaction kinetics and vapor-liquid equilibrium forces must be causing the multi-order type response on the feedtray. Thus, the tray is not responding directly to the increased flow of catalyst but instead to the more complex changes resulting from the esterification reaction and the distillation forces.

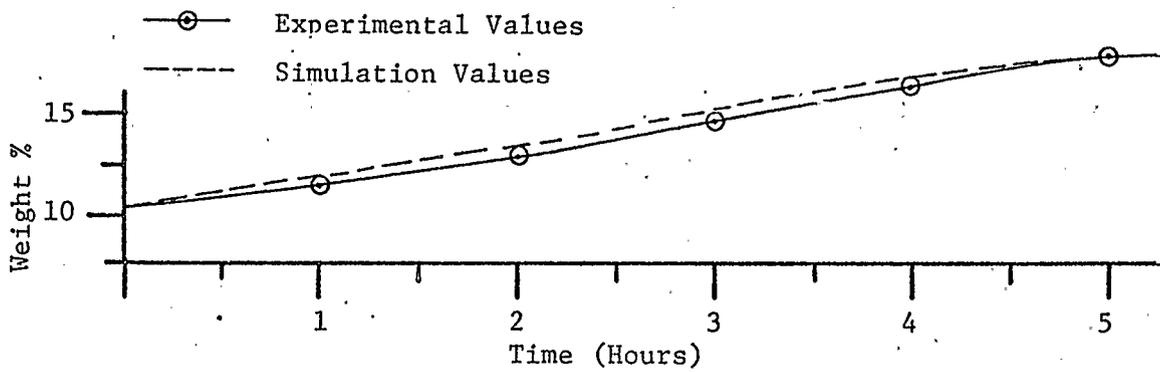
Figures 4.58 and 4.59 give the temperature response to the catalyst step increase for the reboiler and the top or 10th tray of the column, respectively. Figure 4.58 indicates that the water content of the reboiler has dropped very slightly. This is probably due to the higher butyl acetate concentration in the reboiler carrying water up the column. The 10th tray shows the results of the faster reaction (due to increased catalyst) in that its water content increases and the temperature decreases. The time constant resulting from the step increase in catalyst is between 3.0 to 3.5 hours.

4.3.5.2 Steam Step Change

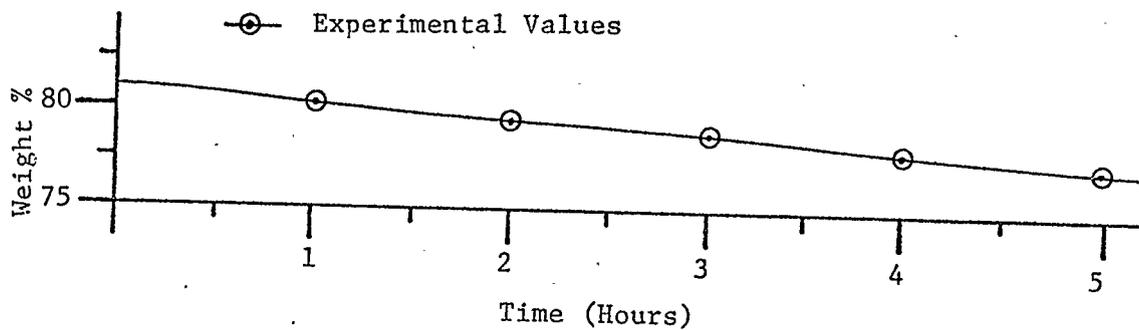
The transient response, due to a step decrease in steam rate from 230 gms/min to 155 gms/min, is illustrated in Figures 4.60 to 4.69 (Tables A7.3 and A7.4). The steady-state conditions that existed at the start and end of the transient are those represented by Runs 9 and 10, respectively, in Figures 4.11 to 4.24 and Tables A4.11 to A4.34.



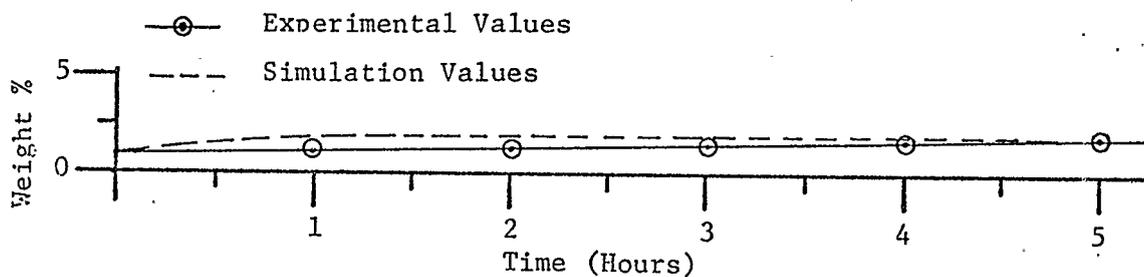
Acetic Acid Transient For Steam Step Change in Reboiler
Figure 4.61



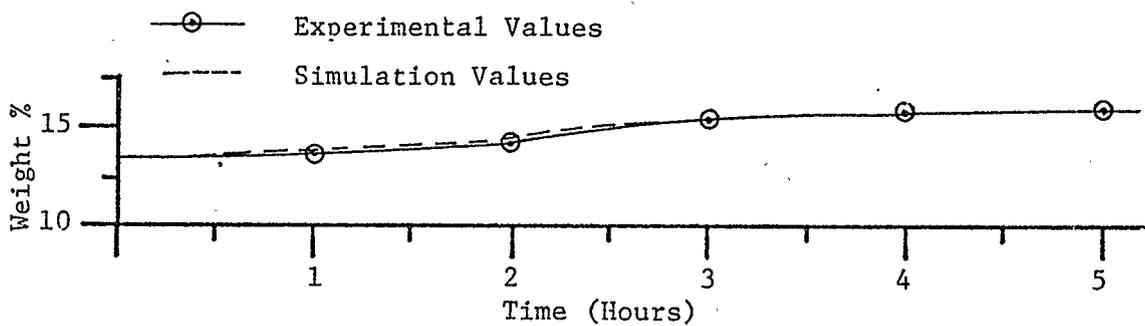
Butanol Transient For Steam Step Change in Reboiler
Figure 4.62



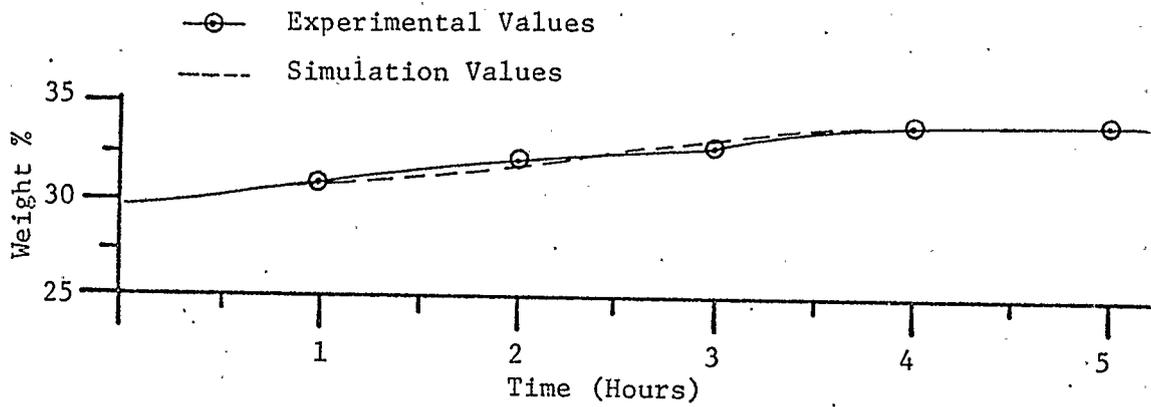
Butyl acetate Transient For Steam Step Change in Reboiler
Figure 4.63



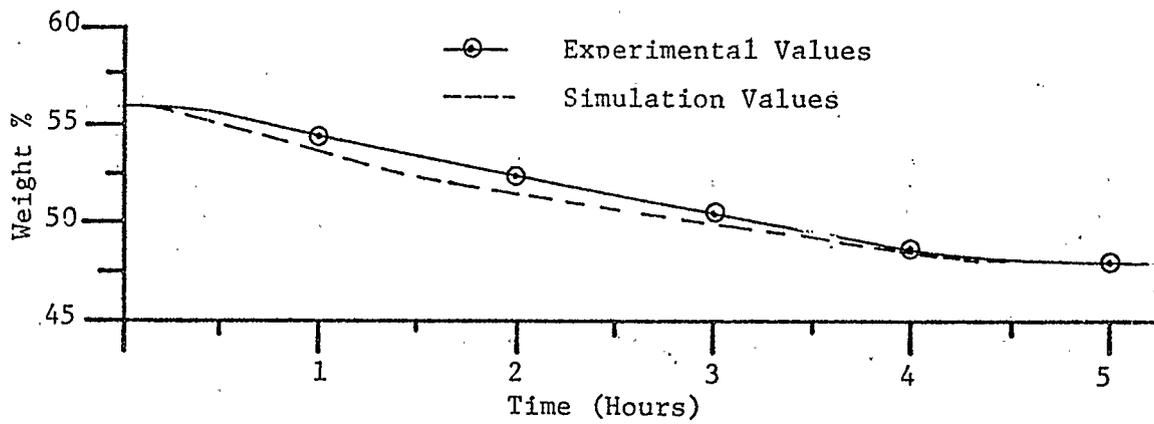
Water Transient For Steam Step Change on Feedtray
Figure 4.64



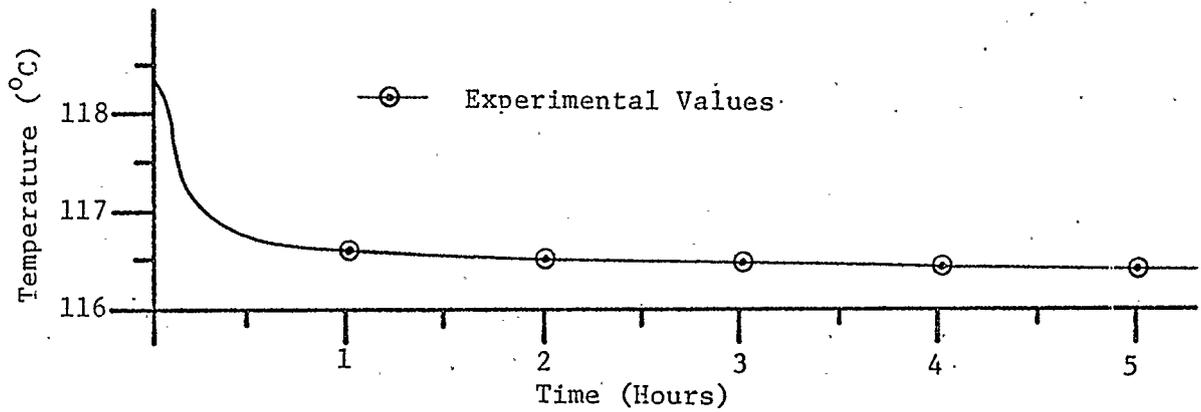
Acetic Acid Transient For Steam Step Change on Feedtray
Figure 4.65



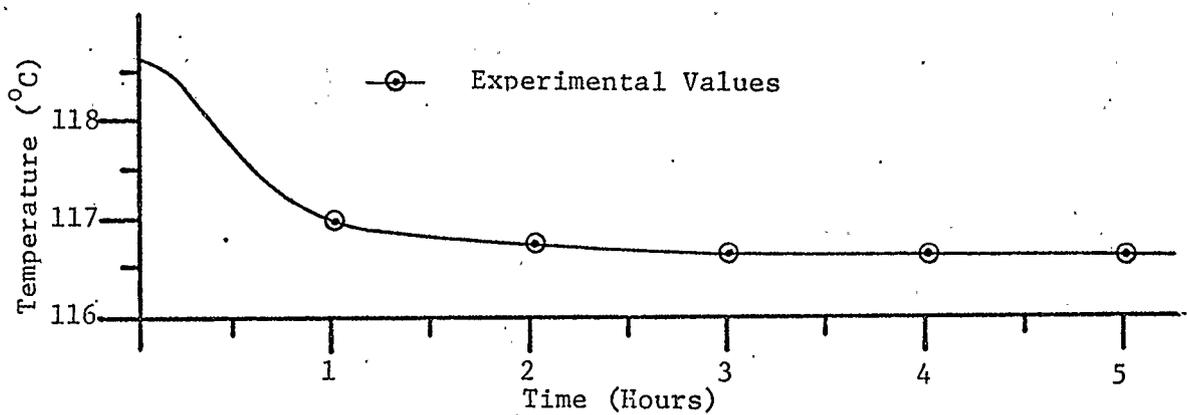
Butanol Transient For Steam Step Change on Feedtray
Figure 4.66



Butyl acetate Transient For Steam Step Change on Feedtray
Figure 4.67



Temperature Transient For Steam Step Change in Reboiler
Figure 4.68



Temperature Transient For Steam Step Change on Tray 10
Figure 4.69

The results of the steam decrease on the reboiler compositions as a function of time are demonstrated in Figures 4.60 to 4.63. The Figures 4.60 to 4.63 show very little deadtime before the steam effects are felt on the reboiler. All response curves describing the reboiler changes have the general shape of a multi-order linear system. The composition in the reboiler changes at an approximately constant rate and then levels out to produce the new steady state of Run 10. A combination of the nonlinear vapor-liquid equilibrium forces and the nonlinear force of the esterification reaction must combine to produce the response. The extra butanol carried down by the 'washing' effect of the acetic acid and butanol negative azeotrope must be such as to cause the acetic acid to decrease in the reboiler in a linear fashion due to the reaction rate, hence, the linear increase in butyl acetate if vapor-liquid equilibrium forces allow it.

The feedtray response in composition for the steam decrease are shown in Figures 4.64 to 4.67. The component responses on the feedtray show a short deadtime. The responses on the feedtray also have the general shape of a multi-order linear system. The response of the water data for the feedtray is in error because of the gas chromatograph, in the author's opinion, as the temperature responded much faster than the water composition indicated by the gas chromatograph. Since the water is at a very low percentage, the smallest drift in the gas chromatograph base line would affect its reading, whereas, the other components' correct values would not be affected because of their higher concentrations. Hence, slow steady drifts in water composition have to be suspect unless they are accompanied by a

steady drift in temperature on the tray concerned.

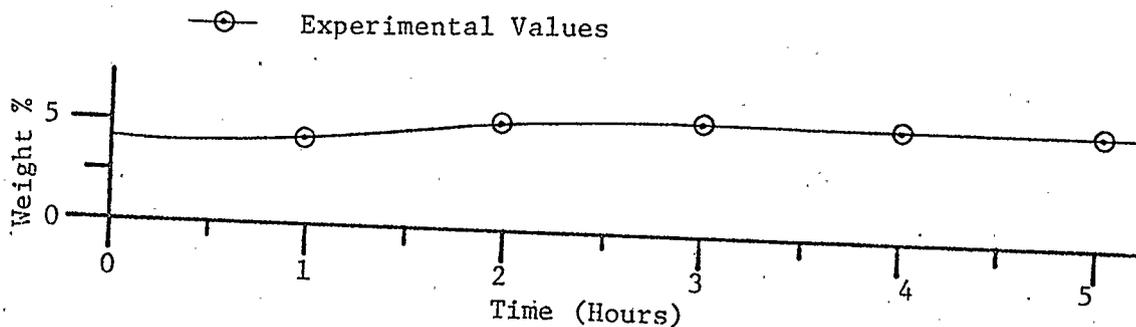
The temperature change in the reboiler shown in Figure 4.68 is immediate and follows the typical under-damped response to a step change for a multi-order linear system. The low temperature in the reboiler is mainly brought about by the increased water concentration in the reboiler due to the fact that the butanol and butyl acetate are not refluxed so heavily as drying agents and, also, a bit by the decrease in pressure. Figure 4.69 shows the response of the temperature on Tray 10. Very little deadtime is evidenced before the lack of high reflux rates of butanol and butyl acetate cause the water content of Tray 10 to increase and the temperature to drop.

4.3.5.3 Feed Flowrate Step Change

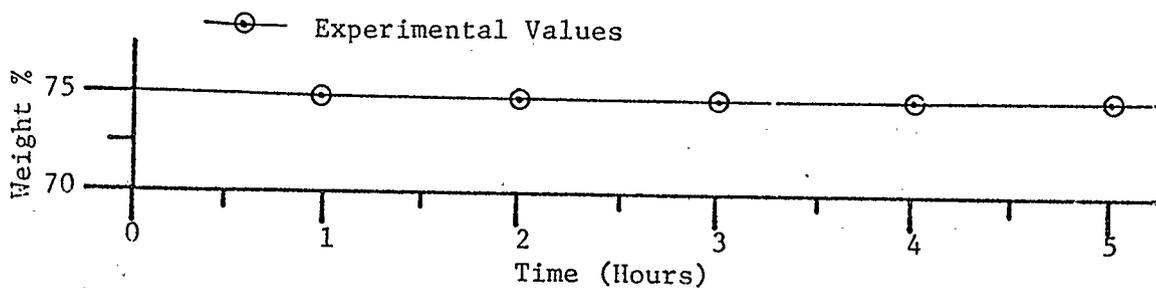
The transient change illustrated by Figures 4.71 to 4.79 (Tables A7.5 and A7.6) is that brought about primarily by increasing the feed flow rate to the esterification column. The steady-state conditions that exist at the start and end of the transient are those of Runs 27 and 28, respectively in Figures 4.11 to 4.24 (Tables A4.11 to A4.34).

The reboiler response to the increased flow as a function of time is given in Figures 4.71 to 4.73. A deadtime or flatness of response due to a multi-order system of $3/4$ of an hour is indicated in the reboiler before the shallow responses occur. Because the responses are not large, it is difficult to make any judgment on the type of response that occurs in the reboiler.

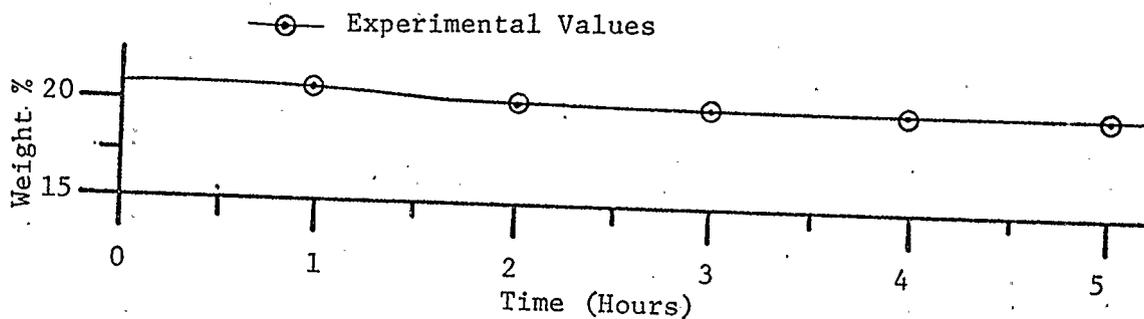
The different compositions' responses on the feedtray are illustrated by Figures 4.74 to 4.77. The flatness of response due to



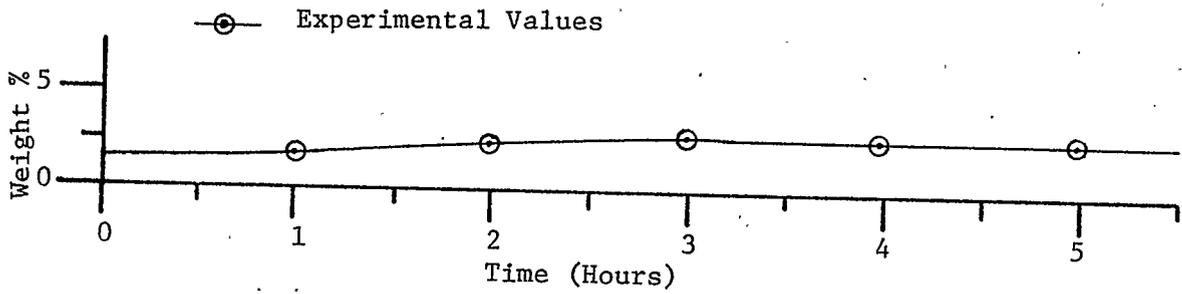
Acetic Acid Transient For Flow-rate Step Change In Reboiler
Figure 4.71



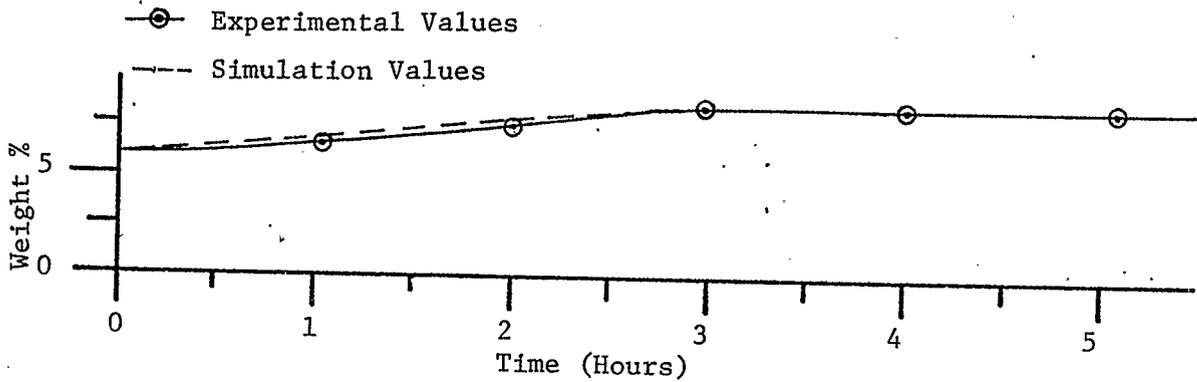
Butanol Transient For Flow-rate Step Change In Reboiler
Figure 4.72



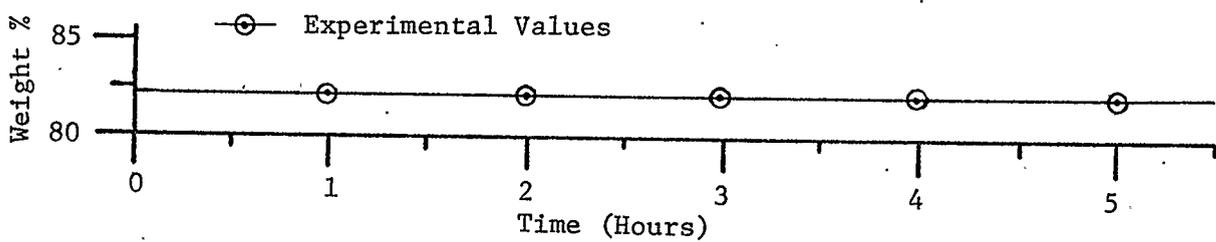
Butyl acetate Transient For Flow-rate Step Change In Reboiler
Figure 4.73



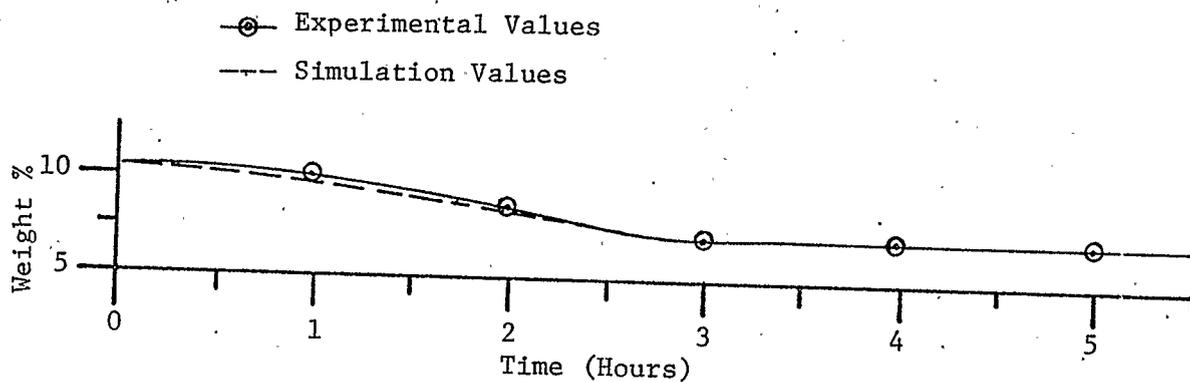
Water Transient For Flow-rate Step Change On Feedtray
Figure 4.74



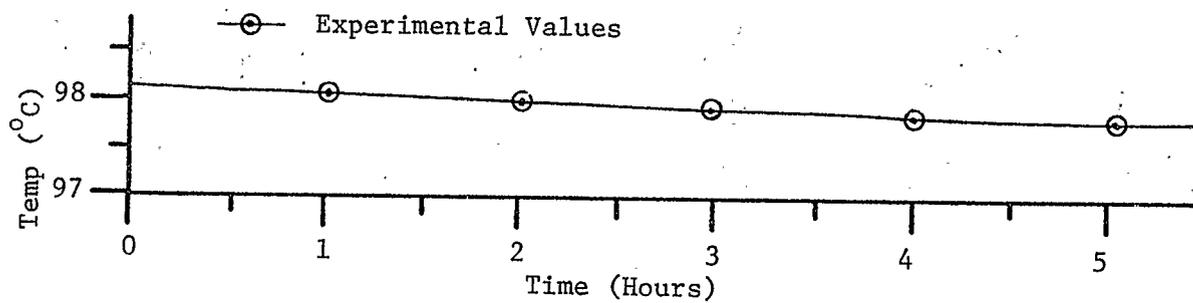
Acetic Acid Transient For Flow-rate Step Change On Feedtray
Figure 4.75



Butanol Transient For Flow-rate Step Change On Feedtray
Figure 4.76



Butyl acetate Transient For Flow-rate Step Change On Feedtray
Figure 4.77



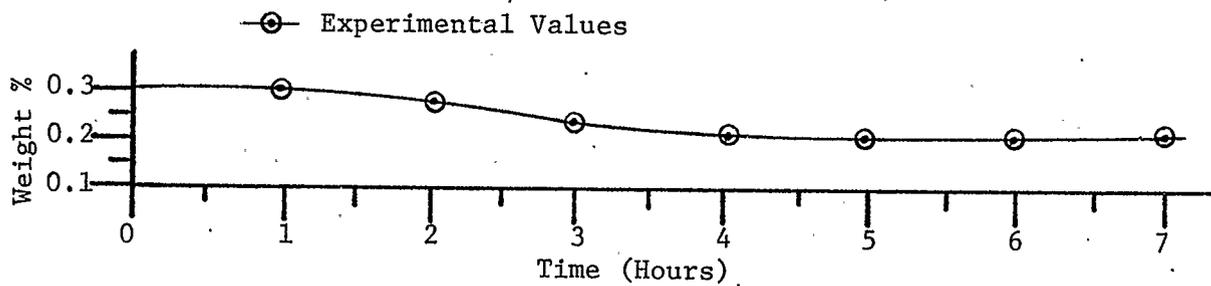
Temperature Transient For Flow-rate Step Change On Tray 10
Figure 4.79

a multi-order system on the feedtray is half an hour. Theoretically there should be at least an immediate small change on the feedtray since the step change enters the column at that position. The reason for the indicated deadtime is probably that the response of the feedtray is that of a high order multi-order system.

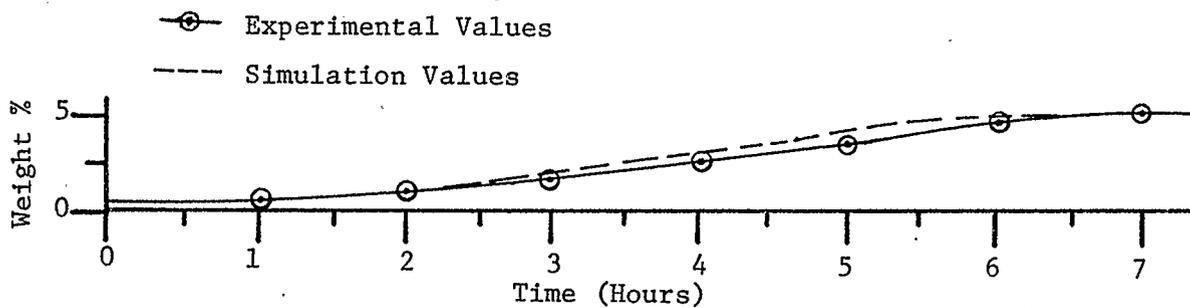
The temperature of the reboiler remained constant throughout the step response from the conditions of Run 27 to those of Run 28. The temperature response of Tray 10 is demonstrated as a function of time in Figure 4.79 . The temperature drifts slowly down indicating an increase in water on the top tray due to the faster reaction rate because of the higher acetic acid concentration in the column. The time constant for the flow step change is from 2 to 3 hours.

