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QUANTITATIVE HEURISTIC DESIGN OF REACTIVE DISTILLATION

by
Muhammad Al-Arfaj

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(Date)

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Abstract

Reactive distillation is an important and challenging process. One of the major deficiencies in this technology is the lack of a quantitative, step-by-step design procedure. A heuristic method to design reactive distillation columns is proposed in this thesis. It is a short-cut method that couples heuristic methods with rigorous simulation. The objective of this design technique is to find an acceptable design that is close to the optimum.

The proposed design method gives initial estimates of the column pressure, the number of reactive stages, the number of rectifying stages and the number of stripping stages. An isothermal PFR simulation is used to generate curves of conversion versus temperature for various reactor holdups or catalyst loading. Heuristic rules are used to select the temperature in the reactive zone and the total holdup or catalyst loading in the reactive zone, which sets the column pressure in some cases. The number of stripping and rectifying trays are estimated from the Fenske equation. Then a rigorous reactive distillation simulator is used to calculate the reflux ratio and the heat input to the reboiler that gives the specifications of product purities.

The design heuristics were developed for two types of chemical reaction systems. The first system, Case I, is the highly exothermic reversible reactions. The second system, Case II, is the irreversible or mildly exothermic reversible reactions. Two examples were studied to generate and check those heuristics. The first example, which represents Case I, is the production of ETBE via reactive distillation. A rigorous reactive distillation program was used to find the optimum design, which was then used to generate the heuristic rules. The second example, which represents Case II, is the methyl acetate process. Eastman Chemical Company patented a

design for the production of methyl acetate by reactive distillation, which was modified to be compared with ours. The heuristic rules were applied and they yielded a design that was close to the modified Eastman design. Our method is not applicable to systems where large excess of one reactants is needed. Furthermore, it does not assess the need for a pre-reactor and the design issues associated with that type of system.

Chapter 1

Introduction

Chemical engineering has a wide range of applications that cover very diverse areas. Separation is one of the most important areas in chemical engineering. From ancient times to recent days, separation processes have been implemented in almost every chemical process. The distillation process is the most popular separation process in the chemical and petroleum industries.

Reactors are also essential parts of any chemical industry. Reactor effluents do not usually meet the specification criteria due to the presence of the unconverted materials. Therefore, it is quite common in industry to see reactors followed by a separation section with recycles. From this point of view, it is important to study and investigate the reactor/ separation/ recycle system. One aspect of studying this system is if the reactor is combined in the separation unit. This is referred to as Reactive Distillation or Catalytic Distillation.

Reactive distillation columns have been given considerable attention in terms of steady-state simulation. However, limited research has been reported in the design aspects of the reactive distillation. The objective of this project is to study the design of reactive distillation columns under no kinetic restrictions and propose a heuristic short-cut method for the design of reactive distillation columns.

Reactive distillation has several advantages over conventional reactors/ separation processes. It is especially suited for those chemical reactions where reaction equilibrium limits the conversion and the products are more and/ or less volatile than the reactants. The reaction can proceed to a much higher level of conversion by continuously separating products from reactants while the reaction is in progress. For instance, if the chemical reaction is equilibrium-limited, the conversion of the limiting reactant can be substantially increased by continual removal of the products from the reacting mixture and thus shifting the reaction from the equilibrium limit. Chemical reactions that are characterized by unfavorable reaction equilibrium, appropriate component volatilities, and significant rates of reaction at distillation temperatures are particularly good candidates for reactive distillation. There are many systems that fall in the applicability region of reactive distillation. The biggest benefit is the reduction in the capital cost. When the chemical reaction and the separation are combined in one unit, a whole unit (the reactor) will be eliminated along with the associated pumps, pipings, and instrumentation. Recycling is sometimes eliminated as well. Other benefits vary depending on the specific chemical system. For azeotropic systems, reactive distillation can sometimes avoid azeotropes and thus overcome the need of having an azeotropic distillation where the separation is difficult and expensive. When the chemical reaction has a significant heat of reaction (exothermic or endothermic), the heat of reaction causes additional mass transfer (vaporization or condensation) between the vapor and liquid phases, over and above the mass transfer occurring for distillation alone. The reaction temperature will be the bubble point of the liquid on the tray. In the case of exothermic reaction, the heat of reaction is utilized directly for the distillation heat requirements, which could reduce energy costs.

Reactions that take place in the column can be homogeneous or heterogeneous. For heterogeneous reactions, simultaneous reaction and separation can be done in several different configurations in reactive distillation. In one configuration, the solid catalyzed chemical reaction and the multistage distillation occur continuously; that is, there is spatial continuity along the length of the column. Both reaction and distillation take place on every tray. Making the reaction and the separation proceed in alternative steps could be another configuration. Here, the reactive section of a column contains both the catalyst contact device where the reaction occurs and the separation device where the reacting phases pass for the vapor/ liquid contact and separation. In both configurations, the section above the reactive section is the rectifying section and the section below reactive section is the stripping section.

Design should not be confused with simulation. Design is a "synthesis" procedure. Simulation is an "analysis" procedure. In design, we specify the state of the feeds to a system together with targets for the product streams (e.g. desired purities of selected components) and the goal is to find equipment sizes and configurations, together with operating conditions that will do the job economically. The biggest difficulty encountered in design is identifying feasible equipment configuration and ranges of operating conditions that are capable of meeting the desired process goals. For complex systems, such as reactive distillation columns, this is a non-trivial problem.

On the other hand, simulation is the complement of design. In simulation, we specify the state of the feeds, the values of all equipment parameters (number of trays) and the values for all independent design variables such as product purities and pressure. Then we calculate the values of the remaining dependent variables: reflux ratios, heat inputs, etc. Design, therefore, is the activity that logically takes place before simulation; the two are complementary in a natural way.

There are many degrees of freedom that one should consider in the design stage of conventional or reactive distillation. Reactive distillation has more degrees of freedom than conventional distillation. In conventional distillation, the system is completely defined when five degrees of freedom are specified: the column pressure, the total number of trays, the feed tray location, the reflux ratio and the heat input to the reboiler. On the other hand, reactive distillation has an additional degree of freedom which is the amount of catalyst (or the liquid holdup).

In this project, we have developed a heuristic short-cut method to obtain an approximate design of reactive distillation columns. The procedure is offered in the same spirit as the "short-cut" method for conventional distillation design. It should yield a design that is close to the optimum and can be used as a good starting point for rigorous simulation optimization.

Chapter 2

Literature Review

The reactive distillation process has been studied for a long time. Most of the studies and the papers that have been published concentrate mainly on steady-state simulation of the process. Increasing interest in reactive distillation has motivated research on other important aspects of this process such as design, dynamic behavior and control strategies. Unfortunately, until now there is a deficiency in the open literature about the design, dynamics and control of this process.

2.1 Steady-State Simulation

Reactive distillation models are extensions of the models of conventional distillation columns. Distillation column models traditionally use equilibrium-based models, which are known as MESH (Material balance, vapor-liquid Equilibria equations, mole fraction Summations, and Heat balance). However, recently non-equilibrium (or rate-based) models have also been explored. Rate-based models, which are known as MERQ (Material balance, Energy balance, Rate equations for mass transfer, and eQuilibrium at the vapor-liquid interface), have been implemented by some researchers. Although MERQ models can more accurately capture the actual behavior of distillation columns, they are more complex and require the estimation of more empirical parameters (some of which may be difficult to obtain) [46]. Generally speaking, both MESH models and MERQ models can be extended to account for chemical reaction in distillation columns. However, most of the work in the literature is based on the MESH models. In our study, a modified MESH model that accounts for reaction is used. Hence the literature review will concentrate on the works that use the modified MESH models.

The first attempt to solve a reactive distillation system numerically was done by Suzuki *et al.* [41]. Simandl and Svrcek [34] as well as Chang and Seader [38] summarized the steady state solving methods and the principal contributors in that area.

2.2 Reactive Distillation Design

Design of reactive distillation columns has not been extensively investigated despite its practical importance in industry. No general quantitative design procedure for reactive distillation has been published. This is a major deficiency in reactive distillation technology. Our main goal in this research is to establish the framework for a heuristic method to design this important process.

While it has been relatively easy to extend *solving* methods developed for conventional distillation columns to reactive distillation columns, it has not been an easy task to extend conventional distillation column *design* techniques to reactive distillation columns. There are several reasons for this. In conventional distillation design, the major design variables are the number of trays in the column, the feed tray location, the operating pressure and the reflux ratio. Tray holdup has no effect on steady-state design. In contrast, in a reactive distillation column, one cannot assume that the holdup volume (or the catalyst load for heterogeneous reactions) is a minor parameter. Furthermore, one cannot assume a constant molar overflow unless the reaction is thermally neutral and stoichiometrically balanced. Also, one cannot assume that the column has a single feed, since an economically optimal reactive distillation column usually features distributed feeds. Column pressure is more critical in reactive distillation than it is in conventional columns due to the direct effect of pressure on column temperature in the reactive zone. Temperature affects both kinetics (reaction rates) and thermodynamics (chemical equilibrium). Thus pressure selection has a major impact on conversion, yield and the amount of catalyst (or liquid holdup) required.

