THE UNIVERSITY OF CALGARY

SIMULATION OF DISTILLATION TOWERS

WITH CHEMICAL REACTIONS

by'

JANA SIMANDL

A THESIS

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DEGREE OF

DOCTOR OF PHILOSOPHY

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DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

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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,

SIMULATION OF DISTILLATION TOWERS WITH CHEMICAL REACTIONS submitted by Jana Simandl in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering

Dr. W.Y. Svrcek (Supervisor) Department of Chemical & Petroleum Engineering

Dr. L.A. Behie Department of Chemical & Petroleum Engineering

Nel

Dr. A.K. Mehrotra Department of Chemical & Petroleum Engineering

Dr. Jim Haslett Department of Electrical Engineering

20

Dr. E. Couch Department of Mathematics & Statistics

Koche ward (

Dr. Ed. Roche, External Examiner Department of Chemical Engineering New Jersey Institute of Technology

611,199

Date

ABSTRACT

Two algorithms previously used for the solution of equations describing steady-state multi-stage equilibrium distillation were applied distillation with chemical reactions. to Both the simultaneous-solution algorithm and the inside-outside tearing algorithm required modifications in order to accommodate the additional terms and equation non-linearities introduced by the presence of chemical reactions. The production of ethyl acetate in a thirteen tray column was used as a test case for the comparison of these algorithms. The domain of initial variable profiles which led to convergence were comparable for both algorithms. However, the inside-outside tearing method proved to be almost three times faster, a significant factor in microcomputer applications. The difference in speed is due in part to a reduction in thermodynamic computations by the two level approach, and also to a readier incorporation of the reaction terms.

Industrial data for a second distillation tower with chemical reactions was tested using the inside-outside tearing algorithm. Depending on the initial starting values, the model predicted two possible steady-states. Two possible causes of this phenomenon were examined: phase splitting of the liquid within the tower and multiple steady-state behaviour similar to continuous-flow, stirred-tank reactors. The later is believed to be the cause of multiple steadystates in distillation towers with reactions.

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NOMENCLATURE

A	constant in K_B model Equation (5.7)
В	constant in K_B model Equation (5.7)
с	number of components
C	constant in K _B model Equation (5.8)
Co	initial concentration
С _р	heat capacity
crit	convergence criterion for the simultaneous-solution algorithm and inner loop of inside-outside algorithm
Da	Damkohler number
Е	activation energy
E ₀₋₄	error terms
f	component feed rate
f _i ^v	component i vapour fugacity
fi	component i liquid fugacity
fi [°]	standard state liquid fugacity
F	total feedstream flowrate
g	component vapour sidestream
·G	vapour sidestream
h	liquid phase enthalpy
H	vapour phase enthalpy
H _f	enthalpy of liquid feed stream
H _R	heat of reaction
i	component counter

j stage counter

k rate of reaction

K phase equilibrium constant

K_R base component phase equilibrium constant

liquid flowrate of component i at stage j

L_j total liquid flowrate at stage j

n number of equilibrium stages

n order of reaction

p stage pressure

q volumetric flowrate

Q heat load

r number of chemical reactions

r_{ij} change in the number of moles of component i due to chemical reactions on tray j

R universal gas constant

 $R_{\rm L}$ stripping factor defined by Equation (3.23)

 $R_{\rm V}$ stripping factor defined by Equation (3.24)

R_{sj} rate of change in number of moles due to chemical reaction s on stage j

s matrix element

S; stripping factor defined by Equation (3.22)

factor defined by Equations (5.4) and (5.5)

vapour flowrate of component i at stage j

. T temperature

u component liquid sidestream

U liquid sidestream

v_{ij}

t

.

xii

V _j tot	al vapour:	flowrate	at	stage	j
--------------------	------------	----------	----	-------	---

V reactor volume

volcrit convergence criterion for outer loop of inside-outside algorithm

w factor defined by Equation (5.3)

wf weighting factor for Equations (4.10), (4.11) and (4.12)

x liquid phase composition

y vapour phase composition

z liquid feed stream composition

 α relative volatility defined by Equation (3.25)

 β coefficient defined by Equation (7.2)

 γ_r activity coefficient

 γ coefficient defined by Equation (7.2)

error vector for energy Equation (3.20)

liquid density

 ϵ

ρ

 $\hat{\phi}_i^v$

fugacity coefficient of i in the vapour phase

CHAPTER 1

INTRODUCTION

Reactive distillation is a unit operation which combines the properties of a reactor and a distillation tower. The process involves the simultaneous occurrence of liquid-phase chemical and vapour-liquid phase separation. reactions The reactiondistillation combination can be used in a complimentary manner, utilizing one mechanism for the improvement of the other. Α criterion for the applicability of the reactive distillation tower is that the reaction must occur at temperatures and pressures suitable to the distillation of the components. The two main applications for reactive distillation towers are: the use of distillation to improve the reactor function of the tower and the use of a reaction to effectuate the separation of closely boiling mixtures.

Distillation can be used to remove the product or products of a liquid phase reaction in order to shift an unfavourable reaction equilibrium or to prevent the product from participating in an undesirable reaction. The desire to improve reaction extents prompted the first recorded uses of reactive distillation: US patents registered to Bacchaus [1] for esterification reactions in the 1920's. More recent examples of this application are the synthesis of epichlorohydrin by the elimination of hydrogen chloride from chlorohydrins [2] and the production of furfural from xylose. The

industrial production of propylene oxide involves the chlorohydrination of propylene followed by the dehydrochlorination of propylene chlorohydrins [3]. The synthesis is carried out in a distillation tower in order to remove the propylene oxide from the reaction environment as quickly as possible, thereby minimising its hydrolysis.

Reactive distillation also promotes separation by using a Large numbers of column trays and high reflux ratios are reaction. required for the separation of mixtures with closely boiling The most common alternative, extractive distillation, components. does not work for components of similar chemical natures. The entrainer is unable to change the relative volatility of components such as isomers. In these cases reactive distillation has been successfully employed, using the selectivity of a specific reactive entrainer toward one of the isomers. The reactive entrainer is chosen in order to preferentially engage one of the isomers in a fast reversible chemical reaction or series of reactions. The separation will work as long as the entrainer has a boiling point higher than the less volatile or lower than the more volatile component. Α second tower can be used to reverse the reaction and strip the entrainer of the reacted isomer. Terrill et al. [4] claim that binary mixtures with a relative volatility of less than 1.06 can be economically separated by using reactive entrainers. They also developed the theory necessary for the selection of reactive entrainers. Saito et al. [5] studied the details of the xylene

isomer process involving the separation of meta-xylene (boiling point = 139.3°C) and para-xylene (boiling point = 138.5°C).

A program which effectively simulates a process unit, in this case distillation towers with chemical reactions, has several applications. A reliable simulator can greatly fascilitate the iterative design procedure required for determining tower parameters such as the number of trays required to achieve a desired degree of component separation. Existing units can be optimized more readily by first testing proposed changes on a simulator and thus minimizing the chances of downtime in the actual unit. Process simulators, particularly dynamic ones, can also be used in the testing of control schemes.

It should be noted that the application for which reactive distillation is chosen, be it reaction enhancement, minimisation of parasitic reactions, or separation of closely boiling mixtures, has no bearing on the simulation of the process. As long as the kinetic and phase equilibrium data are available, the equations describing either process can be solved using the same algorithm. Although reactive distillation is used in industry and has been receiving increased attention, there are few algorithms available for its simulation. Table 1 lists the solution methods available for distillation towers. It is by no means comprehensive since much has been written about distillation without reactions. A more detailed analysis of the solution methods in the literature is given in

Table 1 Summary of the Categories and Principal Authors in the Area of Simulating Steady State Multi-Stage Equilibrium Distillation Towers With and Without Chemical Reactions

Simultaneous Correction Methods

Distillation	Reactive Distillation
Naphtali and Sandholm [8]	Murthy [13]
Ishi and Otto [9]	Simandl and Svrcek [14]
	This Thesis

Relaxation Method

Distillation	Reactive Distillation
Rose et al. [15]	Jelinek and Hlavacek [16]
Ketchum [20]	Komatsu [17]

Continuation-Homotopy Methods

Reactive Distillation

Distillation Bhargava and Hlavacek [19] Salgovic et al. [21] Byrne and Baird [22] Vickery and Taylor [23] Wayburn [24]

Tearing or Equation Decoupling Methods Sequential Modular, Stage to Stage

Distillation	Reactive Distillation
Thiele and Geddes [25]	Davies et al. [28]
Lewis and Matheson [26]	(unsuccessful)
Fonyo et al. [27]	

Equation Solving

Distillation	Reactive Distillation
Wang and Henke [29]	Suzuki et al. [31]
Tomich [32]	Nelson [33]
	Tierney and Riquelme [34]

Kinoshita et al. [35]

Holland [36] Komatsu and Holland [38] Izarraraz et al. [37]

Inside-Outside

Distillation	Reactive Distillation
Boston [39,42,43]	Simandl and Svrcek [50]
Boston and Sullivan [40]	This Thesis
Boston and Brit [41]	
Russell [44]	
Chimowitz and co-workers	
[45,46,47,48]	
Saeger and Bishnoi [49]	

Chapter Two. The simulation of trains of towers and distillation towers with reactions are extensions of the algorithms developed for ordinary distillation. Although numerous approaches are available, only relaxation and some tearing methods have been investigated for use on reactive distillation.

It is the objective of this thesis to examine the applicability of the simultaneous-solution method and the inside-outside tearing method to steady-state distillation with reactions. The equations of the model are developed in Chapter Three. In Chapter Four the equations are solved using the Newton-Raphson simultaneous solution method; in Chapters Five and Six the inside-outside tearing algorithm is used.

In order to perform a simulation of a reactive distillation tower, knowledge of all the parameters involved in ordinary distillation is required, as well as accurate kinetic data. The examples selected for this thesis are the esterification of ethyl acetate and the production of a component here after referred to as "A", whose true identity cannot be revealed due to commercial interests. The objective was not to optimise these processes but merely to use them as test cases in the development of a general algorithm for reactive distillation.

An unexpected but interesting finding was the possible existence of multiple steady-states in some reactive distillation systems. Multiple steady-states were found in the exothermic production of "A"

case but not in the basically athermal ethyl acetate case. The possible causes and implications of this phenomenon are discussed in Chapter Seven. Conclusions and recommendations for further study are presented in Chapter Eight.

CHAPTER 2

LITERATURE REVIEW

The equations which describe the steady-state operation of multi-stage processes with and without chemical reactions are nonlinear and algebraic. The nonlinearity of the sets of equations compels the use of iterative solution methods. The various available computational schemes were first developed for the more common distillation towers without chemical reactions. Some of these methods were then extended to handle more complex cases such as trains of interlinked columns, three phase separators and towers with chemical reactions. The standard methods were tailored to handle such proclivities as additional terms in the equations and greater nonlinearities. Table 1 summarizes the algorithms which have been used for standard distillations and their corresponding reactive distillation extensions. The following sections explain the various approaches in more detail.

2.1 Simultaneous Correction Methods

In the simultaneous-correction class of methods, the equations describing multi-stage separation are first linearised and then solved simultaneously using a single level iterative procedure such as the Newton-Raphson algorithm. When the initial estimates are close enough to the solutions, this algorithm converges very quickly due to its quadratic convergence rate. The greatest drawbacks of this method are the time spent evaluating and inverting a Jacobian matrix at every iteration and the need for a starting value close enough to the solution. Various attempts have been made to improve the efficiency of the Newton-Raphson method by approximating the Jacobian matrix rather than evaluating it rigorously. These modifications include those of Broyden [6], and Brown and Brent as discussed by More and Cosnard [7].

Naphtali and Sandholm [8] were the first to group the linearised mass, energy, and phase equilibrium equations by stage. The resultant coefficient matrix is tridiagonal, which simplifies its handling. The partial derivatives of phase equilibrium and enthalpies with respect to composition are readily included, making the algorithm suitable for non-ideal systems. Naphtali and Sandholm recognised that the primary disadvantage of their rigorous approach was the large computer storage space requirement. Ishii and Otto [9] linearised the model equations assuming enthalpy to be independent of composition. This reduced the number of partial derivatives, and thus the storage requirements and computational effort. Browne et al. [10] and Hofeling and Seader [11] subsequently extended this approach to trains of separation devices. Gallun and Holland [12] later reported some difficulty with convergence of the Ishii-Otto When the Ishii-Otto approximations of partial derivatives approach. were tested on problems involving nonideal solutions, the rate of convergence was extremely slow or divergence occurred.

. 8

There are a few extensions of the Naphtali-Sandholm algorithm to handle separation towers with chemical reactions. Murthy [13] presented a mathematical formulation of the equations and proposed a method of solution, without giving an example of its application. Simandl and Svrcek [14] applied a similar formulation to the esterification of ethanol and acetic acid. Chapter Four presents the simultaneous solution of the equations for reactive distillation and the results of the ethyl acetate test case.

2.2 Relaxation Method

approach which offers great stability Relaxation is an and convergence over а wide range of column conditions and configurations. It extends the domain of convergence of the simultaneous-solution algorithm. The transit from unsteady- to steady-state is simulated with stagewise correction of temperatures and flowrates being applied to the balances at each stage. The resultant new imbalances are again reduced and the process is continually repeated until convergence is reached. A notable algorithm of this class was presented by Rose et al. [15]. The boon of relaxation is that it is extremely stable irrespective of column complexity, dependence of equilibrium ratios on composition, or even the distance of the starting values from the solution. The bane of this method is the deceleration in convergence rate as the solution is approached. Jelinek and Hlavacek [16] and Komatsu [17] applied this method successfully to distillation with reactions.