4.3.5.4 Feed Composition Step Change

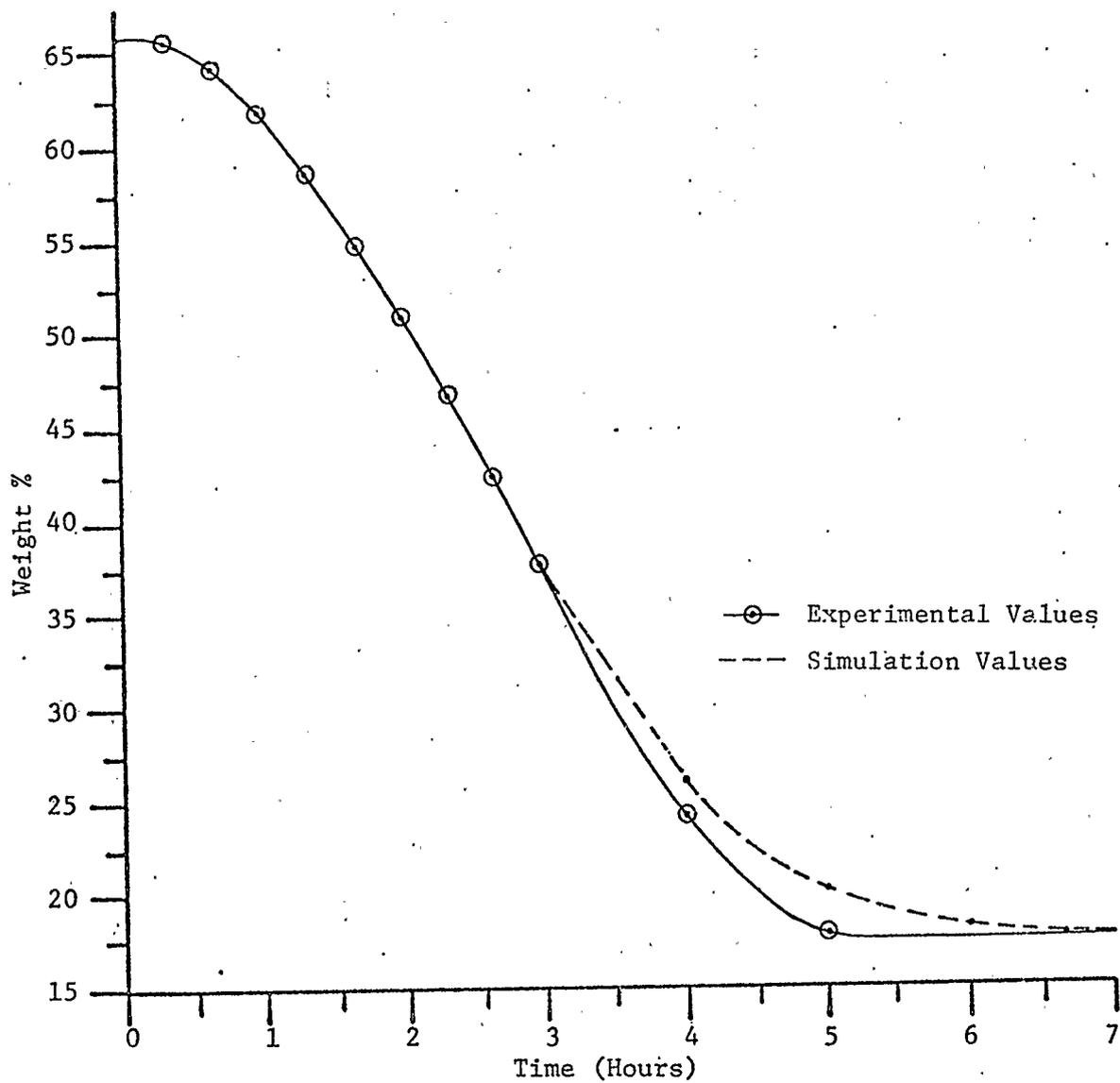
The transient change illustrated by Figures 4.80 to 4.89 (Tables A7.7 and A7.8) is the largest to occur on the column's compositions and is brought about by a 23.0 weight percent increase in acetic acid in the feed. The steady-state conditions that exist at the start and end of the transient are those represented by Runs 6 and 8 respectively, in Figures 4.11 to 4.24 (Tables A4.11 to A4.34). Run 7 indicated in the above figures and tables is actually the peak of a transient. The conditions stated as Run 7 are marked as a steady state because it was thought the column came to steady state in 5 hrs; however on checking by leaving the column alone after such a large transient it was found that the column needed an extra 2 hours to level out at the steady-state conditions marked in Run 8. After the above experience, all



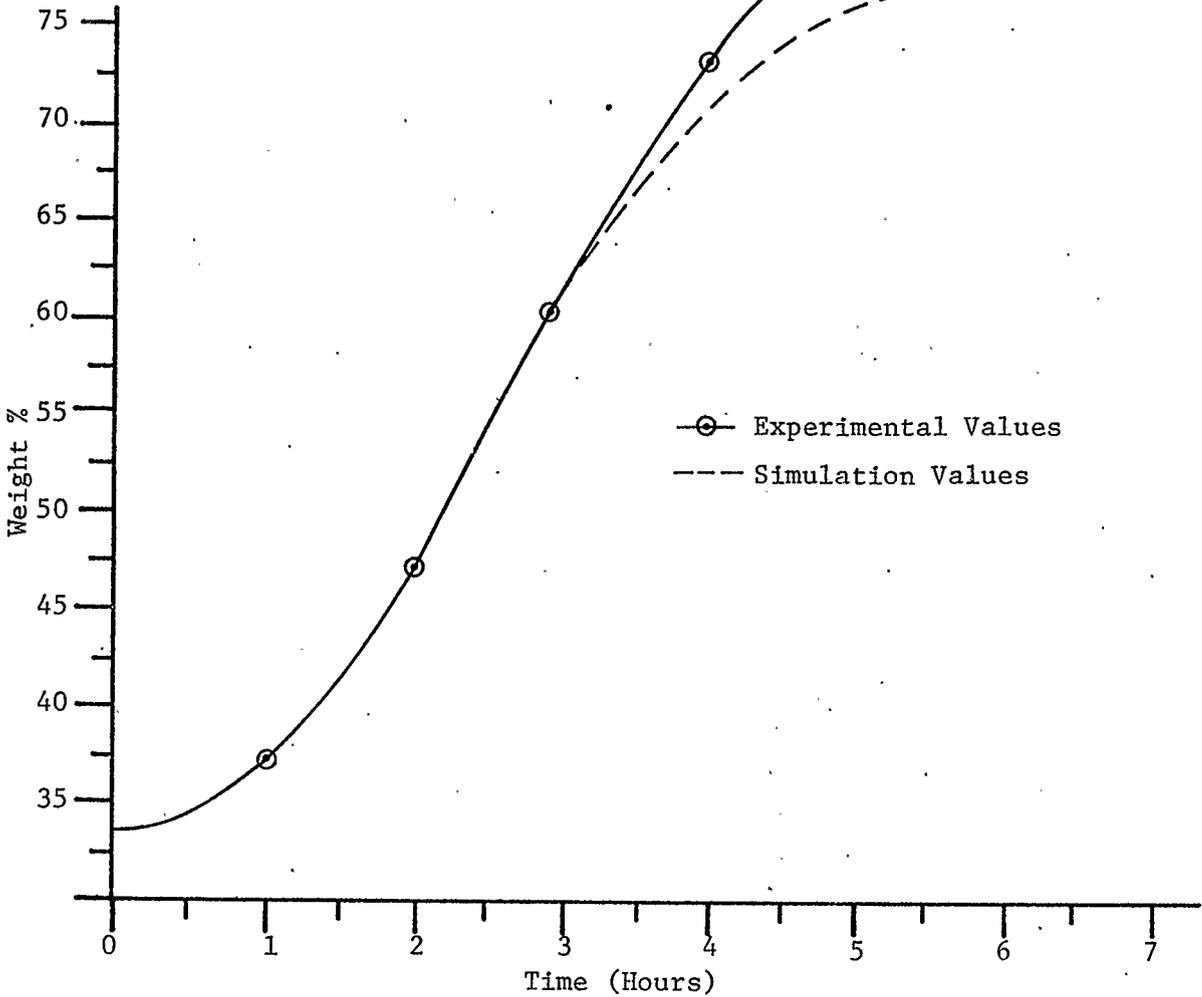
Water Transient For Acetic Acid Feed
Concentration Step Change In Reboiler
Figure 4.80



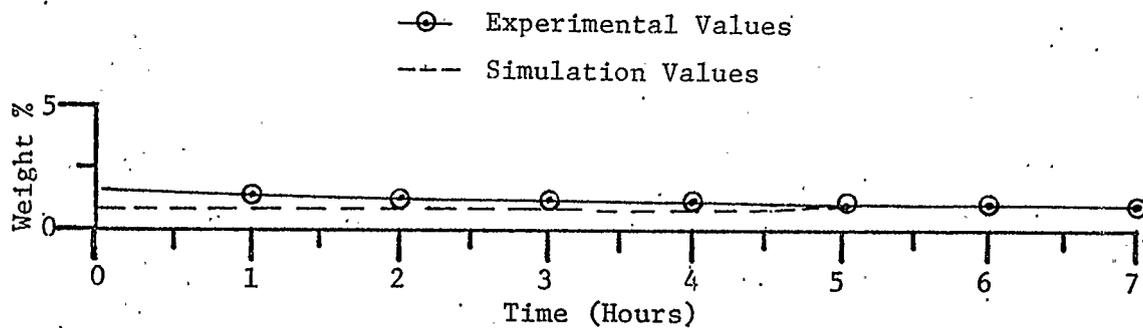
Acetic Acid Transient For Acetic Acid Feed
Concentration Step Change In Reboiler
Figure 4.81



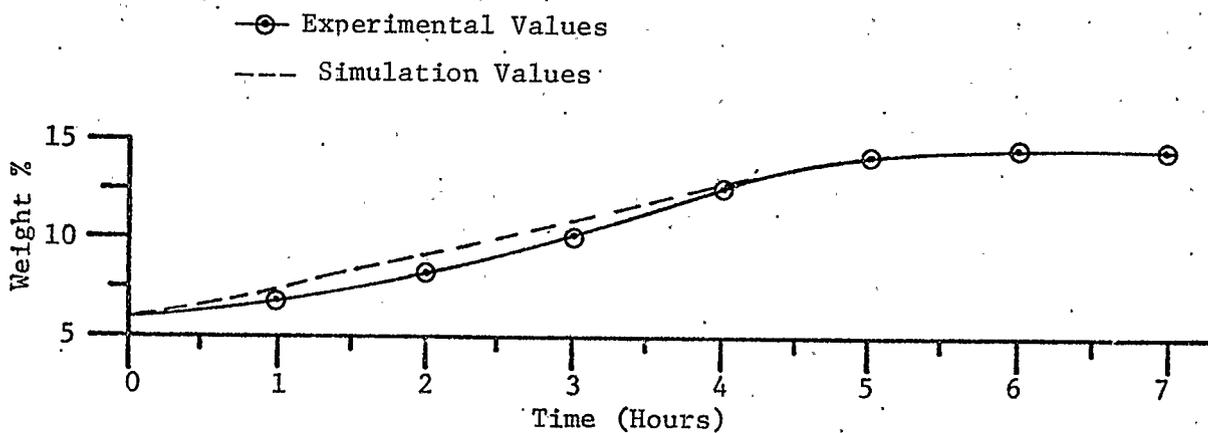
Butanol Transient For Acetic Acid Feed
Concentration Step Change In Reboiler
Figure 4.82



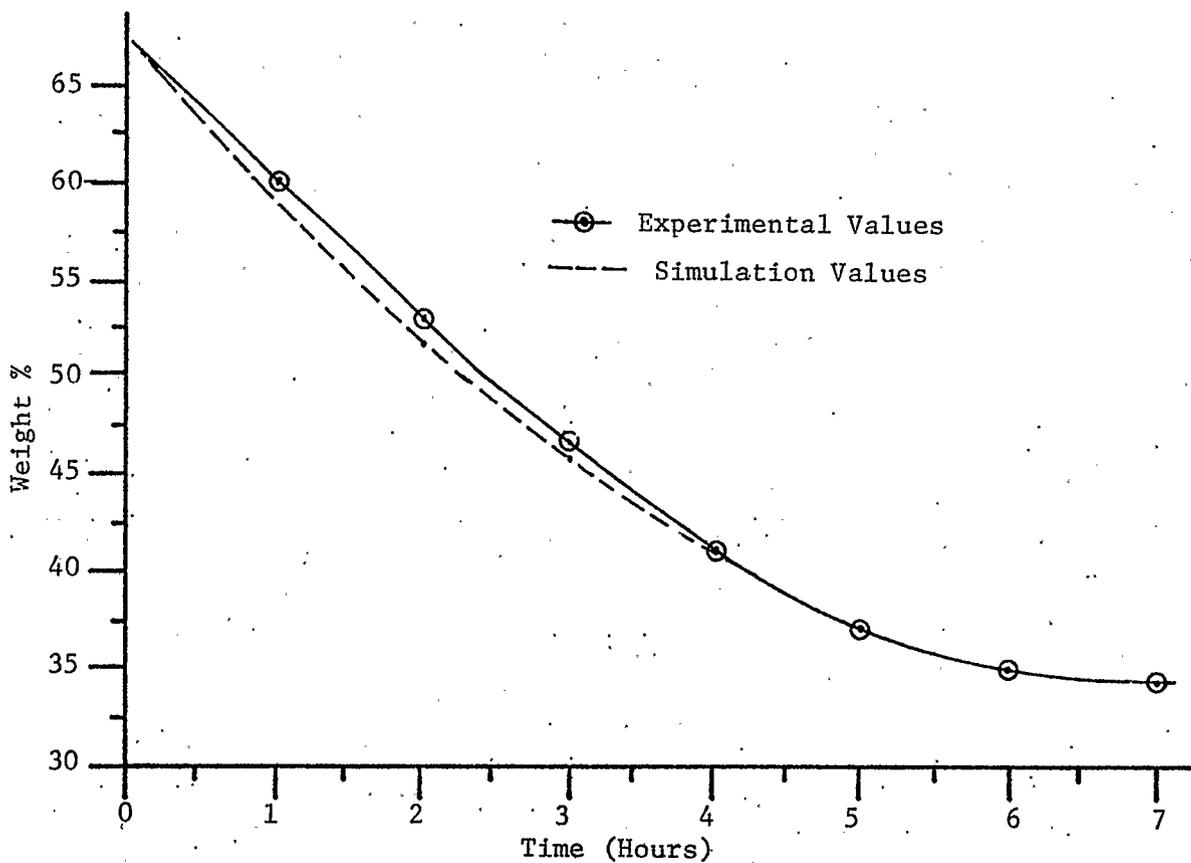
Butyl-acetate Transient For Acetic Acid Feed
Concentration Step Change In Reboiler
Figure 4.83



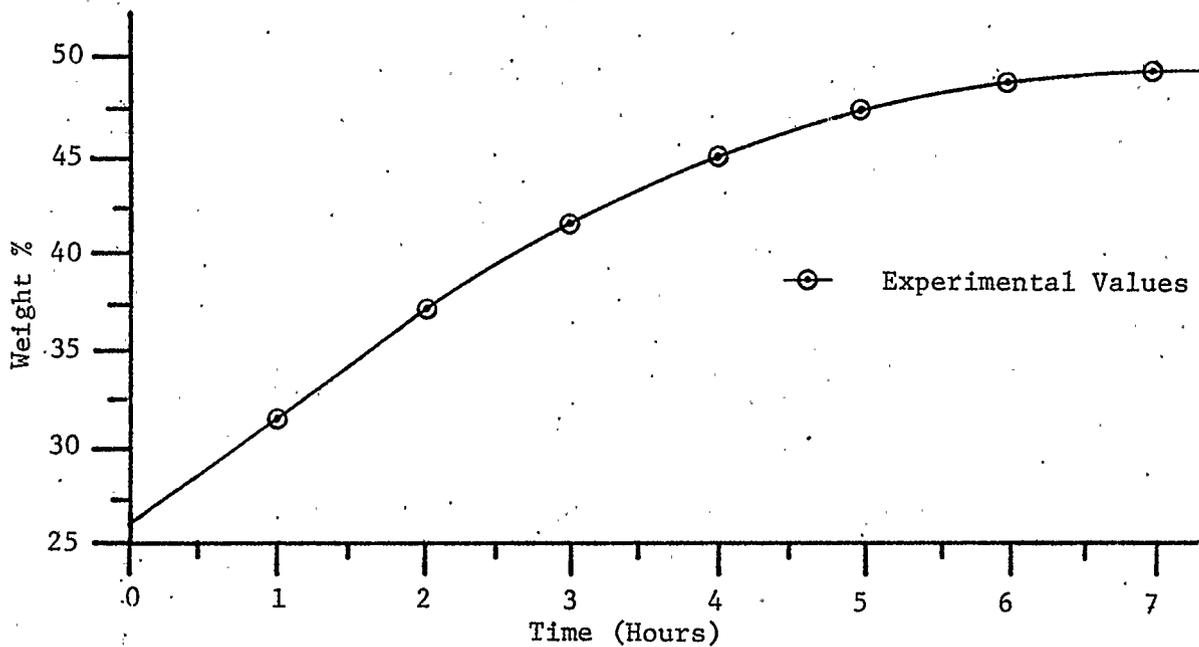
Water Transient For Acetic Acid Feed
Concentration Step Change In Reboiler
Figure 4.84



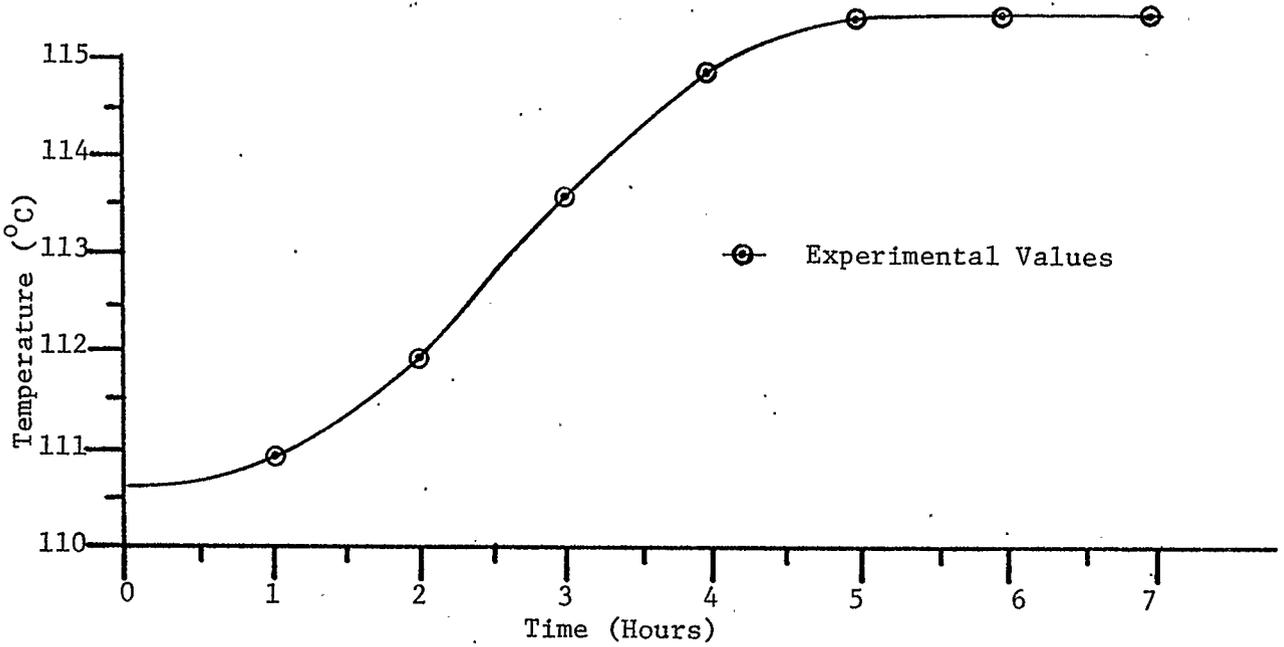
Acetic Acid Transient For Acetic Acid Feed
Concentration Step Change In Reboiler
Figure 4.85



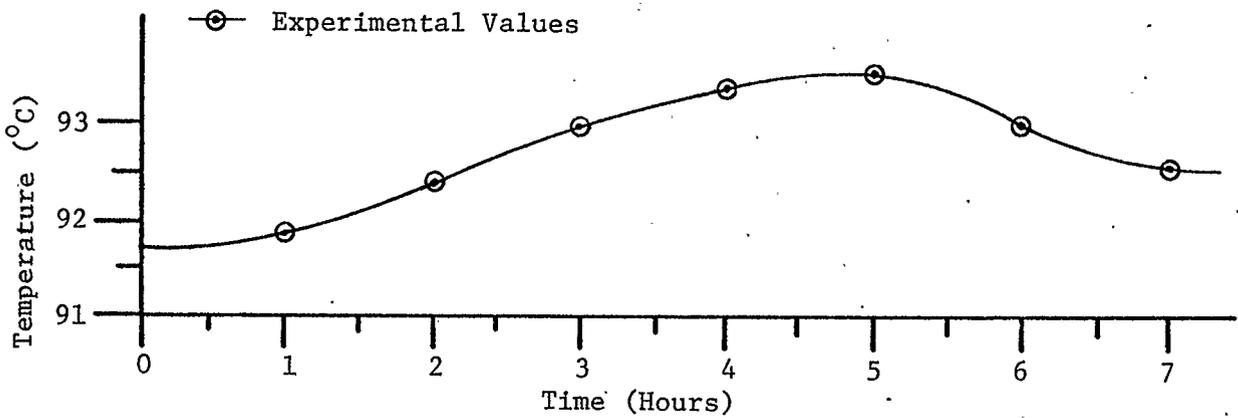
Butanol Transient For Acetic Acid Feed
 Concentration Step Change On Feedtray
 Figure 4.86



Butyl acetate Transient For Acetic Acid Feed
 Concentration Step Change On Feedtray
 Figure 4.87



Temperature Transient For Acetic Acid Feed
Concentration Step In Reboiler
Figure 4.88



Temperature Transient For Acetic Acid Feed
Concentration Step On Tray 10
Figure 4.89

transients were allowed 7 hours to settle; however, none of them needed it. Hence, the non-linear conditions in the column extended the transient for the acetic acid ratio change in the feed. With most changes in the column, the decanter experienced only slight changes; however, when the change was as large as that from Runs 6 to 8, the decanter had to change a great deal. The extra holdup of the decanter might have been the reason for the increased time constant.

The step increase of acetic acid in the feed produced composition transients in the reboiler as illustrated in Figures 4.80 to 4.83 . Because it is felt that the water percentage recorded by the gas chromatograph for this transient in the reboiler was precise over the range it varied (steady gas chromatograph base line), it has been shown in Figure 4.80 on an expanded scale. (By using Figure 4.88, which gives the temperature of the reboiler, a relationship between the water content of the reboiler and the temperature is provided. The precision of water measurements is never better than ± 0.05 weight percent.) Figure 4.81 states the change in acetic acid in the reboiler as a function of time. The reboiler acetic acid response is steady and has a time constant of roughly 4.5 hours. Figure 4.82 illustrates the response of butanol in the reboiler as a function of time. The curve is quite steep and terminates rather abruptly at a time of 5 hours. The curve has a time constant of approximately 3.5 hours. The reason the butanol curve terminates so abruptly is related to the butyl acetate response in the reboiler shown in Figure 4.83 . The butyl acetate composition in the reboiler tends to exhibit the properties of an underdamped linear system. The overshoot of the butyl

acetate in the reboiler shown in Figure 4.83 and the rapid termination of the butanol response in Figure 4.82 are related and are probably the result of the acetic acid and butanol negative azeotrope initially starting down the column; they react to form butyl acetate (only a portion of the butyl acetate goes up with the water), the butyl acetate proceeds to the bottom to form the positive azeotrope with butanol and starts up the column. The abrupt termination of the butanol concentration occurs when the ridge on the ternary vapor-liquid equilibrium diagram of acetic acid, butanol, and butyl acetate is approached and the butyl acetate concentration is increased by reaction which is occurring faster because of the high concentration of both acetic acid and butanol. Once the butanol concentration has decreased, the reaction slows and the column is brought to a new steady state by distillation.

The feedtray response to the acetic acid increase in the feed is shown in Figures 4.84 to 4.87. Figure 4.84 indicates that the water concentration on the feedtray slowly falls and then rises again. This indicates that the reaction rate on the feedtray slowed down and then speeded up again. Since the butanol concentration falls

rapidly (Figure 4.86) initially and then slows down and the acetic acid increases slowly in concentration at first and then faster (Figure 4.85), the reaction must be first slowed by a lack of butanol and then speeded up by the increased acetic acid concentration. The butyl acetate concentration on the feedtray is shown, as a function of time, in Figure 4.87 and tends to increase at a fairly constant rate; hence, because the reaction must have slowed on the feedtray, the

butyl acetate is kept increasing at a steady rate by distillation effects.

As mentioned above, the reboiler temperature as a function of time is illustrated in Figure 4.88 . The temperature of the top or 10th tray is illustrated in Figure 4.89 over the duration of the transient. The top tray increases in temperature indicating a drop in water content and, hence, reaction rate and then decreases in temperature indicating that the reaction has accelerated. (The compositions on the feedtray also indicated a decreasing reaction rate followed by an increasing reaction rate.)

4.4 Discussion of Steady State and Transient Experimental Behaviour of the Esterification Column

This discussion on the data from the esterification column starts by recommending a kinetics equation for predicting the rate of the esterification reaction. A recommendation for operating conditions on the esterification column is then given. A statement on the type of control needed on the esterification column is enunciated. A comment on the high quality data produced by Leyes and Othmer (19) and Brunjes and Furnas (4) is stated. A summary is made of the problems encountered in the study with suggestions on how they might be eliminated in future studies. Attention is drawn to the wide range over which the column is operated in this study.

The kinetics equation given in Section 4.34 of this study is felt to be a better form than that stated by Leyes and Othmer (20). The Leyes and Othmer equation is correct for the range specified for

it; but because of the form of the equation, it can only be used over a very narrow range. (If the catalyst concentration is 0.03 wt %, then the Leyes and Othmer equation gives erroneous negative values for the reaction rate constant when the butanol to acetic acid weight percent ratio is less than 1.969 or less than 1.746 when the catalyst concentration is 0.01 wt %.) Hence, even though there is doubt ($\pm 20\%$) in the constant values given for the kinetics equation of Section 4.3.4, it is without question more precise than the Leyes and Othmer equation when the range is extended to the butanol to acetic acid ratio where the rate constant changes sign. (The data of this study fit the Leyes and Othmer equation with a scatter of $\pm 25\%$ in the range that the equation covered.) The zero catalyst levels used to develop the equation of Section 4.3.4 covered the complete range of acetic acid and butanol concentrations; however, to obtain the rate constant values, k , with catalyst, only the operating range of the esterification column is used. The data gathered (Figure 4.45) shows that sulphuric acid catalyst accelerates the reaction rate at an ever decreasing rate, while it increases tar production (the amount of tar production is unknown).

Two sets of operating conditions for the esterification column are recommended to meet opposing demands on the column. If the object in operating the column is to obtain as much butyl acetate as possible with no more than 1.0% acetic acid and as little sulphuric acid as possible, then the column should be fed 12.0 weight percent acetic acid in the feed with 0.03 weight percent sulphuric acid and operated at a boil-up rate such that the reflux is 1.5 times the feedrate. If the

object is to produce as much butyl-acetate as possible without regard to acetic acid and sulphuric acid levels, then the column should be fed 38.0 weight percent acetic acid in the feed with 0.1 weight percent sulphuric acid and operated at a high boil-up to produce a reflux 5.0 times the feedrate. (Higher levels of acetic acid in the feed might be better but cannot be recommended by this study since they were not investigated.) The first set of operating conditions given will produce a clear product that will not cause fouling and is easily separated downstream from the esterification column. The second set of conditions given, with the high acetic acid and sulphuric acid levels, will produce a small amount of polymer product and salts from Type 316 stainless steel that will cause many fouling problems in all lines and flow meters; separation of the butyl-acetate downstream from the esterification column will not be as simple, either, because of both fouling problems and the fact that acetic acid is introduced into the separation system. Between the two sets of extreme conditions mentioned above, there is the option to compromise, anywhere between the extremes, for the purpose of having a more or less contamination-free product.

The esterification column showed very little need for any type of control beyond the liquid level control needed in the reboiler and decanter phases. The reason the esterification column needs so little control is because of two self-regulating features in the column, namely, its holdup and esterification reaction. If a disturbance occurs in the incoming feed or reflux streams or either of the two product streams the large liquid capacity in the column damps

out the effects of the disturbance. Also the reaction speeds up if more butanol or acetic acid is dumped in the column by noise fluctuations; hence, again smoothing the disturbance so the column is not affected as greatly. Noise in the steam to the column only tends to cause the drying effect by butanol and butyl acetate to fluctuate slightly. Hence, the column, because of its self-regulation, needs no major control system of any type.