The reactive distillation process can sometimes be simplified for the sake of obtaining some working techniques that can be applied if the simplification criteria are met. One of the simplifying assumptions is that the chemical reaction is always at equilibrium. Doherty and co-workers have made pioneering contributions to the analysis and design of the reactive distillation. Barbosa and Doherty ([13], [14], [20]) developed a thermodynamically based approach for analyzing equilibrium limited, thermally neutral (heat of reaction is ignored) reactive distillation systems. This work employed a novel composition coordinate system to transform the problem into a form completely analogous to nonreactive distillation. Using residue curve techniques, they were able to rapidly screen for reactive azeotropes and feasible designs, and to compute the number of trays and the minimum reflux ratio. Doherty and Buzad ([31], [9]) outlined how kinetic effects can be included in this analysis, when the residence time is fixed. In this approach several design parameters, such as the column pressure, Damkohler number and boil up ratio have to be selected in order to get a design. They do not discussed how to select those parameters in order to get a good design. Therefore, this work is an analysis method, not a design method. Ung and Doherty [12] studied the synthesis and feasibility of simple reactive distillation columns containing multiple equilibrium reactions. Recently, Okasinski and Doherty [8] improved the work done by Buzad and Doherty to include the VLE nonideality and the heat of reaction; however their work was analysis, not a design procedure.

Subawalla and Fair [26] have recently made significant contributions to the design of reactive distillation. In their work, they have done a good job in analyzing different design parameters and developing some intuitive guidelines. However, their method is not really a quantitative step-by-step short-cut procedure. They used their method to design a Tert-Amyl Methyl Ether (TAME) process where they end up having a pre-reactor and a reactive distillation column and must feed a large excess of one of the reactants (See Section 7.2).

A general programming method was proposed by Ciric and Gu [7]. In their work, a mixed integer nonlinear programming (MINLP) approach was used to synthesize an optimum reactive distillation column. The MINLP minimizes the total annual cost subject to a MESH model. The solution of this MINLP yields the optimal number of trays, the tray holdups, the feed tray locations, and their feed distribution. The example they considered was the production of ethylene glycol, which yielded a reactive stripper with product removed from the bottom. Although the work was rigorous in terms of the optimization scheme, their results had some practical limitations. The first is the impractical liquid holdups on the reactive stages (42.4 inches). This liquid depth would cause pressure drop problems if implemented. Secondly, the pressure was selected arbitrarily instead of being part of the optimization. Pressure selection should be part of the design process. The thermodynamic and kinetic model that they used in their single example was very simple model, which may not represent the actual system.

Agreda *et al.* ([30], [53]) discussed the use of reactive distillation to produce high purity methyl acetate. In their work they did not design the column based on a design technique but they used an experimental scale-up procedure. In the procedure they started with a bench-scale experiment. After experiments showed promising results, they progressed to a pilot plant that verified the suitability of reactive distillation to produce methyl acetate. They also used a simulator to study the process. Although this procedure will produce the desired product because it goes through all the scale-up tests, the design that they come up with may not be the optimal design. The other backdraw of their work is that it is time, money, and manpower demanding.

Under certain reactive distillation column configurations, multiple steady-states could be observed. Miao and Ciric [6] studied the multiple steady-state behavior in ethylene glycol system. Multiplicities in MTBE reactive distillation was investigated by Hauan *et al.* [49], Nijhuis *et al.* [50] and recently by Guttinger and Morari [37].

Few papers discussed the dynamics and control aspects of reactive distillation. Alejski and Duprat [35] investigated the hydraulic effects in the dynamic behavior of ethyl acetate reactive distillation. Sneesby *et al.* [47] studied the dynamics of the

ETBE reactive system. Scenna *et al.* [36] discussed the dynamics of three reactive systems. Kumar [19] discussed the dynamic behavior and some control aspects of ethylene glycol reactive distillation. The development of effective control structures for reactive distillation columns remains an open area of research.

Chapter 3

Mathematical Models and Numerical Methods

As discussed in Section 2.1, there is more than one way to model steady-state reactive distillation columns and also there is more than one way to solve that model numerically. In this chapter, some of the mathematical models and the way they were solved are discussed. Several other mathematical models, such as the vapor-liquid equilibrium (VLE) model, the Equation Of State (EOS) model, and some numerical methods, such as the Muller method, the Wang-Henke method, and the Newton-Raphson method, were used and can be found in Appendices A and B.

3.1 Isothermal Plug-Flow Reactor (I-PFR) Model

In an I-PFR the reactants are continually consumed as they flow down the length of the reactor at constant temperature. In modeling the I-PFR, we assume that the concentration varies continuously in the axial direction through the reactor at fixed temperature. Consequently, the reaction rate, which is a function of temperature and concentration for all but zero-order reactions, will also vary axially. For I-PFR only mole balance equations are considered. The general mole balance equation is given by:

$$F_{i0} - F_i + \int^V r_i \, dV = \frac{dN_i}{dt} \tag{3.1}$$

where F_{i0}, F_i, r_i and $\frac{dN_i}{dt}$ are the input molar flowrate, the output molar flowrate, the reaction rate, and the molar accumulation, respectively of component i. To develop the PFR design equation we shall divide (conceptually) the reactor into a number of subvolumes so that within each subvolume ΔV, the reaction rate may be considered spatially uniform (See Fig. 3.1). Let $F_i(z)$ represent the molar flow rate of species i into volume ΔV at z and $F_i(z + \Delta z)$ the molar flow of species i out of the volume at the location $(z + \Delta z)$. In spatially uniform subvolume ΔV,

$$\int^{\Delta V} r_i dV = r_i \Delta V \tag{3.2}$$

For a steady-state PFR, Eq. 3.1 becomes

$$F_i(z) - F_i(z + \Delta z) + r_i \Delta V = 0 \tag{3.3}$$

Rearranging Eq. 3.3, simplifying it and taking the limit give:

$$\frac{dF_i}{dV} = r_i \tag{3.4}$$

If we define the conversion of component i to be:

$$X_i = 1 - \frac{Fi}{F_i^{in}} \tag{3.5}$$

where F_i^{in} is the molar feed flow rate of component i, then Eq. 3.4 becomes:

$$\frac{dX_i}{dV} = -\frac{r_i}{F_i^{in}} \tag{3.6}$$

3.2 Reactive Distillation Model

The reactive distillation MESH equations are very similar to conventional distillation MESH equations. The main difference is the addition of the reaction rate term in the total material balance and component material balance as well as the addition of the heat of reaction to total heat balance. Figure 3.2 sketches the reactive equilibrium tray. The reactive MESH equation are:

Total material balance

Total condenser

$$V_{NT} = D(1+RR) \tag{3.7}$$

Tray j

$$V_{j-1} + L_{j+1} + F_j + \sum_i r_{i,j} = (L_j + U_j) + (V_j + W_j) \tag{3.8}$$

Reboiler

$$L_1 = B + V_B \tag{3.9}$$

Component material balance (Component i)

Total condenser

$$V_{NT}\, y_{i,NT} = D(1+RR)x_{i,D} \tag{3.10}$$

Tray j

$$V_{j-1}y_{i,j-1} + L_{j+1}x_{i,j+1} + F_{i,j} + r_{i,j} = (L_j + U_j)x_{i,j} + (V_j + W_j)y_{i,j} \tag{3.11}$$

Reboiler

$$L_1 x_{i,1} = Bx_{i,B} + V_B\, y_{i,B} \tag{3.12}$$

Total energy balance

Total condenser

$$V_{NT}\, H_{NT} = D(1+RR)\, h_D + Q_D \tag{3.13}$$

Tray j

$$V_{j-1}H_{j-1} + L_{j+1}h_{j+1} + F_j H_j^F + Q_j + \sum_i r_{i,j}\, H_j^R = (L_j + U_j)\, h_j + (V_j + W_j)\, H_j \tag{3.14}$$

Reboiler

$$L_1 h_1 + Q_B = B\, h_B + V_B\, H_B \tag{3.15}$$

Vapor Liquid Equilibrium equation

$$y_{i,j} = K_{i,j}\, x_{i,j} = \frac{\gamma_{i,j}\, P_{i,j}^{vap}}{P}\, x_{i,j} \tag{3.16}$$

Summation equation

$$\sum_i y_{i,j} = 1.0 \tag{3.17}$$

$$\sum_i x_{i,j} = 1.0 \tag{3.18}$$

where,

L_j = liquid flowrate of tray j
V_j = vapor flowrate of tray j
F_j = feed flowrate to tray j
U_j = liquid side stream flowrate of tray j
W_j = vapor side stream flow rate of tray j
$x_{i,j}$ = liquid mole fraction of component i in tray j
$y_{i,j}$ = vapor mole fraction of component i in tray j
$x_{F,i}$ = feed mole fraction of component i in tray j
h_j = liquid enthalpy of tray j
H_j = vapor enthalpy of tray j
H^F = feed enthalpy
Q_j = side heating or cooling rate of tray j
$\gamma_{i,j}$ = activity coefficient of component i in tray j
$P_{i,j}^{vap}$ = vapor pressure of component i in tray j
P = total pressure
$r_{i,j}$ = reaction rate of component i in tray j
H_j^R = heat of reaction in tray j