2.3 Continuation or Homotopy Methods

The continuation or homotopy techniques chart a path along which lie mathematical solutions to a family of problems. Although this method has been widely used in other disciplines, its application in chemical engineering has been sporadic. Only recently has is it reemerged in the simulation of separation processes. A recent review of the role of continuation in engineering analysis has been provided by Seydel and Hlavacek [18].

For distillation, the start of the homotopy solution path is an easy, often unrealistic, model. The end of the path is the solution of the more difficult model of interest. The path is generated by varying an artificial or physical parameter. The continuation process involves the prediction of points along the path using a tangent and the correction of the prediction by a Newton-Raphson calculation.

Bhargava and Hlavacek [19] demonstrated the application of the continuation method to difficult countercurrent separation processes. They concluded that it may be sufficient to apply homotopy for one or two iterations only, in order to prevent divergence, and then safely revert to a standard Newton-Raphson algorithm. The Bhargava-Hlavacek approach is based on Ketchum's [20] suggestion of embedding the Newton-Raphson procedure within the relaxation procedure. This produces a more robust algorithm. In cases with very poor initial estimates, Salgovic et al. [21] and Byrne and Baird [22] have found

the continuation method to converge more consistently than Newton-Raphson. For test cases where Newton-Raphson and homotopy both converge, homotopy has been found to be much slower [19]. For this reason Vickery and Taylor [23] recommend that Newton-Raphson be tried first and homotopy used only if Newton-Raphson has failed. Wayburn [24] implemented homotopy for systems of interlinked columns. No example has been found in the available literature of continuationhomotopy having been applied to reactive distillation.

In addition to finding one solution at the end of a path, continuation may be used for following branched paths. This gives it potential for methodically locating multiple solutions without scanning the entire parameter space. Although this may not be of importance in most distillation problems, in light of the possible multiple steady-states discussed in Chapters Six and Seven, continuation methods may find application in simulating towers with chemical reactions.

2.4 Tearing or Equation Decoupling Methods

This class of methods for the solution of equations describing a multi-stage separation unit involves the decoupling of the effects of certain variables and the solution of the equations in a specific order. There are two possible formulations: the equation solving approach and the modular, or stage-to-stage, approach. In the equation solving approach, the equations are grouped according to

type (mass, equilibrium, summation, or energy) and solved for all stages at a time. In the modular approach, the four equations are solved for one stage at a time.

The classical sequential modular approaches were presented by Thiele and Geddes [25] and Lewis and Matheson [26]. The algorithms start with an assumption of the top and bottom concentrations and then work their way, stage by stage, from the two ends of the column to the feed tray. The process is repeated using the last set of calculated values until the feed tray is satisfied or meshed. In the Thiele and Geddes method the material balances are solved for composition, the summation equations for temperature and the heat balances for flowrate. There are several disadvantages to the The method is cumbersome for columns with more modular approach. than one feed stream or multiple side-streams and it is also prone to a buildup of truncation errors. With few exceptions [27], these disadvantages have led to the general abandonment of stage-to-stage calculations in favour of the equation solving approach. One reported attempt was made to apply it to towers with chemical reactions [28]. The calculations progressed from the reboiler to the condenser. Large errors accumulated in the top section, leading the authors to conclude that a different technique should be used.

The equation solving approach does not require mesh points, can easily accommodate multiple feeds and side-stream, and does not suffer from error accumulation. Wang and Henke [29] arranged the

material balances into a tridiagonal matrix for simultaneous solution and used Muller's [30] method for the convergence of tray temperatures. Suzuki et al. [31] extended this method to reactive distillation. Tomich [32] used Broyden's method to replace Muller's for ordinary distillation. For systems with reactions, Nelson [33], Tierney and Riquelme [34], and Kinoshita et al. [35] substituted the Newton-Raphson algorithm for those of Muller and Broyden.

Holland's "theta" method [36] is initialised with assumed temperatures and total liquid to vapour flowrate ratios. The system equations are then solved sequentially in the following order. The material balances are stated in terms of component flowrates and solved. A multiplier called "theta" is then found to place the column in overall material balance and in agreement with tower specifications. The new set of compositions thus obtained is used in the equilibrium equations to determine temperatures. The energy balances and the overall material balance then serve to calculate a new set of total flowrates. The process is repeated until conver-Izarraraz et al. [37] extended the "theta" method gence is reached. to reactive distillation by including as a first step the calculation of reaction extents. In another modification, Komatsu and Holland [38] added a reaction multiplier, similar to "theta". The "theta" method for distillation with or without reactions works well for columns in which mixtures do not deviate too far from ideal solutions.

The last group of tearing methods also uses the equation solving What sets the inside-outside algorithm apart from all the approach. other approaches is the introduction of two levels of computation. An outside loop retains the lengthy rigorous enthalpy and equilibrium calculations while the inside loop uses simple local models for the calculation of these quantities. Since up to 80% of the time of a simulation program can be spent evaluating thermodynamic quantities, this leads to significant acceleration. This approach was pioneered by Boston and several of his co-workers [39, 40, 41, 42, 43]. Russell [44] explored the application of the inside-outside algorithm to a wide range of tower configurations. Chimowitz and his coworkers [45, 46, 47, 48] devoted much attention to the improvement of the local models used in the inner loop. They added explicit composition dependence to models where Boston had used temperature dependence only. This improved the area of validity of the local models. Saeger and Bishnoi [49] also explored the inclusion of composition dependence in the local models. There is no mention in the literature of the inside-outside algorithm's use on distillation with chemical reactions. Chapters Five and Six of this thesis and a related paper [50] explore this area of application.

CHAPTER 3

MATHEMATICAL MODEL OF A REACTIVE DISTILLATION TOWER

3.1 The Column

The schematic column shown in Figure 1 is used in the development of general model equations. It has n plates numbered from the top down. The condenser is plate 1 and the reboiler is plate n. There are c components participating in r reactions.

3.2 The Equilibrium Tray

A diagram of the equilibrium tray is shown in Figure 2. Each tray can have a feed stream F, a vapour side-stream G and a liquid side-stream U. The internal flows are liquid L and vapour V. The tray is assumed to be in equilibrium, the vapour in thermodynamic equilibrium with the liquid. The pressure and temperature are assumed constant at each stage and the concentrations uniform within each phase.

3.3 Defining the System Equations and Variables

The simulation of a distillation tower is complete when the temperature, composition, flowrate and pressure of every vapour and





FIGURE 2 EQUILIBRIUM STAGE

. 17 liquid stream are determined. In order to obtain a solution, the number of independent equations must equal the number of unknown variables.

3.3.1 Degrees of Freedom

The difference between the total number of variables involved in the process and the number of independent equations is referred to as the degrees of freedom. Design variables are the column specifications, equal in number to the degrees of freedom, selected to fully define the separation process. The independent equations describing a distillation tower with chemical reactions can be classified as follows: inherent restrictions, material balances for all components at all stages, energy balances around all stages, phase distributions at all stages and chemical equilibrium restrictions for all reactions present. Inherent restrictions are identities between variables such as equal temperatures for the vapour and liquid streams leaving an equilibrium stage. The remaining equations and restrictions are dealt with in detail in section 3.4.

3.3.2 Design Variables

The following column specifications are required:

1. the number of trays in the column

- 2. the location, temperature, and composition of all feed streams
- 3. the location and rate of all side streams
- 4. the pressure profile of the column
- 5. condenser type: total or partial
- 6. the number of chemical reactions, their rate expressions, and the tray volume in which they occur
- 7. any heat additions or leaks other than reboiler and condenser duties
- 8. the reflux ratio $L_1/(V_1 + U_1)$
- 9. the distillate rate

The last two specifications may be replaced by others such as maximum allowable vapour rate V or V/F, concentration of one or two components, recovery rate of one or two components, reboiler load and condenser load. The specifications listed were the ones used in this thesis. Both numerical examples tested have configurations with a total condenser. This means that V_1 and G_1 are equal to zero and

$$V_2 = L_1 + U_1$$
 (3.1)

3.4 System Equations

Four sets of equations are required for the complete description of each stage: the component material balances, the vapour-liquid equilibrium relationship, the energy balance and the chemical equilibrium equations. The component material balance around stage j for component i may be written as:

$$L_{j-1} x_{i j-1} - (V_j + G_j) y_{ij} - (L_j + U_j) x_{ij} + V_{j+1} y_{ij+1}$$

+ F_j z_{ij} + r_{ij} = 0 (3.2)

where r_{ij} is the net rate of change in the number of moles of component i due to participation in chemical reactions.

The change in the number of moles due to chemical reactions on a given tray is determined as follows. First, the rate of each reaction is calculated using the tray temperature and compositions. For an equilibrium reaction, the expression used includes both a forward and reverse rate constant. The reaction rates, in units of mole/(volume * time), are then multiplied by the holdup on the tray to give R_{sj} . R_{sj} is the rate of change, in moles/time, due to reaction s. The rate of change of component i due to reactions on tray j is r_{ij} . For a system with one reaction, r_{ij} equals R_{1j} if i is a product and $-R_{1j}$ if it is a reactant. When component i participates in several reactions, r_{ij} is positive or negative depending on the role of the component in reaction s. Thus

$$\mathbf{r}_{ij} = \sum_{s=1}^{r} \pm \mathbf{R}_{sj}$$
(3.3)

Using component flowrate notation, Equation 3.2 can be written as:

$$\ell_{j-1} - \ell_j - u_j + v_{j+1} - v_j - g_j + f_j + r_{ij} = 0$$
(3.4)

The overall material balance at stage j is:

$$F_j + L_{j-1} + V_{j+1} - (L_j + U_j) - (V_j + G_j) + \sum_{i=1}^{C} r_{ij} = 0$$
 (3.5)

The vapour-liquid equilibrium ratio is defined by:

$$y_{ij} = K_{ij} x_{ij}$$
(3.6)

This equation can be substituted back into the component mass balance in order to reduce the number of independent variables since

$$v_{j} = y_{j} V_{j} = K_{j} x_{j} V_{j} = K_{j} V_{j} l_{j} / L_{j}$$
 (3.7)

There are two summation equations:

$$\sum_{i=1}^{c} y_{ij} - 1 = 0$$
(3.8)
$$\sum_{i=1}^{c} x_{ij} - 1 = 0$$
(3.9)

The energy balance at stage j is:

$$L_{j-1} h_{j-1} - (V_{j} + G_{j}) H_{j} - (L_{j} + U_{j}) h_{j} + V_{j+1} H_{j+1}$$

+ F_{j} H_{fj} - Q_{j} + $\sum_{s=1}^{r} R_{sj} H_{sj} = E_{0j}$ (3.10)

where h is a liquid phase enthalpy, H is a vapour phase enthalpy, and E_0 is an error term. When the solution is reached, E_0 is close to

zero. Q_j represents any addition of heat or cooling at the tray and heat losses to the surroundings. The sum of the heats of reaction due to all chemical reactions present is accounted for by the last term of the equation.

The preceding equations describe the balances around the equilibrium stage. Depending on the computation method chosen, simultaneous-correction or inside-outside tearing, the equations are handled differently from this point on. For the simultaneouscorrection algorithm the equations are linearized. For the insideoutside algorithm the effects of several variables are combined to create the computational factors used to move the components within the tower during calculation.

3.5 Phase Equilibrium Calculations

The component fugacities of the vapour and liquid phases are defined by:

$$\hat{f}_{i}^{V} - \hat{\phi}_{i}^{V} y_{i}^{P}$$
(3.11)

and

 $\hat{f}_{i}^{L} = \gamma_{i} x_{i} f_{i}^{o} \qquad (3.12)$

where ϕ_i^{V} is the fugacity coefficient of i in the vapour, f_i^{o} is the standard state liquid fugacity, γ_i is the liquid phase activity
coefficient and P is the system pressure. At phase equilibrium the liquid and vapour fugacities are equal. Thus:

$$\hat{\phi}_{i}^{V} y_{i} P = \gamma_{i} x_{i} f_{i}^{0} \qquad (3.13)$$

and

$$K_{i} = \frac{y_{i}}{x_{i}} = \frac{\gamma_{i} f_{i}^{0}}{\phi_{i}^{V} P}$$
 (3.14)

Two simplifying assumptions were made in order to compute K. First, since the column pressures dealt with were low, the vapour phase was assumed to be an ideal gas.

$$b_1 = 1$$
 (3.15)

Second, the fugacity of pure liquid was assumed insensitive to pressure, with compressibility equal to one. Thus

$$f_i^{o} = P_i^{sat} \qquad (3.16)$$

With these simplifications, Equation 3.14 becomes:

$$K_{i} = \frac{y_{i}}{x_{i}} = \frac{\gamma_{i} P^{sat}}{P}$$
(3.17)

Wilson's equation was used to obtain the liquid phase activity coefficients. Vapour pressures were calculated by Antoine's equation. For the ethyl acetate example, explicit formulations for K as a function of temperature, based on experimental data, were also available. They are given in section 3 of Appendix A. The equilibrium constants computed by both methods compared well. For the production of component "A" only Equation 3.17 was used.