The transients illustrated in this study, in Figure 4.50 to 4.89, show how long it takes for a change to occur. The time constants varied in length from 2.5 to 4.5 hours. The transients illustrated are for very large relative changes in any of the four independent variables. The catalyst concentration is stepped 100% in Section 4.3.5.1; the steam is decreased 91.8% in Section 4.3.5.2. The feed flowrate to the column is stepped 17.6% in Section 4.3.5.3 and the acetic acid flowrate in the feed is increased 37.7% in Section 4.3.5.4. Thus very large relative changes are needed on the input streams to bring about the changes that occurred; hence, the column shows a slowness to react to any change and a low sensitivity to any of the input variables. Therefore, the transients provide the evidence as to why automated, high-speed, feedback control is not needed and why manual monitoring and manual control are probably sufficient in most cases.

The column behaved as predicted by the studies of Leyes and Othmer (19) and Brunjes and Furnas (4) for the range their data covered. Thus this study tends to confirm the work by both sets of investigators. The fact that the pilot plant version of the esterification column

agreed well with the laboratory still of Leyes and Othmer indicates that if the column were scaled up further all would probably go as predicted.

The studies done by Leyes and Othmer (19) explored the following: the acetic acid in the feed was changed in concentration from 12.61 to 14.16 wt %; the catalyst concentration was varied from 0.0298 to 0.128 wt %; the feed flowrate was regulated from 528.84 to 1266.3 gms/hr; and the boil-up rate was kept constant. For this study where the equipment is scaled up over the Leyes and Othmer apparatus by a factor of approximately 7, the following ranges were investigated: the acetic acid in the feed was changed in concentration from 9.5 to 37.7 wt %; the catalyst concentration was varied from 0.003 to 0.278 wt %; the feed flowrate was regulated from 7150 to 11500 gms/hr; and the boil-up rate was varied from 120 to 240 (gms steam)/hr. Thus this study explored a much wider set of ranges than the Leyes and Othmer investigation and in so doing showed the many different areas of operation open for use.

The data from the weight scale on the esterification column is not presented. The reason the weight scale data is ignored is because the author does not feel it is precise enough to be meaningful over the 33 runs investigated. Due to the fact that the calibrations and checks on other instruments are more pressing the weight scale is at times neglected and it requires constant attention. The scale does show clearly, however, that the weight of the column increases with increasing boil-up. The 91.8% increase in steam increases the holdup on the trays by approximately 10%.

The problem that causes the greatest amount of trouble during the esterification column studies is that of keeping the gas chromatographs working and properly calibrated. The gas chromatographs were calibrated 4 times for the 33 runs made. During the runs with high concentrations of catalyst and acetic acid, fouling of the filters screening the liquid going into the gas chromatographs occurred. The tar-salt combination produced by the sulphuric and acetic acids proves very difficult to control. If special purpose filters (Appendix 6) had not been made because of lessons learned before the runs, it is highly doubtful if the studies as shown could have been completed. Fouling also affected the flow meter on the bottoms product from the column such that it had to be cleaned twice. At high acetic and sulphuric acid levels serious fouling should always be anticipated or all instruments will rapidly fail and many lines will plug if Type 316 stainless steel is used. Hence, the use of filters is suggested for all exit streams.

All compositions stated for the column trays or streams were calculated by normalizing the analysis results from the gas chromatographs. (The water composition was checked by temperature.) In many cases at steady state it was possible to compare the analysis results from the Beckman gas chromatographs with the results from the Varian gas chromatograph; at times there was a 10% difference in the compositions given for various components by the two makes of gas chromatograph. The steady state Varian analysis results are given in Tables A4.41 to A4.46 and the Beckman analysis results are given in Tables A4.11 to A4.13. In the majority of cases the agreement is

quite good but when a choice between the analysis results of the gas chromatographs is necessary the author chose those resulting from the Beckman instruments because the Beckman machines tend to be less erratic.

No assumptions or approximations were made in the calculations for the mass balance in Section 4.3.2 as all streams were measured and analyzed. The only approximations used in obtaining the heat balance (Section 4.3.3) are that the specific heat of butyl acetate is 0.459, which is the approximate value used by Leyes and Othmer (19), and that exothermic heat given off by the esterification reaction is zero. (The exothermic heat of the reaction was calculated to be less than 0.5% of the heat input to the column.) To obtain the reaction rate equation, 4.3.4, given in Section 4.3.4 the following assumptions had to be made to make the necessary calculations.

- 1) Catalyst concentration in the column is that of the incoming feed and is equal in the five reaction stages.
- 2) There is perfect mixing on all trays.
- 3) Tray distillation efficiency is included in the vapor-liquid equilibrium correlations.
- 4) The reverse reaction (hydrolysis) is not important.
- 5) The temperature in the column is constant and the same for all trays for all runs.

Thus Equation 4.3.4 contains the above assumptions and should not be used in a situation where the temperature deviates much from 111.0°C which is the average temperature of the reaction trays in the column which supplied the kinetic data.

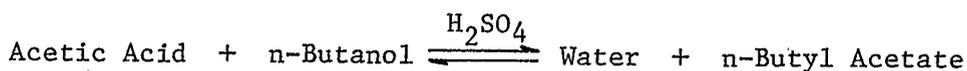
The above information makes it possible to design an esterification column to fit a given system. The type of product for given inputs is stated along with a warning of possible fouling problems. If a simulation is to be done on the system, the kinetics equation necessary has been provided with the references as to the other necessary information. The wide range of acetic acid feed (9.5 wt % to 37.7 wt %) concentrations studied indicated how an esterification column of this type behaves under an excess butanol operation. The fouling problems, which were severe, indicated what would happen if an excess acetic acid esterification column is studied in future investigations.

5.1 Hybrid Model of Esterification Column Outline

The equations and approximations used for the hybrid computer model to simulate the esterification column are described. The digital logic, interface techniques, analog and digital programs are discussed. An analysis is made of a simulated catalyst step change, a steam step change, a flow rate step change, and an acetic acid concentration step change in the feed and the theoretical predictions are compared to the actual experimental results. A summary of the results and information gained concludes the section.

5.2 General Description of the Column and the System Data Used

A schematic of the esterification column is shown in Figure 4.1 . The esterification column and its operation are described in Section 4.2.1 and 4.2.2 . Basically the system is a 10-tray distillation column with a reboiler, total condenser, and a decanter. However, it has the added complication of having chemical reaction on the bottom four trays and in the reboiler. The top 6 trays are for separation. The acetic acid and butanol fed to the feed tray, with the non-volatile sulphuric acid, react to form butyl acetate and water according to the reversible reaction,



Butanol and butyl acetate carry the water up the column; at the top of the column the water is concentrated in the top trays and then

separated out in the decanter as the lower phase. The upper oil phase is sent back into the column as refluxed drying agent.

Butanol is added in excess in the feed to force the above reaction to the right. As a result, the excess butanol and butyl acetate make up the bottom product along with small amounts of acetic acid and sulphuric acid. Because of the importance of all components in the bottoms product, none of the components may be neglected anywhere in the column simulation studies. (The kinetics equation used to calculate the speed of the esterification reaction in producing butyl acetate for the bottoms product stream is Equation 4.34 .)

The total weight of components on each tray is assumed constant for the simulation of a given run. To calculate the mass on a tray for a given run, the average experimental composition is used. Then knowing there is 1200 cc of liquid on a tray and 12000 cc of liquid in the reboiler, the mass is calculated using the density information by Leyes and Othmer (19) repeated here in equation form as:

$$\text{Water Density} = 1.028 - (0.0007)T \text{ gms/cc} \quad (5.21)$$

$$\text{Acetic Acid Density} = 1.070 - (0.0011)T \text{ gms/cc} \quad (5.22)$$

$$\text{Butanol Density} = 0.832 - (0.0009)T \text{ gms/cc} \quad (5.23)$$

$$\text{Butyl acetate Density} = 0.909 - (0.0011)T \text{ gms/cc} \quad (5.24)$$

where $T = \text{degrees centigrade}$

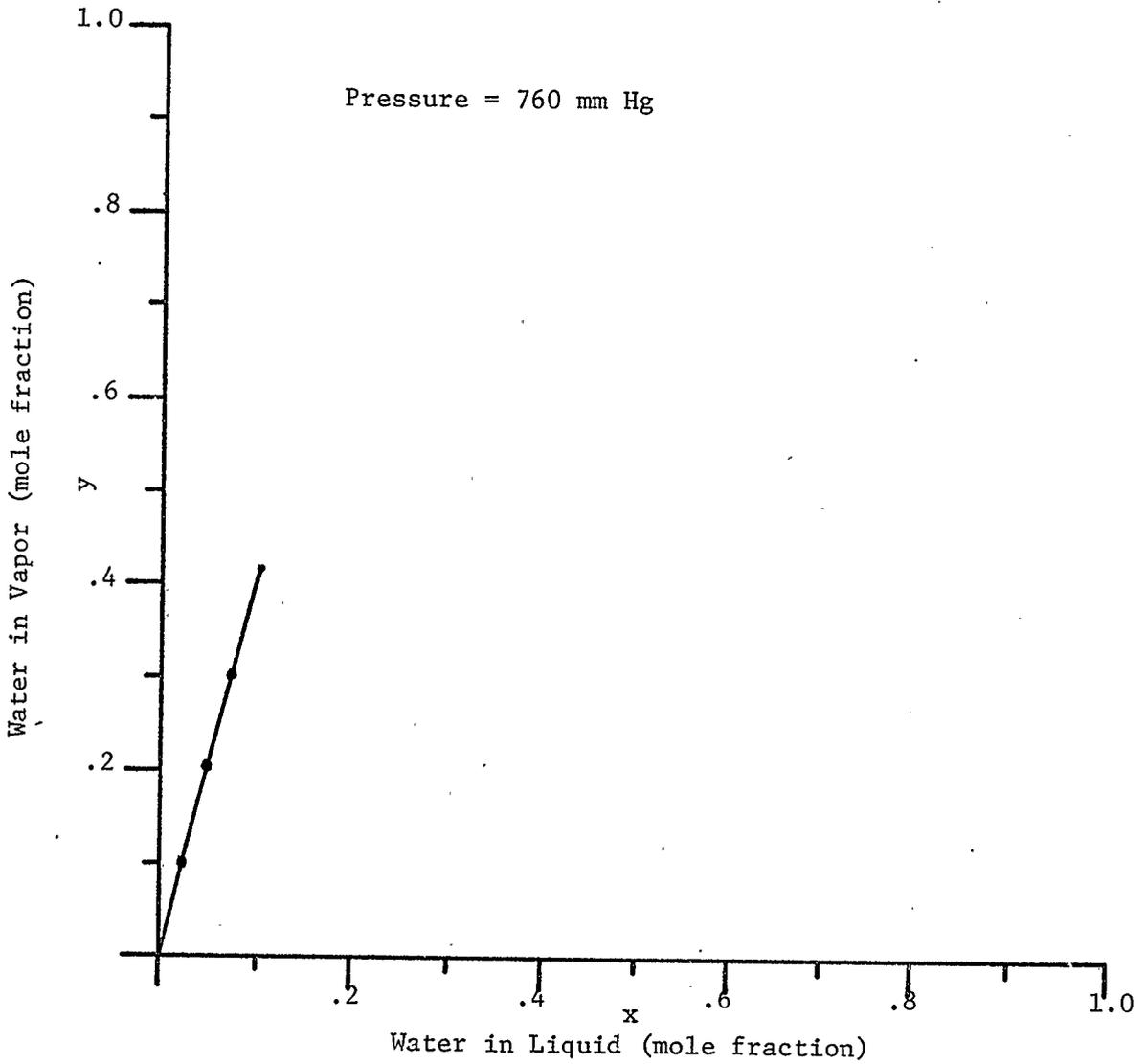
Hence, each tray has a different but constant mass for a given simulation.

The latent and specific heats used in this simulation study are those given by Leyes and Othmer (19) and are as follows:

	Specific Heat cal/gm C	Latent Heat cal/gm
Water	1.004	532.9
Acetic Acid	0.522	96.75
Butanol	0.687	141.26
Butyl acetate	0.459	73.82

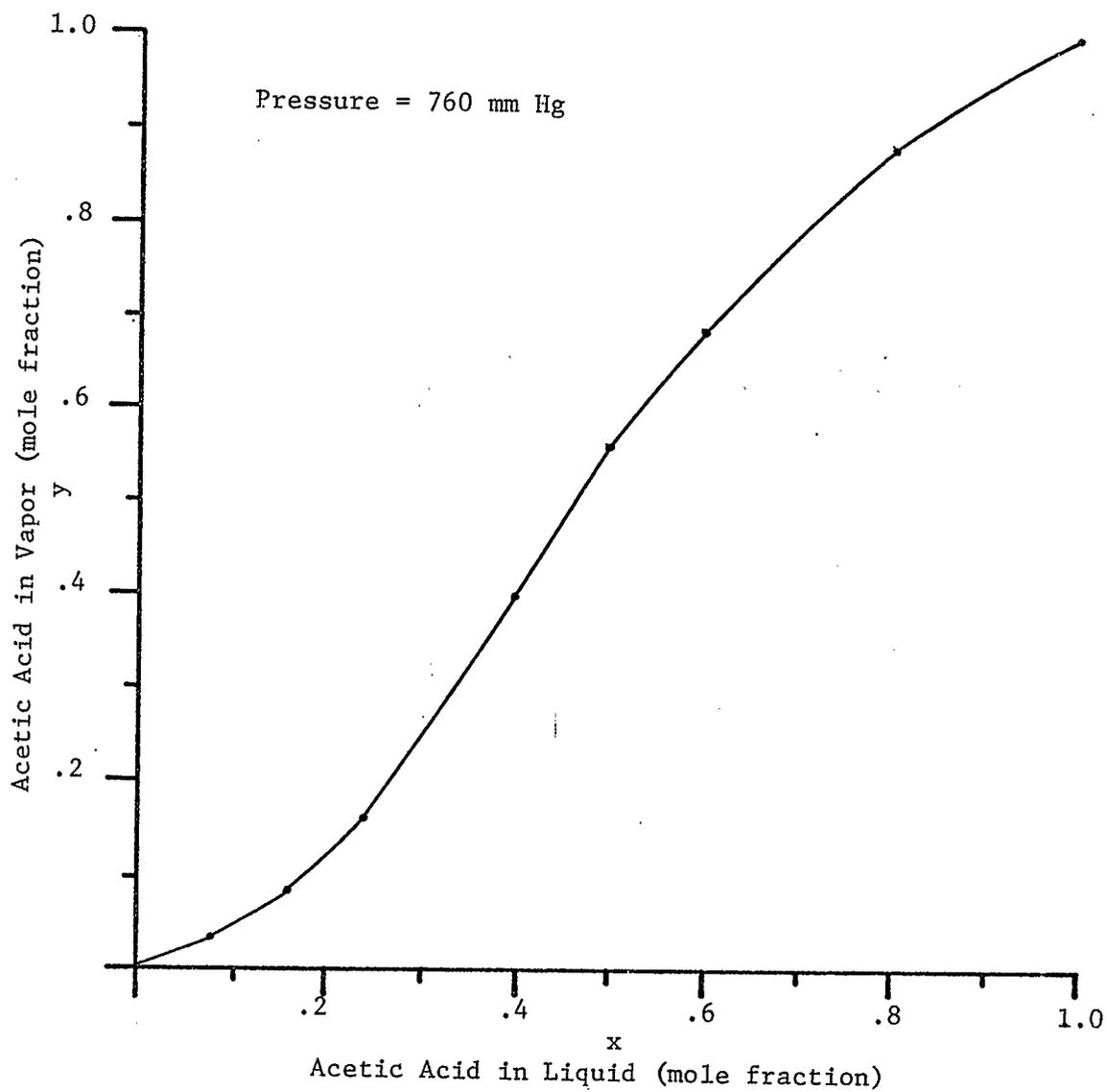
The vapor-liquid equilibrium correlations used in the hybrid computer model are shown in Figures 5.21, 5.22, and 5.23 for water, acetic acid, and butyl acetate respectively.

In the pilot plant column the heat required to provide the column boil-up is supplied through a shell and tube exchanger by condensing steam on the shell side. Any time constant in the reboiler is neglected in the model as the heat is assumed to pass immediately from the steam into the contents of the reboiler. A constant loss of 1400 K - cal/hr of heat is assumed discharged from the column into the surroundings for all runs. (This assumed heat loss is based on the average loss from the experimental column.) Half the heat is assumed lost by the reboiler and hence, the lost heat is just subtracted from the steam input. The other losses are assumed to be evenly spread over the 10 trays; thus, each tray is assumed to discharge 70 K - cal/hr of heat into the surroundings. Therefore, the vapor leaving each tray is cut accordingly.



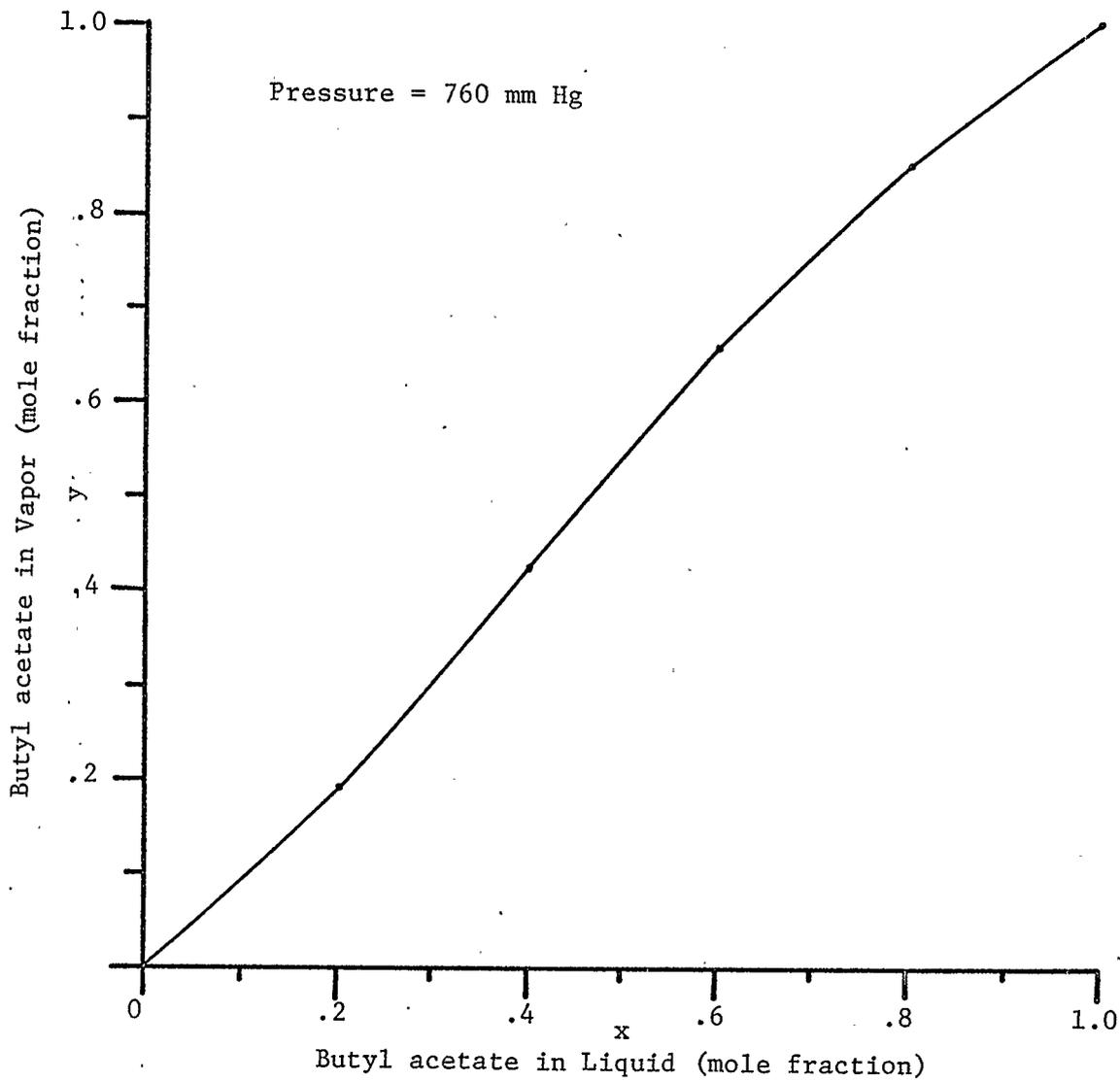
Mole Fraction of Water in the Vapor
as a Function of the Mole Fraction
of Water in the Liquid

Figure 5.21



Mole Fraction of Acetic Acid in the
Vapor as a Function of the Mole
Fraction of Acetic Acid in the Liquid

Figure 5.22



Mole Fraction of Butyl acetate in the Vapor
as a Function of the Mole Fraction
of Butyl acetate in the Liquid

Figure 5.23

5.3 Mathematical Model of the Esterification Column

In writing a mathematical model for a process the dilemma which arises is that of determining exactly what detail is necessary for a particular task. Williams (38) states that a mathematical model for a distillation column must have equations to describe the following:

- 1) A component material balance for each component less one, for each well-mixed region on each tray;
- 2) An enthalpy balance equation for each well-mixed region on each tray;
- 3) An equation relating the liquid dynamics in each well-mixed region on each tray;
- 4) An equation relating the vapor dynamics in each well-mixed region on a tray;
- 5) An equation relating the flow and pressure dynamics of the vapor between trays;
- 6) An enthalpy-balance for the region between the trays;
- 7) An equation relating the fluid dynamics on the liquid flowing between trays; and
- 8) An equation for each well-mixed region on each tray relating the rate of attainment of equilibrium between liquid and vapor in that region.

Since the esterification column has chemical reaction occurring, one more equation must be added to Williams' list:

- 9) An equation for each well-mixed region on each tray relating to the rate of chemical reaction.

The solution of the complex set of equations arising from this very complete dynamic mathematical model of a reaction plate distillation column would be a formidable task. The approach used is to make a number of simplifying assumptions. The assumptions made are generally of two kinds: those made because a phenomenon cannot be measured accurately, and those based on physical considerations such as size, internal arrangement, and operating conditions of the equipment being simulated.

The specific assumptions made which fall into the category of phenomena which are difficult to measure and hence, to correlate accurately are:

- 1) Equilibrium between liquid and vapor is instantaneously realized. This eliminates, from the general set of equations, the equations resulting from Item 8.
- 2) No holdup in the vapor on the trays. Again, from the general set of equations, this assumption would eliminate the equations resulting from Items 4 and 6.

Those assumptions which are based on the size, internal arrangement, and operation of the esterification column are as follows:

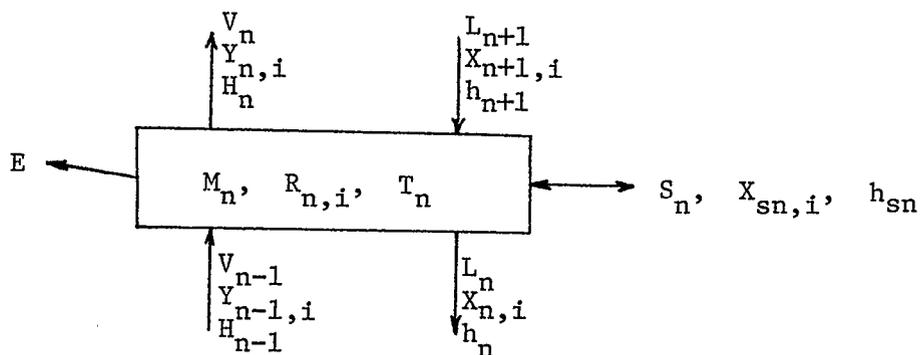
- 3) There is no holdup of vapor between the trays. This assumption eliminates the equation resulting from Item 5.
- 4) No holdup of liquid in the downcomers between the trays. This eliminates the equation arising from Item 7.
- 5) Each tray is considered to be one perfectly mixed cell.
- 6) Mass of liquid on the tray is constant.
- 7) The column operates at a constant pressure.

- 8) There is no liquid entrainment in the vapor.
- 9) The vapor-liquid equilibrium relationships, including tray efficiency can be approximated by an expression of the form $y = f(x)$ represented by Figures 5.21 to 5.23 .
- 10) The trays are at a constant temperature for a given run.
- 11) Sensible heat effects are negligible.
- 12) The sulphuric acid catalyst is totally non-volatile.
- 13) The reverse hydrolysis reaction has no effect.
- 14) The thermal time constant of the reboiler is negligible.
- 15) The composition equations of the two liquid phases that separate in the decanter can be approximated with a series of linear equations.

Assumptions 1 to 8 above are standard for modeling of distillation columns and have been used by Williams (38), Holland (15), and Svrcek (36). Assumptions 9 to 11 are made only after knowing the range over which the esterification column distillation forces vary. Assumption 12 is made because sulphuric acid boils at 338.0 degrees centigrade. The reverse hydrolysis reaction, Assumption 13, has little effect because of the small amount of water present. Svrcek (36) shows that the thermal time constant of a reboiler is roughly one thousand times smaller than the composition response in the reboiler for a binary methanol and water system. Following the same procedure as outlined by Svrcek, it can be shown that the time constant of the esterification column's reboiler is also roughly three orders of magnitude smaller than the time constant of the composition response of

the reboiler, hence, Assumption 14. Assumption 15 is standard linear approximation.

Having made the above assumptions only the equations required by Items 1, 2 and 9 of the general set of equations need be considered. That is, a differential equation, each to describe the component balance, enthalpy balance, and reaction rate for each tray of the column. Furthermore, the assumptions result in the column being considered a series of perfectly mixed cells, Figure 5.31, undergoing an exchange of components and heat with a kinetic reaction rate between components.



Schematic of One Generalized Tray of the Esterification Column

Figure 5.31

Considering the tray model of Figure 5.31, the following differential equations describing the component balance, enthalpy balance, and reaction rate can be written:

1) The component material balance is

$$M_n \frac{dX_{n,i}}{dt} = V_{n-1} Y_{n-1,i} - V_n Y_{n,i} + L_{n+1} X_{n+1,i} - L_n X_{n,i} + R_{n,i} + S_n X_{sn,i} \quad (5.31)$$

n = tray number

i = stands for water, acetic acid, butanol, butyl acetate, sulphuric acid

M_n = total grams weight on tray n (constant)

t = time (minutes)

L_{n+1} = total grams/minute flowing onto tray as liquid

L_n = total grams/minute flowing off tray as liquid to lower tray

V_n = total grams/minute flowing off tray as vapor

V_{n-1} = total grams/minute flowing onto tray as vapor

$X_{n,i}$ = weight percent of component 'i' in liquid flowing off tray

$X_{n+1,i}$ = weight percent of component 'i' in liquid flowing onto tray from upper tray

$Y_{n,i}$ = weight percent of component 'i' in vapor flowing off tray

$Y_{n-1,i}$ = weight percent of component 'i' in vapor flowing onto tray

$X_{sn,i}$ = weight percent of component 'i' in side stream

S_n = total grams/minute flowing onto or off tray as side stream

$R_{n,i}$ = rate at which component 'i' is produced or used in the esterification reaction (grams/minute)

2) The heat balance is

$$M_n \frac{d h_n}{dt} = V_{n-1} H_{n-1} - V_n H_n + L_{n+1} h_{n+1} - L_n h_n - E + S_n h_{sn}$$

since all sensible heat effects inside the esterification column are neglected

$$E = V_{n-1} H_{n-1} - V_n H_n + S_n h_{sn} \quad (5.32)$$

h_{n+1} = enthalpy in liquid flowing onto tray (neglected)

h_n = enthalpy in liquid flowing off tray (neglected)

h_{sn} = enthalpy in side stream

H_n = enthalpy in vapor leaving tray (only latent heat considered) cal/gm

H_{n-1} = enthalpy in vapor flowing onto tray (only latent heat considered) cal/gm

T_n = temperature of tray ($^{\circ}$ C)

E = heat lost to surroundings from tray (cal/min)

3) The reaction rate equation is

$$r = \frac{d X_{AcOH}}{dt} = k (X_{AcOH} X_{BuOH})^2 \quad (5.33)$$

k = constant that is function of catalyst concentration (cc³/(moles³ min))

$$X_{\text{AcOH}} = \text{moles acetic acid/cc}$$

$$X_{\text{BuOH}} = \text{moles butanol/cc}$$

$$r = \text{(grams of component used or produced)/minute(cc)}$$

Hence,

$$R_{n,i} = (r) M_n / \rho_n \quad (5.34)$$

$$\rho_n = \text{average density of components on tray (gms/cc)}$$

Using the above equations and assumptions plus,

$$\sum X_{n,i} = 1 \quad (5.35)$$

$$\sum Y_{n,i} = 1 \quad (5.36)$$

it is possible to mathematically model all trays in the esterification column.