3.3 Kinetic Model

The kinetic models used in reactive distillation vary from system to system depending on the reaction(s) that is taking place. A classical kinetic model is given here for illustration purposes. Assume the following reaction is taking place:

$$A + B \leftrightharpoons C + D \tag{3.19}$$

where the volatilities are the following: $\alpha_C > \alpha_A > \alpha_B > \alpha_D$. The typical model for such a reaction is:

$$r_i = \nu_i \cdot M_{cat} \cdot k \cdot \left[a_A \cdot a_B - \frac{a_C \cdot a_D}{K_{eq}} \right] \tag{3.20}$$

where

$\nu_A = \nu_B = -1$
$\nu_C = \nu_D = 1$
$a_i = \gamma_i \cdot x_i$
$x_i =$ Mole fraction of component i
$\gamma_i =$ Activity coefficient of component i
$M_{cat} =$ Mass of catalyst (g)
$k =$ Reaction constant $\left(\frac{mole}{Hr \cdot g}\right)$
$K_{eq} =$ Equilibrium constant $= f(T)$

3.4 Economic Model

There are several economic models that can be used in order to assess the profitability of a process. The Rate of Return on Investment (RRI) is often used. The RRI is defined as:

$$RRI = \frac{Income - Expenses}{Capital\,Investment} \tag{3.21}$$

In reactive distillation the RRI becomes:

$$RRI = \frac{Value\,of\,products\,(\$/year) - Cost\,of\,Raw\,Materials\,(\$/year) - Total\,Annual\,Cost\,(\$/year)}{Capital\,Investment\,(\$)} \tag{3.22}$$

Total Annual Cost (TAC) is defined as:

$$TAC = SC + CWC + Other\ annual\ expenses + \frac{Capital\,Investment}{Payback\,Period} \tag{3.23}$$

where SC is the steam cost, CWC is the cooling water cost which could be ignored compare to other costs. The *Other anual expenses* is the catalyst cost if assumed to be replaced manually and the raw material cost. The capital investment is defined as:

$$Capital\,Investment = Column\,cost + Trays\,cost + Heat\,Exchangers\,cost \tag{3.24}$$

The capital costs of the column, trays, and heat exchangers are estimated using correlations given by Douglas [23] and updated using Marshall and Swift index of 1997 as follows:

$$\begin{aligned} Column\,cost &= 24920.4 D_c^{1.066} L_c^{0.802} && (3.25) \\ Tray\,cost &= 989.78\, D_c^{1.55} L_c && (3.26) \\ Heat\,Exchangers\,cost &= 13828.13\, \left(A_r^{0.65} + A_c^{0.65}\right) && (3.27) \end{aligned}$$

where the units are in meters. Total Annual Cost could be used for different designs with a fixed production rate to obtain the optimum design which is the one yields the minimum TAC.

The terms involved in the application of the RRI equation were calculated from the following set of assumptions and guidelines:

1. For the calculation of column diameter, an F factor of 1.22 (=1 in engineering units) was assumed. The flooding velocity can be calculated from $F = V_{flood}\sqrt{\rho_V}$.The vapor density was calculated using the average molecule weight and the temperature of the tray that has the largest vapor flow rate. The diameter of the column can then be calculated from Wankat [21]:

$$D_c(m) = 6.26 \times 10^{-3}\ [V\ (mole/Hr)]^{0.5} \left[\frac{T\ (K)\ M_w}{P\ (Pa)}\right]^{0.25} \qquad (3.28)$$

2. The column height can be calculated by assuming a 0.6-m (=2ft) tray spacing and allowing 20% more for column base height: $L_c = 2.4 N_T$.

3. Reboiler area, A_r, was calculated assuming an overall heat transfer coefficient $U = 2044 KJ/(Hr\,K\,m^2)$=$100\,Btu/\,(Hr\,F\,ft^2)$ and a log mean temperature difference of $28^0C\,(=\,50^0F)$. Condenser area, A_c, was calculated using an overall heat transfer coefficient $U = 3066 KJ/(Hr\,K\,m^2)$=$150\,Btu/\,(Hr\,F\,ft^2)$ and a log mean temperature difference of $11^0C\,(=20^0F)$.

4. Energy costs were calculated at a rate of $\$4.74/10^6 KJ$ $(= \$5/10^6 Btu)$ when purchased and at a rate of $\$2.84/10^6$ $(= \$3/10^6 Btu)$ when sold.

5. Cooling water was assumed to be \$264/1000 m^3 (=\$0.1/1000 gal).
6. Stainless steel was assumed to be the material of construction.
7. The plant was assumed to operate for 8160 hrs/year.
8. A 3 year payback period was assumed.

3.5 Distillation Homotopy Continuation Method (DHCM)

The reactive distillation model presented in Section 3.2 is nonlinear and may have multiple solutions. Some of these solutions can be identified with homotopic continuation methods.

A linear homotopy is constructed from two vector functions and a parameter:

$$\mathbf{H}(\mathbf{x}, \alpha) = \alpha \mathbf{f}(\mathbf{x}) + (1 - \alpha)\mathbf{g}(\mathbf{x}) = 0 \tag{3.29}$$

Here, $\mathbf{f}(\mathbf{x})$ is the original nonlinear vector function with one or more roots, $\mathbf{g}(\mathbf{x})$ =0 is a simpler vector function with one unique root, and α is the homotopy parameter. When $\alpha = 0$, the solution of the homotopy lies at the unique root of $\mathbf{g}(\mathbf{x})$ =0. Solutions of $\mathbf{f}(\mathbf{x}) = 0$ correspond to solutions of the homotopy when $\alpha = 1$. Consequently, there is a path between the unique solution of $\mathbf{g}(\mathbf{x})$ =0 and solutions of $\mathbf{f}(\mathbf{x}) = 0$.

All solutions to the homotopy equation $\mathbf{H}(\mathbf{x}, \alpha) = 0$ define a homotopy curve in $(\mathbf{x}, \alpha)$ space. Multiple solutions of the equation $\mathbf{f}(\mathbf{x}) = 0$ are detected when the homotopy curve turns back upon itself and crosses the line $\alpha = 1$ more than once. Differential arc-length continuation methods are commonly used to track a homotopy curve. This approach differentiates the algebraic homotopy equations with respect to an arc length yielding a set of partial differential equations. Integrating these equations gives the homotopy curve.

The DHCM can be used to reach the solution of the complex column starting from a simple column. The desired complex column solution does not necessarily have more than one solution. Therefore, the distillation homotopy continuation method can be used either to find the multiple steady-state solutions or to reach a difficult-to-reach solution. This method was used in a three step procedure:

1. Reaching a non-ideal distillation column from an ideal distillation column.

2. Reaching a reactive distillation column from a non-ideal distillation column.

3. Meeting the product specifications.

To reach the reactive distillation column from a non-reactive distillation column, the vector function $\mathbf{f}(\mathbf{x})$ is set equal to the full reactive distillation model given in Section 3.2. The simpler vector function $\mathbf{g}(\mathbf{x})$ is taken as the model of the non-reactive distillation column given in Appendix A.3. Both models must have the same specifications. The continuation parameter, α, changes from 0 (the non-reactive model) to 1 (the full reactive model). α is applied to the reaction rate term in the reactive distillation model. Therefore, Eqs. 3.8, 3.11 and 3.14 are changed to:

$$V_{j-1} + L_{j+1} + F_j + \alpha \sum_i r_{i,j} = (L_j + U_j) + (V_j + W_j) \tag{3.30}$$

$$V_{j-1} y_{i,j-1} + L_{j+1} x_{i,j+1} + F_{i,j} + \alpha\, r_{i,j} = (L_j + U_j) x_{i,j} + (V_j + W_j) y_{i,j} \tag{3.31}$$

$$V_{j-1} H_{j-1} + L_{j+1} h_{j+1} + F_j H_j^F + Q_j + \alpha \sum_i r_{i,j}\, H_j^R = (L_j + U_j)\, h_j + (V_j + W_j)\, H_j \tag{3.32}$$

Eqs. 3.30, 3.31 and 3.32 together with the rest of the equations in Section 3.2 form the vector function $\mathbf{f}(\mathbf{x})$, while $\mathbf{g}(\mathbf{x})$ are those listed in section A.3.

This homotopy was chosen over a Newton homotopy or a fixed-point homotopy because it provides physically significant information everywhere along the homotopy path. It should be noted that one cannot guarantee that this homotopy will generate all solutions to the desired system, or that "isolas" (where a solution to the system is isolated from the continuous path solution) do not exist.

3.6 The Combined Method

The actual algorithm that was implemented in our research utilizes a combination of numerical methods. Given the fixed parameters (the pressure, the stripping trays, the rectifying trays, and the reactive trays) the algorithm implements the following procedure

1. SOLVE an ideal distillation column by the Wang-Henke method with the distillate flowrate and the reflux ratio fixed.
2. USE the ideal solution as initial conditions and solve a non-ideal column by the Wang-Henke method.
3. USING the non-ideal solution, use DHCM to move to a full reactive distillation column with the distillate flowrate and the reflux ratio fixed.
4. REFORM the functions by specifying $x_{D,HK}$ and $x_{B,LK}$ and use DHCM to find the required distillate flowrate and reflux ratio.