3.6 Equation Handling for Simultaneous-Correction

Before applying the simultaneous-correction algorithm, the equations are linearized as follows:

Overall material balance:

$$\Delta L_{j-1} + \Delta V_{j+1} - \Delta L_j - \Delta V_j = E_{1j}$$
(3.18)

where E_1 is an error term. This equation is used for the computation of total liquid flowrates. When a closed loop is drawn from stage 1 to stage j, the following equation is obtained:

$$\Delta L_{j} = -\sum_{k=1}^{j} E_{1k} + \Delta V_{j+1} - \Delta V_{1}$$
 (3.19)

The component mass balance is linearized as -follows:

$$(L_{j-1}) \Delta x_{i j-1} - \left[(L_{j} + U_{j}) + (V_{j} + G_{j}) \left(K_{ij} + x_{ij} \frac{\partial K_{ij}}{\partial x_{ij}} \right) \right]$$

$$+ \frac{\partial R_{ij}}{\partial x_{ij}} \Delta x_{ij} + V_{j+1} \left(K_{i j+1} + x_{i j+1} \frac{\partial K_{i j+1}}{\partial x_{i j+1}} \right) \Delta x_{i j+1}$$

$$-\left[(V_{j} + G_{j}) \times_{ij} \frac{\partial K_{ij}}{\partial T_{j}} + \frac{\partial R_{ij}}{\partial T_{j}} \right] \Delta T_{j} + \left(V_{j+1} \times_{i j+1} \frac{\partial K_{i j+1}}{\partial T_{j+1}} \right) \Delta T_{j+1}$$
$$+ \times_{i j-1} \Delta L_{j-1} - \times_{ij} \Delta L_{j} - K_{ij} \times_{ij} \Delta V_{j}$$
$$+ K_{i j+1} \times_{i j+1} \Delta V_{j+1} = E_{2j} \qquad (3.20)$$

.25 .

The linearized energy balance is:

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$$\left(\begin{array}{c} L_{j-1} \frac{\partial h_{j-1}}{\partial x_{i \ j-1}} \right) \Delta x_{i \ j-1}$$

$$+ \left[-(\nabla_{j} + G_{j}) \frac{\partial H_{j}}{\partial x_{i \ j}} - (L_{j} + U_{j}) \frac{\partial h_{j}}{\partial x_{i \ j}} + H_{Rj} \frac{\partial R_{j}}{\partial x_{i \ j}} \right] \Delta x_{i \ j}$$

$$+ \left[\nabla_{j+1} \frac{\partial H_{j+1}}{\partial x_{i \ j+1}} \right] \Delta x_{i \ j+1} + \left[L_{j-1} \frac{\partial h_{j-1}}{\partial T_{j-1}} \right] \Delta T_{j-1}$$

$$+ \left[-(\nabla_{j} + G_{j}) \frac{\partial H_{j}}{\partial T_{j}} - (L_{j} + U_{j}) \frac{\partial h_{j}}{\partial T_{j}} + (H_{Rj}) \frac{\partial R_{j}}{\partial T_{j}} \right] \Delta T_{j}$$

$$+ \left[\nabla_{j+1} \frac{\partial H_{j+1}}{\partial T_{j+1}} \right] \Delta T_{j+1} + h_{j-1} \Delta L_{j-1}$$

$$- h_{j} \Delta L_{j} - H_{j} \Delta \nabla_{j} + H_{j+1} \Delta \nabla_{j+1} - E_{3j}$$

$$(3.21)$$

Equation (3.19) can be used to replace the ΔL terms with expressions in ΔV . The summation equation becomes:

$$\sum_{i=1}^{c} \Delta x_{ij} = E_{4j}$$
(3.22)

The relationships used to determine the phase equilibrium ratio and stream enthalpies are functions of temperature, pressure, and composition. The reaction rate term is a function of holdup time, liquid composition, and temperature. For the purposes of linearization:

$$K_{ij} \approx K_{ij} (P_j, T_j, x_{ij})$$
 (3.23)

$$R_{ij} \approx R_{ij} (T_j, x_{ij})$$
(3.24)

$$H_{j} \simeq H_{j} (P_{j}, T_{j}, x_{ij})$$
 (3.25)

$$h_{j} \simeq h_{j} (P_{j}, T_{j}, x_{ij})$$
 (3.26)

When this algorithm was used the derivatives were determined analytically because of the facility of differentiating the thermodynamic expressions utilized (see Appendix A). The computer time required is thus less than if numerical computation of the derivatives had been necessary.

Equations (3.20) and (3.21) are then placed into the following matrix format:

^bil °_{i1} ∆x_{il} ^ai2 b_{i2} c_{i2} ∆x_{i2} ∆x_{ij} ^aij ^bij °ij ^ai n-1 b_{i n-1} c_{i n-l} ∆x_{i n-1} ∆x_{in} ^bin ^ain



(aa _{il} +f _{il})	g_{i1}				ΔV ₁		m _{il}	
^{aa} i2	f _i 2	g _{i2}			ΔV2		^m i2	
,	, 、							•
^{aa} ij		f _{ij}	g _{ij}	-	∆Vj	-	^m ij	(3.27)
		-						
^{aa} i n-1			f _{i n-1}	g _{i n-1}	∆V _{n-1}		^m i n-1	
aa _{in}			*	f _{in}	۵Vn		m _{in}	

27

+



 $\begin{vmatrix} \beta_{i1}+v_{i1} \rangle & w_{i1} \\ \beta_{i2} & v_{i2} & w_{i2} \\ \beta_{ij} & v_{ij} & w_{ij} \\ \beta_{i n-1} & v_{i n-1} & w_{i n-1} \\ \beta_{in} & & v_{in} \end{vmatrix} \begin{vmatrix} \Delta V_{1} \\ \Delta V_{2} \\ \Delta V_{2} \\ \Delta V_{j} \\ \Delta V_{j} \\ \Delta V_{n-1} \\ \Delta V_{n} \end{vmatrix} = \begin{pmatrix} \epsilon_{i1} \\ \epsilon_{i2} \\ \epsilon_{ij} \\ \epsilon_{i n-1} \\ \epsilon_{in} \end{vmatrix} (3.28)$

where m_{ij} is the componential error term E_{2j} , and ϵ_{ij} is the componential error term E_{3j} . The iterative procedure by which these matrices are solved is explained in Chapter Four.

3.7 Equation Handling for the Inside-Outside Algorithm

The system equations are not linearized for the tearing methods; they are merely re-arranged. Substituting Equation (3.7) into Equation (3.4) gives:

$$-\ell_{j-1} + \ell_{j} \left(1 + \frac{U_{j}}{L_{j}} + \frac{K_{j} V_{j}}{L_{j}} + \frac{K_{j} G_{j}}{L_{j}} \right) - \ell_{j+1} \left(\frac{K_{j+1} V_{j+1}}{L_{j+1}} \right) + r_{ij} = f_{j}$$
(3.29)

where l is a component flow rate and f a component feed rate. Several variables are grouped together to form what are called stripping factors. They are defined as:

$$s_{j} = \left(\frac{K_{B} V}{L}\right)_{j}$$
(3.30)

$$R_{Lj} = 1 + \frac{U_j}{L_j}$$
(3.31)

$$R_{vj} = 1 + \frac{G_j}{L_j}$$
 (3.32)

K_R is a base component equilibrium constant such that

$$K_{i} = \alpha_{i} K_{B}$$
(3.33)

where α_i is a relative volatility. The method used for selecting and determining an appropriate base component is described in Chapter Five. Substituting Equations (3.30), (3.31) and (3.32) into Equation (3.29) gives the following mass balance equation:

$$\ell_{j-1} + (R_{Lj} + \alpha_j S_j R_{vj}) \ell_j - (\alpha_{j-1} S_{j-1}) \ell_{j+1} = -f_i - \Sigma \Delta R$$
 (3.34)
Equation (3.26), when written for all column trays, forms the following matrices:

$$\begin{vmatrix} B_{1} & C_{1} \\ -1 & B_{2} & C_{2} \\ & -1 & B_{j} & C_{j} \\ & & -1 & B_{n-1} & C_{n-1} \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

The energy balance, Equation (3.10) is rewritten using the definition of stripping factors:

$$L_{j-1} h_{j-1} - \left[\left(S_j \sum_{i=1}^{c} \alpha_{ij} \ell_{ij} \right) + G_j \right] H_j$$

$$- (L_{j} + U_{j}) h_{j} + \left[S_{j+1} \sum_{i=1}^{c} \alpha_{i j+1} \ell_{i j+1} \right] H_{j+1}$$

+
$$F_{j}H_{fj} - Q_{j} + \sum_{s=1}^{r} \Delta R_{sj}H_{sj} = E_{0j}$$
 (3.36)

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CHAPTER 4

APPLICATION OF A SIMULTANEOUS CORRECTION ALGORITHM TO REACTIVE DISTILLATION

In this chapter the simultaneous correction procedure is first described and then implemented for example Case One, the production of ethyl acetate. The rate of convergence and the domain of convergence of the algorithm are discussed.

4.1 Solution Procedure

An iterative procedure for the solution of the linearized mass and energy balances in matrix form, Equations (3.27) and (3.28), was developed. The procedure combines some aspects of the Ishii-Otto [9] and Tomich [32] algorithms with original handling required by the presence of chemical reaction terms. A flowchart of the procedure is presented in Figure 3.

4.1.1 Variable Initialisation

Prior to the start of iterative calculations, initial values must be assigned to the temperature, vapour flowrate and concentration vectors. The temperature profile was taken to be linear between the assumed condenser and reboiler temperatures. Inter-tray vapor flowrates were initiated at twice the total feed rate. The







initial concentration profiles were linear, their end points determined by the component boiling points. For example, the concentration end points for acetic acid, the least volatile component with a boiling point of 118.1°C, were 0.001 at the condenser and 0.45 at the reboiler. Ethanol, a more volatile component with a boiling point of 78.4°C, had end points at 0.45 for the condenser and 0.3 at the reboiler. The effect of the initial profiles on convergence was examined and is discussed in Section 4.3.1.

4.1.2 Determining the Matrix Elements

Once the temperature, concentration and vapour flowrates have been initialized or updated at the end of a preceding iteration, the values of other variables can be calculated. The reaction rates and phase equilibrium constants are functions of temperature and concentration only and can be determined next. Since expressions for their evaluation are available, (see Appendix A), the reaction rates and phase equilibrium constants are determined explicitly. Their derivatives are also computed analytically, requiring less computer time than a numerical evaluation. The vapour compositions are calculated by applying Equation (3.6). The overall material balance, Equation (3.19), is used to compute the internal liquid flowrates. At this point, all fluid rates and compositions are known and the stream enthalpies and their derivatives at tray temperatures are

determined. This completes the evaluation of all the factors required for the linearized equations in matrix form.

4.1.3 Matrix Solution

The procedure for solving Equations (3.27) and (3.28) is presented using simplified matrix notation. The equations may be written as:

$$\overline{A}_{i} \Delta \overline{x}_{i} + \overline{B}_{i} \Delta \overline{T} + \overline{C}_{i} \Delta \overline{V} = \overline{M}_{i}$$
(4.1)

$$\overline{D}_{i} \Delta \overline{x}_{i} + \overline{E}_{i} \overline{\Delta T} + \overline{F}_{i} \overline{\Delta V} = \overline{P_{i}}$$
(4.2)

The inverses of matrices \overline{A} and \overline{D} are evaluated by the Gauss-Jordan algorithm with partial pivoting. Equations (4.1) and (4.2) are multipled by the inverse of A and the inverse of D respectively to give:

$$\overline{I} \Delta \overline{x}_{i} + \overline{B'_{i}} \Delta \overline{T} + \overline{C'_{i}} \Delta \overline{V} = \overline{M'_{i}}$$

$$(4.3)$$

$$\overline{I} \Delta \overline{x_{i}} + \overline{E'_{i}} \Delta T + \overline{F'_{i}} \Delta V = \overline{P'_{i}}$$
(4.4)

where I is the identity matrix, $\overline{B'_{i}}$ is the product of the inverse of \overline{A} and $\overline{B_{i}}$, $\overline{C'_{i}}$ is the product of the inverse of \overline{A} and $\overline{C_{i}}$, etc. At this point a technique similar to Ishii-Otto [9] is implemented. Equations (4.3) and (4.4) are each summed for all the components.

This gives:

$$\overline{I} \sum_{i=1}^{C} \overline{\Delta x_{i}} + \overline{B''} \overline{\Delta T} + \overline{C''} \overline{\Delta V} = \overline{M''}$$
(4.5)

$$\overline{I} \sum_{i=1}^{C} \overline{\Delta x_{i}} + \overline{E''} \overline{\Delta T} + \overline{F''} \overline{\Delta V} = \overline{P''}$$
(4.6)

where $\overline{B}'' = \sum_{i=1}^{c} \overline{B'_{i}}$, $\overline{C}'' = \sum_{i=1}^{c} \overline{C'_{i}}$, etc.

Equation (3.9) states that $\sum_{i=1}^{c} x_i = 1.0$. For this to hold, the sum of all changes in component concentrations must equal zero. This condition is used to reduce equations (4.5) and (4.6) to:

$$\overline{B^{"}} \overline{\Delta T} + \overline{C^{"}} \overline{\Delta V} = \overline{M^{"}}$$

$$\overline{E^{"}} \overline{\Delta T} + \overline{F^{"}} \overline{\Delta V} = \overline{P^{"}}$$
(4.7)

These two equations are then solved for the ΔV and ΔT vectors:

$$\overline{\Delta V} = (\overline{F}^{"} - \overline{E}^{"} (\overline{B}^{"})^{-1} \overline{C}^{"})^{-1} (\overline{P}^{"} - \overline{E}^{"} (\overline{B}^{"})^{-1} \overline{M}^{"})$$
(4.8)

$$\overline{\Delta T} = (\overline{B}^{"})^{-1} (\overline{M}^{"} - \overline{C}^{"} \Delta \overline{V})$$
(4.9)

Equation (4.3) was then used to determine the values of $\Delta \overline{x_i}$.