In order to complete the mathematical model of the esterification column, it is necessary to have the equations which approximate the separation in the decanter. The composition of the oil phase in the decanter is represented by Equations 5.37 to 5.39 where x stands for the butanol mole fraction and y represents the butyl acetate mole fraction.

$$x_1 = -0.68 y_1 + 0.524 \quad 0 < x_1 < 0.32 \quad (5.37)$$

$$0.30 < y_1 < 0.78$$

$$x_2 = -0.35 y_2 + 0.425 \quad 0.32 < x_2 < 0.40 \quad (5.38)$$

$$0.10 < y_2 < 0.30$$

$$x_3 = +0.4 y_3 + 0.35 \quad 0.35 < x_3 < 0.40 \quad (5.39)$$

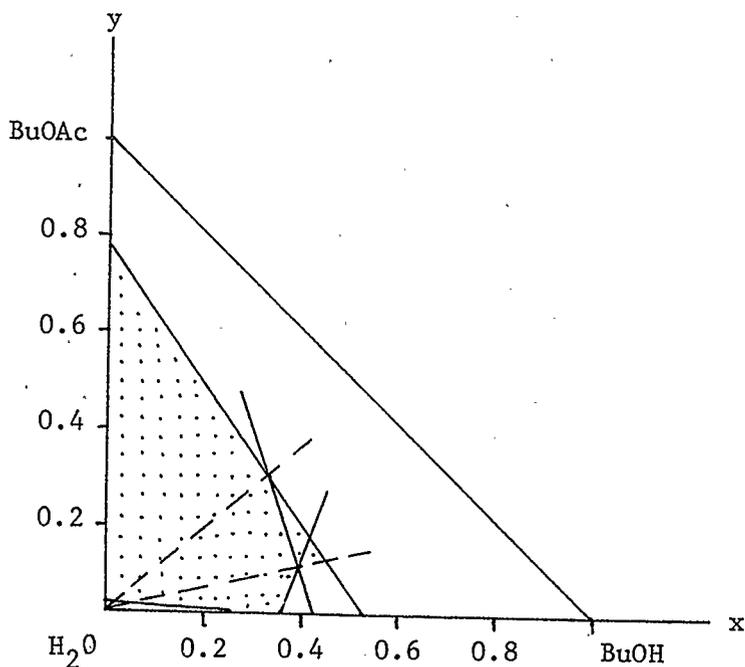
$$0.0 < y_3 < 0.10$$

The composition of the water phase in the decanter is represented by Equation 5.40 where x stands for the butanol mole fraction and y represents the butyl acetate mole fraction. (The water mole fraction is found by subtracting x and y from 1.0)

$$x_4 = -20.0 y_4 + 0.2 \quad 0.0 < x_4 < 0.22 \quad (5.40)$$

$$0.0 < y_4 < 0.01$$

Figure 5.32 illustrates the two-phase region (shaded area) as defined by the above equations. To find the amount of each component in each phase the inverse-level law is used on the tie-lines that radiate out from the x and y origin (100% water).



Schematic of Linear Equations Describing Two-Phase Liquid Region For the Water, Butanol, and Butyl acetate Ternary System

Figure 5.32

The mathematical model of the ten-tray esterification column, reboiler and decanter includes Equations 5.31 through 5.36 for each tray and the reboiler plus the vapor-liquid equilibrium relationships; the decanter model utilizes Equations 5.31, 5.35, 5.37, 5.38, 5.39 and 5.40 . The various solutions to the above set of equations, used for modeling the esterification column, are solved for on a hybrid computer.

5.4 Hybrid Computer Solution of Simulation Equations

The hybrid computer is really a combination of four special purpose computers working together. The 680 analog computer and the 640 digital computer are the standard computational machines with the 690 interface computer and the 680 digital logic computer working as conveyors of information between the 680 and 640. Thus the mathematical modeling equations for the esterification column are solved as a team effort by all four machines.

Because the 690 interface computer only transmits information between machines, its contribution to the solution of the equations will not be discussed. Thus the following discussion will only cover the contribution to the solution of the mathematical model made by the 680 analog computer, the 680 digital logic computer, and the 640 digital computer.

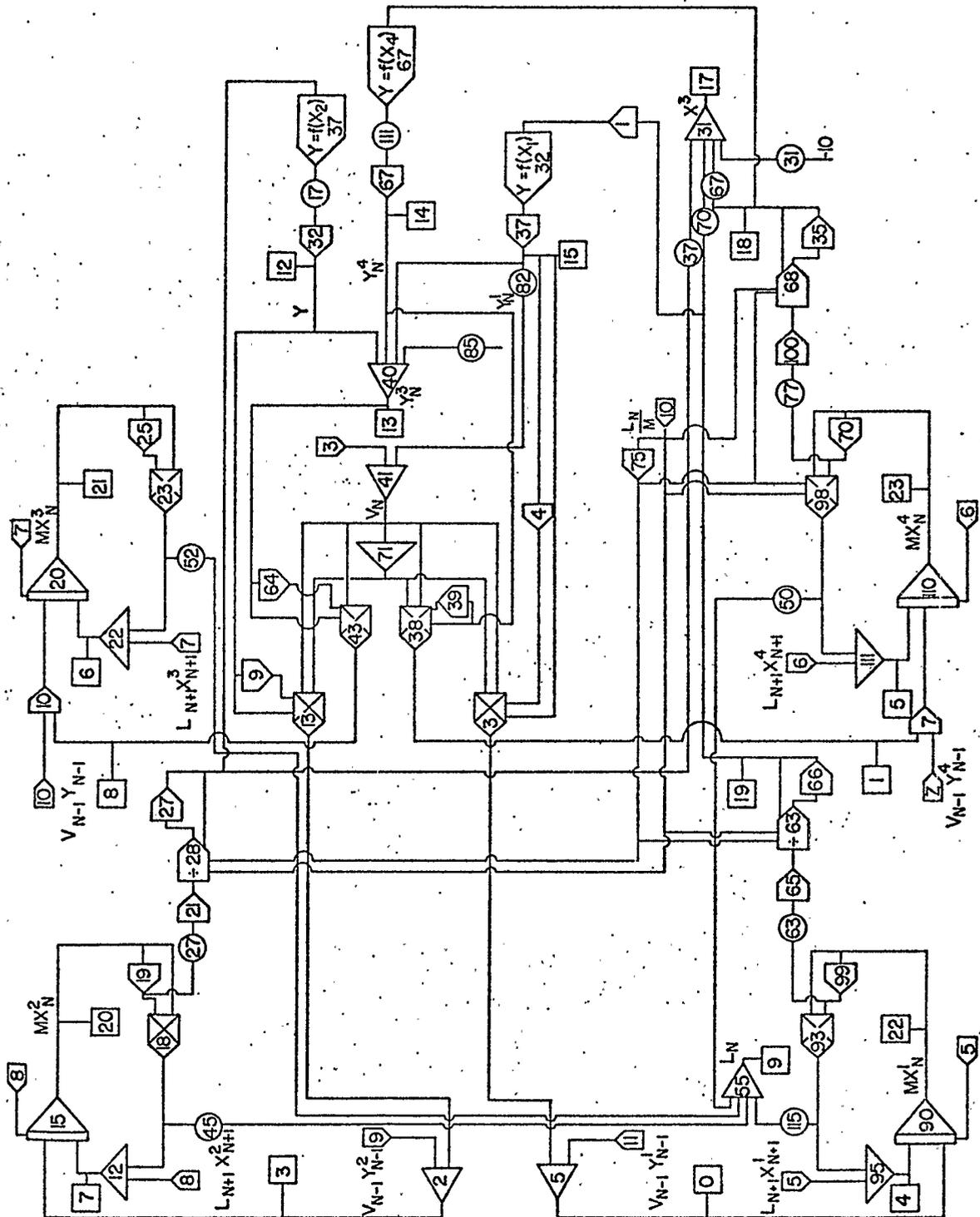
5.4.1 Contribution by the 680 Analog Computer to the Solution of the Mathematical Model

The component balance equations (Equation 5.31) and part of

the enthalpy balance (Equation 5.32) are patched for one tray on the 680 analog computer as shown in Figure 5.41 . (The reaction rate equation and part of the enthalpy balance equation are solved in the 640 digital computer.) All feeds to a given tray on the analog board are treated as forcing functions. The initial conditions are the previous conditions of the tray. Component fluxes, both liquid and vapor, and initial conditions on the tray are transferred to the analog board using digital-to-analog converters and read off the board using analog-to-digital converters.

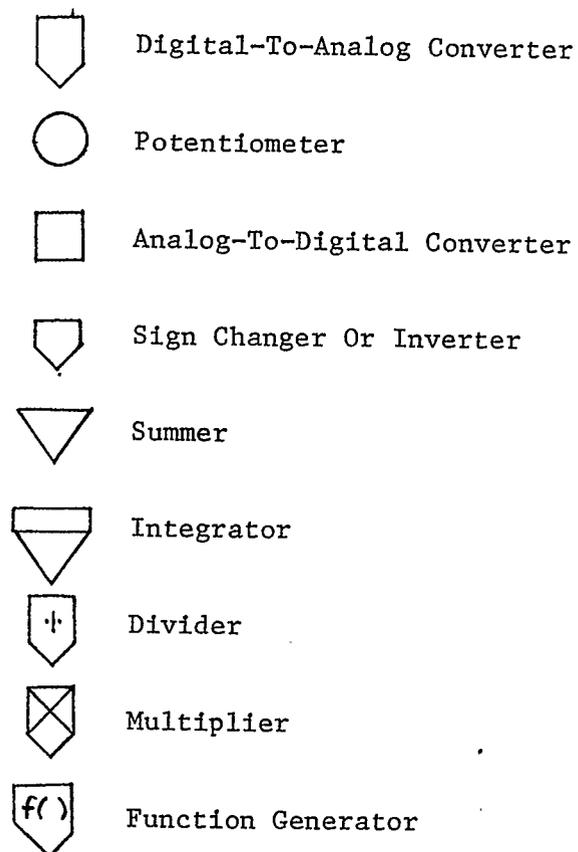
Because the forcing functions loaded into the digital-to-analog converters of the 680 analog computer are calculated in incremental time steps by the 640 digital computer, a time step size must be chosen such that the analog solution resulting from the incremented step changes will not be in error significantly. Ruszkoy and Mitchell (31) suggest a time increment for the forcing functions not greater than 0.1 of the time constant of the system. Since the time constant of the esterification column is at least 2.5 hours, the time increment for the 680 analog forcing functions was chosen at 6.0 minutes. Thus there is a safety factor of being 2.5 times smaller than the value recommended by Ruszkoy and Mitchell. (The time scaling used for the analog solution is 1.0 machine milli-second equals one minute of simulated esterification column time.)

The 680 analog flow chart of Figure 5.41 has its symbols explained in Figure 5.42 .



Analog Flow Chart Of Hybrid Simulation
Figure 5.41

Figure 5.42
Analog Flow Chart Legend



X_N^i = wt % in the liquid of component i on Tray N

Y_N^i = wt % in the vapor of component i on Tray N

L_N = grams/minute of liquid flowing off Tray N

V_N = grams/minute of vapor flowing off Tray N

M = grams of liquid on Tray N

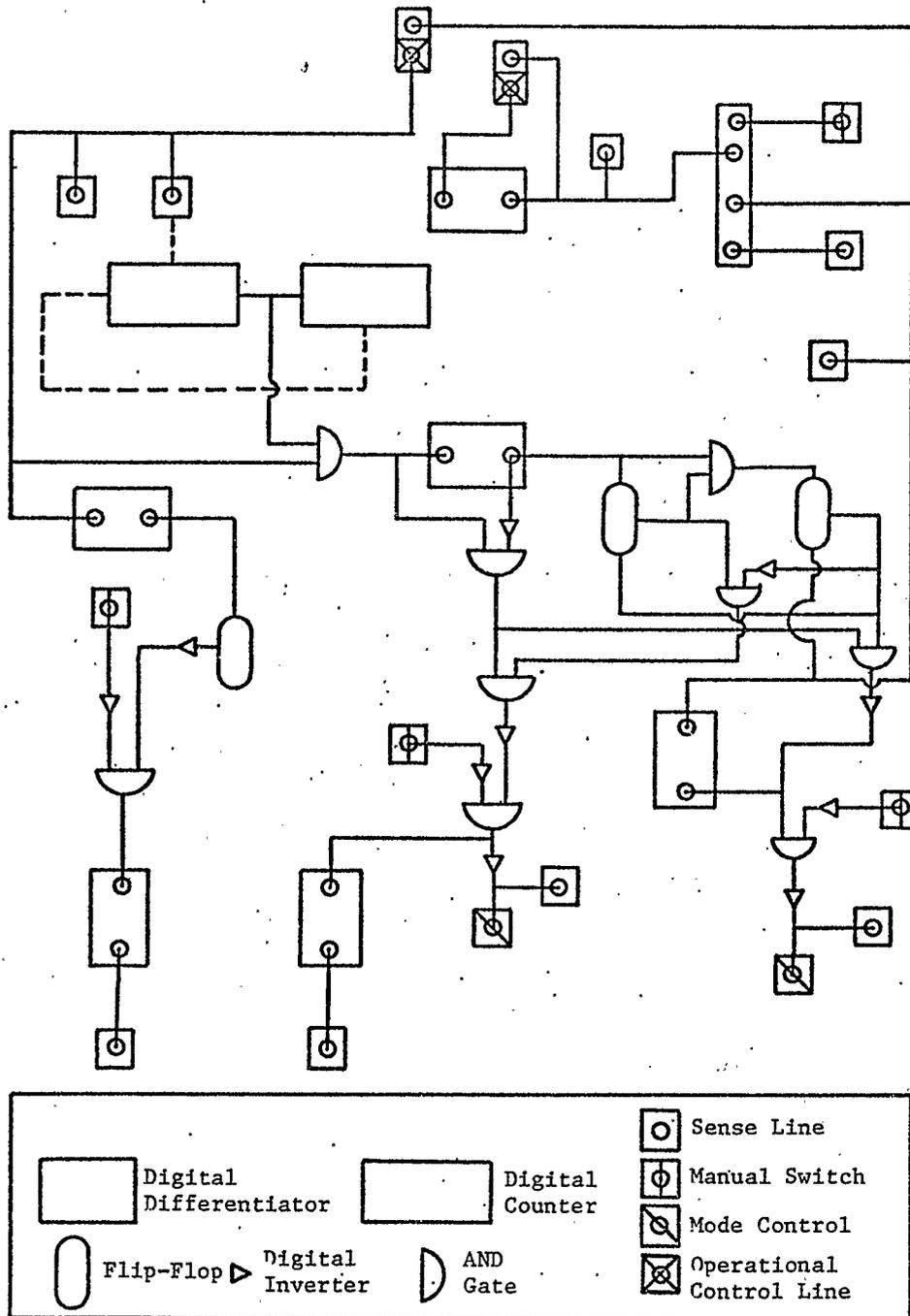
5.4.2 Contribution by the 680 Digital Logic Computer to the Solution of the Mathematical Model

The 680 digital logic computer does not solve any of the mathematical modelling equations of Section 5.3 . However, the 680 digital logic computer does play a very important role in the solution of the equations because it controls the timing sequence of the 680 analog computer and also informs the 640 digital computer of what mode the analog components are in at all times.

The timing sequence that the 680 digital logic patching (Figure 5.43) puts the 680 analog computer through is IC/HOLD/OPERATE/HOLD with each step in the cycle being 6-msec. Because four steps in the timing sequence cycle are used instead of the standard three steps, it is possible to use the same digital-to-analog converters to load the initial conditions and establish the forcing functions. Hence, the extra HOLD between IC (initial conditions) and OPERATE doubles the effective number of digital-to-analog converters available for the programmer. Hence, the 680 digital computer program shown in Figure 5.43 is important if there is a shortage of analog components.

5.4.3 Contribution by the 640 Digital Computer to the Solution of the Mathematical Model

Because of its versatility, the 640 digital computer is used in a number of ways. First and foremost it controls the overall solution of the mathematical equations using the monitor program shown in Figure 5.44 . Second, the 640 digital computer is used to solve Equation 5.34 and part of Equation 5.32 . Third, the 640 is used to



Digital Logic Flow Chart of Hybrid Simulation
Figure 5.43

store and update 680 analog computer values; and, finally, the 640 digital computer is used as the control for all input and output of information to and from the mathematical model.

The monitor program for the 640 digital computer shown in Figure 5.44 initializes all variables; it then calls the appropriate programs to obtain the necessary values for the 680 analog computer and then initiates the loading of the 680 analog. The 640 then waits for each cycle of the 680 analog computer to finish and services the 680 analog as is required. (Interrupts are not used because of the extra core and calculations necessary to use them.) The monitor program then advances the tray number up or down as required, checks if print out is requested, and then repeats the above cycle except for the initializing of the variables.

The 640 digital computer calculates the values required for Equations 5.32 and 5.34 in Programs 25 and 23 respectively of Appendix 1. The 640 digital computer also calculates the necessary changes that must be made when the calculations for the feedtray and reboiler are encountered and these are computed in Programs 27 and 26 respectively. The decanter mathematical model is also solved in the 640 digital computer by using Program 24 to solve for the two phase separation by using Equations 5.37 to 5.40 and the inverse-level low. (Before each set of calculations is attempted on the hybrid system, Program 21 of Appendix 1 is run on the 640 digital computer to make certain the 680 analog and 680 digital computers are functioning properly. This diagnostic test saved a great deal of programmer time.)

5.5 Results of the Hybrid Computer Simulation

The hybrid model, as described above, takes 10 to 30 minutes to run depending on the amount of print out asked for; and the model is used to simulate 8 steady state and 4 transient responses that have previously been discussed for the experimental esterification column. The responses referred to are those represented on Figures 4.50 to 4.89 . Where there is agreement between simulated values and those from the pilot plant column within $\pm 0.25\%$, both responses are represented by the solid line on Figures 4.50 to 4.89 . When the simulated values differ by more than $\pm 0.25\%$ from the actual values, the simulated values are represented by a dashed line on Figures 4.50 to 4.89 . Thus the runs simulated are a step change in catalyst concentration, a step change in boil-up rate, a step change in feed flow rate, and a step change in the acetic acid concentration in the feed.

5.5.1 Simulated Catalyst Step Change

Figures 4.51 to 4.59 represent both the actual and simulated responses for the catalyst step increase from 0.05 wt % in the feed to 0.1 wt %. The simulated model calculated no temperatures; however, the water concentration in the reboiler of the model should have the same response as the temperature in the reboiler since the two are closely related. Since the gas chromatograph could detect no water concentration change in the reboiler of the experimental pilot column, the water concentration has not been plotted for the reboiler. The water concentration of the simulated column decreased 0.01% or for

practical purposes stayed constant as in the experimental column. Hence, the small water decrease computed could possibly be due to noise from the analog computer. Thus the mathematical model implies that the water and temperature of the esterification column reboiler should remain constant. This means that the temperature change increasing in the actual pilot plant column reboiler is caused by the other components or that the simulated model is in error.

The other three components in the reboiler represented by Figures 4.51, 4.52, and 4.53 demonstrate that the simulated and experimental compositions for the reboiler are in excellent agreement. The deadtime and time constants of the transient responses are identical for practical purposes in the reboiler.

The feedtray simulated responses (Figures 4.54, 4.55, 4.56, and 4.57) do not have quite as tight a fit to the experimental values in the reboiler. The experimental values of the response of the feedtray indicate a higher order system than the faster responding simulated values for the feedtray. Also, the simulated response on the feedtray is more even and gradual than the actual response.

To make the above simulated responses agree accurately with the experimental values the 'k' value for the kinetics equation is reduced from 0.814 to 0.714 for 0.1 weight % catalyst. Hence, the rate equation is modified to make the simulated responses very close to the actual experimental results. The 'k' value is changed according to Figure 4.45 as the catalyst concentration increases on a given tray.

5.5.2 Simulated Boil-up Step Change

A step decrease in the steam feed rate (230 gms/min to 155 gms/min) for both the experimental and simulated esterification column is represented in Figures 4.60 to 4.69 for the compositions versus time for the reboiler and feedtray. As previously stated the temperature is not calculated in the simulated responses. When the simulated values disagree with the experimental by $\pm 0.25\%$, they are represented by dashed lines on the figures.

The reboiler responses for the experimental and simulated component responses are in disagreement because of an early and constant displacement in Figures 4.61 and 4.62. Since the heat transfer time constant in the reboiler is one thousand times smaller than the composition response in the reboiler, the displacement is not due to heat transfer deadtime but most likely due to the vapor-liquid equilibrium correlations not being sufficiently precise. Figure 4.63 is in good agreement.

Figures 4.64 to 4.67 show the component response as a function of time on the feedtray. The acetic acid and butanol responses from the model are fairly accurate on the feedtray as evidenced by Figures 4.65 and 4.66. However, the butyl acetate and water responses indicate that they are in error slightly as evidenced by Figures 4.64 and 4.67. Since the temperature responses of the experimental column are as shown in Figures 4.68 and 4.69, they give evidence that the experimental water concentration changed faster than indicated by Figure 4.64. The simulated water (Figure 4.64) response tends to follow the approximate temperature responses indicated

by Figures 4.68 and 4.69 . Hence, because the temperature indicates a water composition change, it is probable that the gas chromatograph is out slightly on the experimental water response. Thus because the water composition response in the column is likely faster experimentally than indicated in Figure 4.64, the simulated values of 4.64 and 4.67 are probably not in error as much as indicated.

In all cases (except possibly the water response) the time constants of the simulated and experimental values are in excellent agreement. The reboiler indicates a time constant of approximately 3.25 hours and that of the feedtray is roughly 3 hours. The initial value, 0.603, picked for the reaction rate constant 'k' ($\text{cc}^3/\text{moles}^3\text{hr}$) is kept for this simulation since the simulated and experimental steady states are in excellent agreement.

5.5.3 Simulated Flow Rate Change

The reboiler and feedtray composition responses to a step change in feedflow rate, from 9650 cc/hr to 11,350 cc/hr, as a function of time are illustrated in Figures 4.71 to 4.79 for both experimental and simulation runs. When differences of over $\pm 0.25\%$ occur the simulated values are indicated by a dashed line. No temperatures are calculated by the mathematical model simulation.

The simulated reboiler response to the change in flow rate between Runs 27 and 28 is very close to the experimental response. Not much change is needed, however, and the 'k' ($\text{cc}^3/\text{moles}^3\text{hr}$) of the kinetics equation (Equation 4.34) is changed from 0.0722 to 0.0692 to make the results agree as presented.

The only slight difference between the simulated and experimental results shown for the feedtray is that the simulated results again have less deadtime before responding. The responses are almost in perfect agreement.

Both the feedtray and the reboiler display short time constants of approximately 2.5 hours. The shorter time constant, as compared to the time constant of the other transients, that matches the experimental value is an indication that the model has the versatility to describe the column properly.

5.5.4 Simulated Acetic acid Concentration Change in the Column Feed

The change in the compositions of the reboiler and feedtray versus time are illustrated in Figures 4.80 to 4.89 for a step change in the acetic acid feed concentration from 13 weight percent to 36 weight percent. No temperatures are calculated in the simulation and the simulation results are represented by dashed lines on the above figures when they differ from the experimental results by $\pm 0.25\%$.

Figures 4.80 to 4.83 show the concentration change of the four components as a function of time in the reboiler for the feed concentration step change. The expanded water composition scale of Figure 4.80 shows the simulated and experimental results in total agreement and also the water curve responds the same as the temperature of Figure 4.88. Hence all three curves tend to indicate the close relationship of water and temperature. The acetic acid response in the reboiler (Figure 4.81) shows approximately the same shape for both the experimental and simulated runs with the simulated run having

an approximate 0.3 hours faster time constant. The butanol and butyl acetate transients shown in Figures 4.82 and 4.83 show the largest absolute error between simulated and experimental transient curves. The butyl acetate transient (Figure 4.83) is the worst showing a 3.4% maximum difference between simulated and experimental results. The reason for the large differences is that the model is not able to simulate the rapid flattening of the butanol transient or the slight 'oscillation' of the butyl acetate response. (The crude vapor-liquid equilibrium correlations are probably the reason for the difference between the experimental and simulated responses.) Both the butanol and butyl acetate transients for the simulation tend to have slightly larger time constants than the experimental transients.

The feedtray transients shown in Figures 4.84 to 4.87 are in excellent agreement except for the slight difference of the acetic acid transient and the small but important difference of the water response curve (Figure 4.84). The simulated water transient only rises and, hence, does not change directions as does the experimental response as indicated by both composition measurements (Figure 4.84) and temperature measurement (Figure 4.89). Thus, the model fails to predict the most interesting nonlinearities that occur in the esterification column and this is probably due to the crude vapor-liquid equilibrium correlations.

The kinetics rate constant ' k ' $\text{cc}^3/\text{m}^3\text{hr}$ is kept at the original value found for it in the kinetics studies of 0.603 for a catalyst concentration of 0.05 weight percent in the above simulations. The time constant for the above simulated transients is approximately 3.5 to

4.0 hours which is again close to the actual values.

5.6 Summary and Conclusions to the Simulation Studies

The fact that the time constants obtained, from the hybrid simulation of the esterification column varied with the different step changes, in agreement with the experimental column, shows that the mathematical model is able to represent the experimental column quite precisely over a wide range. Therefore, the assumptions and approximations made in development of the model must be tolerable. The only case where moderately large errors occur is when the acetic acid in the feed is step changed 23 percent. Thus, overall, the mathematical model does an excellent job of simulating the four transients examined.

The largest absolute error that occurs in the simulation studies results when the butyl acetate values calculated from the model do not follow the small oscillation or overshoot that occurs in the experimental column. The value of the error is 3.25%. For the overall average, the results are within 1.0% relative error which, according to Williams (38), is very good for such studies. However, it must be remembered that, to make the results agree as shown, the value of the 'k' (cc /moles hr) constant on the reaction rate equation is modified twice. If the values had not been adjusted, the results would have been in error accordingly.

Four valuable lessons are learned about the hybrid computer in this simulation study. The first is the need for a program that actively checks the analog patchboard before any complex problem is

run. If this is not done the results can be in error due to faults in the analog and digital logic components. The second point is that interrupts should be used only when necessary since the use of interrupts requires the allocation of large amounts of core to store variables and run special tests which limits the capability of the 640 digital computer accordingly. The third lesson is that the 680 analog timing sequence should consist of four mode steps in cycle instead of three. If four are used, double usage can be made of the digital-to-analog converters; hence, a large number of amplifiers are freed for problem solving and debugging. The fourth lesson is that the hybrid computer requires a great deal more effort by the programmer to set up and solve a problem. The main reason is that debugging between the four computers that make up the hybrid computer is more complex. (Timing the four computers making up the hybrid, in the proper sequence and exchanging information between them, introduces many bugs.) Hence, the hybrid computer should be used only on problems that have to be solved a large number of times and where there is a great deal of integration at which the hybrid excels.

6.1 Summary and Conclusions Relating to the Total Study on the Water, Acetic Acid, n-Butanol, and n-Butyl acetate System

This study was presented in three parts so that, in the interests of clarity, the information on vapor-liquid equilibrium, experimental pilot plant production, and simulation studies could be discussed separately. The initial purpose of the study was to find wide ranging information on the production of n-butyl acetate using excess butanol in a reaction distillation column so that the column could be fitted into a larger operation with predictable results as to steady state and transient behaviour.

In summary, the results derived from the investigation into the production of n-butyl acetate with excess n-butanol in a reaction distillation column are as follows:

- 1) A new design for a vapor-liquid equilibrium still, capable of handling slow reactions and two liquid phase systems, is put forth and verified.
- 2) Using the still mentioned in (1) above, vapor-liquid equilibrium data were gathered for the following four binary and two ternary systems:
 - i) n-butanol and n-butyl acetate
 - ii) n-butanol and acetic acid
 - iii) n-butyl acetate and acetic acid
 - iv) water and acetic acid

- v) water, acetic acid, and n-butanol
 - vi) acetic acid, n-butanol, and n-butyl acetate
- 3) The Margules, Renon, Wilson, and Van Laar activity coefficient equations are tested for their ability to curve fit and predict the experimental vapor-liquid equilibrium data of the systems involved in this study. The equations all fail to precisely fit or predict the experimental data. Of the four equations involved, the Margules equation is shown to be the best for practical purposes.
 - 4) A kinetics rate equation for the esterification reaction is obtained from experimental data. The range of the equation makes it applicable to any operation using excess butanol.
 - 5) Steady state data varying over almost the complete excess butanol range of operation of the esterification column is collected. The data illustrates how four times the n-butyl acetate may be produced from the same column if the resulting separation and fouling problems can be tolerated in the product stream.
 - 6) A successful simulation of the pilot plant esterification column is operated on the hybrid computer. Attention is also drawn to the lessons learned about the practical use of hybrid computers.
 - 7) The experimental and simulated studies on the esterification column showed that the column needed few controllers

due to the self-regulation resulting from a large holdup, distillation forces, and kinetics reaction, and also a low sensitivity to input variable changes.

A brief discussion is now given on each of the above points.

The new still presented in this study has the features necessary to examine vapor-liquid equilibrium relationships in this system, namely, a fast transient to equilibrium and the ability to handle two liquid phases. The temperature measurement system and the heating procedure combine to produce the fast transient to equilibrium in the still; and the use of the dry ice cooled syringes makes possible the handling of two liquid phase samples collected from the still.

The four sets of binary data collected from the still agree fairly well with the work done by previous workers. Since the ternary data collected is original, all that can be said is that it behaves as one would expect from binary information; and it has few apparent inconsistencies. The precision of the data is unknown.