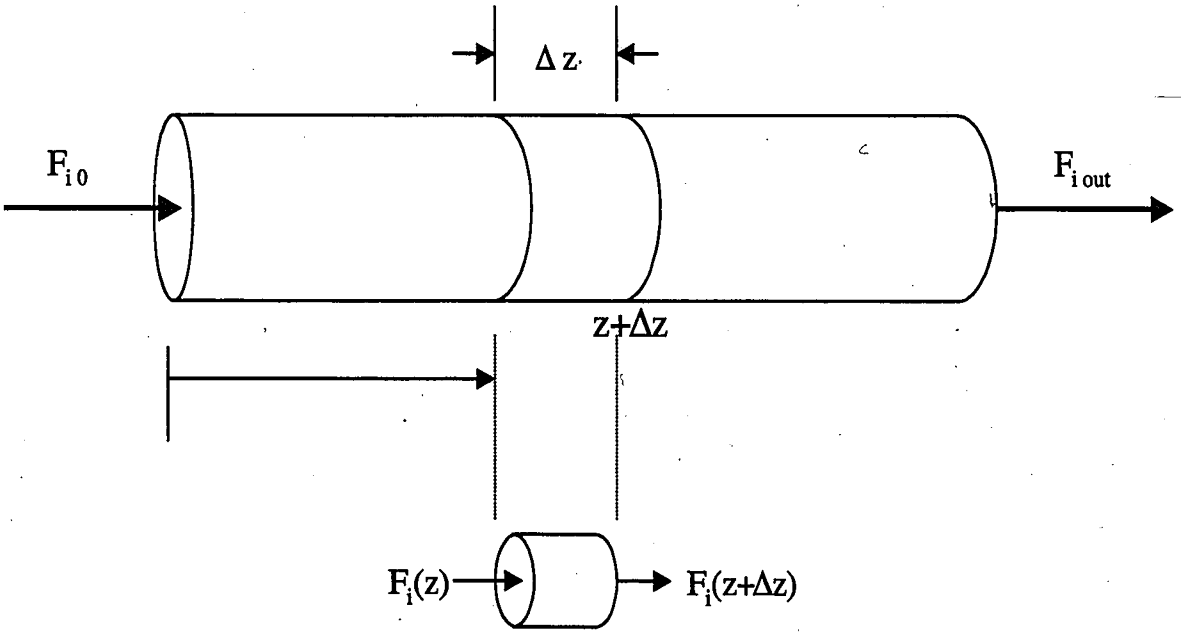

Figure 3.1: Plug- Flow Reactor (PFR)

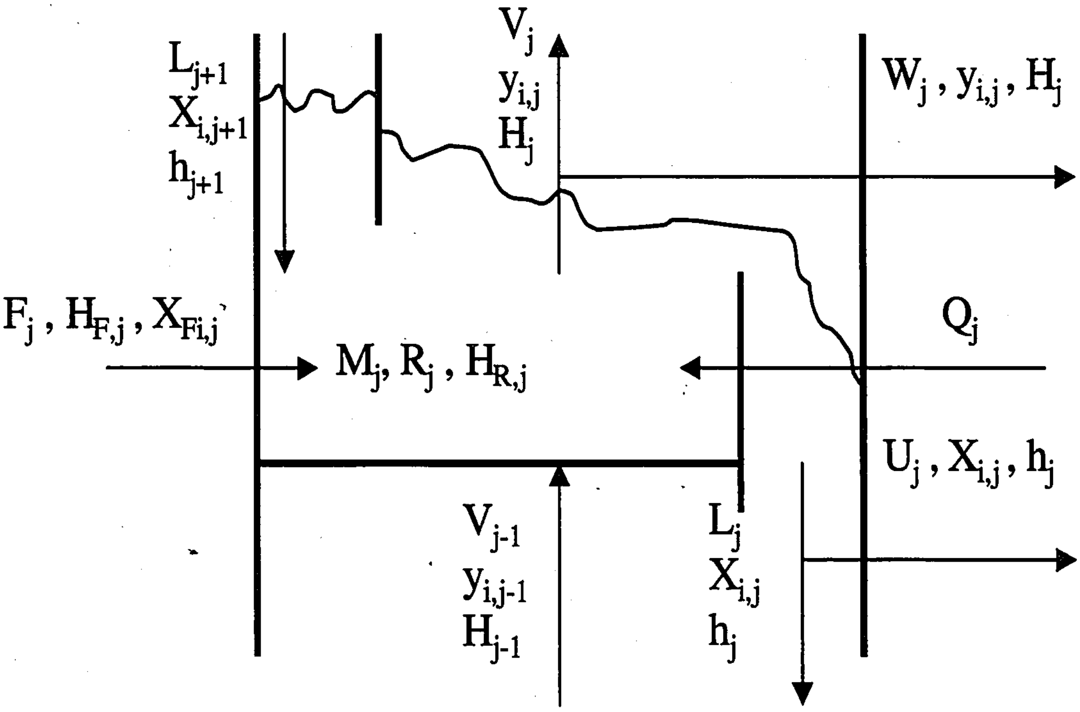

Figure 3.2: Reactive Equilibrium Tray

Chapter 4

Reactive Distillation Heuristic Design Technique

4.1 Introduction

One of the major deficiencies in reactive distillation technology is the lack of a quantitative, step-by-step design procedure. Our main goal is to develop this type of design methodology for this important process. Our technique couples heuristic methods with rigorous simulation. The method should give a rough estimate of the design parameters: pressure, reactive trays, rectifying trays, and stripping trays. Existing methods rely on experimental testing and iterative simulation studies. Our technique can lead the designer to an area close to the optimum design. Obtaining the optimum design is much more difficult task and cannot be achieved without a fully rigorous optimization simulation. It is very important to emphasize that this method is not meant to give the final design but to give a reasonable design.

This method is offered based on the limited data available in the literature for reactive distillation systems, which is due to the proprietary nature of the data. Therefore, this method needs refinement by applying it to different systems to obtain better heuristic parameters. We offer a practical framework to approach the problem of the design of reactive distillation. The basic tools needed are:

1. A small program to simulate an isothermal plug-flow reactor.
2. The chemical kinetics for the specific reactions and the VLE data.

With our heuristic design method, one can easily find the following:

1. An initial estimate of the total pressure of the column.
2. Number of reactive trays.
3. Number of stripping trays.
4. Number of rectifying trays.

Our method, however, does not give the reflux ratio needed and the heat input to the reboiler. These are determined later by using a rigorous reactive distillation simulator. In addition, our method does not currently handle the cases where a large excess of one reactant is essential and it does not address the need for a pre-reactor.

We classify reactive distillation systems into two cases (which we will refer to as Case I and Case II) based on the chemical reaction taking place:

1. Highly exothermic reversible reactions. $[K_{eq} = f(T)]$
2. Mildly exothermic and the irreversible reactions. $[K_{eq} \neq f(T)]$

4.2 Conventional versus Reactive Design

Short-cut, heuristic design of a conventional distillation column is very well known and understood. In conventional distillation, the operating pressure is usually set such that we can use cooling water in the condenser or that a maximum temperature is not violated in the reboiler. Other design parameters such as total number of trays and reflux ratio are found using short-cut methods such as the Fenske equation, the Underwood equations and the Gilliland correlation. The feed is introduced on the tray that minimizes energy consumption. Tray holdup is not a design parameter in conventional columns.

Unfortunately, short-cut methods are not available for reactive distillation. The interaction between the chemical reaction and the physical separation makes it hard to come up with simple short-cut methods. For example, column pressure is more critical in reactive distillation than in conventional distillation. Pressure affects the temperatures inside the column and therefore affects the reaction rate and the reaction equilibrium constant for reversible reactions. Pressure also affects the relative volatilities. It appears that reactive distillation is more sensitive to the operating pressure than to the design configuration, i.e., the number of stripping, rectifying and reactive trays. This makes the selection of the pressure more important than the other design parameters. This sensitivity to pressure is illustrated in the ETBE example discussed later in Chapter 5.

While tray holdup was not a design parameter in conventional column, it is a crucial design parameter in reactive columns. A large liquid holdup (or a large amount of catalyst) requires many reactive stages. Too little holdup may result in the reaction not attaining the required conversion.

Placement of the reactive zone inside the column is another parameter that is not present in conventional systems. The chemical reaction depends on the temperature and the concentration of the components. Therefore, it is important to place the reactive zone in the optimal location that produces high conversion and gives the desired product purities.

4.3 Conversion-Temperature Diagram (CTD)

The CTD is a diagram that shows how the conversion in an isothermal PFR changes with respect to the temperature of the reaction at a fixed amount of catalyst or volume holdup. The CTD varies in its behavior depending how exothermic or endothermic the reaction is and whether the reaction is reversible or irreversible. Depending on the nature of the reaction, the CTD can lead directly or indirectly to the holdup or catalyst load needed in the reactive zone.

CTD is generated using the isothermal PFR as follows:

1. Pack the PFR with certain catalyst load (or specify a fixed volume).
2. Assume a temperature and obtain the corresponding conversion.
3. Vary the temperature and get the corresponding conversion.
4. Plot the conversion profile over the selected temperature range at a fixed catalyst load (or volume).
5. Change the catalyst load (or volume holdup) and repeat the procedure.