4.1.4 Updating the Variables

Once the values of $\overline{\Delta V}\,,~~\overline{\Delta T}$ and $\overline{\Delta x}$ have been computed, they are

used for the updating of the vapour flowrates, tray temperatures, and liquid compositions:

$$T_j^{k+1} = T_j^k + wf^k * \Delta T_j$$
(4.10)

$$V_{j}^{k+1} = V_{j}^{k} + wf^{k} \star \Delta V_{j}$$
(4.11)

$$x_{ij}^{k+1} = x_{ij}^{k} + wf^{k} * \Delta x_{ij}$$
(4.12)

where k is the iteration counter and wf is a weighting factor used to dampen the changes between iterations and to guide the computation process to convergence. The weighting factor ranges from -1 to +1 with the actual value used determined by a sequential testing approach. The selection of the weighting factor is further discussed in section 4.3.2.

4.1.5 Convergence Criterion

The criterion for convergence used is the second norm of the normalized energy balances errors from Equation (3.10). The sum of the heat inputs onto the tray is used to normalize the criterion at different stages:

crit =
$$\sum_{j=1}^{n} (E_{0j} / (F_{j}H_{fj} + Q_{j} + L_{j-1} h_{j-1} + V_{j+1} H_{j+1} + \sum_{s=1}^{r} R_{sj} H_{sj}))^{2}$$
 (4.13)

Convergence was assumed to be complete when:

crit ≤ 10.0 .

4.2 Results from the Simulation of Case 1: Ethyl Acetate

The algorithm described in the previous sections was programmed in the FORTRAN language and implemented on the University of Calgary Multics Honeywell Computer. The program contained 2600 lines of code.

The results from the simulation of the thirteen-tray ethyl acetate column, shown in Figure 4, are presented in Figures 5, 6, 7 The complete column specifications are given in Appendix A. and 8. Figure 5 shows the composition profiles of the four components: ethanol, acetic acid, water, and ethyl acetate. The column specifications originate from tests performed by Komatsu et al. [51] and thus liquid composition data at five stages are available for comparison. In all cases, the predicted values match the experimental data within 15%. The largest discrepancies occur with water below the feed tray and acetic acid near the reboiler. The differences between the experimental and modelled results are caused by the expressions used in the evaluation of thermodynamic properties and kinetic data. For example, the Wilson coefficients given in Appendix A had been developed from binary and tertiary data and then extended to this quaternary system. Unfortunately, no experimental



Figure 4 Case 1: Production of Ethyl Acetate



Figure 5 Predicted Composition Profiles and Available Experimental Data from Komatsu et al. [51]





Figure 8 Predicted Reaction Rate for Case 1

data are available for comparison with the temperature, flowrate and reaction extent profiles. Only the simulated profiles are presented in Figures 6, 7, and 8. It is believed that they are satisfactory since any significant deviations from actual values would have adversely affected the concentration profiles.

4.3 Achieving Convergence

The average run within the domain of convergence would take approximately 12 iterations although up to 20 iterations were required when starting near the domain's edges. The approach to convergence of a typical run is shown in Figure 9. The computer time taken in this case was 73 cpu seconds. Convergence and its rate depended on two factors: the initial values of the temperature, liquid composition and vapour flow rate profiles, and the choice of weighting factor used in the updating of variables between iterations.

4.3.1 Domain of Convergence

The domain of convergence of the algorithm was investigated by varying the initial profiles of temperature, liquid composition and vapour flowrates. Convergence was least sensitive to changes in the temperature profile. Linear profiles within a 30°C band of the final profile gave good convergence (Figure 10). The relative band width was narrower for the initial vapour flowrate profile. The initial

Figure 9 Approach to Convergence of the Simultaneous Correction Algorithm

values had to be within 15% of the final values for convergence (Figure 11). The initial concentration profiles had the strongest effect in determining whether or not convergence would occur. The narrow bands within which a linear initial profile had to fall are shown in Figures 12, 13, 14 and 15.

4.3.2 Variable Updating

The choice of weighting factor wf for the updating of calculation variables via Equations (4.10), (4.11) and (4.12) is crucial. It can determine whether or not convergence is reached for a given set of initial values. Figure 16 illustrates this effect. It represents the behaviour of the convergence criterion defined by equation (4.13) with respect to selected values of wf at point A of the run represented in Figure 9. After eight iterations of the run, . the value of the convergence criterion was 1066.0. Figure 16 shows what the value of the criterion would be following the next iteration depending on which value is selected for wf. A weighting factor of -0.2 or 0.8 would have flung the program far from convergence. Factors between -1.0 and -0.6 and between 0.0 and 0.2 improve the criterion. In this case 0.0 was used.

The selection of the weighting factor became a major difficulty in the implementation of this program. The irregular nature of the function made it difficult to navigate from iteration to iteration. An error in weighting factor could endanger convergence. Different

Correction Algorithm

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Correction Algorithm

Correction Algorithm

methods of normalising the energy error in equation (4.13) were examined but the behaviour of the criterion with respect to the weighting factor did not improve. Ishii and Otto [9] and Tomich [32] had used Broyden's algorithm for determining the weighting factor in their variable updating routines for non-reactive distillation problems. Attempts to apply Broyden's algorithm in this case failed, probably due to the added complexity of the function caused by additional non-linearities present due to the chemical reaction What finally proved adequate was a sequential testing of the terms. weighting factors. The standard sequence used was: 0.0, +1.0, -1.0, +0.3, -0.3, +0.6 and -0.6. A weighting factor which would decrease the value of the criterion was usually found within three or four trials. One would expect a weighting factor of 0.0 to produce the same criterion value as was obtained by the previous iteration. This is not the case because the calculation of reaction extents lags by one iteration, using old temperatures and liquid compositions. If a weighting factor of 0.0 is applied twice in a row, then there is no change in the criterion. This somewhat primitive approach for selecting weighting factors did not map the quickest path to the solution; however, it did lead to it.

4.4 The Effect of Chemical Reactions on the Algorithm

The presence of chemical reactions strongly affects the convergence behaviour of the algorithm. As was mentioned in the previous section, the reaction extent calculations create a lag

within the convergence mechanism. An additional problem is the fact that reaction extents are a strong function of concentration. Small changes in liquid concentration are thus amplified. This is probably the cause of the high sensitivity of convergence to the initial concentration profiles. The introduction of a lag into the iterative process and greater non-linearities between equations make the simulation of distillation towers with chemical reactions more difficult than distillation towers without reactions.

CHAPTER 5

APPLYING THE INSIDE-OUTSIDE ALGORITHM

TO REACTIVE DISTILLATION

The inside-outside algorithm was applied to two reactive distillation towers: the ethyl acetate producing column which had been used to test the simultaneous-solution algorithm, and a tower for the industrial production of component "A". The design variables listed in Section 3.3.2 were used in both cases. This chapter describes the procedure which was used to implement the insideoutside algorithm, and the effect of initialization methods and convergence criteria on convergence behaviour. A flowchart of the inside-outside algorithm used is presented in Figure 17. This program was also written in FORTRAN and implemented on the Multics Honeywell Computer. It contained 3500 lines of code.

5.1 Initialisation of the Variables

There are two parts to the initialisation of iterations for the inside-outside algorithm. First, the temperature, total liquid flowrates and liquid compositions profiles are determined. The values of the temperature and composition initial profiles were the same as those used in simultaneous-correction, Section 4.1.1. The internal liquid flowrates were initialised at twice the feed rate.

Figure 17 Flowchart of the Inside-Outside Algorithm

The second part of the initialisation involves the outer loop parameters. The values of the rigorous phase equilibrium constants K can be evaluated from explicit equations, as was the case in both examples used in this thesis, or from more involved thermodynamic computations. The outer loop parameters used are the relative volatilities defined by

$$\alpha_{i} = K_{i}/K_{B}$$
(5.1)

where K_i is the rigorous phase equilibrium constant and K_B is the value of the equilibrium for a base component. More complex expressions than the one above have been proposed by Chimowitz et al. [46] and Saeger and Bishnoi [49]. The simple form defined above performed satisfactorily in the cases studied.

5.2 Selecting the Initial Base Component K_R

Selecting the proper starting value for the base component K_B is very important, since it is used in the initialisation of the outer loop parameter: the relative volatilities. The base component can be a predominant or weighted-average component. Several configurations were tried before a generally applicable one was found.

The first tests done on this inside-outside algorithm involved a thirteen-tray, eleven-component hydrocarbon column similar to Example 2 of Russell [44]. Since this example did not involve chemical reactions, it is not elaborated in this thesis. What is of interest

to the present discussion is that it was possible to successfully use a component of average volatility, appearing in both the distillate and bottoms, as the base component. Initialising K_B as the calculated K of this component led to good results.

In the simulation of the ethyl acetate column this approach did not work. All four components, water, ethanol, acetic acid and ethyl acetate, were tested as possible base components. None of them was present in significant concentrations on all trays and the resultant evaluations of initial volatility from Equation (5.1) were not adequate. The relative volatilities computed from equation (5.1) are kept constant throughout the inner loop calculations until the inner loop has converged. If the relative volatility is not a monotonic function over the temperature range of the column, its use in the inner loop calculations can lead to poor convergence or divergence. Defining K_B as the algebraic mean of the four K_i 's worked well for the ethyl acetate case. An algebraic mean worked for the nonreactive column as well. Figure 18 shows the relationship between K_{R} and 1/T for some of the K_R configurations which were tested on Case One.

The second reactive example used in this thesis is the production of component "A". When the inside-outside algorithm was tested on this tower, none of the previous K_B initialisation methods proved successful. The approach recommended by Boston [39] and Russell [44] for evaluating the initial K_B value is:

$$ln K_{\rm B} = \sum w_{\rm i} ln K_{\rm i}$$
 (5.2)

where

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$$= t_i / \sum t_i$$
 (5.3)

$$t_{i} = y_{i} \partial (ln K_{i}) / \partial (1/T)$$
(5.4)

This formulation worked on the non-reactive tower but did not work on the two reactive ones.

The following definition of t worked for the reactive columns:

$$t_{i} = \partial \left(\ln K_{i} \right) / \partial t \tag{5.5}$$

Since this definition of t_i was arrived at heuristically rather than from first principles, it is not possible to state whether it will work for all reactive distillation cases. It was the only formulation which worked for the two reactive examples simulated in this thesis. Equations (5.2), (5.3) and (5.4) are used only once, in the first computation of the outer loop volatilities. Subsequently K_B is determined from:

$$K_{\rm B} = 1 / \sum_{i=1}^{\rm c} \alpha_i x_i$$
 (5.6)

5.3 The K_B Model

The K_B model is used within the inner loop to calculate temperatures which satisfy the phase equilibrium and Equation (5.6). Both Boston [39] and Russell [44] modelled the relationship between

 K_B and temperature with an equation of the Clausius-Clapeyron form:

$$ln K_{\rm R} = A - (B/T)$$
 (5.7)

They used a unique K_B model for each stage of the tower. There were thus as many linearised segments on the $ln \ K_B$ vs. 1/T curve as there were trays. Chimowitz et al. [47] proposed an algorithm for varying the size of the linearised segments depending on the behaviour of ln K_B with respect to 1/T. This would be beneficial for cases with exotic equilibrium behaviour. The relationship between $ln \ K_B$ and 1/T for the two cases was not tortuous and fixed step sizes handled it well. It was found that longer linearised segments, covering two or three trays, could be used without detriment to the computations.

The following expression, of the Antoine equation form, was also tested:

$$ln K_{B} = A - \frac{B}{T+C}$$
(5.8)

On a graph of T versus K_B one linear segment defined by Equation (5.8) would cover the span of two segments defined by Equation (5.7). However, no significant change in computing time was found.

5.4 Inner Loop Calculations

 \cdot The inner loop is entered with a set of fixed relative volatilities, $K_{\rm B}$ model constants, temperature and liquid composition

profiles and stripping factors. The stripping factors were computed from Equations (3.30), (3.31) and (3.32) at the start of the program and then updated in subsequent iterations.

5.4.1 Solving the Mass Balances

The reaction rates are calculated at the start of the inner loop using the kinetic expressions in Appendices A and B. At this point, all the elements necessary for the component mass balances are now available. Equation (3.35) is solved for the component liquid flowrates using LINPACK's [52] Gaussian elimination with partial pivoting. The resultant vector contains the component liquid flowrates.

5.4.2 Evaluating Total Liquid Flowrates and Compositions

The total liquid flowrates are the sum of the individual component flowrates:

$$L_{j} = \sum_{i=1}^{c} \ell_{ij}$$
 (5.9)

The component liquid compositions are obtained from:

$$\mathbf{x}_{ij} = \ell_{ij} / \mathbf{L}_{j} \tag{5.10}$$

5.4.3 Determining Temperature from the K_B Model

Equation (5.6) is used to evaluate new K_B 's using the latest liquid compositions and the outer loop relative volatilities. Equation (5.7) is used to evaluate the tray temperatures.