Contrary to the predictions of References (16), (27) and (29), the least-squares curve fitting of the experimental data for the miscible ternary of this study showed that the Wilson activity coefficient equation could not perform as well as the Margules equation. Moreover, the Renon equation fails to fit the immiscible systems as well as the Margules equation. Since the Margules activity coefficient equation does not use temperature and the Renon and Wilson equations do, it is possible that the Wilson and Renon equations might have performed badly due to the temperature being in error, from reaction effects, in the two ternaries with reaction. However, in the water,

n-butanol, and n-butyl acetate ternary no reaction could occur and the Renon and Wilson equations still performed badly. The Wilson equation can be excused since it is supposed to apply only to miscible liquid systems, but the Renon equation which is purported to be able to handle immiscible systems must be labelled a failure from the results of this study. Since none of the activity coefficient equations could fit the experimental data, their predictive capabilities were useless.

The kinetics rate equation developed in this study for the esterification of n-butyl acetate from n-butanol and acetic acid (Equation 4.34) was developed primarily for the hybrid computer simulation studies. As a result, the final values picked for the constant, k , in Equation 4.34 for a given catalyst concentration (Figure 4.45) were picked so as to make the hybrid simulation results agree with the pilot plant experimental results. Thus two data points in Figure 4.45 were changed to suit the hybrid computer model; 0.714 was previously 0.814 and 0.0692 was previously 0.0722 from kinetics studies alone. The changed values resulted in the hybrid computer studies agreeing with the pilot plant experimental results and also in producing a smooth curve for Figure 4.45 .

Even though the hybrid computer simulation results agree well with the experimental results there is still a degree of uncertainty in the kinetics equation. This is due to the fact that the vapor-liquid equilibrium correlations used to obtain the kinetics rate constants, k , for various catalyst levels, are also the same correlations used in the simulation studies. Hence, the kinetics equation could possibly be correcting for errors in the vapor-liquid equilibrium.

correlations which do not show up because the correlations are used both to calculate the kinetics correlation and in the simulation studies. Thus no estimate of the precision of the kinetics equation is known.

The steady state data collected from the pilot plant esterification column demonstrated two extreme choices open for its operation. The column could be fed about 12 weight percent acetic acid in the feed with 0.05 weight percent catalyst and the output stream would be clear, easily separated, and free of serious fouling problems; or the column could be fed 38 weight percent acetic acid in the feed stream with 0.1 weight percent catalyst and the output stream would be clouded, difficult to separate, and present a serious fouling problem due to tar and salts. The second choice mentioned, with a high acetic acid feed, would produce four times the n-butyl acetate from the same esterification column. (An acetic acid feed concentration between the two extremes mentioned above could provide the best economical balance between corrosion and better production of butyl acetate.)

The simulation studies done on the hybrid computer showed that the mathematical model used represented the experimental esterification column quite accurately. Thus the 15 assumptions enunciated in Section 5.3 are reasonable for the modeling of the esterification column.

Because of the effects of self-regulation and a low sensitivity to input variables, the esterification column needs high-speed,

automatic control only to keep liquid in the reboiler and proper liquid levels in the decanter. Thus the column needs little automatic control and could probably be operated properly with manual valves on the input and exit streams. A continual monitoring of the composition of the output stream would be essential every half hour to allow an operator to adjust the necessary manual controllers.

BIBLIOGRAPHY

1. Asselineau, L. et Renon, H., "Extension de l'équation NRTL pour la représentation de l'ensemble des données d'équilibre binaire, liquide-vapeur et liquide-liquide", Chem Engg Sc, 25, 1211-1223, 1970.
2. Bekey, G. A. and Karplus, W. J., Hybrid Computation, John Wiley & Sons Inc, Toronto, 1968.
3. Brown, G. G., Unit Operations, John Wiley & Sons Inc, New York, 1950.
4. Brunjes, A. S. and Furnas, C. C., "Commercially Important Systems of Organic Solvents", I&EC, 28, (5), 573-580, 1936.
5. Brunjes, A. S. and Furnas, C. C., "Vapor-Liquid Equilibrium Data for Commercially Important Systems of Organic Solvents", I&EC, 27, (4), 396-400, 1935.
6. Cobb, C. B., "A Comparison of Digital, Analog, and Hybrid Techniques for Solving Unsteady State Distillation Problems", Monsanto Co, St. Louis, Missouri, 1968.
7. Cohen, G. et Renon, H., "L'équation NRTL pour la calcul des équilibres liquide-liquide à n-constituants", Cdn Jour of Chem Engg, 48, (3), 291-297, 1970.
8. Cornell, W. I. and Montanna, R. E.; "Studies in Distillation II.", I&EC, 25, (12), 1331-1335, 1933.
9. Garwin, L. and Hutchison, K. E., "Separation of Acetic Acid and Water by Distillation", I&EC, 42, (4), 727-730, 1950.
10. Gilmont, R. and Othmer, D. F., "Composition of Vapors from Boiling Binary Solutions", I&EC, 36, (11), 1061-1064, 1944.

11. Hála, E., Pick, J., Fried, V. and Vilim, O., "Liquid-Vapor Equilibriums. XIII, Phase Equilibriums in the System Water-Butanol-Butyl-acetate", *Chemické Listy*, 49, 1112-1116, 1955.
12. Hála, E., Pick, J., Fried, V. and Vilim, O., Vapour Liquid Equilibrium, second ed., Pergamon Press, Toronto, 1967.
13. Hirata, M. and Hirose, Y., "Physical Properties of Ternary System Acetic Acid-Water-Butyl-acetate", *Chem Engg (Japan)*, 27, (6), 407-413, 1963.
14. Hirata, M. and Hirose, Y., "Vapor-Liquid Equilibria of Ternary System Water-Acetic Acid-n-Butyl-acetate", *Chem Engg (Japan)*, 30, (2), 121-128, 1966.
15. Holland, C. D., Unsteady State Processes with Applications in Multicomponent Distillation, Prentice Hall Inc, New Jersey, 1966.
16. Holmes, M. J. and Van Winkle, M., "Prediction of Ternary Vapour-Liquid Equilibria from Binary Data", *I&EC*, 62, (1), 1970.
17. Hybrid Computation, Applications Reference Library, Electronic Associates Inc.
18. Lange, N. A., Handbook of Chemistry, tenth ed, McGraw-Hill Book Co, New York, 1967.
19. Leyes, C. E. and Othmer, D. F., "Continuous Esterification of Butanol and Acetic Acid, Kinetic and Distillation Considerations", *Am Inst Chem Engrs*, 157-195, April, 1945.
20. Leyes, C. E. and Othmer, D. F., "Esterification of Butanol and Acetic Acid", *I&EC*, 37, (10), 968-977, 1945.
21. Marek, J., "Rectification with a Chemical Reaction. I. Calculation of the Number of Theoretical Plates for Continuous Plate Columns", *Collec Czech Commun*, 19, 1055-1074, 1954.

22. Marquardt, D. W., "An Algorithm for Least-Squares Estimation of Non-linear Parameters", J SIAM, 11, (2), 1963.
23. Nagata, I. and Ohta, T., "Isobaric Vapor-Liquid Equilibria for Three Binary and Two Ternary Systems", J Chem Engg Data, 16, (2), 1971.
24. Othmer, D. F., "Composition of Vapors from Boiling Binary Solutions", I&EC, 20, (7), 743-746, 1928.
25. Othmer, D. F., Silvis, S. J. and Spiel, A., "Composition of Vapors from Boiling Binary Solutions", I&EC, 44, (8), 1864-1872, 1952.
26. Perry, J. H., Chemical Engineers' Handbook, third ed, McGraw-Hill Book Company, Toronto, 1950.
27. Prausnitz, J. M., Eckert, C. A., Orye, R. V. and O'Connell, J. P., Computer Calculations for Multicomponent Vapor-Liquid Equilibria, Prentice Hall Inc, New Jersey, 1967.
28. Redlich, O., Kister, A. T. and Turnquist, C. E., Chem Engg Progr Symp Ser 48, (2), 49, 1952.
29. Renon, H. and Prausnitz, J. M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", AIChE, 14, (1), 135-144, 1968.
30. Rius, A., Otero, J. L. et Macarron, A., "Equilbes liquide-vapeur de mélanges binaires donnant une reaction chimique: systèmes methanol-acide acétique; n-butanol-acide acétique", Chem Engg Sc, 10, 105-111, 1959.
31. Ruszkay, R. and Mitchell, E. E. L., "Hybrid Simulation of a Reacting Distillation Column", Proc - Spring Joint Computer Conf, 389-399, 1966.

32. Smith, B. D., Design of Equilibrium Stage Processes, McGraw-Hill Book Co Inc, Toronto, 1963.
33. Smith, J. M., Chemical Engineering Kinetics, McGraw-Hill Book Co Inc, Toronto, 1956.
34. Smith, T. E. and Bonner, R. F., "Vapor-Liquid Equilibrium Still for Partially Miscible Liquids", I&EC, 41, (12), 2867-2871, 1949.
35. Stainthorp, F. P., "Comments on the Pilot Plant and Hybrid Computer Installed in the Faculty of Engineering, University of Calgary", Dept Chem Engg, Univ Calg, 1971.
36. Svrcek, W. Y., "Dynamic Response of a Binary Distillation Column", PhD Thesis, Univ Alta, July 1967.
37. Volk, W., Applied Statistics for Engineers, McGraw-Hill Book Co, New York, 1969.
38. Williams, T. J., Chemical Engineering Symposium Series, (46), 59, 1-8, 1963.
39. Williams, T. J., "Computers and Process Control", I&EC, 62, (2), 28-40, 1970.
40. York, R. and Holmes, R. C., "Vapor-Liquid Equilibria of the System Acetone-Acetic Acid-Water", I&EC, 34, (3), 345-350, 1942.

APPENDICES

APPENDIX 1

COMPUTER PROGRAMS USED IN STUDIES

A.1.1 Vapor-Liquid Equilibrium Program

1) Component Addition to Still

(Language: FORTRAN)

This program calculates the contents of the still and the likely amount and composition removed with each sample taken from the still. The program's purpose is to calculate the next composition which should be investigated in a ternary system. Because of the above purpose, the program does a mass balance and prints out the amount of fresh component or components to be added. The program greatly expedited the experimental work.

2) Raw Data Processing for Vapor-Liquid Equilibrium

(Language: FORTRAN)

This program first creates a set of calibration curves for each component to match the areas under the gas chromatograph response. Once the calibration curves are established the program calculates the weight percent of all components in all vapor and liquid samples. The weight percents are then converted to make mole fractions. Using the temperature readings from the experiments and the vapor pressure curves from Reference 13, the activity coefficients at each point are calculated. Relative volatility values are then calculated for all components at all points. All related values are plotted against one another on graphs.

3) Regression Routine for Curve Fitting

(Language: PL/1)

The least-squares regression technique of Reference 22 uses a combination of steepest descent and Taylor Series approximations. The degree to which either of the above methods is used is controlled by the programmer. Once a curve has been fit, the program calculates the deviation between calculated and actual values. A plot of the differences is also made by the program. Any type of linear or non-linear equation can be handled by this program.

4) Binary Margules Equation

(Language: PL/1)

The Margules equation for the activity coefficient in a binary solution

$$\ln \lambda_1 = x_2^2 [A_{12} + 2x_1 (A_{21} - A_{12})]$$

is provided by this program. Program 3 uses the equation this program provides in its algorithm to calculate the values of A_{12} and A_{21} . Thus Programs 3 and 4 are used together to fit binary data to the Margules equation. (The usual cycling of subscripts is used for the second activity coefficient.)

5) Binary Renon Equation

(Language: PL/1)

The Renon equation for the activity coefficient in a binary solution

$$\ln \lambda_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{(x_1 + x_2 G_{21})^2} \right) + \tau_{12} \left(\frac{G_{12}}{(x_2 + x_1 G_{12})^2} \right) \right]$$

is provided by this program. The necessary relationships applied in Reference 20, namely in the expressions

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT}; \quad \tau_{21} = \frac{g_{21} - g_{11}}{RT}$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}); \quad G_{21} = \exp(-\alpha_{21} \tau_{21})$$

we have $\alpha_{12} = \alpha_{21}$ and $g_{12} = g_{21}$.

Program 3 uses the equation, thus provided, in its algorithm to calculate the values of

$$g_{12} - g_{22} \text{ and } g_{21} - g_{11}$$

since the value of α_{12} and α_{21} is picked by the programmer according to the rules of Reference 29. Thus Programs 3 and 5 are used in conjunction with one another to fit the experimental activity coefficients to the Renon equation. (The usual cycling of subscripts is used for the second activity coefficient.)

6) Binary Van Laar Equation

(Language: PL/1)

The Van Laar equations for the two activity coefficients in a binary solution

$$\ln \lambda_1 = \frac{1}{T} \left[\frac{A_{21}}{\left(1 + A_{12} \frac{x_1}{x_2}\right)^2} \right]$$

and

$$\ln \lambda_2 = \frac{1}{T} \left[\frac{A_{12} A_{21}}{\left(A_{12} + \frac{x_1}{x_2}\right)^2} \right]$$

are provided by this program. Programs 3 and 6 are used in conjunction with one another to fit the experimental data to the above equations by optimizing to find the best values of A_{12} and A_{21} .

7) Wilson Binary Equation

(Language: PL/1)

The Wilson equation for the activity coefficient in a binary solution

$$\ln \lambda_1 = -\ln[x_1 + \Lambda_{12} x_2] + x_2 \left[\frac{\Lambda_{12}}{(x_1 + \Lambda_{12} x_2)} - \frac{\Lambda_{21}}{(x_2 + \Lambda_{21} x_1)} \right]$$

is provided by this program. The relationships given in Reference 16 are applied, namely, that in the expression

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left[-\frac{(\gamma_{12} - \gamma_{11})}{RT}\right]$$

and

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left[-\frac{(\gamma_{21} - \gamma_{22})}{RT}\right]$$

we have $\gamma_{12} = \gamma_{21}$

The molar volumes v_1 and v_2 are also provided by the program as a function of temperature. Program 3 is used with this program to calculate the values of

$$\gamma_{12} - \gamma_{11} \text{ and } \gamma_{21} - \gamma_{22}$$

and thus fit the experimental data to the Wilson equation. (A cycling of subscripts is used to calculate the second activity coefficient.)

8) Margules Ternary Equation

(Language: PL/1)

The Margules equation for the activity coefficient for a component in a ternary system

$$\begin{aligned} \ln \lambda_1 = & x_2^2 [A_{12} + 2x_1 (A_{21} - A_{12})] + x_3^2 [A_{13} + 2x_1 (A_{31} - A_{13})] \\ & + x_2 x_3 [A_{21} + A_{13} - A_{32} + 2x_1 (A_{31} - A_{13}) + 2x_3 (A_{32} - A_{23}) \\ & - C(1 - 2x_1)] \end{aligned}$$

is provided by this program. Using this program, the algorithm of Program 3 calculates the best values of the A's and of C to fit the experimental data to the Margules expression for the activity coefficient. The subscripts are cycled to obtain the second and third activity coefficient expressions.

9) Renon Ternary Equation

(Language: PL/1)

This program provides the Renon equation for the activity coefficient of a component in a ternary system.

$$\begin{aligned} \ln \lambda_1 = & \frac{\tau_{21} G_{21} x_2 + \tau_{31} G_{31} x_3}{x_1 + G_{21} x_2 + G_{31} x_3} + x_1 \left(\frac{-x_2 \tau_{21} G_{21} - x_3 \tau_{31} G_{31}}{(x_1 + G_{21} x_2 + G_{31} x_3)^2} \right) \\ & + \frac{x_3 G_{13}}{G_{12} x_1 + x_2 + G_{32} x_3} \left(\tau_{13} - \frac{(x_1 \tau_{12} G_{13} + x_3 \tau_{32} G_{32})}{(G_{12} x_1 + x_2 + G_{32} x_3)} \right) \\ & + \frac{x_3 G_{13}}{G_{13} x_1 + G_{23} x_2 + x_3} \left(\tau_{13} - \frac{(x_1 \tau_{13} G_{13} + x_2 \tau_{23} G_{23})}{(G_{13} x_1 + G_{23} x_2 + x_3)} \right) \end{aligned}$$

The same equations necessarily apply here as in the binary system.

Therefore:

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \quad \text{and} \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$\text{and} \quad g_{ij} = g_{ji} \quad ; \quad \alpha_{ij} = \alpha_{ji}$$

where $i = 1, 2, 3$

$j = 1, 2, 3$

The algorithm of Program 3 calculates the optimized values of

$$g_{ij} - g_{jj}$$

to make the experimental data for the activity coefficient fit the above expression. Cycling of subscripts is used to calculate the expression

for the other activity coefficients.

10) Wilson Ternary Equation

(Language: PL/1)

This program provides the Wilson equation for the activity coefficient of a component in a ternary system

$$\ln \lambda_1 = 1 - \ln[x_1 + \Lambda_{12}x_2 + \Lambda_{13}x_3] - \left[\frac{x_1}{x_1 + \Lambda_{12}x_2 + \Lambda_{13}x_3} \right] \\ - \left[\frac{\Lambda_{21}x_2}{\Lambda_{21}x_1 + x_2 + \Lambda_{23}x_3} \right] - \left[\frac{\Lambda_{31}x_3}{\Lambda_{31}x_1 + \Lambda_{32}x_2 + x_3} \right]$$

As in the binary equation, the interacting energies are equal; hence:

$$\gamma_{ij} = \gamma_{ji} \quad ; \quad i = 1, 2, 3 \quad ; \quad j = 1, 2, 3$$

and the expressions for v_1 , v_2 , and v_3 are known. Because of the above relationships there are only six different values of the expression:

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\left[-\frac{(\gamma_{ij} - \gamma_{ii})}{RT}\right], \quad i = 1, 2, 3 \quad ; \quad j = 1, 2, 3$$

The algorithm of Program 3 calculates the 6 best values for the above expression to make the Wilson equation fit the experimental data for the activity coefficient. By cycling the subscripts, Program 10, in conjunction with 3, is used to fit all three activity coefficients to the experimental data.

11) Check on Binary Curve Fitting

(Language: FORTRAN)

This program uses the calculated curves for the activity coefficients and the vapor pressure curves from the literature to

calculated vapor and liquid compositions in equilibrium with one another. The calculated values are then compared against experimental values. All values are printed for observation. The correlation coefficient and the variance of estimate of the vapor compositions are calculated.

12) Check on Ternary Curve Fitting

(Language: FORTRAN)

Using the equations for the ternary activity coefficients and the vapor pressure equations from the literature, this program calculates vapor-liquid equilibrium relationships. The values calculated are then compared against actual experimental values. All values are printed for observation. The correlation coefficient and the variance of estimate of the calculated versus the experimental vapor compositions are calculated.

13) Check on the Curve Fitting of Reference 12

(Language: FORTRAN)

Using the Margules equation suggested by Reference 12, this program calculated constant vapor composition lines for a ternary diagram. The values are then compared to the experimental work of Reference 12. There is very little similarity between the calculated and experimental diagrams.

14) Conversion Routines

(Language: FORTRAN)

Eight small programs convert data by other authors into units

and areas suitable for comparison with work done in this study. Extrapolation of others' work is never used but a great deal of interpolation is employed so that direct comparisons, especially in binary systems, could be made.

A.1.2 Esterification Column and Model Programs

15) Kinetics Calculation from Still Data

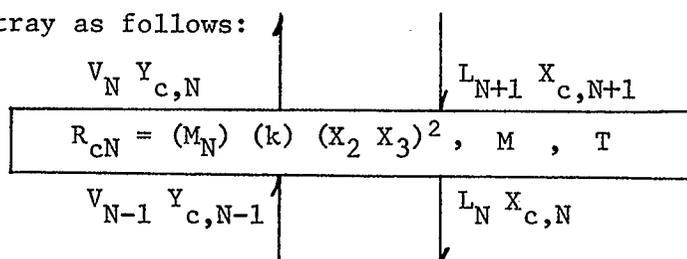
(Language: FORTRAN)

This program uses data which is taken from the still 0.5 to 12.0 minutes after acetic acid and butanol are mixed at the boiling point. The program assumes constant temperature and that the composition of acetic acid and butanol remains constant. The amount of water and butyl-acetate formed is assumed to be the rate of reaction for the above concentration of acetic acid and butanol in a batch reaction.

16) Kinetics Calculation from Column Data

(Language: FORTRAN)

Using a steady state model of the esterification column, this program calculates the rate of reaction obtained under conditions within the column. A balance for each component is done in moles for each tray as follows:



$$R_{c,N} = L_{N+1} X_{c,N+1} + V_{N-1} Y_{c,N-1} - V_N Y_{c,N} - L_N X_{c,N}$$

Since the total number of moles on each tray (M_N) is known, the rate

can be and is calculated from $R_{c,N}$. The composition and rate of the two exit streams from the above tray depend heavily on the vapor-liquid equilibrium data which is taken from Reference 20 ($Y_{c,N} = f(X_{c,N})$). The vapor-liquid equilibrium data from the above reference fluctuates 10 to 20 percent. Hence, the fact that the kinetics data obtained from the column fluctuates an equal amount is not surprising. The usual corrections to the above balance are made for the feed tray, reboiler, and condenser.

17) Calculation of Steady State Compositions Throughout Column

(Language: FORTRAN)

Samples are taken from each tray of the esterification column when it reaches steady state. The samples are analysed by a technical assistant and the results given to the author in calibrated integral strokes. This program converts the integral strokes to weight percent and then to mole fraction statements on the column's composition.

18) Mass Balance Check on Esterification Column

(Language: FORTRAN)

This program is given all experimental steady state flows and compositions into and out of the esterification column. It then calculates the overall mass balance from weight percent considerations and then from mole fraction considerations. The amount of absolute error, as well as the relative percent error, is printed out for observation and study. All flows are also printed out for easy accessibility.

19) Heat Balance on Esterification Column

(Language: FORTRAN)

All steady state flows, temperatures, and compositions are fed to this program to enable it to calculate the overall heat balance on the esterifications column. The difference between the heat injected by the steam and that not extracted by the cooling water is printed out along with the percentage of the heat it represents. All other values of importance to the heat balance are printed for ease of acquisition.

20) HOI Debug Routine for Hybrid

(Language: HOI (Hands on Interrupter))

This program is applied to remove any obvious analog patching errors in the analog portion of the hybrid model for the esterification column. The program gives the programmer the ability to check any part of the analog circuit in an on-line mode. The ability to change the program as debugging progresses greatly enhances the speed at which the initial phases of debugging are done.

21) FORTRAN Debug Routine for Hybrid

(Language: FORTRAN)

This program is used to check the analog patch panel before the digital half of esterification model is applied. It loads a standard set of values through the DAC's and integrates for six machine seconds. The values are printed out and if there is any error due to a faulty component or loose wire, it can be corrected easily. This

program saves a great deal of time.

22) Hybrid Monitor Program

(Language: FORTRAN)

This program provides the general overall control of the hybrid model of the esterification column. First it reads in and initializes all variables. It then proceeds to control the timing of when different routines are run and when the analog board is operated. The decision of when to output results and in which direction to calculate through the column is also controlled by the program. This program treats all programs from number 23 to 27 as subroutines. Figure 5.44 shows the detail calling and timing sequence of the program.

23) Reaction Rate Calculation for Hybrid Model

(Language: FORTRAN; Subroutine name: REA)

This program calculates the rate of reaction for the hybrid model with the equation:

$$r = k (X_2 X_3)^2$$

where X_2 and X_3 are the mole fractions of acetic acid and butanol respectively and k takes the values of 0.714, 0.603, 0.474, 0.0692, and 0.0152 for catalyst concentrations of 0.1, 0.05, 0.03, 0.003, and 0.0 percent sulfuric acid respectively. The above equations developed in this study make it possible to calculate the mole rate of reaction which is then converted into grams for the analog portion of the hybrid model. Thus each time this program is called by the monitor, it corrects for reaction on the tray. Since there are two calculations

for each tray for each time period, the reaction program works in 3 minutes and not 6.

24) Decanter Calculations for Hybrid Model

(Language: FORTRAN; Subroutine name: COND)

This program calculates the phase separation of the totally condensed overhead product from the esterification hybrid model. The separation of the phases is first calculated in mole fractions and then converted to grams. The amount of material going into the upper oil layer and reflux is calculated as well as that into the lower water layer which is discharged. The information for the above calculations came from Reference 11.

25) Vapor Rate Calculations for Hybrid Model

(Language: FORTRAN; Subroutine name: VAP)

This program simulates the heat loss from the column by cutting back on the amount of vapor leaving each tray in the hybrid model. Half of the column's heat losses are assumed to occur from the reboiler. The other half is assumed to be lost evenly over the 10 trays of the column. Hence the vapor flow is cut enough from each tray to make up for the calories lost. A constant amount of heat is assumed lost from the column for all simulated runs.

26) Reboiler Adjustment for Hybrid Model

(Language: FORTRAN; Subroutine name: REB)

This program provides the corrections to the analog patch board so that the reboiler calculations can be done similar to a tray.

The total mass in grams is increased 10 times and the incoming vapor streams are set to zero. The quantity of vapor leaving the reboiler is calculated. The amount and flow rate of product leaving the reboiler is noted.

27) Feedtray Adjustment for Hybrid Model

(Language: FORTRAN; Subroutine name: FEED)

This program corrects the model for the incoming streams of butanol, acetic acid, and sulphuric acid catalyst. The liquid feed is added to the input onto the tray. The heat required to bring the liquid to a boil is obtained by cutting the outgoing vapor stream enough to provide the required calories.

Note: A copy of any of the above programs may be obtained from the Hybrid Lab of the Faculty of Engineering, at the University of Calgary.