For Case I, where the reaction is reversible and exothermic, the conversion will reach a maximum as the temperature changes for a fixed amount of catalyst load due to the inverse effect of temperature on the equilibrium constant. Plotting the same profile for different amount of catalyst load will yield different maxima. Connecting those maxima will give a curve of the maximum conversion at each temperature but under different catalyst loads. As illustrated in Fig. 4.1, for a given amount of catalyst or liquid holdup, conversion is low at low temperatures. Increasing temperature, increases conversion until the equilibrium constraint is reached. Further increases in temperatures result in a decrease in conversion. For a given temperature, increasing the amount of catalyst or holdup gives an increase in conversion (unless the equilibrium constraint has been reached).

For mildly exothermic reactions and irreversible reactions, the maximum conversion curve at high temperature will be almost flat due to the absence of equilibrium limitations at higher temperatures. For endothermic reversible reactions, conversion increases as temperature increases because the equilibrium constant increases with temperature. Irreversible reactions and endothermic reactions go to completion as temperature increases. Figure 4.2 shows a schematic sketch of such reactions.

4.4 Design Heuristics for Case I

4.4.1 The Column Pressure

In Case I, as pressure increases, temperature increases, reaction rate increases and less catalyst is needed. On the other hand, as temperature increases the equilibrium constant decreases. Therefore, in this case setting the pressure to achieve the needed temperature in the reactive zone may be more important than being able to use cooling water in the condenser. We propose the following procedure to select the operating pressure:

Step 1: From 80-85 % of the maximum conversion in the CTD, get the catalyst load or the volume holdup needed and the reactor temperature (T_R). The catalyst load or the volume holdup is the minimum amount needed in the reactive zone. See Step 4 below.

Step 2: Run the isothermal PFR under the conditions found in Step 1 and obtain the reactor effluent liquid mole fraction x_{PFR}.

Step 3: Select the initial column pressure to be equal to the bubble point pressure of a liquid with mole fraction x_{PFR} at the reactor temperature (T_R) found in Step 1.

4.4.2 The Reactive Zone

To design the reactive zone for this case, follow those steps:

Step 4: Set the amount of catalyst or holdup volume equal to 7 times the minimum required found in Step 1.

Step 5: Estimate the vapor flowrate to be around double the total feed flowrate. This factor may change depending on the relative volatilities in the system. Using an F factor of 1.22 (unity in engineering units) and assuming ideal gas, estimate the column diameter using Eq. 3.28

Step 6: From the catalyst density and assuming a height of catalyst or liquid on trays around 7.5 centimeters and using 70-80% of the column cross sectional area, calculate the catalyst per tray. Then calculate the total number of reactive trays, N_{rxn}.

4.4.3 The Separation Zones

Designing the separation zones uses the heuristic design method for the conventional distillation. The Fenske equation is used to determine the minimum number of trays in both the rectifying and the stripping sections. The recommended number of trays is twice the minimum number of trays.

The critical factors are how to determine the relative volatilities in both sections and how to estimate the compositions at the top and the bottom of reactive zone. The compositions of key components at the bottom of the rectifying section and at the top of the stripping section are taken to be the pseudo liquid compositions leaving the PFR. These are used because they provide a conservative estimate of the number of trays. The material leaving the PFR is essentially at chemical equilibrium, so the mixture contains both reactants and products. In a reactive distillation column, there should be lower concentrations of reactants. Thus the separation requirements in reactive column should be less than those used in this procedure. This gives a conservative estimate of the number of trays.

A typical reactive distillation is sketched in Fig. 4.3 where the following reaction is taking place:

$$A + B \rightleftharpoons C + D \tag{4.1}$$

and the volatilities are as follows: $\alpha_C > \alpha_A > \alpha_B > \alpha_D$. The light reactant (A) is introduced in the bottom of the reactive zone while the heavier reactant (B) is introduced in the top of reactive zone and the light product is collected in the top whereas the heavier one is collected in the bottom. In reactive distillation, the light reactant will be almost completely reacted as it goes up through the reactive zone; therefore, the heavy reactant is typically the heavy-key component in the top of the reactive zone. Therefore, for the rectifying section, the key components are typically the light reaction product and the heavy reactant. The same analogy is also valid for the heavy reactant and thus the light-key component in the bottom of the reactive zone is the light reactant. The key components in the stripping section are typically the heavy reaction product and the light reactant. However, there could some special cases where this analysis does not apply, for example, when the light reactant feed contains large amounts of inert. In this case the inert and the heavy reaction product are the key components. The presence of azeotropes could also lead to different key components.

The Fenske equation estimates the minimum number of trays needed to achieve a certain separation between two key components. It is important to note that the key components to be separated in the rectifying zone need not to be the same as those in the stripping zone. The following guidelines are the design procedure for the separation zones:

Step 7: From the liquid mole fractions x_{PFR} calculate the pseudo binary mole fractions at the bottom of the rectifying section for the two key components needed to be separated in the rectifying zone.

Step 8: Using the VLE for the two binary key components at a fixed pressure equivalent to the design pressure found in Step 3, calculate relative volatilities at the two ends of the rectifying section. At the top of the rectifying section use the distillate product specifications to determine the pseudo binary components.

Step 9: Use a geometric average relative volatility and the pseudo mole fractions in the Fenske equation to calculate the minimum number of trays needed in the rectifying zone. Set the total number of trays in the rectifying zone at twice the minimum.

Step 10: Repeat Steps 7, 8, and 9 to determine the number of stripping trays. Use the liquid mole fractions x_{PFR} and the bottom product specifications to find the pseudo binary compositions for the two key components in the stripping zone.

4.4.4 Finishing Touches and Concerns

Upon the completion of the heuristic design, the design is finalized by using a rigorous reactive distillation simulator to find the required reflux ratio and heat input to the reboiler to meet the product specifications. From the rigorous simulation one can also find the value of the economic function used as an objective function to be maximized or minimized. Then with trays fixed, the final column pressure is found by running few simulations at different pressures around the initial one found in Step 3. The optimum pressure is the one produces an optimum economic function (maximum RRI or minimum TAC).

There are two points that are worth mentioning at this point;

1. The procedure we outlined in selecting the pressure could lead to using refrigeration in the condenser. This may be justified if conversion is extremely important. However, in most cases this is not justified because the required catalyst load or volume holdup becomes large due to the low temperatures inside the column.

2. If the catalyst is very expensive, the number of reactive trays can be reduced. However, this reduction in catalytic trays will result in lower conversion and its associated economic penalty.

4.5 Design Heuristics for Case II

4.5.1 The Column Pressure

In Case II, the pressure cannot be selected as in Case I because the chemical equilibrium (if it exists) does not limit the pressure from being high. The upper pressure limit is set such that a maximum temperature in the reboiler is not violated or based on heat source limitations. The higher the pressure, the higher the temperature and the less catalyst needed. If the catalyst is expensive, a higher pressure could be used to reduce the amount of catalyst. There is a lower limit on column pressure.

This lower pressure limit is set by the use of cooling water in the condenser which requires a reflux drum temperature around 330K (57°C).

Step 1: Unless the catalyst is very expensive, set the initial column pressure at the lower limit pressure.

4.5.2 The Reactive Zone

For Case II, it is more difficult to get the reactor temperature due to the flatness of the maximum conversion curve in the CTD. Therefore, another approach is proposed to design the reactive zone.

Step 2: Find the set of T_R and the catalyst loads (or volume holdups) where the equilibrium bubble point pressure of the PFR effluent liquid mole fraction x_{PFR} is equal to the column pressure found in Step 1. At each T_R, find the ratio of the conversion achieved at the catalyst load found to the maximum achievable conversion (Conv/Conv$_{max}$). Plot T_R and catalyst loads (or volume holdups) for each Conv/Conv$_{max}$ and generate Modified CTD (MCTD). A general sketch of MCTD is shown in Fig. 4.4. Using the MCTD and a conversion ratio around 93%, find the catalyst load or volume holdup (minimum required) and the reactor temperature (T_R).

Step 3: Run the isothermal PFR under the conditions found in Step 1 and obtain the reactor effluent liquid mole fraction x_{PFR}.

Step 4: Follow step 4 to 6 from Case I.

4.5.3 The Separation Zones

Follow Case I design steps 7-11 discussed in Section 4.4.3.

4.5.4 Finishing Touches and Concerns

As in Case I, the design is finalized by using a rigorous reactive distillation simulator to find the required reflux ratio and heat input to the reboiler to meet the product specifications as well as the value of the economic function.

4.6 Concluding Remarks

In this chapter, our purposed quantitative heuristic design method was introduced. This design method has been tested in several reactive systems and it produced satisfactory designs that are close to the optimum. However, we are not claiming that our method is going to work well in each and every reactive distillation system. It could be true that the basic approach is a global method but as of now we cannot guarantee it. More testing is required. The method has the potential to save time and money. Further studies might suggest more cases and more heuristics.

The other point that should be emphasized is that this method is not meant to be a rigorous method or a method to produce the optimum design. However, it is a heuristic method that should put the designer close to the optimum design.