5.4.4 Enthalpy Evaluations

The most recent values of component flowrates and temperatures are used to evaluate the stream enthalpies and heats of reaction. The heat of reaction for ethyl acetate is zero, however, for the production of component "A" it is significant. Expressions in Appendices A and B were used for these calculations.

5.4.5 Inner Loop Convergence and Variable Updating

As in the simultaneous-correction method, errors in the energy balances were used as convergence criteria in the inner loop. The errors were computed using Equation (3.36). The inner loop criterion was defined in the same manner as in Section 4.1.4.

The inside-outside algorithm uses the stripping factors as the primary computation variables. These factors are updated between inner loop iterations by applying a Newton-Raphson algorithm to the energy balances. The derivatives of the tray error terms E_0 with respect to the stripping factors for the Jacobian are determined

numerically. Broyden's algorithm is used to update the Jacobian. The Jacobian elements are re-determined numerically at the start of every set of inner loops corresponding to one outer loop in order to improve stability and prevent numerical fouling. Only (n-1) equations are used in the updating of stripping factors. Since both columns are equipped with total condensers, V_1 is zero and so is S_1 . The energy equation around the first tray is used to calculate the condenser heat duty.

5.5 Outer Loop Calculations

Once the inner loop convergence criterion is satisfied, the most recent values of temperature and composition are used to re-evaluate the relative volatilities. A comparison of the new volatilities with the ones which had been kept constant in the last set of inner loops was used to determine the approach to convergence. This is a relative rather than an absolute criterion.

$$\sum_{j=1}^{n} \sum_{i=1}^{c} (\alpha_{ij}^{k+1} - \alpha_{ij}^{k}) / \alpha_{ij}^{k})^{2} \leq \text{volcrit}$$
(5.11)

volcrit = 0.002 * n

where n is the number of stages within the column.

When the above criterion is met, the outer loop has converged and the problem is considered solved. If the criterion is not met, new K_B

constants are computed from Equation (5.7) and the inner loops are reconverged using the latest relative volatilities.

5.6 Convergence Behaviour

Tearing methods exhibit convergence behaviour different from simultaneous-correction methods and care must be taken to prevent "creeping". Creeping involves small but definite relative changes of a monitored parameter between iterations. The sum of these small changes continued over many iterations becomes significant. The danger here is that the relative changes in outer loop parameters may fall below volcrit even though the solution has not been reached. To verify the validity of the criterion volcrit, the program was allowed to run for up to 500 outer loops, well past the volcrit limit. Although some creeping occurred, below the volcrit of 0.002 * n the approach to convergence was asymptotic.

There is significant interaction between the inner loop and outer loop convergence criteria and overall convergence behaviour. If the inner loop criterion is too loose, creeping is more likely to set in. Figure 19 shows three approaches to equilibrium for the ethyl acetate example.

In Run A, the inner loop criterion crit (Equation (4.13)) was set at 20.0 and volcrit at $0.002 \times n$. In Run B, the inner loop criterion was set at 10.0 and volcrit remained the same. The



Figure 19 Outside Algorithm Due to Inner Loop Criteria

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difference in convergence behaviour is dramatic. With the looser inner loop criterion, the program uses fewer inner loops per outer loop but creeping occurs. When the inner loop criterion is strict, two to three times as many inner loops are needed per outer loop but there are fewer outer loops and no creeping.

A gradual tightening of the inner loop criterion resolved this behaviour. The value of crit would start at 20 but was reduced to 10 within four outer loop iterations. This progressive tightening of the inner loop criterion kept down the number of inner loops required per outer loop while preventing creeping. Curve C results from this approach.

CHAPTER 6

RESULTS OF REACTIVE DISTILLATION SIMULATIONS USING THE INSIDE-OUTSIDE ALGORITHM

This chapter presents the results obtained for the ethyl acetate and component "A" towers with the inside-outside algorithm. The performances of this algorithm and the simultaneous-correction algorithm are compared for the ethyl acetate case.

6.1 Results from the Simulation of Case 1: Ethyl Acetate

The same final temperature, composition, flowrate and reaction rate profiles were obtained with the inside-outside algorithm as with the simultaneous-correction algorithm. This is not surprising since the same property subroutines based on Appendix A had been used. There were, however, differences in the time required to reach the solution and in the domain of convergence.

6.1.1 Computer Time Requirements

The strongest feature of the inside-outside algorithm is its speed. The acceleration is particularly significant in cases where large amounts of time are-spent on thermodynamic evaluations. In the two reactive cases simulated, the calculations were explicitly formulated and only about 20% of the computer time was spent on evaluating these functions.

For initial conditions which took 73 cpu seconds to converge by simultaneous-correction, only 26 cpu seconds were required by the inside-outside algorithm. Similar reductions took place for all runs with identical starting values. This 64% reduction cannot be attributed solely to a reduction in thermodynamic calculations. A major factor slowing down the simultaneous-correction algorithm is the variable updating mechanism. No weighting factor was required in updating the stripping factors within the inside-outside method; the changes obtained by Broyden's algorithm were applied directly.

The computer time reduction is of less importance when the program is run on a mainframe computer, but it becomes significant for the ubiquitous micro-computers.

6.1.2 Domain of Convergence

A second important point upon which the two algorithms should be compared is the domain of convergence or robustness. Once again the sensitivity of convergence to initial profiles was examined. Figures 20, 21, 22, 23, 24 and 25 show the domains of convergence for linear initial profiles of temperature, liquid flowrate and composition. The temperature convergence band is of similar width to that of the simultaneous-solution method except for a shift to one side. The initial composition profiles convergence bands are slightly more finical. The range in initial liquid flowrates is similar to the



Figure 20 Domain of Initial Temperature Profiles which Lead to Convergence by the Inside-Outside Algorithm



Figure 21 Final Liquid Flowrate Profile for Case 1 and Domain of Covergence by the Inside-Outside Algorithm



Figure 22 Domain of Initial Acetic Acid Composition Profiles which Lead to Convergence by the Inside-Outside Algorithm re 23 Domain of Initial Ethanol Composition Profiles which Lead to Convergence by the Inside-Outside Algorithm



Convergence by the Inside-Outside Algorithm

Algorithm

range in initial vapour flowrates. In this respect, the two algorithms are comparable.

6.2 Results from the Simulation of Case 2: Component "A"

A second column was simulated with the inside-outside algorithm. The details of the process components cannot be revealed due to its proprietary nature. A schematic diagram of the tower is shown in Figure 26. The same version of the inside-outside algorithm was used as for the ethyl acetate case. Equations (5.2), (5.3) and (5.5) were used for initializing the $K_{\rm R}$ model.

6.2.1 Final Temperature and Concentration Profiles

The final temperature profiles obtained are presented in Figure 27. Two different profiles were obtained depending on the initial values used. The higher calculated temperature profile, Profile A, was in good agreement with the results presented by Roat et al. [53]. The second profile, B, has no data to support it. The domains of initial temperature values which converge to the two final solutions are also indicated in Figure 27. The band for the supported profile is narrower than for the second one. It is because the regions border on each other that the second profile was found while testing the sensitivity of convergence to initialisation.

The two different temperature profiles have correspondingly different liquid composition distributions. These are shown in



Figure 26 Case 2: Production of Component "A"



Figure 27 Two Steady-State Temperature Profiles for Component "A" and their Domains of Convergence

Figures 28 and 29. The profile for steady-state A is close to the available data. It is superior to steady-state B in that a higher purity of component "A" is achieved in the distillate. If indeed both steady-states are physically possible, the difference in product quality between them makes proper control of the tower very important. Some possible reasons for the presence of two steady-states are discussed in Chapter 7.

6.2.2 Computer Time

The computer time required to reach steady-state A from within its convergence band ranged from 92 to 120 cpu seconds. Convergence to steady-state B was slower, ranging from 96 to 212 cpu seconds. Up to 25 outer loop iterations were required, with most runs requiring about 16.



Steady State A. Data Points from Downs [74]



CHAPTER 7

ON THE EXISTENCE OF MULTIPLE STEADY-STATE SOLUTIONS

The existence of multiple steady-states under the same operating conditions has been noted in chemical reactors, fluid flow problems, elasticity theory and biological models. However, awareness of the possible existence of multiple steady-states in separation processes is a recent development. As was mentioned in previous chapters, one set of temperature and concentration profiles was found to satisfy the model equations of the simulated ethyl acetate column but two sets were found for the component "A" column.

For the component "A" column, a domain of initial profiles around each of the two steady-states which leads exists to convergence at that steady-state. Convergence was not reached with initial profiles outside of these two domains. Unfortunately, a full mapping of the domains of convergence for the solutions could not be carried out since n(c-1) initial concentration values and n temperature values are involved. A systematic but not complete search from physically possible combinations of starting points located the two steady-states mentioned. Although only two solutions were found, the possible existence of others cannot be categorically Various avenues were explored to find an explanation for denied. this behaviour.

7.1 System Configuration

Chavez et al. [54] found multiple steady-state solutions in interlinked separation systems. Using a continuation algorithm, they discovered four sets of internal flow distributions which satisfied the specifications of a Petlyuk system for benzene, toluene and ortho-xylene separation. These multiple solutions were found to exist when two sections of the system shared a specification in order to satisfy local degrees of freedom. Since the component "A" production tower simulated was a single column with no interlinking, the sharing of specifications is not a possible source of multiple solutions.

In addition, Doherty and Perkins [55] showed, by analysing dynamic models, that for homogeneous distillation with constant molar overflow multiple steady-state solutions are a consequence of multiple components and multiple stages. Multiple steady-states were not exhibited by binary distillation in multistage columns or multicomponent flash distillations. The component "A" system involved four components in a column with 26 trays.

7.2 Azeotropic Distillation Columns

The first report of multiple steady-state solutions in separation processes involved ethanol-benzene-water and ethanolpentane-water azeotropic distillation towers simulated by Magnussen

et al. [56]. They found that, within a limited range of input specifications, three different sets of independent temperature and composition profiles satisfied the component balances coupled with equilibrium relationships as well as the total stage mass balance. Propakis and Seider [57] tried to duplicate the three regimes of the ethanol-benzene-water system but were unable to do so since they used UNIQUAC equation parameters different from those of Magnussen et al. [56]. They did, however, find two similar regimes.

In a subsequent paper, Propakis and Seider [58] reported on the dynamic simulation of the ethanol-benzene-water azeotropic process. They noted the extreme sensitivity of the overhead vapour composition and steep composition and temperature fronts in response to small changes in variables. The first experimental data for an industrial azeotropic distillation tower were presented by Kovach and Seider [59] for the dehydration of secondary butyl alcohol. Two distinct steady-state solutions over a small range of reflux ratios were found: one with a sole liquid phase on all trays and one with two liquid phases on the majority of trays. The presence of these two solutions, located fairly close together, conformed with the erratic experimental behaviour of the tower in that region.

Van Dongen and Doherty [60] examined the total Gibbs free energy of closed systems and found multiple equilibrium solutions for nonideal mixtures. They theorised that one possible cause of this phenomenon is the presence of multiple metastable solutions to the

phase equilibrium equations in the vicinity of heterogeneous azeotropes, and that the asymptotic stability of each steady state in the phase plane is directly related to the material stability of each phase in the mixture.

All of the cases which have been reported to exhibit multiple steady-states have involved two liquid phases at some point in the tower, if only in the condenser. The experimental data available on component "A" and ethyl acetate do not indicate heterogeneity in the towers simulated. The esterification of higher order alcohols, for example butanol to butyl acetate [61], does involve two liquid phases. It must also be noted that the component "A" and ethyl acetate towers did not involve azeotropes since the concentration of potential azeotropic components throughout the tower remained relatively low due to their consumption in the reaction.

7.3 Analysis for a Continuous-Flow Stirred Tank Reactor

The analysis presented in the previous section was based on the available literature for distillation towers where only phase equilibrium occurred. However, the trays of the reactive distillation tower can also be viewed as a complex set of continuous stirred tank reactors (CSTRs) in series.

7.3.1 Multiple Steady States in CSTRs

Multiple steady-states in CSTRs have been widely reported in literature since the work of van Heerden [62] and Bilous [63]. It was therefore decided to check whether some part of this theory is applicable for reactive distillation towers.

Exothermic reactions occurring in a CSTR can under certain conditions have three steady states: two stable and one metastable. Two CSTRs in series have been experimentally found by Horak et al. [64] to have three stable and two metastable steady-states for the reaction of bi-trichloromethyl-trisulphide with aniline in methanol. The existence of more than one steady-state in exothermic reacting systems is caused by three points of intersection between the mass and energy balances.

7.3.2 Criteria for the Prediction of Multiple Steady States in CSTR's

In recent years, criteria have been developed via the catastrophe and singularity theories with a distinguished parameter to predict the existence of multiple steady-states in CSTRs [65-69]. Six possible multiplicity patterns have been predicted by Balakataiah and Luss [70]. The shape of the multiplicity pattern is determined by the Damkohler number:

$$Da = \frac{VkC_o^{n-1}}{q}$$
(7.1)

where V is the volume of the reactor, q is the volumetric flowrate, k is the rate of the reaction, C_0 the initial concentration, and n the order of the reaction. Only the S-shaped pattern has been observed experimentally. This is also the only pattern possible for an adiabatic reactor.