APPENDIX 2

ACTIVITY COEFFICIENT CURVE FITTING TABLES

TABLE A2.11

WATER(1) - ACETIC-ACID(2) SYSTEM

		Constants	Correlation ln	Coefficients* Arithmetic	Variance ln	of Estimate* Arithmetic	
Margules Equation	ln λ_1	0.0921749 0.199716	0.99991	0.99894	0.00032	0.00013	
	ln λ_2	0.385178 0.179018	0.99859	0.99220	0.00576	0.00101	
Constant = 0.2							
Renon Equation	ln λ_1	614.389 -422.024	0.99991	0.99880	0.00032	0.00015	
	ln λ_2	147.175 39.9828	0.99825	0.98810	0.00715	0.00154	
	Constant = 0.3						
	ln λ_1	171.018 - 40.7268	0.99990	0.99852	0.00037	0.00019	
	ln λ_2	186.262 1.72906	0.99822	0.98781	0.00729	0.00158	
	Constant = 0.47						
Van Laar Equation	ln λ_1	255.902 - 12.1411	0.99942	0.99502	0.00928	0.00016	
	ln λ_2	120.133 5107.06	0.98073	0.96207	0.31361	0.00295	
	ln λ_1	5808.99 28685.7	0.99976	0.99597	0.00094	0.00052	
	ln λ_2	699.074 38798.1	0.99911	0.99863	0.00362	0.00017	
Wilson Equation	ln λ_1	583.414 -328.579	0.99992	0.99918	0.00029	0.00010	
	ln λ_3	1397.71 -1098.49	0.99862	0.99135	0.00563	0.00112	

* See Appendix 5

TABLE A2.12

		WATER(1) - BUTANOL(3) SYSTEM			Variance of Estimate	
		Constants	Correlation Coefficients		ln	Arithmetic
			ln	Arithmetic		
Margules Equation	ln λ_1	0.61 1.34	0.97592	0.39346	0.17023	0.03697
	ln λ_3	0.61 1.34	0.99782	0.81646	1.84132	0.01458
	ln λ_1	1.21873 2.51029	0.99819	0.89514	0.01288	0.00269
	ln λ_3	0.677078 3.13434	0.99945	0.95328	0.46122	0.00399
Renon Equation	Constant = 0.2					
	ln λ_1	2562.24 - 322.997	0.99839	0.90391	0.01147	0.00800
	ln λ_3	2462.68 - 156.275	0.99944	0.96051	0.47245	0.00338
	Constant = 0.3					
	ln λ_1	2316.21 67.1232	0.99842	0.90530	0.01125	0.00789
	ln λ_3	2181.44 137.166	0.99444	0.96615	0.47376	0.00291
Van Laar Equation	Constant = 0.47					
	ln λ_1	2374.68 532.074	0.99823	0.89229	0.01259	0.00836
	ln λ_3	714.438 1901.64	0.99942	0.96667	0.48361	0.00286
	ln λ_1	0.434081 1142.85	0.99839	0.90423	0.01144	0.00797
Wilson Equation	ln λ_3	0.452486 528.253	0.99944	0.96502	0.47222	0.00300
	ln λ_1	1569.12 13067.4	0.99832	0.90161	0.0120	0.00818
	ln λ_3	2245.37 565.484	0.99940	0.94862	0.50306	0.00438

TABLE A2.13

		WATER(1) - BUTYL ACETATE(4) SYSTEM					
		Constants	Correlation Coefficient	Variance of Estimate			
			ln	ln	Arithmetic		
			Arithmetic				
Margules Equation	ln λ_1	2.01 0.81	0.99409	0.77777	0.12149	0.03126	
	ln λ_4	2.01 0.81	0.99972	0.88636	9.85990	0.01696	
	ln λ_1	1.49986 2.77886	0.99988	0.99539	0.00235	0.00072	
	ln λ_4	2.91222 5.28674	0.99999	0.99673	0.00717	0.00051	
Constant = 0.2							
Renon Equation	ln λ_1	2871.03 - 178.805	0.99994	0.99788	0.00114	0.00033	
	ln λ_4	3341.94 638.07	0.99999	0.99669	0.00508	0.00052	
	Constant 0.3						
	ln λ_1	3811.29 331.959	0.99996	0.99815	0.00082	0.00029	
	ln λ_4	3246.41 961.681	0.99999	0.99602	0.0071	0.00062	
	Constant = 0.47						
Van Laar Equation	ln λ_1	2148.94 716.949	0.99926	0.96242	0.01516	0.00583	
	ln λ_4	3424.4 1131.63	0.99999	0.99334	0.01527	0.00104	
	ln λ_1	0.48055 1.24372	0.89107	-1.11651	2.125	0.17777	
	ln λ_4	0.538016 1047.9	0.99999	0.99702	0.00437	0.00047	
Wilson Equation	ln λ_1	2086.93 2416.5	0.99961	0.97900	0.00800	0.00328	
	ln λ_4	2998.85 1980.08	0.99999	0.98344	0.04538	0.00259	

TABLE A2.14

ACETIC ACID(2) - BUTANOL(3)

		Constants	Correlation ln	Coefficients Arithmetic	Variance ln	of Estimate Arithmetic	
Margules Equation	ln λ_2	-0.442085 -0.6813	0.99999	0.99997	0.00001	0.00000	
	ln λ_3	-0.971325 -0.429764	0.99991	0.99982	0.00020	0.00003	
		Constants = 0.2					
Renon Equation	ln λ_2	631.373 -908.999	0.99995	0.99992	0.00011	0.00001	
	ln λ_3	- 88.4521 - 1.74999	0.95418	0.99037	0.11211	0.00214	
			Constant = 0.3				
	ln λ_2	832.384 -954.245	0.99999	0.99999	0.00000	0.00000	
	ln λ_3	932.575 -1097.37	0.99991	0.99989	0.00021	0.00002	
			Constant = 0.47				
Van Laar Equation	ln λ_2	899.351 -871.203	0.99999	0.99999	0.00000	0.00000	
	ln λ_3	715.462 -877.704	0.99999	0.99999	0.00000	0.00000	
	ln λ_2	0.61375 -287.641	0.99971	0.99751	0.00066	0.00055	
	ln λ_3	0.528616 -208.312	1.00000	0.99999	0.00000	0.00000	
Wilson Equation	ln λ_2	-237.087 - 53.9886	0.99999	0.99998	0.00001	0.00000	
	ln λ_3	-319.306 - 48.1989	0.99999	0.99999	0.00000	0.00000	

TABLE A2.15

ACETIC ACID(2) - BUTYL ACETATE(4)

		Constants	Correlation Coefficient		Variance of Estimate	
			ln	Arithmetic	ln	Arithmetic
Margules Equation	ln λ_2	-0.072703 0.396954	0.99700	0.99600	0.00814	0.00075
	ln λ_4	-0.229405 -0.0265388	0.99926	0.99681	0.00198	0.00060
Renon Equation	Constant = 0.2					
	ln λ_2	2060.74 -1246.98	0.99660	0.99576	0.00925	0.00080
	ln λ_4	- 54.1806 - 32.9436	0.99899	0.99645	0.00270	0.00067
	Constant = 0.3					
	ln λ_2	1617.4 - 874.783	0.99665	0.99576	0.00911	0.00080
	ln λ_4	1371.71 - 954.25	0.99925	0.99681	0.00199	0.00060
Van Laar Equation	Constant = 0.47					
	ln λ_2	1235.45 - 585.005	0.99661	0.99580	0.00922	0.00079
	ln λ_4	1050.80 - 685.655	0.99925	0.99678	0.00200	0.00060
	ln λ_2	-1738.42 76.0237	0.99468	0.98900	0.01445	0.00207
	ln λ_4	8526.57 -150852.0	0.99888	0.99421	0.00299	0.00109
	ln λ_2	33.1873 812.095	0.99645	0.99589	0.00964	0.00077
Wilson Equation	ln λ_4	449.661 -455.369	0.99856	0.99569	0.00385	0.00081

TABLE A2.16

		BUTANOL(3) - BUTYL ACETATE(4) SYSTEM				
		Constants	Correlation Coefficients		Variance of Estimate	
			ln	Arithmetic	ln	Arithmetic
Margules Equation	ln λ_3	0.676165 0.548205	0.99993	0.99933	0.00017	0.00005
	ln λ_4	0.325345 0.837174	0.99792	0.99789	0.00018	0.00018
	ln λ_3	0.22 0.24	0.99461	0.98204	0.01366	0.00156
	ln λ_4	0.22 0.24	0.97494	0.98719	0.08225	0.00111
Renon Equation	Constant = 0.2					
	ln λ_3	-200.077 755.885	0.99993	0.99929	0.00016	0.00006
	ln λ_4	1612.68 -766.117	0.99826	0.99812	0.00576	0.00016
	Constant = 0.3					
	ln λ_3	- 1.55488 534.802	0.99993	0.99939	0.00016	0.00005
	ln λ_4	1266.06 -481.742	0.99829	0.99795	0.00567	0.00017
Van Laar Equation	Constant = 0.47					
	ln λ_3	63.6286 486.957	0.99993	0.99933	0.00015	0.00005
	ln λ_4	949.764 -228.849	0.99834	0.99819	0.0055	0.00015
	ln λ_3	1.27728 214.577	0.99993	0.99933	0.00016	0.00005
Wilson Equation	ln λ_4	0.435682 154.782	0.99849	0.99803	0.00500	0.00017
	ln λ_3	779.811 -226.133	0.99994	0.99937	0.00014	0.00005
	ln λ_4	- 3.99977 805.353	0.99851	0.99720	0.00493	0.00024

TABLE A2.31

RENON
 TERNARY WATER(1) - ACETIC-ACID(2) - BUTANOL(3)

Renon Equation (1 set of constants)
 (Constant = 0.2)

		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	1510.49		
	2)	- 41.436		
	3)	3622.56	same	same
	4)	-1364.76		
	5)	299.126		
	6)	- 607.418		
Correlation Coefficient of Logs		0.98278	0.73408	0.97417
Correlation Coefficient of Arithmetic Values		-1.02544	0.55792	0.63881
Variance of Estimate of Logs		0.05161	0.60649	0.67071
Variance of Estimate of Arithmetic Values		0.02043	0.00855	0.00593

Renon Equation (3 sets of constants)
 (Constant = 0.2)

		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	-499.441	- 61.5849	-242.324
	2)	716.706	478.854	- 71.3222
	3)	2016.31	4605.13	3220.43
	4)	-161.251	20635.7	-809.601
	5)	-557.448	2889.91	124.629
	6)	-519.85	-2085.0	-666.072
Correlation Coefficient of Logs		0.99857	0.98671	0.99942
Correlation Coefficient of Arithmetic Values		0.87935	0.98626	0.94607
Variance of Estimate of Logs		0.00429	0.03470	0.01513
Variance of Estimate of Arithmetic Values		0.00225	0.00033	0.00044

TABLE A2.32

RENON
 TERNARY WATER(1) - ACETIC-ACID(2) - BUTANOL(3)

Renon Equation (1 set of constants)
 (Constant = 0.3)

		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	70.4629		
	2)	720.703		
	3)	1826.11	same	same
	4)	- 13.1788		
	5)	15.3911		
	6)	- 862.374		
Correlation Coefficient of Logs		0.01721	0.09767	0.09397
Correlation Coefficient of Arithmetic Values		0.00714	0.00139	0.00105
Variance of Estimate of Logs		0.99429	0.96215	0.99642
Variance of Estimate of Arithmetic Values		0.53141	0.94235	0.86572

Renon Equation (3 sets of constants)
 (Constant = 0.3)

		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	-296.74	670.594	-37.9482
	2)	408.534	-213.209	155.633
	3)	1746.6	3638.34	2158.31
	4)	150.023	-548.513	33.362
	5)	-502.297	1977.22	-429.942
	6)	-709.477	-1605.13	- 95.5374
Correlation Coefficient of Logs		0.99857	0.98585	0.99916
Correlation Coefficient of Arithmetic Values		0.87871	0.98667	0.91020
Variance of Estimate of Logs		0.00429	0.03694	0.02191
Variance of Estimate of Arithmetic Values		0.00226	0.00032	0.00072

TABLE A2.33

RENON
TERNARY WATER(1) - ACETIC-ACID(2) - BUTANOL(3)

Renon Equation (1 set of constants)
(Constant = 0.47)

		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	1858.36		
	2)	0.18		
	3)	24034.3	same	same
	4)	9.73558		
	5)	- 64.8711		
	6)	- 0.97		
Correlation Coefficient of Logs		0.97022	0.54861	0.92284
Correlation Coefficient of Arithmetic Values		-1.29524	0.43903	-1.02438
Variance of Estimate of Logs		0.08874	0.91939	1.95191
Variance of Estimate of Arithmetic Values		0.02667	0.01002	0.00863

Renon Equation (3 sets of constants)
(Constant = 0.47)

		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	298.261	7.81719	- 28.2797
	2)	-215.053	315.091	6741.43
	3)	1354.13	2097.53	2372.75
	4)	1129.1	367.71	190.809
	5)	205.421	1291.98	- 2.13516
	6)	-1034.6	-1170.66	-385.975
Correlation Coefficient of Logs		0.99873	0.98509	0.99947
Correlation Coefficient of Arithmetic Values		0.89279	0.98608	0.94323
Variance of Estimate of Logs		0.00381	0.03890	0.01386
Variance of Estimate of Arithmetic Values		0.00202	0.00034	0.00046

TABLE A2.34

WILSON
 TERNARY WATER(1) - ACETIC-ACID(2) - BUTANOL(3)

Wilson Equation (3 sets of constants)		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	472025.0	29806.8	22234.2
	2)	28685.7	28685.7	28685.7
	3)	5.8095	0.434329	1543.7
	4)	9431.19	15722.2	15733.9
	5)	0.61375	0.61375	0.61375
	6)	-4512.54	-1388.02	11531.8
Correlation Coefficient of Logs		0.92220	0.27770	0.99821
Correlation Coefficient of Arithmetic Values		-2.21590	-1.42434	0.89826
Variance of Estimate of Logs		0.22616	1.41669	0.04685
Variance of Estimate of Arithmetic Values		0.05887	0.03761	0.00081
Wilson Equation (1 set of constants)		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)	472025.0		
	2)	28685.7		
	3)	5.8095	same	same
	4)	9431.19		
	5)	0.61375		
	6)	-4512.54		
Correlation Coefficient of Logs		0.92220	0.79809	1.75241
Correlation Coefficient of Arithmetic Values		2.21590	1.20373	2.52186
Variance of Estimate of Logs		0.22616	2.15301	53.56060
Variance of Estimate of Arithmetic Values		0.05887	0.03041	0.03101

TABLE A2.35

WILSON
 TERNARY WATER(1) - ACETIC-ACID(2) - BUTANOL(3)

Wilson Equation (1 set of constants)		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)		29006.8	
	2)		28685.7	
	3)	same	0.434329	same
	4)		15722.2	
	5)		0.61375	
	6)		-1388.02	
Correlation Coefficient of Logs		0.92140	0.27770	0.21384
Correlation Coefficient of Arithmetic Values		-2.22050	-1.42434	-1.77879
Variance of Estimate of Logs		0.22839	-1.41669	-12.5551
Variance of Estimate of Arithmetic Values		0.05907	0.03761	0.01755
Wilson Equation (1 set of constants)		$\ln \lambda_1$	$\ln \lambda_2$	$\ln \lambda_3$
Constants	1)			22234.2
	2)			28685.7
	3)	same	same	1543.7
	4)			15733.9
	5)			0.61375
	6)			11531.8
Correlation Coefficient of Logs		0.95086	-1.21136	0.99821
Correlation Coefficient of Arithmetic Values		-3.02731	-2.82560	0.89826
Variance of Estimate of Logs		0.14498	-3.24529	0.04685
Variance of Estimate of Arithmetic Values		0.10125	0.11158	0.00081

TABLE A2.36

RENON
 TERNARY ACETIC-ACID(2) - BUTANOL(3) - BUTYL ACETATE(4)

Renon Equation (1 set of constants) (Constant = 0.2)		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	4427.88		
	2)	-2250.89		
	3)	2112.92		
	4)	-1125.3	same	same
	5)	- 31.97		
	6)	342.863		
Correlation Coefficient of Logs		0.99370	0.98528	0.98523
Correlation Coefficient of Arithmetic Values		0.98015	0.97311	0.98703
Variance of Estimate of Logs		0.01510	0.03485	0.03534
Variance of Estimate of Arithmetic Values		0.00202	0.00242	0.00055
Renon Equation (3 sets of constants) (Constant = 0.2)		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	-952.496	- 23.5687	-127.044
	2)	555.927	-292.137	- 68.4743
	3)	-929.655	968.403	-587.366
	4)	1341.89	486.379	714.213
	5)	-432.463	93.799	- 10.0276
	6)	1000.73	658.791	412.491
Correlation Coefficient of Logs		0.99594	0.99757	0.99354
Correlation Coefficient of Arithmetic Values		0.99280	0.99572	0.99420
Variance of Estimate of Logs		0.00973	0.00577	0.01552
Variance of Estimate of Arithmetic Values		0.00073	0.00039	0.00024

TABLE A2.37

RENON
TERNARY ACETIC-ACID(2) - BUTANOL(3) - BUTYL ACETATE(4)

Renon Equation (1 set of constants) (Constant = 0.3)		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	-635.944		
	2)	- 8.70597		
	3)	539.466	same	same
	4)	-215.822		
	5)	-202.397		
	6)	693.971		
Correlation Coefficient of Logs		0.99479	0.98833	0.98265
Correlation Coefficient of Arithmetic Values		0.99034	0.98293	0.97543
Variance of Estimate of Logs		0.01250	0.02766	0.04148
Variance of Estimate of Arithmetic Values		0.00099	0.00154	0.00104
Renon Equation (3 sets of constants) (Constant = 0.3)		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	-602.645	- 68.258	0.61375
	2)	121.074	-270.615	-242.369
	3)	-953.035	555.904	-522.682
	4)	1722.18	763.835	688.030
	5)	-140.496	- 23.9119	69.4621
	6)	433.077	903.987	353.595
Correlation Coefficient of Logs		0.99586	0.99759	0.99357
Correlation Coefficient of Arithmetic Values		0.99226	0.99576	0.99403
Variance of Estimate of Logs		0.00994	0.00573	0.01545
Variance of Estimate of Arithmetic Values		0.00079	0.00038	0.00025

TABLE A2.38

RENON
TERNARY ACETIC-ACID(2) - BUTANOL(3) - BUTYL ACETATE(4)

Renon Equation (1 set of constants) (Constant = 0.47)		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	-637.363		
	2)	17.5763		
	3)	203.315	same	same
	4)	44.3099		
	5)	- 4.31263		
	6)	486.455		
Correlation Coefficient of Logs		0.99473	0.98889	0.98199
Correlation Coefficient of Arithmetic Values		0.99093	0.97993	0.97520
Variance of Estimate of Logs		0.01264	0.02635	0.04304
Variance of Estimate of Arithmetic Values		0.00093	0.00181	0.00105
Renon Equation (3 sets of constants) (Constant = 0.47)		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	-548.66	-224.025	-366.07
	2)	36.881	-114.195	- 28.2442
	3)	-709.661	490.963	- 17.5186
	4)	1348.11	799.744	20.6062
	5)	1.27728	- 2.81989	-157.153
	6)	- 9.35261	1129.95	674.887
Correlation Coefficient of Logs		0.99584	0.99763	0.99361
Correlation Coefficient of Arithmetic Values		0.99243	0.99580	0.99337
Variance of Estimate of Logs		0.00998	0.00564	0.01534
Variance of Estimate of Arithmetic Values		0.00077	0.00038	0.00028

TABLE A2.39

WILSON
 TERNARY ACETIC-ACID(2) - BUTANOL(3) - BUTYL ACETATE(4)

Wilson Equation (3 sets of constants)				
		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	0.61375	0.61375	-332.615
	2)	-597.746	-343.861	- 0.956363
	3)	-256.706	759.537	226.782
	4)	2103.03	1184.16	125.752
	5)	1.27728	1.27728	1.2772
	6)	-247.889	818.698	423.629
Correlation Coefficient of Logs		0.99510	0.99534	0.98481
Correlation Coefficient of Arithmetic Values		0.99013	0.98876	0.98935
Variance of Estimate of Logs		0.01176	0.01106	0.03634
Variance of Estimate of Arithmetic Values		0.00101	0.00102	0.00045
Wilson Equation (1 set of constants)				
		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	0.61375		
	2)	-597.746		
	3)	-256.706	same	same
	4)	2103.03		
	5)	1.27728		
	6)	-247.889		
Correlation Coefficient of Logs		0.99510	0.99389	0.96069
Correlation Coefficient of Arithmetic Values		0.99013	0.99336	0.95488
Variance of Estimate of Logs		0.01176	0.01452	0.09293
Variance of Estimate of Arithmetic Values		0.00101	0.00060	0.00190

TABLE A2.40

WILSON
TERNARY ACETIC-ACID(2) - BUTANOL(3) - BUTYL ACETATE(4)

Wilson Equation (1 set of constants)		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)		0.61375	
	2)		-343.861	
	3)	same	759.537	same
	4)		1184.16	
	5)		1.27728	
	6)		818.698	
Correlation Coefficient of Logs		0.93769	0.99534	0.74826
Correlation Coefficient of Arithmetic Values		0.84006	0.98876	0.42809
Variance of Estimate of Logs		0.14536	0.01106	0.53073
Variance of Estimate of Arithmetic Values		0.01518	0.00102	0.01762
Wilson Equation (1 set of constants)		$\ln \lambda_2$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)			-322.615
	2)			- 0.956363
	3)	same	same	226.782
	4)			125.752
	5)			1.2772
	6)			423.629
Correlation Coefficient of Logs		0.99258	0.99453	0.98481
Correlation Coefficient of Arithmetic Values		0.98885	0.99030	0.98935
Variance of Estimate of Logs		0.01777	0.01299	0.03634
Variance of Estimate of Arithmetic Values		0.00114	0.00088	0.00045

TABLE A2.41

RENON
TERNARY WATER(1) - BUTANOL(3) - BUTYL ACETATE(4)

Renon Equation (1 set of constants)				
(Constant = 0.2)				
		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	2445.98		
	2)	595.362		
	3)	12745.7	same	same
	4)	- 1100.71		
	5)	1876.22		
	6)	0.598368		
Correlation Coefficient of Logs		0.97787	0.42014	0.93140
Correlation Coefficient of Arithmetic Values		-1.69103	-1.82029	0.78954
Variance of Estimate of Logs		0.71990	1.07834	0.61362
Variance of Estimate of Arithmetic Values		0.09763	0.04736	0.00791
Renon Equation (3 sets of constants)				
(Constant = 0.2)				
		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	579.182	1058.95	- 171.511
	2)	1472.39	- 46.4773	1119.48
	3)	5569.04	-31987.3	814.732
	4)	-529.91	2716.8	922.755
	5)	5016.16	11233.2	71913.1
	6)	14301.4	18523.7	480.336
Correlation Coefficient of Logs		0.99373	0.99389	0.99921
Correlation Coefficient of Arithmetic Values		0.21370	0.96284	0.98680
Variance of Estimate of Logs		0.20560	0.01594	0.00728
Variance of Estimate of Arithmetic Values		0.02414	0.00080	0.00055

TABLE A2.42

RENON
TERNARY WATER(1) - BUTANOL(3) - BUTYL ACETATE(4)

Renon Equation (1 set of constants) (Constant - 0.3)				
		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	2713.37		
	2)	85.1471		
	3)	5892.75	same	same
	4)	7.74888		
	5)	1139.62		
	6)	19.5056		
Correlation Coefficient of Logs		0.97957	0.91661	0.98824
Correlation Coefficients of Arithmetic Values		-1.06787	0.64839	0.92077
Variance of Estimate of Logs		0.66539	0.20928	0.10824
Variance of Estimate of Arithmetic Values		0.05414	0.00636	0.00319
Renon Equation (3 sets of constants) (Constant - 0.3)				
		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	- 1.22162	886.788	95896.9
	2)	1596.75	40.1918	60.1491
	3)	7495.11	174070.0	953.041
	4)	-238.365	3012.63	533.999
	5)	5841.28	213995.0	270770.0
	6)	-2598.26	10845.7	10330.1
Correlation Coefficient of Logs		0.98677	0.99382	0.99900
Correlation Coefficient of Arithmetic Values		0.55968	0.96061	0.99078
Variance of Estimate of Logs		0.43229	0.01612	0.00918
Variance of Estimate of Arithmetic Values		0.03322	0.00084	0.00038

TABLE A2.43

RENON
 TERNARY WATER(1) - BUTANOL(3) - BUTYL ACETATE(4)

Renon Equation (1 set of constants)
 (Constant = 0.47)

		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	1716.77		
	2)	14.1649		
	3)	3234.24	same	same
	4)	125.798		
	5)	1554.22		
	6)	217.019		
Correlation Coefficient of Logs		0.97152	0.91455	0.98577
Correlation Coefficient of Arithmetic Values		-1.66375	0.49283	0.92187
Variance of Estimate of Logs		0.92383	0.21421	0.13082
Variance of Estimate of Arithmetic Values		0.09532	0.00831	0.00315

Renon Equation (3 sets of constants)
 (Constant = 0.47)

		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	1101.4	1262.4	19206.3
	2)	1724.65	- 6.23226	- 500.365
	3)	4560.2	-2099.09	1068.66
	4)	64.81	1897.66	3824.85
	5)	5645.8	30431.3	30431.3
	6)	20847.2	392.351	5528.04
Correlation Coefficient of Logs		0.98270	0.98900	0.99880
Correlation Coefficient of Arithmetic Values		0.63232	0.93829	0.98891
Variance of Estimate of Logs		0.56428	0.02863	0.01107
Variance of Estimate of Arithmetic Values		0.03541	0.00131	0.00046

TABLE A2.44
 WILSON
 TERNARY WATER(1) - BUTANOL(3) - BUTYL ACETATE(4)

Wilson Equation (3 sets of constants)				
		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	1297.63	1412.44	1412.4
	2)	10500.0	10500.0	10500.0
	3)	129272.0	129272.0	129272.0
	4)	7155.57	7155.57	7155.0
	5)	1871.12	1871.12	110.259
	6)	- 728.287	- 728.287	798.144
Correlation Coefficient of Logs		0.96199	0.96411	0.99906
Correlation Coefficient of Arithmetic Values		-1.27990	0.89900	0.98889
Variance of Estimate of Logs		1.22684	0.09229	0.00861
Variance of Estimate of Arithmetic Values		0.06673	0.00210	0.00046
Wilson Equation (1 set of constants)				
		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	1297.63		
	2)	10500.0		
	3)	129272.0	same	same
	4)	7155.57		
	5)	1871.12		
	6)	- 728.287		
Correlation Coefficient of Logs		0.96199	0.97156	0.98652
Correlation Coefficient of Arithmetic Values		-1.27990	0.90947	0.97989
Variance of Estimate of Logs		1.22684	0.07342	0.12395
Variance of Estimate of Arithmetic Values		0.06673	0.00189	0.00083

TABLE A2.45
 WILSON
 TERNARY WATER(1) - BUTANOL(3) - BUTYL ACETATE(4)

Wilson Equation (1 set of constants)		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)		1412.44	
	2)		10500.0	
	3)	same	129272.0	same
	4)		7155.57	
	5)		1871.12	
	6)		- 728.287	
Correlation Coefficient of Logs		0.966245	0.96411	0.98652
Correlation Coefficient of Arithmetic Values		-1.22354	0.89900	0.97989
Variance of Estimate of Logs		1.21227	0.09229	0.12395
Variance of Estimate of Arithmetic Values		0.06316	0.00210	0.00083
Wilson Equation (1 set of constants)		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)			1412.4
	2)			10500.0
	3)	same	same	129272.0
	4)			7155.57
	5)			110.259
	6)			798.144
Correlation Coefficient of Logs		0.96245	0.97056	0.99906
Correlation Coefficient of Arithmetic Values		-1.22356	0.81490	0.98889
Variance of Estimate of Logs		1.21227	0.07596	0.00861
Variance of Estimate of Arithmetic Values		0.06316	0.00368	0.00046

TABLE 2.46

WILSON
 TERNARY WATER(1) - BUTANOL(3) - BUTYL ACETATE(4)

Wilson Equation (1 set of constants)		$\ln \lambda_1$	$\ln \lambda_3$	$\ln \lambda_4$
Constants	1)	3512.2		
	2)	10500.0		
	3)	1299.19	same	same
	4)	1373.15		
	5)	73.2833		
	6)	2351.17		
Correlation Coefficient of Logs		0.98407	0.81817	0.96552
Correlation Coefficient of Arithmetic Values		-0.77245	-0.99240	0.89565
Variance of Estimate of Logs		0.51989	0.43290	0.31380
Variance of Estimate of Arithmetic Values		0.04039	0.02179	0.00415

APPENDIX 3

VAPOR-LIQUID EQUILIBRIUM DATA

TABLE A3.11

EXPERIMENTAL DATA FOR TERNARY
VAPOR-LIQUID EQUILIBRIUM SYSTEM
ACETIC ACID, BUTANOL, AND BUTYL ACETATE

Pressure = 760 mm Hg)

Vapor Composition In Mole Fraction			Liquid Composition In Mole Fraction			Temperature °C
AcOH	BuOH	BuOAc	AcOH	BuOH	BuOAc	
0.82983	0.05913	0.10484	0.80902	0.07712	0.11590	119.13
0.06122	0.06030	0.16866	0.72519	0.08685	0.18422	120.42
0.58863	0.08481	0.30810	0.53987	0.11842	0.34158	120.64
0.79530	0.13355	0.06307	0.75103	0.17654	0.06702	120.10
0.72109	0.15492	0.12190	0.67175	0.20143	0.12723	120.21
0.66282	0.13476	0.19133	0.61215	0.19582	0.19356	120.64
0.53956	0.19009	0.26069	0.51106	0.21373	0.27544	121.07
0.67276	0.24235	0.06746	0.60360	0.27653	0.11965	120.42
0.59284	0.26950	0.12604	0.56088	0.31524	0.12319	120.21
0.66994	0.07880	0.24315	0.63158	0.08610	0.28162	120.21
0.50241	0.28517	0.20006	0.51023	0.30556	0.18290	120.42
0.56333	0.35177	0.07494	0.54775	0.37885	0.07235	120.64
0.46156	0.39556	0.13130	0.47663	0.40885	0.11468	120.42
0.44903	0.46670	0.06611	0.46118	0.47834	0.06081	121.07
0.17561	0.17326	0.63931	0.17561	0.10269	0.71988	121.28
0.14997	0.32178	0.51931	0.16215	0.25187	0.58522	120.42
0.12786	0.42698	0.43035	0.14847	0.35686	0.48999	119.56
0.11166	0.52416	0.35122	0.14376	0.48274	0.37470	118.70
0.28725	0.26128	0.43288	0.30705	0.23013	0.45778	120.64
0.25170	0.37100	0.35141	0.28893	0.34673	0.36173	119.99
0.21643	0.46917	0.29281	0.26887	0.44499	0.28178	119.56
0.48272	0.10860	0.39999	0.44085	0.11368	0.44299	121.07
0.42175	0.21101	0.33863	0.38332	0.23631	0.37523	120.64
0.36035	0.33297	0.28253	0.38247	0.33601	0.27872	120.31
0.07647	0.76970	0.14392	0.13243	0.73770	0.12905	118.70
0.09861	0.67925	0.20939	0.13730	0.67153	0.19052	118.70
0.17405	0.73745	0.07670	0.23303	0.69052	0.07276	120.64
0.19269	0.62636	0.15822	0.23671	0.62787	0.13275	119.56
0.19881	0.55221	0.22707	0.24995	0.54642	0.20818	118.70
0.31384	0.50371	0.16284	0.35357	0.50845	0.13407	119.74
0.29356	0.45492	0.24476	0.35390	0.44229	0.19868	119.12
0.38559	0.52995	0.08101	0.41131	0.51929	0.06541	121.07
0.38559	0.52995	0.08101	0.41131	0.51929	0.06541	121.07
0.30823	0.61434	0.08330	0.33317	0.59306	0.07111	120.85
0.30823	0.61434	0.08330	0.33317	0.59306	0.07111	120.85

TABLE A3.12

EXPERIMENTAL DATA FOR TERNARY
VAPOR-LIQUID EQUILIBRIUM SYSTEM
WATER, ACETIC ACID, AND BUTANOL

(Pressure = 760 mm Hg)