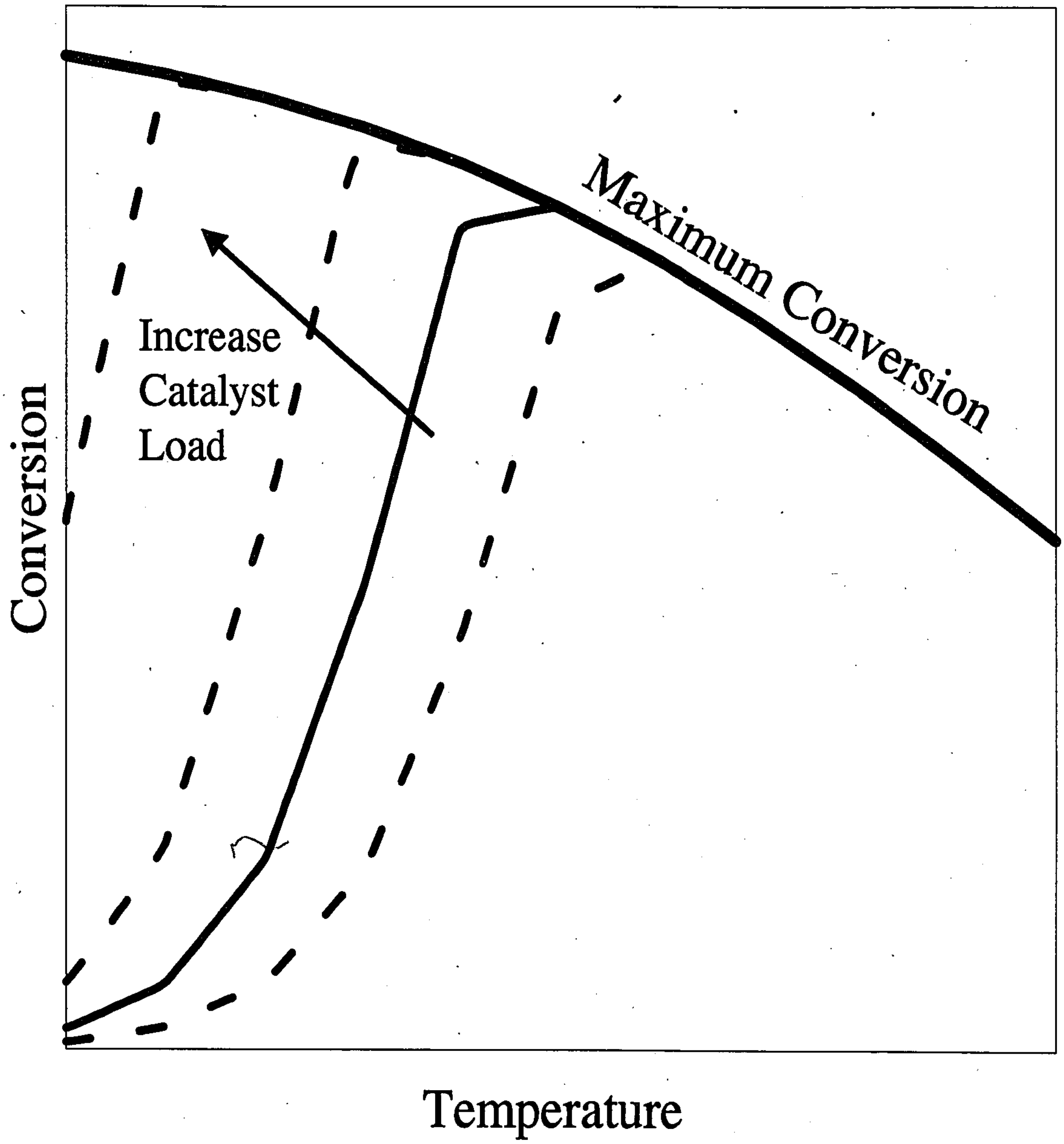

Figure 4.1: Conversion- Temperature Diagram (reversible exothermic reactions)

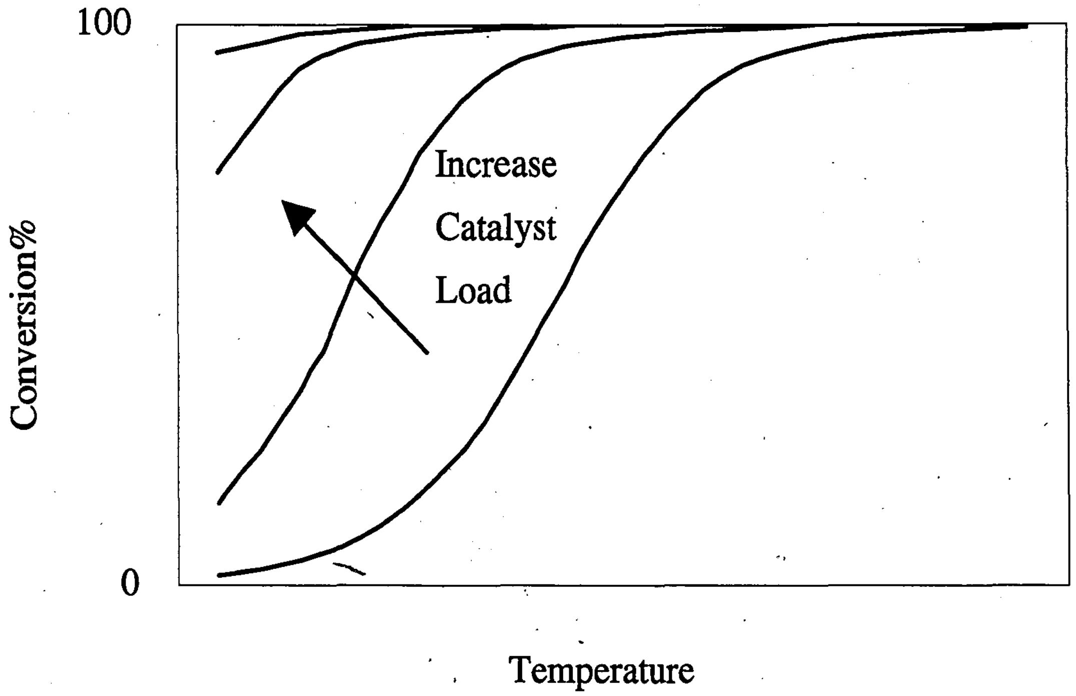

Figure 4.2: Conversion- Temperature Diagram (irreversible and endothermic reactions)