Two parameters are required in order to determine whether multiple steady-states are possible for a specific system at some value of the Damkohler number. These parameters are:

$$\beta = \frac{(-\Delta H)C_o}{\rho C_p T_o}, \quad \gamma = \frac{E}{RT_o}$$
 (7.2)

where ρ is the density, C_p the heat capacity, E the activation energy, ΔH the heat of reaction, C_o and T_o the composition and temperature of the feed entering the system, and R the universal gas constant. Using these two parameters, Tsotsis and Schmitz [67] and Van Den Bosch and Luss [68] have developed charts, for reactions of order zero to three, which define the boundaries of possible multiplicity. Their analysis was applied to one adiabatic component "A" tower tray. The calculations are given in Appendix C. When a component "A" tower tray is treated as a CSTR, the conditions for multiple solutions at some value of the Damkohler number are

satisfied when the concentration of the reactants at the tray is above a minimum value found to be 0.58 lbmole/ft³. This condition is satisfied at the feed trays. If stable multiple steady-states are possible at the feed trays, the tower can have multiple steady-state profiles corresponding to those on the feed trays. When the CSTR method of steady-state analysis is applied to the ethyl acetate case, it predicts only one steady-state solution because the heat of reaction is negligible. Only one steady-state was found for the ethyl acetate tower.

7.4 Conclusion

The model equations used to describe the exothermic component "A" system were found to have two solutions. It is not known whether these are the only two which exist. Equations 7.1 and 7.2 detect whether steady-states are possible but cannot predict the number of such states. Only one solution was found for the athermal ethyl acetate system. An iterative search of all physically possible permutations of the input variables is impractical due to their vast number. In addition, the search grid would have to be very fine in order not to miss steady-states with small domains of convergence. The new continuation methods, although having limitations, may prove to be the best approach for the simulation of reactive distillation towers if they have multiple solutions.

Analysing a single adiabatic tower tray as if it were a CSTR has

led to the conclusion that the heat of reaction of component "A" production as well as the residence time on the trays augur the existence of multiple steady-states. The heat of reaction of the ethyl acetate reaction is negligible, thus making only one steadystate possible if taking place in a CSTR. These observations agree with the behaviour found in the towers simulated. Phase equilibrium behaviour and liquid phase splitting seem to be the cause of multiple solutions in azeotropic distillation towers however no phase splitting was seen in the reactive towers studied. It is thus more likely that the mutliple steady-states observed in the exothermic case were caused by the same phenomena as multiple steady-states in CSTRs.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

- 8.1 Conclusions
- Both the simultaneous-correction algorithm and the inside-outside successive substitution algorithm can be extended for use in the steady state simulation of distillation towers with chemical reactions.
- 2. The inside-outside successive substitution algorithm runs several times faster than the simultaneous-correction algorithm for distillation with reactions, not only because time spent on thermodynamic computation is reduced, but because it handles the inclusion of chemical reaction terms more readily.
- 3. The two algorithms tested have similar domains of covergence. However, the inside-outside algorithm requires stricter internal control over convergence criteria in its two levels of computation in order to achieve proper convergence.
- 4. The presence of chemical reaction terms within the model equations has a strong effect upon the convergence behaviour of the algorithm. A lag is introduced between iterations by the reaction rate calculations. Also, errors in component

concentrations can be amplified, making the programs sensitive to initial conditions.

- 5. The K_B model within the inside-outside algorithm is flexible enough to accommodate the changes required by reactive distillation. However, the initialization procedure for K_B necessitated major modifications before it could be applied to reactive distillation.
- 6. In the simultaneous solution algorithm, weighting factors are required for the updating of variables between iterations. A systematic heuristic scheme was developed for the determination of these weighting factors.
- 7. The model developed for simulating esterification towers predicts one solution for a distillation tower producing ethyl acetate and two steady-states for a tower producing component "A". The effect of possible phase splitting on multiple steady-states in distillation as reported by other workers azeotropic was examined. Also, criteria for the existence of multiple steadystates in continuously stirred tank reactors (CSTRs) were applied to a single tray of the component "A" tower and predicted multiple solutions. Behaviour similar to CSTRs is believed to cause the multiple steady-states observed in reactive distillation.

8.2 Recommendations

- 1. There is no mention in the literature of multiple steady-states existing for a distillation tower with chemical reactions. Now that the possible existence of this phenomenon has been predicted, it should be experimentally verified. A wide range of chemical reactions should be tested. This would also provide much needed data for the testing of model equations and solution methods.
- 2. The use of equilibrium trays within a process model assumes that perfect contacting exists between the phases. This is not the case in actual distillation units. Although such tools as Murphree efficiences have been used on standard distillation towers, their applicability to towers with reactions must be tested. Any effects which the presence of chemical reactions may have on tray efficiencies should be investigated.
- 3. The use of equilibrium trays within the column model also implies perfect mixing upon the trays. Since this does not occur in practice, various models of tray behaviour ranging from CSTR to plug flow should be tested and validated through experiments. The quantification of this non-ideality would be of particular significance in determining the reaction extents of slow reactions occurring on distillation trays.

- 4. The new continuation homotopy methods should be tried on the model equations of towers with reactions as these methods may prove capable of locating multiple steady-states.
- 5. Just as there are now criteria available for the prediction of multiple steady-states in CSTRs, accessible criteria should be developed for the prediction of multiple steady-states in distillation towers.

REFERENCES

- Bacchaus, A. A., US Patents 1 400 849, 1 400 850, 1 400 851, 1921; 1 403 224, 1 403 225, 1 425 624, 1 425 625, 1922; 1 454 462, 1 454 463, 1923.
 - Carra, S., Santacesaria, E., Morbidelli, M., Schwarz, P., and Divo, C., "Synthesis of Epichlorohydrin by Elimination of Hydrogen Chloride from Chlorohydrins", Ind. Eng. Chem. Process Des. Dev., <u>18</u>, (3), 424-433, 1979.
 - Carra, S., Santacesaria, E., Morbidelli, M., and Cavalli, L.,
 "Synthesis of Propylene Oxide From Propylene Chlorohydrins",
 Chemical Engineering Science, <u>34</u>, pp 1123-1132, 1979.
 - Terrill, D. L., Sylvestre, L. F., and Doherty, M. F., "Separation of Closely Boiling Mixtures by Reactive Distillation", Ind. Eng. Chem. Process Des. Dev., <u>24</u>, 1062-1071, 1985.
 - Saito, S., Michishita, T., and Maeda, S., "Separation of Metaand Para-Xylene Mixture by Distillation Accompanied by Chemical Reactions", Journal of Chemical Engineering of Japan, <u>4</u>, (1), 37-43, 1971.
 - Broyden, C. G., "A Class of Methods for Solving Nonlinear Simultaneous Equations", Mathematics of Computation, <u>19</u>, 577 - 594, 1965.

- More, J.J., and Cosnard, M.Y., "Numerical Solution of Nonlinear Equations", ACM Transactions on Mathematical Software, <u>5</u>, (1), 64-85, 1979.
- Naphtali, L. M. and Sandholm, D. P., "Multicomponent Separation Calculations by Linearization", AIChE Journal, <u>17</u>, (1) 148-153, 1971.
- Ishii, Y. and Otto, F. D., "A General Algorithm for Multistage Multicomponent Separation Calculations", The Canadian Journal of Chemical Engineering, <u>51</u>, 601-606, 1973.
- 10. Browne, D. W., Ishii, Y. and Otto, F. D., "Solving Multicolumn Equilibrium Stage Operations by Total Linearization", The Canadian Journal of Chemical Engineering, <u>55</u>, 307-312, 1977.
- 11. Hofeling, B. S. and Seader, J. D., "A Modified Naphtali-Sandholm Method for General Systems of Interlinked, Multistaged Separators", AIChE Journal, <u>24</u>, 1131-1134, 1978.
- 12. Gallun, S. E. and Holland, C. D., "Solve More Distillation Problems: Part 5 - For Highly Nonideal Mixtures", Hydrocarbon Processing, <u>55</u>, (1), 134-144, 1976.
- Murthy, A. K. S., "Simulation of Distillation Column Reactors", Proceedings of the Summer Computer Simulation Conference, Boston, Mass., 630-635, July 23-25, 1984.

- 14. Simandl, J. and Svrcek, W. Y., "Simulation of Multi-Stage Reaction Towers", Proceedings of the Summer Computer Simulation Conference, Chicago, Illinois, 347-352, July 22-24, 1985.
- 15. Rose, A., Sweeny, R. F. and Schrodt, V. N., "Continuous Distillation Calculations by Relaxation Method", Industrial and Engineering Chemistry, <u>50</u>, (5), 737-740, 1958.
- 16. Jelinek, J. and Hlavacek, V., "Steady State Countercurrent Equilibrium Stage Separation with Chemical Reaction by Relaxation Method", Chemical Engineering Communications, <u>2</u>, 79-85, 1976.
- Komatsu, H., "Application of the Relaxation Method for Solving Reacting Distillation Problems", Journal of Chemical Engineering of Japan, <u>10</u>, (3), 200-205, 1977.
- 18. Seydel, R. and Hlavacek, V., "Role of Continuation in Engineering Analysis", Chemical Engineering Science, <u>42</u>, (6), 1281-1295, 1987.
- 19. Bhargava, R. and Hlavacek, V., "Experience with Adopting One-Parameter Imbedding Methods Toward Calculation of Countercurrent Separation Processes", Chemical Engineering Communications, <u>28</u>, 165-179, 1984.

20. Ketchum, R. G., "A Combined Relaxation-Newton Method as a New

Global Approach to the Computation of Thermal Separation Processes", Chemical Engineering Science, <u>34</u>, 387-395, 1979.

- 21. Salgovic, A., Hlavacek, V. and Ilavsky, J., "Global Simulation of Countercurrent Separation Processes via One-Parameter Imbedding Techniques", Chemical Engineering Science, <u>36</u>, 1599-1604, 1981.
- 22. Byrne, G. D. and Baird, L. A., "Distillation Calculations Using a Locally Paramaterized Continuation Method", Computers and Chemical Engineering, <u>9</u>, (6), 593-599, 1985.
- Vickery, D. J. and Taylor, R., "Path-Following Approaches to the Solution of Multicomponent, Multistage Separation Process Problems", AIChE Journal, <u>32</u>, (4), 547-556, 1986.
- 24. Wayburn, T. L., <u>Modeling Interlinked Distillation Columns by</u> <u>Differential Homotopy-Continuation</u>, Ph.D. Thesis, The University of Utah, 1983.
- 25. Thiele, E. W. and Geddes, R. L., "Computation of Distillation Apparatus for Hydrocarbon Mixtures", Industrial and Engineering Chemistry, <u>25</u>, (3), 289-295, 1933.
- 26. Lewis, W.K., and Matheson, G.L., "Studies in Distillation Design of Rectifying Columns for Natural and Refinery Gasoline", Ind. Eng. Chem., <u>24</u>, 494, 1932.
- 27. Fonyo, Z., Nishimura, H., and Yamashita, Y., "New Simultaneous Modular Method for Calculating Multistage Multicomponent Separation Processes", AIChE Journal, <u>29</u>, (4), 538-544, 1983.
- 28. Davies, B., Jenkins, J.D., and Dilfanian, S., "Distillation with Chemical Reaction - Distillation of Formaldehyde Solutions in a Sieve Plate Column", I. Chem. E. Symp. Ser., No. 56, pp. 4.2/65 - 4.2/79.
- 29. Wang, J.C., and Henke, G.E., "Tridiagonal Matrix for Distillation", Hydrocarbon Processing, <u>45</u>, (8), 155-163, 1966.
- 30. Muller, D.E., "A Method for Solving Algebraic Equations Using an Automatic Computer", Mathematical Tables and Other Aids to Computation, <u>10</u>, 208-215, 1956.
- 31. Suzuki, I., Yagi, H., Komatsu, H., and Hirata, M., "Calculation of Multicomponent Distillation Accompanied by a Chemical Reaction", Journal of Chemical Engineering of Japan, <u>4</u>, (1), 26-33, 1971.
- 32. Tomich, J.F., "A New Simulation Method for Equilibrium Stage Process", AIChE Journal, <u>16</u>, (2), 229-232, 1970.
- 33. Nelson, P.A., "Countercurrent Equilibrium Stage Separation with Reaction", AIChE Journal, <u>17</u>, (5), 1043-1049, 1971.
- 34. Tierney, J.W., and Riquelme, G.D., "Calculation Methods for

Distillation Systems with Reaction", Chem. Eng. Commun., <u>16</u>, 91-108, 1982.

- 35. Kinoshita, M., Hashimoto, I., and Takamatsu, T., "A New Simulation Procedure for Multicomponent Distillation Column Processing Nonideal Solutions or Reactive Solutions", Journal of Chemical Engineering of Japan, <u>16</u>, (5), 370-377, 1983.
- 36. Holland, C.D., <u>Fundamentals of Multicomponent Distillation</u>, McGraw-Hill Book Company, 1981.
- 37. Izarraraz, A., Bentzen, G.W., Anthony, R.G., and Holland, C.D., "Solve More Distillation Problems: Part 9 - When Chemical Reactions Occur", Hydrocarbon Processing, <u>59</u>, (4), 195-203, 1980.
- 38. Komatsu, H., and Holland, C.D., "A New Method of Convergence for Solving Reacting Distillation Problems", Journal of Chemical Engineering of Japan, <u>10</u>, (4), 292-297, 1977.
- 39. Boston, J.F., <u>A New Class of Quasi-Newton Solution Methods for</u> <u>Multicomponent</u>, <u>Multistage Separation Processes</u>, Ph.D. Thesis, Tulane University, 1970.
- 40. Boston, J.F., and Sullivan, S.L., "A New Class of Solution Methods for Multicomponent, Multistage Separation Processes", The Canadian Journal of Chemical Engineering, <u>52</u>, (2), 52-63, 1974.