Vapor Composition In Mole Fraction			Liquid Composition In Mole Fraction			Temperature °C
Water	AcOH	BuOH	Water	AcOH	BuOH	
0.42914	0.50699	0.06018	0.24267	0.64326	0.10887	109.85639
0.62758	0.31130	0.05778	0.46552	0.47318	0.05890	105.32838
0.76628	0.16081	0.06905	0.63206	0.31259	0.05452	102.52546
0.81441	0.10682	0.07457	0.73549	0.22058	0.04272	101.01606
0.83584	0.07983	0.08108	0.79330	0.16514	0.04047	99.93806
0.51120	0.38616	0.09874	0.26557	0.58466	0.14770	108.13148
0.70565	0.20151	0.08993	0.46651	0.41740	0.11393	103.81910
0.77126	0.12293	0.10212	0.63226	0.27610	0.08970	100.80043
0.80264	0.07484	0.12014	0.70911	0.20570	0.08443	99.07557
0.57512	0.28308	0.13808	0.28067	0.49848	0.21787	106.19087
0.72123	0.14148	0.13456	0.46382	0.35621	0.17631	101.01606
0.78166	0.08108	0.13580	0.62835	0.22999	0.14083	98.85993
0.60994	0.21402	0.17253	0.28444	0.42935	0.28264	105.54408
0.73925	0.10039	0.15853	0.47787	0.28164	0.23897	99.63618
0.62114	0.15661	0.22001	0.36294	0.31001	0.32287	103.38789
0.81745	0.02723	0.14994	0.92820	0.04044	0.03081	94.33193
0.82880	0.02896	0.14151	0.93112	0.03730	0.03161	93.90077
0.82880	0.02896	0.14151	0.91785	0.04040	0.04178	93.90077
0.81093	0.02900	0.15931	0.87514	0.04388	0.08101	94.00862
0.77717	0.02810	0.19479	0.84816	0.04731	0.10456	93.68519
0.79376	0.02247	0.18383	0.77614	0.05694	0.16697	94.11634
0.86172	0.04008	0.09578	0.90264	0.06961	0.02779	98.64430
0.80238	0.04437	0.15093	0.86042	0.07878	0.06083	98.21315
0.77289	0.03837	0.18786	0.79647	0.09342	0.10982	97.78187
0.78979	0.04021	0.16925	0.79647	0.09342	0.10982	97.78187
0.80201	0.04184	0.15593	0.74247	0.10075	0.15661	97.67402
0.84186	0.06834	0.08794	0.83861	0.12060	0.04083	100.15364
0.79437	0.07628	0.12721	0.80550	0.12627	0.06766	99.50679
0.81645	0.06703	0.11499	0.74766	0.14014	0.11179	99.29121
0.69062	0.03888	0.27001	0.28958	0.14174	0.56798	100.69270
0.73299	0.03415	0.23292	0.53501	0.08578	0.37927	97.13502
0.70244	0.03338	0.26425	0.53009	0.08290	0.38707	97.13502
0.64193	0.06646	0.29168	0.27998	0.22159	0.49852	102.09413
0.71429	0.04491	0.24018	0.31392	0.13208	0.55331	98.10530
0.73786	0.04260	0.21898	0.31392	0.13208	0.55331	98.10530
0.75410	0.04465	0.20083	0.64072	0.11816	0.24082	97.24287
0.61835	0.11211	0.26833	0.28345	0.24736	0.46812	103.28010
0.72481	0.07929	0.19482	0.42810	0.22954	0.34001	100.04585
0.74405	0.07457	0.18023	0.61539	0.17702	0.20689	98.85993

TABLE A3.21

PREDICTED TERNARY VAPOR COMPOSITION
USING MARGULES EQUATION

VAPOR COMPOSITION IN MOLE FRACTION

Water	AcOH	BuOH
0.43293	0.38874	0.05948
0.62995	0.22356	0.06037
0.76951	0.13810	0.06841
0.81653	0.10642	0.06784
0.83500	0.08552	0.07798
0.50876	0.31151	0.09153
0.70099	0.16891	0.10302
0.77444	0.10713	0.09733
0.78466	0.08189	0.10474
0.57318	0.22906	0.14200
0.69914	0.12092	0.13071
0.76343	0.07676	0.12734
0.59906	0.18130	0.18572
0.71333	0.08493	0.15686
0.69513	0.10644	0.20956
0.76498	0.02557	0.11737
0.75480	0.02339	0.12111
0.74797	0.02371	0.14192
0.73121	0.02113	0.19283
0.71157	0.02021	0.19982
0.69898	0.01957	0.20229
0.87573	0.04712	0.10178
0.84426	0.04333	0.15634
0.80856	0.04007	0.17964
0.80856	0.04007	0.17964
0.78955	0.03676	0.18744
0.88004	0.06953	0.10074
0.85228	0.06246	0.13055
0.83169	0.05715	0.15369
0.73635	0.02887	0.28885
0.74227	0.02160	0.20777
0.74482	0.02070	0.20959
0.61628	0.05923	0.27519
0.70039	0.02543	0.25392
0.70039	0.02543	0.25392
0.74973	0.03481	0.18311
0.61965	0.07383	0.27374
0.70284	0.06582	0.19644
0.78028	0.05488	0.16450

TABLE A3.22

PREDICTED TERNARY VAPOR COMPOSITION
USING MARGULES EQUATION

VAPOR COMPOSITION IN MOLE FRACTION

AcOH	BuOH	BuOAc
0.82836	0.06151	0.09846
0.77341	0.07127	0.16193
0.56895	0.11256	0.30288
0.78875	0.15281	0.06169
0.69221	0.17549	0.11691
0.62969	0.17905	0.17882
0.51681	0.21973	0.25922
0.61041	0.25267	0.11371
0.55213	0.29372	0.11848
0.49212	0.29930	0.17491
0.54870	0.35912	0.07194
0.45002	0.40133	0.11337
0.44674	0.47874	0.06427
0.18257	0.20105	0.63425
0.14175	0.41080	0.54330
0.11138	0.50902	0.47777
0.09187	0.59757	0.38354
0.28807	0.31321	0.42244
0.23964	0.43252	0.34989
0.20316	0.52450	0.28664
0.46872	0.13330	0.40083
0.36593	0.28142	0.34927
0.34029	0.37475	0.27189
0.07554	0.79365	0.13876
0.07819	0.74412	0.20836
0.17368	0.75960	0.08087
0.16704	0.67951	0.14351
0.17232	0.59063	0.20983
0.28428	0.63094	0.07910
0.28428	0.63094	0.07910
0.29326	0.52765	0.13532
0.28888	0.45703	0.19236
0.38405	0.53277	0.06871
0.66916	0.07083	0.24498
0.64763	0.03981	0.22410
0.38405	0.53277	0.06871
0.34519	0.46142	0.09123
0.30328	0.41751	0.09623

TABLE A3.23

VAPOR COMPOSITION IN MOLE FRACTION GIVING ONLY
THE FIRST TWO CONCENTRATIONS FOR THE TERNARY
WATER, BUTANOL, AND BUTYL ACETATE

Experimental Values of Concentration		Values Predicted By Author's Margules Equation		Values Predicted By Hala et al Using Margules Equation	
Water	Butanol	Water	Butanol	Water	Butanol
0.67805	0.18313	0.68224	0.19235	0.32654	0.22358
0.70775	0.16295	0.55894	0.20497	0.24404	0.23574
0.52126	0.30674	0.55383	0.29755	0.22743	0.33479
0.41120	0.40945	0.41338	0.42602	0.16156	0.46888
0.68537	0.16267	0.58565	0.19805	0.28826	0.23368
0.61528	0.23451	0.46340	0.28945	0.20842	0.32694
0.16465	0.57544	0.33702	0.48508	0.14797	0.52098
0.70765	0.13862	0.61975	0.12778	0.48457	0.12762
0.71228	0.13761	0.62735	0.13071	0.47965	0.13060
0.70295	0.14546	0.70474	0.13043	0.36330	0.15121
0.69877	0.15399	0.71242	0.13956	0.30483	0.16655
0.67051	0.17959	0.67941	0.15832	0.23954	0.18811
0.67519	0.17719	0.59642	0.17204	0.18484	0.19989
0.63824	0.20083	0.45238	0.19221	0.12299	0.21556
0.72961	0.22557	0.85005	0.20558	0.50240	0.19490
0.73093	0.22649	0.87813	0.22238	0.51168	0.20999
0.72872	0.23021	0.87492	0.23251	0.50473	0.21905
0.69427	0.02222	0.63103	0.02183	0.40999	0.01817
0.72397	0.23187	0.68362	0.25839	0.42747	0.24211
0.69241	0.28234	0.51659	0.30171	0.39792	0.29041
0.71498	0.13846	0.73094	0.17439	0.50697	0.17346
0.71517	0.18513	0.74423	0.18161	0.50267	0.18050
0.71864	0.19868	0.75182	0.18926	0.49045	0.18663
0.72026	0.19447	0.75623	0.19992	0.48018	0.19702
0.71733	0.19868	0.71823	0.20569	0.44945	0.20365
0.67371	0.23540	0.68283	0.22681	0.43240	0.22548
0.69895	0.04412	0.77696	0.04278	0.46230	0.03490
0.69778	0.04362	0.77602	0.04317	0.45830	0.03538
0.68048	0.11223	0.07426	0.09761	0.38423	0.11311
0.67675	0.11771	0.74004	0.10076	0.35321	0.12131
0.67531	0.12661	0.78219	0.10980	0.31947	0.13423
0.65299	0.14304	0.78272	0.13116	0.25512	0.15786
0.59019	0.19445	0.56520	0.18096	0.13993	0.19889
0.68359	0.07958	0.63788	0.07045	0.35451	0.07892
0.63837	0.10981	0.65318	0.10985	0.36719	0.12323
0.00291	0.12463	0.00293	0.12124	0.21907	0.07772

TABLE A3.31
BINARY DATA FOR n-BUTANOL AND n-BUTYL ACETATE
(Pressure = 760 mm Hg)

Vapor Composition (Wt. % Butanol)	Liquid Composition (Wt. % Butanol)	Temperature (°C)
28.05	18.66	120.371
40.26	31.65	118.862
48.82	41.29	117.783
56.69	53.11	117.283
66.57	64.57	116.421
63.38	60.15	116.637
69.83	68.64	116.637
79.85	79.42	116.852
88.18	89.42	116.852

TABLE A3.32
BINARY DATA FOR ACETIC ACID AND BUTANOL
(Pressure = 760 mm Hg)

Vapor Composition (Wt. % Acetic Acid)	Liquid Composition (Wt. % Acetic Acid)	Temperature (°C)
6.53	10.71	120.332
6.53	12.5	120.332
11.83	18.55	121.794
11.90	18.67	121.794
21.34	28.21	122.440
21.86	27.66	122.440
21.71	27.66	122.440
59.51	54.59	123.177
65.39	60.37	123.177
87.85	79.58	120.862

TABLE A3.33
 BINARY DATA FOR ACETIC ACID AND n-BUTYL ACETATE
 (Pressure = 760 mm Hg)

Vapor Composition (Wt. % Acetic Acid)	Liquid Composition (Wt. % Acetic Acid)	Temperature (°C)
11.62	9.73	125.719
11.59	9.00	125.719
25.54	22.06	125.204
25.48	22.06	125.204
36.71	32.34	124.596
35.97	32.26	124.596
51.66	46.98	123.280
51.76	46.98	123.280
58.18	49.77	122.541
65.27	60.66	121.171
71.00	60.66	121.171
65.71	60.19	121.171
77.51	69.48	120.093
82.66	79.12	119.662
92.28	89.52	118.599
92.28	89.61	118.599
91.21	89.50	118.599

TABLE A3.34
BINARY DATA FOR ACETIC ACID AND WATER
(Pressure = 760 mm Hg)

Vapor Composition (Mole Fraction) Water	Liquid Composition (Mole Fraction) Water	Temperature (°C)
0.3291	0.2023	109.77
0.3472	0.2023	108.78
0.3151	0.1943	110.28
0.4834	0.3271	107.05
0.5952	0.4546	105.76
0.6536	0.5237	104.79
0.7665	0.6563	103.06
0.8017	0.7003	102.41
0.8274	0.7334	101.66
0.8524	0.7793	101.23
0.8564	0.7772	101.32
0.9725	0.9623	100.15
0.9445	0.9201	100.37
0.9334	0.9069	100.58
0.9178	0.8815	100.58
0.9185	0.8815	100.58
0.9201	0.8815	100.58
0.9085	0.8687	100.91
0.8739	0.8155	101.45

APPENDIX 4

PILOT PLANT ESTERIFICATION DATA

TABLE A4.11

WEIGHT PERCENT COMPOSITION OF REBOILER AT STEADY STATE

Run	Water	Acetic Acid	Butanol	Butyl acetate
1	0.20	0.0	63.8	36.0
2	0.20	0.5	64.0	35.3
3	0.20	1.5	64.8	32.5
4	0.20	2.0	71.0	26.8
5	0.20	2.0	70.8	27.0
6	0.20	0.5	65.3	33.5
7	0.20	3.5	17.5	78.8
8	0.20	5.0	17.3	77.5
9	0.20	8.5	10.0	81.3
10	0.25	4.0	17.25	82.5
11	0.45	2.5	65.5	31.55
12	0.45	1.5	67.05	31.0
13	0.40	1.5	67.05	31.0
14	0.20	4.3	27.0	68.5
15	0.40	6.5	70.5	22.6
16	0.20	1.5	69.0	29.3
17	0.20	5.0	55.0	39.8
18	0.20	3.5	50.5	45.8
19	0.20	3.8	45.0	51.0
20	0.20	3.8	45.5	50.5
21	0.20	3.8	49.5	46.5
22	0.20	3.0	73.8	23.0
23	0.20	0.5	73.3	26.0
24	0.20	0.5	73.8	25.5
25	0.20	1.0	73.8	25.0
26	0.20	0.5	75.3	24.0
27	0.20	3.8	75.0	21.0
28	0.20	5.3	74.5	20.0
29	0.20	2.3	73.0	24.5
30	0.20	2.0	73.0	24.3
31	0.20	1.5	74.5	23.8
32	0.20	2.5	66.0	31.3
33	0.20	3.5	63.5	32.8

TABLE A4.12

WEIGHT PERCENT COMPOSITION OF FEED PLATE AT STEADY STATE

Run	Water	Acetic Acid	Butanol	Butyl acetate
1	1.2	4.0	72.0	22.8
2	2.6	6.0	73.0	18.4
3	1.2	5.0	78.0	25.8
4	0.5	3.0	74.5	22.0
5	3.0	3.0	72.0	22.0
6	1.8	6.0	66.2	26.0
7	1.5	14.0	36.5	48.0
8	2.0	14.5	34.5	49.0
9	2.0	13.5	28.5	56.0
10	2.2	16.0	34.0	47.8
11	2.4	7.5	72.6	17.5
12	2.4	12.0	67.6	18.0
13	1.5	10.0	72.5	16.0
14	2.4	12.5	72.6	17.5
15	2.3	13.0	77.7	7.0
16	2.7	9.0	73.3	15.0
17	4.0	10.0	70.0	16.0
18	3.0	9.0	66.0	22.0
19	4.2	7.0	63.8	25.0
20	4.1	7.0	62.9	26.0
21	2.6	9.5	66.9	21.0
22	2.2	5.0	79.8	13.0
23	3.7	4.0	77.3	15.0
24	3.0	4.0	79.0	14.0
25	3.0	4.0	80.0	13.0
26	3.2	4.5	77.3	15.0
27	1.3	6.0	82.2	10.5
28	2.6	8.5	81.9	7.0
29	3.1	7.5	78.4	11.0
30	3.4	7.5	78.1	11.0
31	3.4	5.5	78.1	13.0
32	3.4	8.5	69.6	18.5
33	4.0	9.5	67.5	19.0

TABLE A4.13

WEIGHT PERCENT COMPOSITION
OF OIL LAYER IN DECANter AT STEADY STATE

Run	Water	Acetic Acid	Butanol	Butyl acetate
1	12.0	0.0	52.0	36.0
2	12.0	0.0	52.0	36.0
3	12.0	0.0	52.0	36.0
4	12.0	0.0	52.0	36.0
5	12.0	0.0	52.0	36.0
6	11.6	0.0	52.2	36.2
7	9.5	0.0	44.8	45.7
8	13.2	0.5	35.5	50.8
9	13.2	0.5	35.5	50.8
10	13.2	0.5	35.5	50.8
11	12.8	0.0	52.2	35.0
12	12.0	0.0	53.0	35.0
13	12.0	0.0	52.0	36.0
14	13.0	0.0	54.0	33.0
15	12.7	0.0	49.0	38.3
16	13.0	0.0	53.0	34.0
17	12.3	0.0	48.6	39.1
18	11.0	0.0	51.5	37.5
19	11.0	0.0	51.0	38.0
20	13.4	0.0	45.8	40.8
21	11.0	0.0	51.5	37.5
22	12.2	0.0	54.3	33.5
23	13.2	0.0	54.0	32.8
24	14.0	0.0	58.0	28.0
25	14.0	0.0	58.0	28.0
26	12.3	0.0	50.9	36.8
27	12.8	0.0	54.5	32.7
28	15.4	0.0	57.2	27.4
29	13.9	0.0	55.8	30.3
30	14.6	0.0	54.0	31.4
31	14.4	0.0	54.0	31.6
32	13.7	0.0	52.5	33.8
33	12.9	0.0	49.1	38.0

TABLE A4.21

TEMPERATURE OF ESTERIFICATION, COLUMN PLATES AT
STEADY STATE IN DEGREES CENTIGRADE

Run	Reboiler	Plate 2	Plate 4	Plate 8	Plate 10
1	111.1	110.0	108.8	104.5	94.2
2	110.5	110.1	109.7	106.9	96.0
3	111.6	110.3	109.7	106.9	96.1
4	112.0	111.3	109.9	107.1	98.1
5	111.6	110.4	109.0	106.5	96.1
6	110.6	108.9	105.9	100.0	91.7
7	115.4	110.5	108.8	104.0	93.5
8	115.4	110.0	108.2	103.5	92.5
9	118.3	115.4	113.5	110.3	98.2
10	116.5	113.5	111.6	106.3	96.2
11	111.6	110.5	110.1	107.8	98.1
12	113.0	112.1	111.3	109.7	98.1
13	112.2	111.4	111.3	109.5	98.1
14	114.5	112.3	111.8	110.3	108.2
15	115.4	112.5	111.6	109.7	99.1
16	112.5	110.5	110.3	107.8	95.4
17	112.0	110.5	109.9	105.1	94.4
18	112.5	109.8	109.0	104.9	93.9
19	113.5	112.6	111.6	108.3	97.3
20	113.5	112.6	111.3	107.9	95.4
21	113.0	110.5	109.7	104.8	99.1
22	112.0	111.0	110.5	108.4	97.9
23	111.6	110.5	110.1	107.8	96.9
24	110.8	110.1	109.7	107.5	95.4
25	111.7	110.4	109.7	107.9	95.9
26	112.5	112.0	111.8	109.7	98.1
27	112.5	111.9	111.6	109.6	97.9
28	113.5	112.3	111.8	109.0	97.3
29	112.7	111.8	111.0	108.3	95.4
30	111.5	111.0	110.1	106.7	94.5
31	112.0	111.5	110.8	108.0	97.3
32	112.5	111.3	110.4	106.9	95.5
33	112.0	110.6	109.8	105.4	94.7

TABLE A4.22

COLUMN D/P, REFLUX RATE, COOLING WATER RATE,
AND. COOLING WATER TEMPERATURE CHANGE

Run	D/P Across Column inches H ₂ O	Reflux cc./hr.	Cooling Water lb/min	Cooling Water Change in Temperature °C
1	14.0	14250	9.2	8.5
2	14.0	12800	9.2	10.0
3	14.0	13500	7.7	12.5
4	19.0	14250	5.15	20.5
5	16.0	14250	5.5	13.6
6	17.0	12000	4.5	18.0
7	23.0	12000	4.5	23.0
8	24.0	12000	4.5	21.5
9	56.0	31000	6.85	26.0
10	25.0	16500	6.20	13.0
11	19.0	20000	7.20	12.4
12	37.0	29000	6.70	21.5
13	21.0	16000	6.70	11.4
14	21.0	15000	6.70	11.1
15	19.0	13500	6.70	10.6
16	21.0	15750	6.70	12.8
17	21.5	15000	6.85	12.3
18	22.0	15500	6.85	12.5
19	48.0	32000	6.85	26.0
20	48.0	31000	6.85	24.0
21	24.0	15500	7.00	14.0
22	22.0	19500	7.10	12.5
23	21.5	18000	7.20	13.5
24	21.0	17000	7.30	12.6
25	21.0	17500	7.60	13.0
26	28.0	19500	7.70	17.5
27	27.0	26250	7.75	16.8
28	25.0	24500	7.82	15.0
29	26.0	20000	7.90	15.2
30	19.0	16500	7.90	11.0
31	17.0	16000	8.00	9.3
32	18.0	16000	8.00	10.3
33	17.5	15750	8.00	12.0

TABLE A4.31
STEADY STATE MASS BALANCE IN GRAMS

Run	Feed in Gms/hr			Output in Gms/hr			Error %
	AcOH	BuOH	Water	AcOH	BuOH	BuOAc	
1	1095.7	5470.1	232.49	0	4059.2	2283.3	0.14
2	949.6	5672.7	199.94	34.33	4394.37	2437.5	-6.69
3	918.3	6321.1	213.89	101.89	4415.1	2275.47	3.22
4	887.0	5996.9	320.84	130.77	4642.22	1765.35	0.36
5	887.0	5996.9	320.4	130.77	4642.22	1765.35	0.36
6	887.0	5996.9	320.4	32.20	4250.16	2157.28	1.80
7	2483.7	4457.1	502.19	207.66	1038.3	4687.2	7.28
8	2483.7	4457.1	502.19	296.66	1038.3	4598.19	7.30
9	2577.6	4376.1	706.79	513.05	603.58	4919.2	3.04
10	2577.6	4376.1	544.04	238.24	1072.06	4645.6	6.53
11	939.2	5794.3	252.44	159.66	4183.1	2043.65	1.41
12	939.2	5794.3	294.64	91.2	4104.02	1976.01	3.97
13	939.2	5794.3	89.00	91.2	4104.02	1976.01	7.03
14	939.2	5794.3	139.49	275.01	4186.3	1650.07	7.17
15	939.2	5794.3	140.39	405.58	4399.0	1435.13	5.25
16	939.2	5994.3	140.39	93.51	4301.5	1839.05	5.33
17	1617.5	5024.4	395.24	302.75	3330.3	2422.04	2.88
18	1617.5	5024.4	427.79	205.07	2958.8	2695.14	5.35
19	1617.5	5024.4	544.04	253.84	2855.65	3236.4	-3.73
20	1617.5	5024.4	502.19	249.85	2842.08	3154.4	-1.61
21	1617.5	5024.4	283.64	253.76	3140.32	2950.0	0.2
22	730.5	6118.5	139.49	190.69	4703.7	1461.96	5.16
23	730.5	6118.5	139.49	31.96	4698.0	1662.16	4.63
24	730.5	6118.5	139.49	31.86	4715.8	1625.04	4.92
25	730.5	6118.5	139.49	65.0	4810.3	1625.10	3.05
26	730.5	6118.5	74.4	31.72	4789.8	1522.58	6.29
27	851.82	7131.5	139.49	315.06	5907.4	1654.07	-0.4
28	1346.2	8103.1	242.2	520.04	7043.7	1890.93	-2.62
29	1346.2	8103.1	322.64	327.78	6943.2	2330.25	-4.07
30	1346.2	8103.1	236.4	459.01	6701.6	2295.07	-2.59
31	772.2	7131.5	190.64	115.5	5736.5	1848.0	0.17
32	1168.8	4862.3	292.54	136.53	3604.5	1720.33	4.6
33	1669.7	6240.0	512.09	243.0	4408.7	2291.14	5.75

TABLE A4.32

STEADY STATE MASS BALANCE IN MOLES

Run	Feed Moles/hr			Output Moles/hr			Error %
	AcOH	BuOH	Water	AcOH	BuOH	BuOAc	
1	18.24	73.80	12.90	0	54.77	19.66	5.12
2	15.81	76.53	11.09	0.57	59.28	20.98	9.78
3	15.29	85.28	11.87	1.70	59.65	19.59	8.01
4	14.77	80.90	17.80	2.18	62.63	15.2	-2.24
5	14.77	80.90	17.80	2.18	62.63	15.2	-2.24
6	14.77	80.90	17.80	0.54	57.34	18.57	1.48
7	41.36	60.13	27.86	3.46	14.01	40.35	14.99
8	41.36	60.13	27.86	4.94	14.01	39.59	14.87
9	42.92	59.04	39.22	8.54	8.14	42.35	3.64
10	42.92	59.04	30.19	3.97	14.46	39.99	13.09
11	15.64	78.17	14.01	2.66	56.44	17.59	3.32
12	15.64	78.17	16.35	1.52	55.37	17.01	3.79
13	15.64	78.17	4.94	1.52	55.37	17.01	15.96
14	15.64	78.17	7.74	4.58	56.48	14.21	11.51
15	15.64	78.17	7.79	6.75	59.35	12.35	8.07
16	15.64	78.17	7.79	1.56	58.03	15.83	11.30
17	26.93	67.78	21.93	5.04	44.93	20.85	1.96
18	26.93	67.78	23.74	3.41	39.92	23.20	4.69
19	26.93	67.78	30.19	4.23	38.53	27.86	-6.44
20	26.93	67.78	27.86	4.16	38.34	27.16	-2.97
21	26.93	67.78	15.74	4.23	42.37	25.40	7.36
1a	12.16	82.54	7.74	3.18	63.46	12.59	8.16
23	12.16	82.54	7.74	0.53	63.38	14.31	9.23
24	12.16	82.54	7.74	0.53	63.62	13.99	9.31
25	12.16	82.54	7.74	1.08	64.90	13.99	7.38
26	12.16	82.54	4.12	0.53	64.62	13.11	13.01
27	14.19	96.22	7.74	5.25	79.70	14.23	3.16
28	22.42	109.32	13.44	8.66	95.03	16.28	-1.27
29	22.42	109.32	17.90	3.96	93.68	20.06	-2.93
30	22.42	109.32	13.12	7.64	90.42	19.76	0.61
31	12.86	96.21	10.57	1.92	77.12	15.91	3.25
32	19.46	65.6	16.23	2.27	48.63	14.81	3.67
33	27.80	84.18	28.42	4.05	59.48	19.72	0.28

TABLE A4.33
 STEADY STATE HEAT BALANCE ON
 ESTERIFICATION COLUMN

Run	Heat Added K-cal/hr	Heat Removed K-cal/hr	Heat Loss K-cal/hr	Heat Loss %
1	4333.05	2410.54	1922.51	44.37
2	4303.26	2752.84	1550.42	36.03
3	4297.47	2881.06	1416.41	32.96
4	4511.34	3190.44	1320.90	29.28
5	4489.43	2320.65	2168.78	48.31
6	3543.93	2365.14	1178.79	33.26
7	3397.07	3040.15	356.92	10.51
8	3405.13	2872.09	533.04	15.65
9	6476.05	5235.75	1240.30	19.15
10	4360.62	2730.30	1630.32	37.39
11	4341.02	2648.50	1692.52	38.99
12	5784.08	4260.44	1523.64	26.34
13	4347.03	2261.84	2085.19	47.97
14	4349.65	2199.77	2149.88	49.43
15	4347.71	2096.22	2251.49	51.79
16	4358.42	2525.08	1833.34	42.06
17	4320.68	2454.64	1866.04	43.19
18	4362.15	2513.95	1848.20	42.37
19	6320.23	5176.93	1143.3	18.09
20	6337.18	4825.52	1511.66	23.85
21	4370.00	2850.48	1519.43	34.77
22	4348.08	2630.56	1717.52	39.50
23	4342.68	2854.72	1487.96	34.26
24	4349.13	2707.76	1641.38	37.74
25	4352.03	2899.14	1452.89	33.38
26	4852.69	3916.64	936.05	19.29
27	4918.83	3858.55	1060.28	21.56
28	4904.65	3495.99	1408.66	28.72
29	4921.86	3535.37	1386.49	28.17
30	3973.87	2578.54	1395.33	35.11
31	3707.01	2221.36	1485.65	40.08
32	3687.67	2417.12	1270.55	34.45
33	3726.83	2814.87	911.96	24.47

TABLE A4.34

STEADY STATE HEAT TRANSFER
COEFFICIENT AND TEMPERATURE DIFFERENCE

Run	Heat Transfer Coefficient (hA) K-cal/(hr °C)	(T _{column} - T _{surface}) average
1	22.65	85.0
2	17.95	86.4
3	16.45	86.0
4	15.30	86.3
5	25.60	84.7
6	14.41	81.5
7	4.22	84.3
8	6.25	85.3
9	14.05	88.3
10	18.49	88.1
11	19.50	86.9
12	17.15	88.8
13	23.35	89.3
14	24.25	88.6
15	25.35	88.7
16	21.25	86.4
17	21.85	85.4
18	21.90	84.4
19	13.14	87.0
20	17.36	87.1
21	17.53	86.6
22	19.67	87.3
23	16.98	87.6
24	18.99	86.5
25	16.81	86.5
26	10.68	87.7
27	11.88	89.2
28	15.66	89.9
29	15.55	89.1
30	15.50	89.0
31	16.97	87.6
32	14.68	86.5
33	10.88	83.8