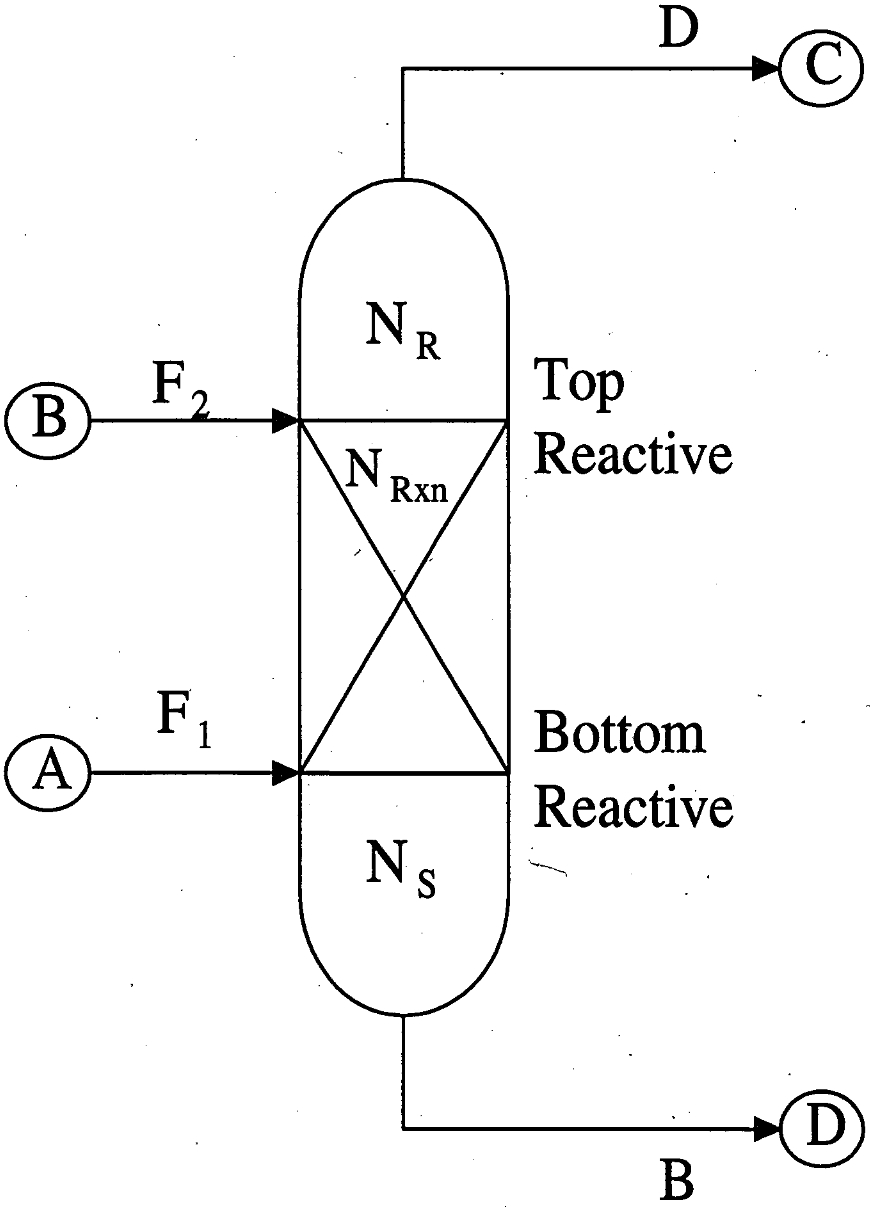

Figure 4.3: Reactive Distillation

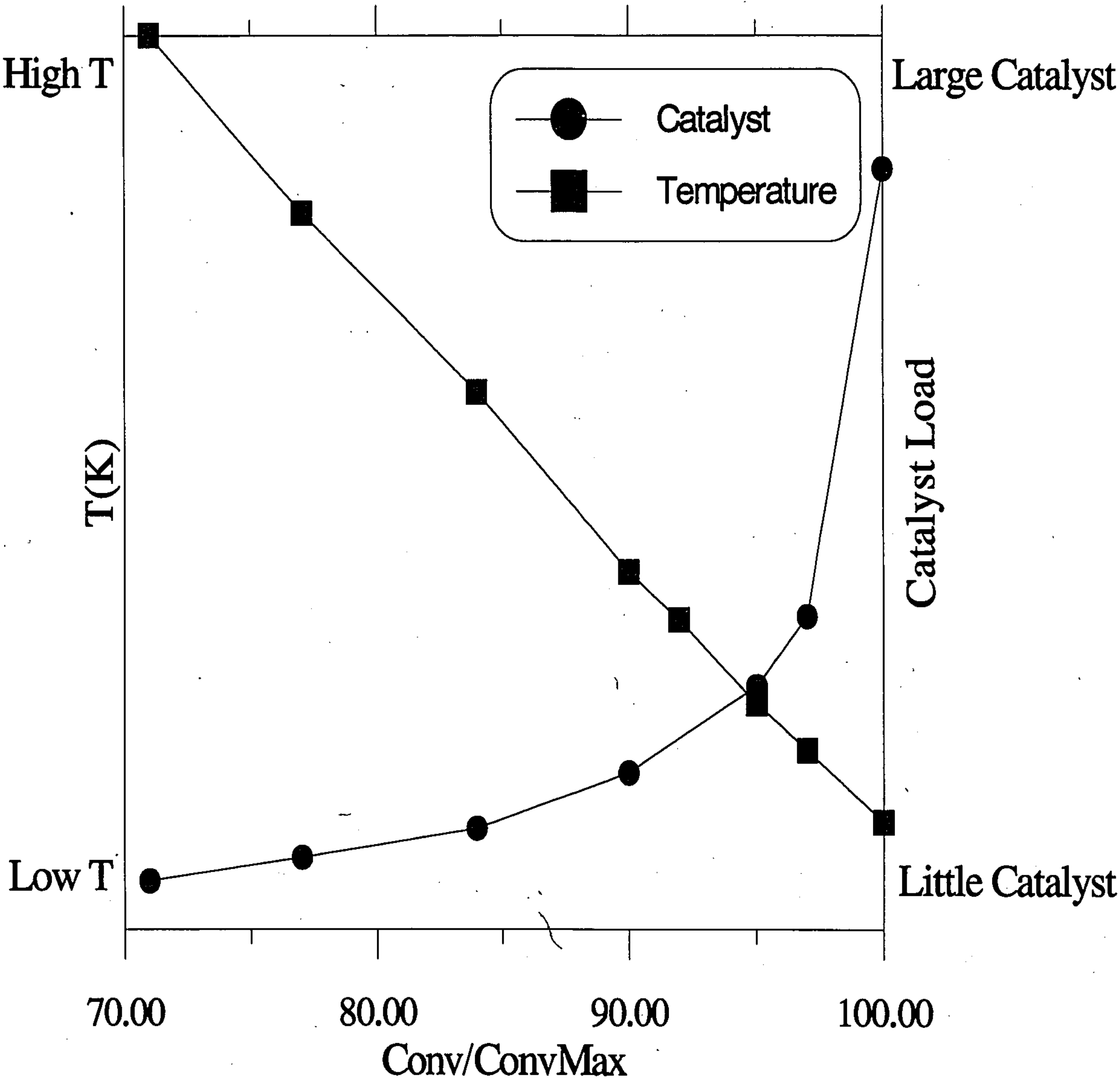

Figure 4.4: Modified Conversion-Temperature Diagram (irreversible and mild exothermic reactions)

Chapter 5

Design of ETBE Reactive Distillation Column

5.1 The ETBE Process

5.1.1 Introduction

Changing worldwide regulations are encouraging the addition of oxygenates to gasoline sold in heavily urbanized areas to reduce emissions of carbon monoxide and unburned hydrocarbons in an attempt to combat smog and ground level ozone. The high octane rating of many oxygenates can also be utilized to eliminate leaded octane enhancers, such as tetramethyllead (TML) and tetraethyllead (TEL), from gasoline blends. To date, methyl tert-butyl ether (MTBE) and ethanol have been the most widely used oxygenates. MTBE appears to offer the best combination of oxygen content, low Reid vapor pressure (RVP), high octane, high energy content, and low cost, but ethanol has been used in gasoline for many years and has attracted particular interest as an environmentally friendly alternative to fossil fuels because it can be produced from biomass. Many governments also offer ethanol subsidies to offset the cost differential with MTBE. Ethyl tert-butyl ether (ETBE) has merged more recently as a potential oxygenate.

Compared with MTBE, ETBE has a higher octane rating and a lower volatility.

It is also less hydrophilic than either MTBE or ethanol and, therefore, less likely to permeate and pollute groundwater supplies. Volatile organic compounds (VOC) emissions are also lessened by ETBE's lower volatility compared with MTBE. ETBE has a slightly lower oxygen content than MTBE (and much lower than ethanol) so that larger volumes are required, but its higher cost of production remains its principal disadvantage when compared with either MTBE or ethanol. When ETBE is produced via reactive distillation technology, this disadvantage could disappear and ETBE could be a competitive alternative to MTBE (See Section 5.2).

ETBE is produced via reactive distillation by either feeding a pre-reacted mixture to the column or by feeding fresh reactants directly to the column. To utilize the full capacity of the reactive column, we feed the fresh reactants directly to the column. The hydrocarbon feed is obtained from either fluidized catalatic cracker (FCC) unit, steam cracker unit or an isobutane dehydrogenation unit. In any of these units the butene product contains isobutene, n-butene, and others. Therefore, the butene feed to the column contains large amounts of inerts which are collected at the top of the column. The ethanol feed should be essentially pure to minimize side reactions.

5.1.2 The Reaction Kinetics

ETBE is produced from the reversible reaction of isobutene and ethanol over an acid catalyst, such as the acidic ion-exchanger resign, Amberlyst 15:

$$(CH_3)_2C = CH_2 + C_2H_5OH \leftrightharpoons (CH_3)_3COC_2H_5 \tag{5.1}$$

The reaction is equilibrium limited in the industrially significant range of temperatures, so that the equilibrium conversion from a stoichiometric mixture of reactants at 70 ^0C is only 84.7% [46].

Datta [2] has recently published a paper that studies the chemical equilibrium and the kinetics of the ETBE reaction. He provided expressions for the equilibrium constants and developed the reaction kinetics for the liquid-phase synthesis of ETBE based on the Langmuir-Hinshelwood/ Hougen-Watson (LHHW) model. The proposed reaction mechanism involves two adsorbed ethanol sites reacting with one adsorbed isobutene in a rate-determining step, giving a total of three active sites. Based on Datta's results, the following expressions are used in our simulation:

Reaction equilibrium constant

$$K_{ETBE} = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.0191544\,T + 5.28586 \times 10^{-5}\,T^2 - 5.32977 \times 10^{-8}\,T^3 \tag{5.2}$$

Adsorption equilibrium constant

$$\ln K_A = -1.0707 + \frac{1323.1}{T} \tag{5.3}$$

Reaction rate constant (gmole/hr/g of catalyst)

$$k_{rate} = 7.418 \times 10^{12} \exp\left(\frac{-60.4 \times 10^3}{RT}\right) \tag{5.4}$$

Generalized rate equation (gmole/hr)

$$r_{ETBE} = \frac{M_{cat}\, k_{rate}\, a_{EtOH}^2 \left(a_{iBut} - \frac{a_{ETBE}}{K_{ETBE}}\right)}{\left(1 + K_A\, a_{EtOH}\right)^3} \tag{5.5}$$

where a_i (the activity) = γ_i (liquid activity coefficient) × x_i (liquid mole fraction), R is the gas constant (Joule/gmole K), M_{cat} is the mass of the catalyst (g) and T is the temperature (K).

The ETBE reaction system also includes an unavoidable side reaction: the dimerization of isobutene to produce diisobutene (DIB):

$$(CH_3)_2C = CH_2 + (CH_3)_2C = CH_2 \rightleftharpoons [(CH_3)_2C = CH_2]_2 \tag{5.6}$$

However, in practice, some ethanol excess is used to prevent such significant side reactions involving isobutene. The LHHW reaction model predicts a large adsorption equilibrium constant for ethanol, which implies that, at ethanol excesses of 4 mole % and above, the catalyst surface is largely covered with ethanol. Under these conditions, the dimerization of isobutene is essentially eliminated. Therefore, as a first assumption in our simulation, the ethanol is fed to the column with about 4-5 mole % excess and the dimerization reaction is ignored.