- 41. Boston, J.F., and Britt, H.I., "A Radically Different Formulation and Solution of the Single-Stage Flash Problem", Computers and Chemical Engineering, <u>2</u>, 109-122, 1978.
- 42. Boston, J.F., "Inside-Out Algorithms for Multicomponent Separation Process Calculations", <u>Computer Applications to</u> <u>Chemical Engineering</u>, American Chemical Society, 135-151, 1980.
- 43. Fournier, R.L., and Boston, J.F., "A Quasi-Newton Algorithm for Solving Multiphase Equilibrium Flash Problems", Chem. Eng. Commun., <u>15</u>, 305-326, 1981.
- Russell, R.A., "A Flexible and Reliable Method Solves Single-Tower and Crude-Distillation-Column Problems", Chemical Engineering, <u>90</u>, October 17, 53-59, 1983.
- 45. Chimowitz, E.H., Bielinis, R.Z., and Jobsky, R.W., "Speed up Micro-computer Design Calculations", Chemical Engineering, <u>90</u>, December 26, 43-45, 1983.
- 46. Chimowitz, E.H., Anderson, T.F., Macchietto, S., and Stutzman, L.F., "Local Models Representing Phase Equilibria in Multicomponent, Nonideal Vapour-Liquid and Liquid-Liquid Systems. 1. Thermodynamic Approximation Functions", Ind. Eng. Chem. Process Des. Dev., <u>22</u>, (2), 217-225, 1983.
- 47. Chimowitz, E.H., Macchietto, S., Anderson, T.F., and Stutzman, L.F., "Local Models for Representing Phase Equilibria in Multi-

component, Nonideal Vapour-Liquid and Liquid-Liquid Systems. 2. Application to Process Design", Ind. Eng. Chem. Process Des. Dev., <u>23</u>, (3), 609-618, 1984.

- 48. Macchietto, S., Chimowitz, E.H., Anderson, T.F., and Stutzman, L.F., "Local Models for Representing Phase Equilibria in Multicomponent Nonideal Vapour-Liquid and Liquid-Liquid Systems. 3. Parameter Estimation and Update", Ind. Eng. Chem. Process Des. Dev., <u>25</u>, (3), 674-682, 1986.
- .49. Saeger, R.B., and Bishnoi, P.R., "A Modified 'Inside-Out' Algorithm for Simulation of Multistage Multicomponent Separation Processes Using the UNIFAC Group-Contribution Method", The Canadian Journal of Chemical Engineering, <u>64</u>, (10), 759-767, 1986.
- 50. Simandl, J., and Svrcek, W.Y., "Simulation of Reactive Distillation by the Inside-Outside Method", Proceedings of the Thirty Seventh Chemical Engineering Conference, Montreal, 365 -367, May 18-22, 1987.
- 51. Komatsu, H., Suzuki, I., Ishikawa, T., and Hirata, M., "Distillation Accompanied by Esterification of AcOH-EtOH", Kagaku Kogaku, <u>34</u>, (1), 45-52, 1970.
- 52. Dongarra, J.J., Bunch, J.R., Moler, C.B., and Stewart, G.W., LINPACK User's Guide, SIAM, 1979.

- 53. Roat, S.D., Downs, J.J., Vogel, E.F., and Doss, J.E., "The Integration of Rigorous Dynamic Modeling and Control System Synthesis for Distillation Columns: An Industrial Approach", Paper presented at the Third International Conference on Chemical Process Control (CPC-III), Asilomar, California, January 12-17, 1986.
- 54. Chavez, R. F., Seader, J. D., and Wayburn, T. L., "Multiple Steady-State Solutions for Interlinked Separation Systems", Ind. Eng. Chem. Fundam., <u>25</u>, 566-576,1986.
- 55. Doherty, M. F. and Perkins, J. D., "On the Dynamics of Distillation Processes-IV", Chemical Engineering Science, <u>37</u>, (3), 381-392, 1982.
- 56. Magnussen, T., Michelsen, M. L., and Fredenslund, Aa., "Azeotropic Distillation Using UNIFAC", "I. Chem. E. Symp. Ser.", No. 56, pp 4.2/1-4.2/19, 1979.
- 57. Propakis, G. J. and Seider, W. D., "Feasible Specifications in Azeotropic Distillation", AIChE Journal, <u>29</u>, (1), 49-60, 1983.
- 58. Propakis, G. J. and Seider, W. D., "Dynamic Simulation of Azeotropic Distillation Towers", AIChE Journal, <u>29</u>, (6), 1017-1029, 1983.
- 59. Kovach III, J. W. and Seider, W. D., "Heterogeneous Azeotropic

Distillation: Experimental and Simulation Results", AIChE Journal, <u>33</u>, (8), 1300-1314, 1987.

- 60. Van Dongen, D. B., Doherty, M. F., and Haight, J. R., "Material Stability of Multicomponent Mixtures and the Multiplicity of Solutions to Phase-Equilibrium Equations", Ind. Eng, Chem. Fundam., <u>22</u>, 472-485, 1983.
- 61. Arrison, L.N., <u>Butyl Acetate System</u>, Ph.D. Thesis, University of Calgary, 1972.
- 62. Van Heerden, C., "The Character of the Stationary State of Exothermic Processes", <u>Chemical Reaction Engineering</u>, Vol 1, Twelfth Meeting of the European Federation of Chemical Engineering, Amsterdam, 7th, 8th, and 9th May, 133-145, 1957.
- 63. Bilous, O. and Amundson, N. R., "Chemical Reactor Stability and Sensitivity", AIChE Journal, <u>1</u>, (4), 513-521, 1955.
- 64. Horak, J., Jiracek, F., and Krausova, L., "Experimental Study of the Behaviour of an Isothermal Continuous Stirred Tank Reactor in the Course of an Autocatalytic Reaction", Chemical Engineering Science, <u>26</u>, 1-10, 1971.
- 65. Uppal, A., Ray, W. H., and Poore, A. B., "On the Dynamic Behaviour of Continuous Stirred Tank Reactors", Chemical Engineering Science, <u>29</u>, 967-985, 1974.

- 66. Chang, H-C. and Calo, J. M., "Exact Criteria for Uniqueness and Multiplicity of an nth Order Chemical Reaction via a Catastrophe Theory Approach", Chemical Engineering Science, <u>34</u>, 285-299, 1979.
- 67. Tsotsis, T. T. and Schmitz, R. A., "Exact Uniqueness and Multiplicity Criteria for a Positive-order Arrhenius Reaction in a Lumped System", Chemical Engineering Science, <u>34</u>, 135-137, 1979.
- 68. Van Den Bosch, B. and Luss, D., "Uniqueness and Multiplicity Criteria for an nth Order Chemical Reaction", Chemical Engineering Science, <u>32</u>, 203-212, 1977.
- 69. Leib, T. M. and Luss, D., "Exact Uniqueness and Multiplicity for an nth Order Reaction in a CSTR", Chemical Engineering Science, <u>36</u>, 210-212, 1981.
- 70. Balakataiah, V., and Luss, D., "Analysis of the Multiplicity Patterns of a CSTR", Chem. Eng. Commun., <u>13</u>, 111-132, 1981.
- 71. Arnikar, H.J., Rao, T.S., and Bodne, A.A., "A Gas Chromatographic Study of the Kinetics of the Uncatalysed Esterification of Acetic Acid by Ethanol", J. Chromatog., <u>47</u>, 265-268, 1970.
- 72. Suzuki, I., Komatsu, H., and Hirata, M., "Formulation and Prediction of Quaternary Vapor-Liquid Equilibria Accompanied by

Esterification", Journal of Chemical Engineering of Japan, <u>3</u>, (2), 152-157, 1970.

- 73. Barbosa, D., and Doherty, M.F., "The Influence of Equilibrium Chemical Reactions on Vapor-Liquid Phase Diagrams", 1986 Annual AIChE Meeting, Miami Beach, Florida, November 2-7, 1986.
- 74. Downs, Dr. James, Tennessee Eastman Company. Private Communication.

APPENDIX A

Data for Case 1: Production of ethyl acetate via the uncatalysed

esterification of acetic acid by ethanol

1. Column Specification [51]:

13 trays including the reboiler and a total condenser : 10 Reflux ratio Column pressure : 1 atm : Holdup (clear 1.0 Liters for reboiler : 0.3 Liters for each plate and condenser liquid volume) Distillate Rate : 0.0208 moles/min Feed Tray 6 : Feed Rate 0.1076 moles/min, at boiling point : Feed Composition : 1. Acetic Acid 0.4963 2. Ethanol 0.4808 0.0229 3. Water 4. Ethyl Acetate 0.0

2. Reaction Data [71]:

 $\begin{array}{rcl} CH_{3}COOH + C_{2}H_{5}OH = CH_{3}COOC_{2}H_{5} + H_{2}O \\ k_{1} &= 4.85 \times 10^{2} \exp \left(-14.300/\text{RT}\right) & 1/\text{mole sec} \\ k_{2} &= 1.23 \times 10^{2} \exp \left(-14.300/\text{RT}\right) & 1/\text{mole sec} \\ \end{array}$ where T is in K R = 1.987 cal/mole K reaction rate = $k_{1}C_{A}C_{B} - k_{2}C_{C}C_{D}$ C is the component concentration in gmole/1 heat of reaction = 0

3. Vapour-Liquid Equilibrium [72]:

 $\begin{array}{rcl} K_1 & = & 2.25 \times 10^{-2} \text{ T} - 7.812 & \text{T} > 347.6 \\ K_1 & = & 0.001 & \text{T} \\ \log K_2 & = & -2.3 \times 10^3 \text{ / T} + 6.588 \\ \log K_3 & = & -2.3 \times 10^3 \text{ / T} + 6.484 \\ \log K_4 & = & -2.3 \times 10^3 \text{ / T} + 6.742 \\ \text{T in K} \end{array}$

4. Enthalpies, cal/mol, [36]:

Vapour: H₁ = -2421.29 + 2.0142 T + 2.80325 x 10⁻² T² - 0.11363 x 10⁻⁴ T³ + 0.002005 x 10⁻⁶ T⁴ H₂ = -3003.24 + 4.750 T + 2.503 x 10⁻² T² - 0.8263 x 10⁻⁵ T³ + 1.1975 x 10⁻³ T⁴ H₃ = 7.19136 x T + 10737.1 H₄ = -4981.59 + 10.31 T + 30.495 x 10⁻³ T² - 5.390 x 10⁻⁶ T³

T in K

Latent Heats of Vaporization [36], cal/mole using Watson's correlation:

ΔH_2	$\left(1 - T_{r2}\right)$
ΔH_1	$\left(1 - T_{r1}\right)$

where T _r	= T/T _C	T in K
Component	∆H ₁	T _c K
1	5600	594.4
2	9260	516.2
3	9717	647.3 [.]
4	7700	523.2

Liquid enthalpies are calculated from the latent heat and vapour enthalpies.

5. Activity Coefficients:

The Wilson equation is used with parameters from reference [73]

$$\ln \gamma_{r} = 1 - \ln \left[\sum_{j=1}^{c} x_{j} \Lambda_{rj} \right] - \sum_{i=1}^{c} \left[\frac{x_{i} \Lambda_{ir}}{\sum_{j=1}^{c} x_{j} \Lambda_{ij}} \right]$$

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \left[\frac{-A_{ij}}{T}\right]$$

m³/mole K

APPENDIX B

Data for Case 2: Production of component "A" via a catalysed

reaction. Data from source [74]:

1. Column Specifications:

26 trays including the reboiler and a total condenser Reflux ratio : 2.0 Column pressure : top : 850 torr : bottom: 1073 torr Holdup (clear 1 ft³ on all trays : liquid volume) Distillate Rate : 50 lbmoles/hr Feed Tray 6 : rate 50 lbmoles/hr temperature 25°C : composition : 0.9999 D 0.0001 A Feed Tray : 10 : 0.5 lbmole/hr rate temperature : 25°C - composition : 1.0 catalyst E Feed Tray : 20 rate : 50 lbmoles/hr temperature 50°C : composition 0.9999 B : 0.0001 C

2. Reaction Data:

B + D = A + Cliquid catalyst : E $k_2 = 69.7 \exp(-9.198/RT)$ $k_1 = 13.38 \exp(-9.198/RT)$ where T is in K R = 1.987

reaction rate = $k_1 C_E C_B C_D - k_2 C_E C_A C_C$ lbmole/hr ft³

C is the component concentration in ${\rm lbmole/ft}^3$ heat of reaction, ${\rm Btu/hr\ ft}^3$

hrxn = 1687 * reaction rate

3. Enthalpies

liquid enthalpy, Btu/lb [.]