TABLE A4.41
COMPOSITION OF ESTERIFICATION PLATES AT
STEADY STATE IN WEIGHT PERCENT

Run Number 4				
Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.052	0.40	67.47	32.08
1	0.07	0.43	67.42	32.07
2	0.10	0.65	69.62	29.63
3	1.18	1.10	66.36	31.36
4	0.41	2.17	68.68	28.74
5	0.26	1.30	70.43	28.01
6	0.77	0.59	69.15	29.49
7	5.76	0.43	65.04	28.78
8	0.27	0.06	67.25	32.42
9	0.62	0.00	65.66	33.72
10	1.09	0.00	64.09	34.83

Run Number 6				
Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.18	0.80	65.0	34.02
1	0.07	1.03	66.55	32.35
2	0.20	1.39	65.47	32.93
3	0.23	1.75	66.82	31.20
4	0.32	3.28	69.99	26.41
5	0.34	1.45	69.96	28.25
6	1.34	0.59	68.64	29.43
7	0.48	0.21	68.51	30.81
8	0.38	0.0	67.76	31.85
9	0.69	0.0	66.57	32.74
10	1.04	0.0	64.53	34.43

Run Number 8				
Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.10	2.38	11.31	86.21
1	0.14	6.39	19.30	74.17
2	0.20	9.20	26.99	63.59
3	0.27	12.09	33.09	54.55
4	0.67	15.66	35.95	47.72
5	0.46	11.37	40.73	47.44
6	0.49	7.13	42.63	49.75
7	0.45	3.82	45.45	50.27
8	0.49	1.88	47.43	50.20
9	0.70	0.72	48.61	49.97
10	1.09	0.35	48.01	50.56

TABLE A4.42
COMPOSITION OF ESTERIFICATION PLATES AT
STEADY STATE IN WEIGHT PERCENT

Run Number 9

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.12	7.33	6.18	86.37
1	0.14	10.70	12.44	76.73
2	0.12	14.26	17.98	67.65
3	0.52	8.97	25.27	65.25
4	0.17	15.84	26.08	57.91
5	0.22	13.46	30.42	55.90
6	0.23	7.37	39.56	52.83
7	0.22	5.15	41.20	53.43
8	0.17	5.12	39.04	55.66
9	0.28	2.42	43.71	53.59
10	0.93	1.18	43.99	53.89

Run Number 11

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.15	2.03	64.30	33.53
1	0.11	2.93	66.68	30.28
2	0.07	3.27	69.57	27.09
3	0.15	3.84	69.76	26.25
4	0.29	4.04	69.08	26.59
5	0.11	1.85	72.0	26.04
6	0.11	0.79	71.42	27.68
7	0.13	0.39	70.05	29.43
8	0.12	0.18	68.87	30.83
9	0.23	0.08	67.62	32.07
10	1.03	0.04	65.15	33.77

Run Number 15

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.22	7.40	71.63	20.75
1	0.10	5.94	76.29	17.68
2	0.07	5.87	77.36	16.70
3	0.10	5.36	79.48	15.06
4	0.10	5.84	80.67	13.39
5	0.13	2.58	79.16	18.14
6	0.15	1.34	80.17	18.33
7	0.13	0.45	76.09	23.34
8	0.11	0.26	75.88	23.75
9	0.23	0.05	73.17	26.55
10	0.97	0.04	69.12	29.87

TABLE A4.43
COMPOSITION OF ESTERIFICATION PLATES AT
STEADY STATE IN WEIGHT PERCENT

Run Number 17

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.19	5.74	48.08	45.98
1	0.14	7.42	55.18	37.26
2	0.17	8.77	58.42	32.64
3	0.28	4.04	74.21	21.47
4	0.29	5.80	68.05	25.86
5	0.29	5.26	67.37	27.08
6	0.21	1.61	78.02	20.16
7	0.21	0.52	74.36	24.91
8	0.33	0.52	66.97	32.17
9	0.56	0.18	66.41	32.84
10	1.16	0.06	66.69	32.09

Run Number 20

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.18	3.32	39.43	57.06
1	0.32	4.85	46.64	48.19
2	0.19	5.39	53.21	41.22
3	0.35	6.01	58.32	35.32
4	0.35	7.60	56.03	36.02
5	0.20	3.89	56.63	39.28
6	0.25	2.15	68.80	28.79
7	0.20	0.79	62.80	36.20
8	0.16	0.45	61.14	38.24
9	0.37	0.30	60.17	39.16
10	1.24	0.07	59.54	39.16

Run Number 22

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.53	3.99	70.94	24.53
1	0.18	3.99	73.16	22.67
2	0.12	3.95	75.63	20.30
3	0.11	4.26	76.69	18.94
4	0.18	4.31	79.29	16.22
5	0.09	2.16	78.83	18.92
6	0.08	1.02	76.24	22.67
7	0.12	0.42	75.12	24.34
8	0.15	0.17	73.54	26.13
9	0.20	0.07	72.26	27.47
10	0.88	0.03	69.07	30.03

TABLE A4.44
COMPOSITION OF ESTERIFICATION COLUMN PLATES AT
STEADY STATE IN WEIGHT PERCENT

Run Number 23

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.10	0.59	73.56	25.75
1	0.10	2.05	74.63	23.21
2	0.13	2.56	75.65	21.67
3	0.15	3.28	76.61	19.96
4	0.22	3.57	78.31	17.89
5	0.27	1.59	78.59	19.55
6	0.15	0.84	76.90	22.11
7	0.01	0.02	75.70	24.27
8	0.21	0.11	73.62	26.06
9	0.32	0.08	71.96	27.63
10	1.34	0.02	68.07	30.57

Run Number 26

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.27	1.19	75.09	23.45
1	0.09	2.32	76.67	20.93
2	0.10	2.95	77.81	19.15
3	0.20	2.60	78.45	18.76
4	0.13	3.16	79.38	17.33
5	0.11	1.28	78.92	19.69
6	0.14	0.64	78.57	20.65
7	0.11	0.32	75.92	23.64
8	0.14	0.12	75.12	24.63
9	0.29	0.08	73.05	26.57
10	0.96	0.04	70.05	28.95

Run Number 28

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.45	5.77	73.74	20.04
1	0.08	6.07	76.21	17.64
2	0.09	6.26	77.99	15.66
3	0.18	5.23	79.61	14.98
4	0.31	5.74	81.41	12.54
5	0.11	3.10	83.61	13.18
6	0.13	1.31	83.08	15.48
7	0.17	0.44	82.01	17.38
8	0.15	0.17	79.89	19.79
9	0.30	0.09	77.41	22.20
10	1.27	0.04	72.58	26.10

TABLE A4.45

COMPOSITION OF ESTERIFICATION COLUMN PLATES
STEADY STATE IN WEIGHT PERCENT

Run Number 29

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.14	2.41	70.13	27.32
1	0.17	3.47	73.02	23.34
2	0.17	4.25	74.74	20.84
3	0.20	5.22	76.13	18.45
4	0.25	5.51	78.69	15.55
5	0.18	2.42	80.16	17.24
6	0.19	1.10	80.23	18.48
7	0.19	0.46	78.16	21.19
8	0.27	0.16	76.96	22.61
9	0.43	0.09	75.14	24.34
10	1.44	0.06	71.20	27.30

Run Number 30

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.20	2.15	70.57	27.08
1	0.14	3.77	72.69	23.40
2	0.19	4.86	73.76	21.20
3	0.25	5.65	76.56	17.54
4	0.32	3.49	81.34	14.85
5	0.26	2.89	80.64	16.21
6	0.24	1.38	79.58	18.80
7	0.27	0.44	78.10	21.20
8	0.37	0.17	76.35	23.11
9	0.56	0.08	73.63	25.73
10	1.42	0.06	70.44	28.07

Run Number 32

Plate	Water	Acetic Acid	Butanol	Butyl acetate
Reboiler	0.17	1.89	62.72	35.22
1	0.21	4.19	65.39	30.21
2	0.18	5.53	67.21	27.08
3	0.22	2.55	75.79	21.44
4	0.36	7.94	70.71	21.00
5	0.32	3.42	73.69	22.57
6	0.29	1.26	75.69	22.75
7	0.23	0.48	75.66	23.63
8	0.34	0.22	72.65	26.79
9	0.56	0.06	70.83	28.55
10	1.48	0.03	67.73	30.76

TABLE A4.46

COMPOSITION OF ESTERIFICATION COLUMN PLATES AT
STEADY STATE IN WEIGHT PERCENT

Run Number 33

Plate	Water	Acetic Acid	Butanol	Butyl acetate
1	0.25	5.55	58.86	35.34
2	0.26	7.47	62.45	29.83
3	0.73	5.42	67.29	26.56
4	0.33	10.11	67.45	22.12
5	0.44	5.10	70.67	23.79
6	0.47	2.16	71.28	26.09
7	0.61	1.31	71.72	26.36
8	0.54	0.39	68.71	30.36
9	0.67	0.13	67.68	31.52
10	1.61	0.05	71.00	27.34

APPENDIX 5
STATISTICS TERMS USED

The correlation coefficient, r , used in this study is given by Volk (37) and is defined as:

$$r = \sqrt{1 - \frac{(y - \hat{y})^2}{(y - \bar{y})^2}}$$

The variance of estimate is also discussed by Volk (37) and is defined as:

$$s(\hat{y}) = \frac{(y - \hat{y})^2}{N - k - 1}$$

where N = number of observations of y

k = number of independent variables on which y depends

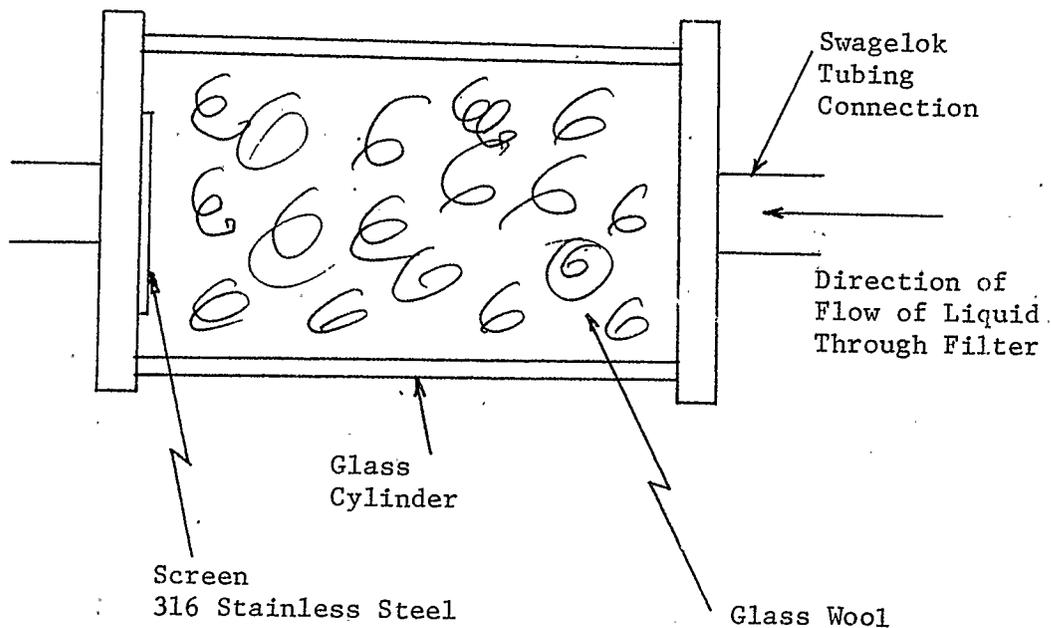
\hat{y} = estimate of y from regressions plane

\bar{y} = estimate of population mean or sample mean

APPENDIX 6

FILTER USED ON ESTERIFICATION COLUMN EXIT LINES

The filters used to remove the polymer and salt from the streams coming out of the esterification column consisted of a glass cylinder packed with glass wool with stainless steel (Type 316) screens at one end to stop the glass wool from being washed from the glass cylinder. The filters were piped in parallel so that one filter could be removed for cleaning without disturbing the flow on the stream in question. A drawing of a typical filter is given below.



Schematic of Filter Used
To Remove Polymer and Salts

APPENDIX 7

ESTERIFICATION COLUMN TRANSIENT DATA

TABLE A7.1

TRANSIENT FOR CATALYST STEP CHANGE IN REBOILER

Time (mins)	Experimental Data (wt %)			Temperature °C Reboiler
	Acetic Acid	Butanol	Butyl Acetate	
0	5.0	55.0	39.8	112.5
9	5.0	55.0	39.8	112.5
18	5.0	55.0	39.8	112.5
27	5.0	54.9	39.9	112.5
36	5.0	54.9	39.9	112.5
45	5.0	54.9	40.0	112.5
54	5.0	54.9	40.1	112.5
63	5.0	54.7	40.2	112.6
72	5.0	54.4	40.4	112.6
81	5.0	54.1	40.5	112.6
90	5.0	53.8	40.8	112.6
99	5.0	53.5	41.1	112.6
108	5.0	53.2	41.5	112.7
117	4.9	53.0	42.0	112.7
126	4.7	52.8	42.3	112.7
135	4.5	52.7	42.6	112.7
144	4.3	52.6	42.9	112.7
153	4.1	52.4	43.2	112.8
162	4.0	52.3	43.5	112.8
171	3.9	52.1	43.8	112.8
180	3.8	52.0	44.0	112.8
189	3.7	51.8	44.2	112.8
198	3.6	51.7	44.4	112.8
207	3.6	51.6	44.6	112.9
216	3.6	51.4	44.8	112.9
225	3.6	51.3	45.0	112.9
234	3.6	51.2	45.1	112.9
243	3.6	51.1	45.2	112.9
252	3.5	51.0	45.4	112.9
261	3.5	50.9	45.5	112.9
270	3.5	50.8	45.6	113.0
279	3.5	50.7	45.7	113.0
288	3.5	50.6	45.7	113.0
297	3.5	50.5	45.8	113.0

TABLE A7.2

TRANSIENT FOR CATALYST STEP CHANGE ON FEEDTRAY

Time (mins)	Experimental Data (wt %)				Temperature °C Tray 10
	Water	Acetic Acid	Butanol	Butyl Acetate	
0	4.0	10.0	70.0	16.0	94.4
9	4.0	10.0	70.0	16.0	94.4
18	4.0	10.0	70.0	16.0	94.4
27	4.0	9.9	69.9	16.1	94.4
36	4.0	9.9	69.9	16.2	94.4
45	4.0	9.9	69.9	16.2	94.4
54	4.0	9.8	69.8	16.3	94.4
63	4.0	9.8	69.8	16.3	94.3
72	4.0	9.8	69.7	16.5	94.3
81	4.0	9.7	69.6	16.8	94.3
90	3.9	9.7	69.4	17.1	94.3
99	3.9	9.7	69.3	17.4	94.3
108	3.9	9.6	69.1	17.7	94.2
117	3.9	9.6	69.0	18.0	94.2
126	3.8	9.6	68.7	18.3	94.2
135	3.8	9.5	68.5	18.6	94.2
144	3.8	9.5	68.2	18.9	94.2
153	3.7	9.5	68.0	19.2	94.1
162	3.7	9.4	67.8	19.6	94.1
171	3.6	9.4	67.6	19.9	94.1
180	3.6	9.4	67.5	20.2	94.1
189	3.5	9.3	67.3	20.5	94.1
198	3.5	9.3	67.1	20.8	94.0
207	3.4	9.3	67.0	21.0	94.0
216	3.4	9.2	66.8	21.2	94.0
225	3.3	9.2	66.7	21.4	94.0
234	3.3	9.2	66.6	21.6	94.0
243	3.2	9.2	66.5	21.7	93.9
252	3.2	9.1	66.3	21.7	93.9
261	3.1	9.1	66.1	21.8	93.9
270	3.1	9.1	66.1	21.8	93.9
279	3.0	9.0	66.0	21.9	93.9
288	3.0	9.0	66.0	21.9	93.9
297	3.0	9.0	66.0	22.0	93.9

TABLE A7.3

TRANSIENT FOR STEAM STEP IN REBOILER

Time (mins)	Experimental Data (wt %)			Temperature °C Reboiler
	Acetic Acid	Butanol	Butyl Acetate	
0	8.5	10.0	81.3	118.3
9	8.5	10.2	81.3	118.0
18	8.4	10.4	81.3	117.0
27	8.3	10.6	81.4	116.7
36	8.2	10.8	81.4	116.6
45	8.1	11.1	81.4	116.6
54	8.0	11.3	81.5	116.6
63	7.9	11.5	81.5	116.6
72	7.8	11.7	81.5	116.6
81	7.7	11.8	81.6	116.6
90	7.5	11.9	81.6	116.6
99	7.4	12.1	81.6	116.5
108	7.2	12.3	81.7	116.5
117	7.0	12.5	81.7	116.5
126	6.8	12.7	81.8	116.5
135	6.6	12.9	81.8	116.5
144	6.5	13.1	81.9	116.5
153	6.4	13.3	81.9	116.5
162	6.2	13.5	81.9	116.5
171	6.1	13.7	82.0	116.5
180	6.0	13.9	82.0	116.5
189	5.8	14.1	82.1	116.5
198	5.7	14.4	82.1	116.5
207	5.5	14.7	82.1	116.5
216	5.4	15.0	82.2	116.5
225	5.2	15.3	82.2	116.5
234	5.1	15.6	82.2	116.5
243	5.0	15.9	82.3	116.5
252	4.8	15.2	82.3	116.5
261	4.7	16.5	82.4	116.5
270	4.5	16.8	82.4	116.5
279	4.3	17.0	82.4	116.5
288	4.1	17.2	82.5	116.5
297	4.0	17.3	82.5	116.5

TABLE A7.4

TRANSIENT FOR STEAM STEP ON FEEDTRAY

Time (mins)	Experimental Data (wt %)				Temperature °C Tray 10
	Water	Acetic Acid	Butanol	Butyl Acetate	
0	2.0	13.5	29.5	56.0	98.2
9	2.0	13.5	29.6	55.9	98.0
18	2.0	13.6	29.8	55.7	97.7
27	2.0	13.6	29.9	55.5	97.2
36	2.0	13.6	30.1	55.3	96.8
45	2.0	13.7	30.2	55.0	96.5
54	2.0	13.7	30.3	54.7	96.4
63	2.0	13.7	30.5	54.4	96.4
72	2.0	13.8	30.7	54.1	96.3
81	2.0	13.8	30.9	53.8	96.3
90	2.0	13.9	31.1	53.4	96.3
99	2.0	13.9	31.2	53.0	96.3
108	2.0	14.0	31.3	52.7	96.3
117	2.0	14.2	31.5	52.3	96.3
126	2.0	14.4	31.6	52.0	96.3
135	2.0	14.6	31.7	51.7	96.3
144	2.0	14.8	31.8	51.5	96.2
153	2.0	15.0	32.0	51.2	96.2
162	2.1	15.2	32.1	50.9	96.2
171	2.1	15.4	32.3	50.7	96.2
180	2.1	15.5	32.5	50.5	96.2
189	2.1	15.6	32.6	50.2	96.2
198	2.1	15.7	32.8	49.9	96.2
207	2.1	15.7	33.0	49.6	96.2
216	2.1	15.8	33.2	49.3	96.2
225	2.1	15.8	33.4	49.0	96.2
234	2.1	15.8	33.6	48.8	96.2
243	2.1	15.9	33.8	48.5	96.2
252	2.1	15.9	33.9	48.3	96.2
261	2.1	15.9	33.9	48.1	96.2
270	2.2	15.9	34.0	47.9	96.2
279	2.2	16.0	34.0	47.9	96.2
288	2.2	16.0	34.0	47.8	96.2
297	2.2	16.0	34.0	47.8	96.2

TABLE A7.5

TRANSIENT FOR FLOW-RATE STEP CHANGE IN REBOILER

Time (mins)	Experimental Data (wt %)			Temperature °C Reboiler
	Acetic Acid	Butanol	Butyl Acetate	
0	3.8	75.0	21.0	112.5
9	3.8	75.0	21.0	112.5
18	3.8	75.0	20.9	112.5
27	3.8	75.0	20.9	112.6
36	3.9	75.0	20.9	112.6
45	3.9	74.9	20.9	112.6
54	4.0	74.9	20.8	112.7
63	4.1	74.9	20.8	112.7
72	4.2	74.9	20.8	112.7
81	4.3	74.9	20.7	112.8
90	4.4	74.9	20.6	112.8
99	4.5	74.8	20.5	112.8
108	4.7	74.8	20.4	112.8
117	4.8	74.8	20.3	112.9
126	4.9	74.8	20.3	112.9
135	4.9	74.8	20.3	112.9
144	4.9	74.7	20.2	112.9
153	4.9	74.7	20.2	113.0
162	5.0	74.7	20.2	113.0
171	5.0	74.7	20.1	113.0
180	5.0	74.7	20.1	113.1
189	5.1	74.7	20.1	113.1
198	5.1	74.7	20.1	113.1
207	5.1	74.7	20.1	113.1
216	5.1	74.6	20.1	113.2
225	5.2	74.6	20.0	113.2
234	5.2	74.6	20.0	113.2
243	5.2	74.6	20.0	113.3
252	5.2	74.6	20.0	113.3
261	5.3	74.6	20.0	113.3
270	5.3	74.6	20.0	113.4
279	5.3	74.6	20.0	113.4
288	5.3	74.5	20.0	113.4
297	5.3	74.5	20.0	113.5

TABLE A7.6

TRANSIENT FOR FLOW-RATE STEP CHANGE ON FEEDTRAY

Time (mins)	Experimental Data (wt %)				Temperature °C Tray 10
	Water	Acetic Acid	Butanol	Butyl Acetate	
0	1.3	6.0	82.2	10.5	97.9
9	1.3	6.1	82.2	10.4	97.9
18	1.3	6.2	82.2	10.3	97.9
27	1.3	6.3	82.2	10.2	97.9
36	1.4	6.4	82.2	10.1	97.8
45	1.4	6.5	82.2	10.0	97.8
54	1.5	6.6	82.2	9.8	97.8
63	1.5	6.7	82.2	9.7	97.8
72	1.6	6.8	82.2	9.5	97.7
81	1.6	7.0	82.2	9.4	97.7
90	1.7	7.1	82.2	9.2	97.7
99	1.7	7.2	82.1	9.0	97.7
108	1.8	7.3	82.1	8.8	97.6
117	1.8	7.4	82.1	8.6	97.6
126	1.9	7.5	82.1	8.4	97.6
135	1.9	7.7	82.1	8.2	97.6
144	2.0	7.8	82.1	8.0	97.6
153	2.0	7.9	82.1	7.8	97.5
162	2.1	8.0	82.1	7.6	97.5
171	2.1	8.1	82.0	7.4	97.5
180	2.2	8.3	82.0	7.2	97.5
189	2.2	8.3	82.0	7.1	97.5
198	2.3	8.4	82.0	7.1	97.5
207	2.3	8.4	82.0	7.1	97.4
216	2.4	8.4	82.0	7.1	97.4
225	2.4	8.4	82.0	7.0	97.4
234	2.5	8.4	82.0	7.0	97.4
243	2.5	8.5	82.0	7.0	97.4
252	2.6	8.5	81.9	7.0	97.4
261	2.6	8.5	81.9	7.0	97.3
270	2.6	8.5	81.9	7.0	97.3
279	2.6	8.5	81.9	7.0	97.3
288	2.6	8.5	81.9	7.0	97.3
297	2.6	8.5	81.9	7.0	97.3

TABLE A7.7

TRANSIENT FOR ACETIC ACID FEED CONCENTRATION STEP CHANGE IN REBOILER

Time (mins)	Experimental Data (wt %)				Temperature °C Reboiler
	Water	Acetic Acid	Butanol	Butyl Acetate	
0	0.30	0.5	65.3	33.5	110.6
9	0.30	0.5	65.1	33.8	110.7
18	0.30	0.5	64.7	34.5	110.7
27	0.30	0.6	64.2	35.2	110.7
36	0.30	0.6	63.8	36.0	110.8
45	0.29	0.6	63.2	36.5	110.9
54	0.29	0.7	62.6	37.0	111.0
63	0.29	0.7	62.0	37.5	111.1
72	0.29	0.7	61.0	38.5	111.2
81	0.28	0.8	60.0	40.0	111.3
90	0.28	0.8	59.0	41.5	111.4
99	0.28	0.9	57.0	43.0	111.5
108	0.27	1.0	55.0	44.5	111.6
117	0.27	1.1	53.0	45.5	111.8
126	0.26	1.1	51.0	47.0	112.0
135	0.26	1.3	49.0	49.5	112.3
144	0.25	1.4	47.0	51.0	112.6
153	0.25	1.5	44.0	54.5	112.9
162	0.24	1.7	42.0	57.0	113.2
171	0.24	1.9	40.0	59.0	113.5
180	0.23	2.1	37.5	61.5	113.7
189	0.23	2.3	35.5	63.0	113.8
198	0.23	2.5	33.5	64.5	113.9
207	0.22	2.7	31.0	66.0	114.1
216	0.22	2.9	29.0	67.5	114.3
225	0.22	3.0	27.0	69.5	114.4
234	0.22	3.1	25.0	71.5	114.5
243	0.21	3.2	24.0	73.0	114.7
252	0.21	3.4	23.0	74.0	114.8
261	0.21	3.5	32.0	75.2	114.9
270	0.21	3.6	21.0	76.5	115.0
279	0.21	3.7	20.0	77.2	115.1
288	0.21	3.8	19.0	77.9	115.2
297	0.21	3.9	18.0	78.8	115.3
306	0.20	4.1	17.5	78.7	115.4
315	0.20	4.2	17.4	78.6	115.4
324	0.20	4.3	17.4	78.4	115.4
333	0.20	4.5	17.3	78.2	115.4
342	0.20	4.6	17.3	78.1	115.4
351	0.20	4.7	17.3	78.0	115.4
360	0.20	4.8	17.3	77.9	115.4
369	0.20	4.9	17.3	77.8	115.4
378	0.20	5.0	17.3	77.7	115.4
387	0.20	5.0	17.3	77.6	115.4

TABLE A7.8

TRANSIENT FOR ACETIC ACID FEED CONCENTRATION STEP CHANGE ON FEEDTRAY

Time (mins)	Experimental Data (wt %)				Temperature °C Tray 10
	Water	Acetic Acid	Butanol	Butyl Acetate	
0	1.8	6.0	66.2	26.0	91.7
9	1.8	6.0	65.4	26.7	91.7
18	1.8	6.1	64.6	27.5	91.7
27	1.8	6.1	63.8	28.2	91.7
36	1.8	6.1	63.0	29.0	91.7
45	1.8	6.2	62.2	29.8	91.8
54	1.8	6.2	61.4	31.5	91.8
63	1.7	6.2	60.6	32.3	91.8
72	1.7	6.3	59.4	33.0	91.9
81	1.7	6.3	58.2	33.7	91.9
90	1.7	6.3	57.0	34.4	92.0
99	1.7	6.4	55.8	35.1	92.0
108	1.7	6.4	54.6	35.8	92.1
117	1.7	6.5	53.4	36.5	92.2
126	1.7	6.5	52.2	37.2	92.3
135	1.7	7.2	51.3	38.0	92.4
144	1.7	7.9	50.5	38.8	92.5
153	1.7	8.6	49.6	39.6	92.6
162	1.6	9.0	48.7	40.4	92.7
171	1.6	9.5	47.8	41.2	92.8
180	1.6	10.0	47.0	42.0	92.9
189	1.6	10.4	46.2	42.4	93.0
198	1.6	11.0	45.4	42.9	93.1
207	1.6	11.3	44.6	43.3	93.2
216	1.6	11.6	43.8	44.7	93.3
225	1.6	11.9	43.0	45.1	93.3
234	1.6	12.2	42.2	45.4	93.4
243	1.6	12.5	41.5	45.6	93.4
252	1.6	12.8	49.7	46.0	93.4
261	1.5	13.0	39.9	46.4	93.4
270	1.5	13.3	39.1	46.8	93.5
279	1.5	13.6	38.2	47.2	93.5
288	1.5	13.8	37.3	47.6	93.5
297	1.5	14.0	36.5	48.0	93.5
306	1.5	14.1	36.0	48.1	93.4
315	1.5	14.2	35.7	48.2	93.3
324	1.6	14.3	35.4	48.3	93.2
333	1.6	14.4	35.1	48.4	93.1
342	1.7	14.5	34.8	48.5	93.0
351	1.7	14.5	34.7	48.6	92.9
360	1.8	14.5	34.6	48.7	92.8
369	1.9	14.5	34.5	48.8	92.7
378	1.9	14.5	34.5	48.9	92.6
387	2.0	14.5	34.5	49.0	92.5