 $h_{i} = 1.8 (A_{i} * T + B_{i}/2 * T^{2} + C_{i}/3 * T^{3})$ where T is in °C

Component	А	В	C
A	0.4540	1.43 E-3	0.0
В	0.53	2.83 E-3	0.0
C	1.0034	-2.11 E-4	2.26 E-6
D	0.4710	7.70 E-4	0.0
Ε	1.00	0.0	0.0

 $h = \sum x_i h_i$

latent heats of vaporization, Btu/lb

 $\Delta H_{i} = A_{vi} + B_{vi} * T + C_{vi} * T^{2}$

where	component	A _v	B_v	Cv
	А	195.0	-0.317	0.0
	В	529.00	-0.867	0.0
	С	1056.32	-3.59	1.30 e-3
	D	201.00	-0.232	0.0
	Е	200.0	0.0	0.0

vapour enthalpy, Btu/lb

4. Activity Coefficients:

Wilson equation

$$ln \gamma_{i} = 1 - ln \left(\sum_{j} x_{j} A_{ij}\right) - \sum_{j} \frac{x_{j} A_{ji}}{\sum_{k} x_{k} A_{jk}}$$

values of A_{ij}:

	A	В	C	, D	E
A	1.0	0.58950	0.21480	1.7405	1.0
B	0.5577	1.0	0.4284	1.987	1.0
C	0.2520	1.0565	1.0	1.4826	1.0
D	0.30650	0.40610	0.3157	1.0	1.0
E	1.0	1.0	1.0	1.0	1.0

5. Vapour Pressure:

$$P_{i} = \exp \left[A_{vpi} + \frac{B_{vpi}}{T + C_{vpi}} \right]$$

where P_i is in torr T is in °C

Component	Avpi	Bvp	Ċvp
A	16.26831	-2665.54	219.73
В	18.718570	-3720.83	242.66
С	18.67190	-4030.92	235.00
D	16.80518	-3404.0	216.75
E	2.00	-0.01	

APPENDIX C

CSTR ANALYSIS FOR AN ADIABATIC TRAY

The criteria for multiple steady-states in CSTRs of Tsotsis and Schmitz [67] and Van Den Bosch and Luss [68] is applied to a single adiabatic tray of the component "A" producing tower.

Damkohler number
$$Da = \frac{VkC_0^{n-1}}{q}$$
 (C.1)

$$\beta = \frac{(-\Delta H)C_o}{\rho C_p T_o}, \quad \gamma = \frac{E}{RT_o}$$
(C.2)

The bifurcation curves for γ and β according to Tsotsis and Schmitz are given in Figure 30. Unique steady states exist below the curves and multiple steady-states above for some values of the Damkohler number. For the production of "A":

$$\gamma = \frac{(-9198)}{(1.987)(303)} = 15.3$$
(C.3)

From Figure 30 it can be seen that β must be greater or equal to 0.4 for multiplicity to occur. For a feed stream of pure "B":

$$(\rho)(C_p) = (49.47 \text{ lb/ft}^3)(1.1 \text{ Btu/lb}^\circ\text{C}) = 54.42 \text{ Btu/ft}^3^\circ\text{C}$$
 (C.4)

and for pure "D":





$$(\rho)(C_p) = (65.53 \text{ lb/ft}^3)(0.9 \text{ Btu/lb}^\circ\text{C}) = 58.98 \text{ Btu/ft}^3 \circ\text{C}$$
 (C.5)

The higher value is used for the worst possible scenario. Thus for multiple steady-states to exist:

$$\beta \ge 0.55 \tag{C.6}$$

$$\beta = \frac{(1687 \text{ Btu/lb mole})(C_0)}{(58.98 \text{ Btu/ft}^3 \circ C)(30 \circ C)} \ge 0.55$$
(C.7)

$$\beta = 0.953 \text{ C}_{0} \ge 0.55$$
, $C_{0} \ge \frac{0.55}{0.9853} = 0.58 \text{ lbmole/ft}^{3}$ (C.8)

The criteria of Tsotsis and Schmitz is satisfied for cases when the feed stream concentration is greater than 0.58 $lbmole/ft^3$. This is the case for the feed trays.

The bifurcation curve for second order reactions according to Van Den Bosch and Luss [68] is given in Figure 31. The dashed curve represents the relationship between $(\beta\gamma)(1 + \beta)$ and β for the case where γ equals 15.3. This is the value of γ for the component "A" reaction. From this it can be seen that multiplicity occurs for some Damkohler numbers when β is greater than approximately 0.55. This agrees with the criterion value from the Tsotsis and Schmitz calculations.



Figure 31 Multiplicity Criteria for a Second Order Reaction, from Van Den Bosch and Luss [68]

APPENDIX D RESULTS FOR CASE 1: ETHYL ACETATE PRODUCTION

	Temperature (C)	Liquid Flowrate (moles/min)	Reaction Rate (moles/min/liter)
1	72.6	0.208	0.00
2	72.7	0.207	0.00
3	73.4	0.205	0.00
4	73.6	0.202	0.00
5	74.6	0.196	0.00
`6	80.0	0.302	0.45e-3
7	80.2	0.301	0.47e-3
8	80.5	0.300	0.48e-3
9	80.8	0.299	0.50e-3
10	81.2	0.300	0.52e-3
11	82.3	0.301	0.64e-3
12	85.3	0.308	0.97e-3
13	92.0	0.087	8.26e-3

VAPOUR PHASE COMPOSITIONS

tray	Acetic Acid	Ethanol	Water	Ethyl Acetate
1	0.00000	0.54656	0.00876	0.42715
2	0.00000	0.62322	0.01282	0.34498
3	0.00000	0.69404	0.01770	0.27723
4	0.00001	0.74342	0.02343	0.22431
5	0.00075	0.77743	0.03003	0.18464
6	0.02288	0.78162	0.03671	0.15299
7	0.02266	0.76584	0.04499	0.16099
8	0.02266	0.74913	0.05658	0.16671
9	0.02299	0.72959	0.07309	0.17028
10	0.02406	0.70441	0.09680	0.17164
11	0.02810	0.66875	0.13057	0.17037
12	0.04801	0.61013	0.17563	0.16437
13	0.14394	0.49150	0.21855	0.14463

LIQUID PHASE COMPOSITIONS

	Acetic Acid	Ethanol	Water	Ethyl Acetate
1	0.00000	0.62822	0.01282	0.34498
2	0.00000	0.70071	0.01820	0.27037
3	0.00001	0.75521	0.02452	0.21196
4	0.00083	0.79283	0.03180	0.16809
5	0.02524	0.79752	0.03920	0.13309
6	0.18996	0.67402	0.04029	0.09270
7	0.18908	0.66120	0.04944	0.09766
8	0.18850	0.64632	0.06213	0.10106
9	0.18849	0.62735	0.07999	0.10288
10	0.19056	0.60082	0.10509	0.10287
11	0.20341	0.55776	0.13860	0.09984
12	0.26740	0.47083	0.17254	0.08913
L3	0.47028	0.30064	0.17014	0.06216

APPENDIX E:

tray	Source [74]	Steady State A	Sțeady State B
1	60.0	58.6	53.6
2	59.9	58.5	52.9
3	60.5	59.2	53.4
4	61.4	60.4	54.2
5	64.0	63.7	54.7
6	73.6	71.8	70.1
7	73.9	72.4	71.6
8	74.2	72.9	72.5
9	74.5	73.5	72.6
10	74.9	73.8	72.8
11	. 75.1	73.9	73.4
12	75.4	74.2	73.9
13	75.6	74.3	74.2
14	75.7	74.6	75.3
15	75.8	74.6	75.4
16	75.7	74.6	75.2
17	75.3	74.5	74.8
18	74.3	73.7	73.5
19	72.3	71.6	72.1
20	68.8	70.1	70.4
21	68.6	69.5	69.5
22	69.4	69.1	68.2
23	73.7	72.7	68.9
24	87.8	86.9	70.2
25	103.4	102.7	72.5
26	108.9	108.2	81.2

TEMPERATURES (C)

LIQUID PHASE MOLE FRACTIONS STEADY STATE A

tray	component A	component B	component C	component D	component E
1	0.974	0.025	0.005	0.005	0.000
2	0.976	0.024	0.002	0.007	0.000
3	0.973	0.024	0.001	0.008	0.000
4	0.937	0.016	0.001	0.052	0.000
5	0.829	0.008	0.002	0.155	0.000
, 6	0.531	0.009	0.003	0.458	0.000
7	0.530	0.012	0.009	0.452	0.000
8	0.526	0.015	0.011	0.454	0.000
9	0.515	0.014	0.011	0.459	0.000
. 10	0.507	0.010	0.019	0.462	0.0032
11	0.509	0.012	0.026	0.447	0.0033
12	0.506	0.009	0.031	0.452	0.0032
13	0.496	0.017	0.047	0.428	0.0033
14	0.487	0.020	0.064	0.423	0.0033
15	0.472	0.033	0.114	0.387	0.0032
16	• 0.423	0.051	0.146	0.381	0.0032
17	0.378	0.063	0.220	0.365	0.0031
18	0.352	0.069	0.246	0.336	0.0032
19	0.348	0.106	0.284	0.268	0.0030
20	0.342	0.254	0.216	0.192	0.0030
21	0.324	0.296	0.243	0.147	0.0028
22	0.293	0.325	0.297	0.130	0.0029
23	0.256	0.308	0.407	0.115	0.0028
24	0.071	0.164	0.683	0.092	0.0027
25	0.005	0.025	0.892	0.076	0.0028
26	0.001	0.001	0.936	0.065	0.0090

LIQUID PHASE MOLE FRACTIONS STEADY STATE B

tray	component A	component B	component C	component D	component E
1	0.101	0.895	0.008	0.002	0.000
2	0.100	0.892	0.008	0.002	0.000
3	0.110	0.883	0.009	0.001	0.000
4	0.093	0.848	0.009	0.052	0.000
5	0.058	0.765	0.012	0.168	0.000
6	0.056	0.404	0.013	0.543	0.000
7	0.053	0.405	0.011	0.549	0.000
8	0.052	0.400	0.010	0.545	0.000
9	0.046	0.413	0.013	0.544	0.000
10	0.045	0.412	0.015	0.542	0.0033
11	0.047	0.410	0.018	0.538	0.0033
12	0.045	0.416	0.021	0.548	0.0032
13	0.039	0.412	0.028	0.543	0.0032
14	0.035	0.413	0.037	0.532	0.0031
15	0.032	0.413	0.035	0.534	0.0032
16	0.032	0.414	0.041	0.051	0.0032
17	0.029	0.396	0.048	0.532	0.0033
18	0.025	0.392	0.103	0.486	0.0031
19	0.024	0.384	0.132	0.457	0.0031
20	0.024	0.356	0.183	0.442	0.0029
21	0.021	0.415	0.196	0.367	0.0028
22	0.020	0.513	0.226	0.247	0.0029
23	0.013	0.426	0.335	0.235	0.0028
24	0.009	0.337	0.504	0.148	0.0027
25	0.005	0.206	0.725	0.0,63	0.0026
26	0.001	0.183	0.756	0.062	0.0086

LIQUID PHASE MOLE FRACTIONS DATA FROM SOURCE [74]

tray	component A	component B	component C	component D	component E
1	0.978	0.018	0.005	0.0003	0.000
2	0.986	0.009	0.003	0.002	0.599e-17
3	0.983	0.007	0.003	0.007	0.139e-16
4	0.961	0.006	0.003	0.030	0.109e-14
5	0.863	0.006	0.003	0.127	0.919e-13
6	0.566	0.007	0.005	0.422	0.792e-11
7	0.561	0.009	0.009	0.422	0.112e-8
8	0.556	0.009	0.013	0.421	0.160e-6
9	0.550	0.010	0.020	0.420	0.233e-4
10	0.543	0.010	0.028	0.415	0.0034
11	0.536	0.012	0.037	0.412	0.0034
12	0.526	0.015	0.048	0.408	0.0034
13	0.515	0.018	0.060	0.404	0.0035
14	0.502	0.023	0.075	0.397	0.0035
15	0.486	-0.029	0.094	0.387	0.0035
16	0.467	0.039	0.119	0.371	0.0035
17	0.445	0.055	0.151	0.345	0.0035
18	0.418	0.085	0.193	0.300	0.0036
19	0.382	0.150	0.240	0.225	0.0037
20	0.339	0.314	0.230	0.114	0.0027
21	0.346	0.296	0.265	0.091	0.0027
22	0,299	0.300	0.322	0.077	0.0027
23	0.161	0.276	0.497	0.064	0.0028
24	0.031	0.129	0.795	0.042	0.0026
25	0.003	0.028	0.940	0.026	0.0025
26	0.0005	0.004	0.964	0.021	0.0099

REACTION RATES (lbmole/hr/ft**3)

tray	Source [74] (calculated)	Steady State A	Steady State B
1	0.0	0.0	0.0
2	-1.0e-16	0.00	0.00
3	-1.8e-16	0.00	0.00
4	-9.9e-15	0.00	0.00
5	8.4e-13	0.00	0.00
6	1.3e-9	0.00	0.00
7	2.9e-5	0.00	0.00
8	3.6e-3	0.00	0.00
9	3.6e-3	0.00	0.00
10	0.34	0.33	0.07
11	0.31	0.30	0.06
12	0.35	0.34	0.06
13	0.45	0.43	0.08
14	0.62 .	0.59	0.12
15	0.92	0.88	0.13
16	1.5	1.4	0.3
17	2.6	2.5	0.5
18	4.8	4.7	0.9
19	8.9	8.7	1.3
20	9.0	9.5	1.2
21	4.2	4.4	0.6
22	2.8	2.8	0.3
23	3.3	3.1	0.12
24	4.7	4.5	0.32
25	3.0	2.9	0.2
26	1.2	1.1	0.11