The ETBE reaction rate also depends on the activity of the catalyst, which is susceptible to both deactivation (slow aging) and poisoning (fast aging). Poisoning is potentially a serious problem as water and especially salts neutralize active catalyst sites. Deactivation occurs over a much longer period and is accelerated by thermal degradation caused by hot spots due to inadequate mixing. In our study, the catalyst was assumed to be replaced annually.

5.1.3 Vapor-Liquid Equilibrium

The choice of physical property routines is important due to the highly non-ideal nature of the ether-alcohol-alkene system. The UNIFAC model has been used successfully to predict liquid phase activities by several researchers including the developers of the reaction equilibrium constant expression and rate equation for the ETBE [2]. The vapor phase is assumed to behave ideally due to the moderate operating pressure.

The ETBE system is susceptible to azeotropes due to non-idealities in the liquid phase. Azeotropes between ethanol and isobutene and between ethanol and ETBE have been recorded experimentally [54]. The UNIFAC model predicts the presence of these azeotropes and also suggests an azeotrope between ethanol and n-butene. The literature data are incomplete, but the UNIFAC model indicates that the azeotropes between ethanol and butenes only exist at high pressure. Figs. C.1 to C.5 in the appendix show the binary vapor-liquid equilibrium for all components. Isobutene and n-butene are almost identical in volatility, so their VLE lies in the 45^0 line.

5.2 The Optimum Design

Optimization of reactive distillation is very important. No reports have appeared in the literature of the optimization of the ETBE reactive distillation system. We assumed that the optimum design is the one that gives the minimum TAC for a fixed ETBE production rate of 700 Kg mole/Hr. In this optimization, the TAC included the raw material cost as they vary to meet the ETBE production rate. The price of the ETBE was not easily obtainable, so the optimization results were based on the assumption that the ETBE price is the same as MTBE. The economic data used were:

1. Ethanol price: \$15/Kgmole.
2. Butenes (iso + normal) price: \$8.25/Kgmole.
3. ETBE price: \$25.3/Kgmole.
4. Catalyst (Amberlyst 15) price: \$7.7/Kg (=\$3.5/lb).

The specifications in the distillate and in the bottom are taken to be:

1. 0.5% mole fraction $nC_4^=$ in the bottom product.
2. 0.5% mole fraction ethanol in the distillate product.

In the ETBE process, the distillate, which is mainly n-butene, can be utilized as a fuel. Therefore, the value of the distillate is evaluated based on the heat of combustion of the butenes and on a selling value of \$2.84/10^6 KJ (=\$3/10^6 Btu). The standard heat of combustion of butenes is approximately equal to 2.74×10^6 Joule/mole. The other costs, such as the TAC and the TCC, are calculated as given in Section 3.4.

In order to get the optimum design for the ETBE case, a brute-force simulation was carried out where the pressure, the total number of trays, the number of reactive trays and the reactive zone location were varied. A minimum of 3 rectifying trays and 3 stripping trays were always maintained in all the simulations. In each run, the specifications in the distillate and in the bottom were met. The optimization algorithm is shown in Fig. 5.1. A hybrid strategy was used to solve the non-ideal reactive distillation column equations. The algorithm, shown in Fig. 5.2, used a sequence of different methods. The optimization program covered the range of NT from 9 trays up to 30 trays and a pressure from 6.5 atm to 11 atm. Solving for each and every case by the algorithm shown in Fig. 5.2 was not easy, especially the part where the continuation is done on the specifications. The optimization problem is computationally very demanding where a single case takes about an hour in Pentium Pro II machine. The optimum case was the case yielding the minimum TAC.

The Process Flow Diagram (PFD) of the optimum design and the temperature, composition, and flow rate profiles are given in Figs. 5.3 to 5.5. About 1000 Kg of catalyst was assumed in each reactive tray, which gave a liquid height on each reactive tray of about 7.5 centimeters.

5.3 Development of Heuristics From the ETBE Process

The ETBE reaction is highly exothermic reaction; therefore, the ETBE case falls under Case I. The ETBE CTD is shown in Fig. 5.9. In this case the optimum design was used to obtain the heuristics. Other cases are given in later chapters. Although the heuristic rules were obtained from the optimum design, this demonstrates very well the basic idea and approach. It should be possible to apply the method to a board range of reactive distillation systems as more data become available. The basic steps in the method should be useful for obtaining a shortcut design.

The two key components in the rectifying zone are selected as they are selected in a typical case. In other words, the heavy reactant ethanol, (which is fed in the bottom of the rectifying section) and the light product (which is in this case an inert, n-butene) are the key components in the rectifying section. The two key components in the stripping section are ETBE and n-butene. This selection does not violate the typical arrangement discussed in Section 4.4.3. The n-butene which is an inert that is fed with the light reactant (i-butene) was selected because it has the same volatility as the i-butene and since it does not react, it has a higher concentration at the top of the stripping section than the i-butene.

In the ETBE case, we chose the TAC for a fixed ETBE production rate to be our cost function and thus the needed feed flowrate is not known a *priori*. Therefore, to make the CTD independent of the feed flowrate, we used the ratio of catalyst weight to limiting reactant feed flowrate instead of the explicit catalyst load discussed in Section 4.3. In order to obtain the amount of catalyst needed, first we will use the heuristics to obtain the catalyst-to-feed ratio. Secondly, we will assume a 100% conversion from which we can find the limiting reactant feed flowrate and then back calculates the amount of catalyst.

Following the 11 steps outlined in Section 4.4, the following are obtained for each step:

Step 1: The ETBE CTD is shown in Fig. 5.9. At 80% conversion, catalyst-to-feed ratio $= 3\,\frac{Kg}{Kgmole/Hr}$ and $T_R = 350K$. Assuming feed flowrate = desired ETBE production rate = 700 Kg mole/Hr, $(M_{cat})_{min} = 3\,\frac{Kg}{Kgmole/Hr} \cdot 700 Kgmole/Hr$ $= 2100\,Kg$.

Step 2: From PFR calculation at 350K and 2100Kg catalyst: $\{x_{nC_4^=} = 0.556;\ x_{iC_4^=} = 0.073;\ x_{EtOH} = 0.073;\ x_{ETBE} = 0.299\}$

Step 3: Initial pressure = pressure of x_{PFR} at T_R : $P_i = 7.77$ atm

Step 4: $M_{cat} = 7\ (M_{cat})_{min} = 14700Kg$

Step 5: $V_{max} = 2\cdot$ total feed $= 2 \cdot (700 Kgmole\, EtOH/Hr + 1750 Kgmole\ mixed\ C_4^=/Hr) = 4900 Kgmole/Hr$. Using $T_R = 350K$, $P = 7.77\,atm$ and average molecular weight $= \frac{102.2+46.07+2\cdot 56.11}{4} = 65$ on Eqn. 3.28 results in $D_c = 5.7m$

Step 6: Catalyst per tray $= \rho_{cat}\,\frac{\pi D_c^2}{4}\,(0.07m)(0.7) \simeq 1000kg/tray$. Therefore, $N_{Reactive} = \frac{M_{cat}}{\text{cat per tary}} \simeq 15$

Step 7: $\left(\tilde{x}_{EtOH}\right)_{BottomRectifying} = \frac{0.073}{0.073+0.556} = 0.116$ and $\left(\tilde{x}_{nc4}\right)_{BottomRectifying} = 1 - 0.116 = 0.884$ also the top specs are $\left(\tilde{x}_{EtOH}\right)_D = 0.005$ and $\left(\tilde{x}_{nc4}\right)_D = 1 - 0.005 = 0.995$

Step 8: The relative volatility between n-butene and ethanol at 7.77 atm at the top of the column is 1.81 and at the bottom of the rectifying zone is 3.62. The geometric average relative volatility = 2.56

Step 9: $N_R = 2\left(N_R\right)_{min} = 2\left[\ln\left(\frac{0.995}{0.005}/\frac{0.884}{0.116}\right) \div \ln 2.56\right] = 7$

Step 10: Following steps 7-9 for the stripping section gives:

- $\left(\tilde{x}_{nc4}\right)_{TopStripping} = \frac{0.556}{0.556+0.299} = 0.650$ and $\left(\tilde{x}_{ETBE}\right)_{TopStripping} = 1-0.650 = 0.350$ also the bottom specs are $\left(\tilde{x}_{nc4}\right)_B = 0.005$ and $\left(\tilde{x}_{ETBE}\right)_B = 0.995$
- The relative volatility between n-butene and ETBE at 7.77 atm at the bottom of the column is 5.95 and at the top of the stripping zone is 9.8. The geometric average relative volatility = 7.64
- $N_S = 2\left(N_S\right)_{min} = 2\left[\ln\left(\frac{0.650}{0.350}/\frac{0.005}{0.995}\right) \div \ln 7.64\right] = 6$

The heuristic design yielded a bigger rectifying and stripping sections than the optimum and thus it is a conservative design. The initial pressure (7.77 atm) was obtained by following the rules in Section 4.4.1. The optimum pressure for this design configuration which is found by exploring a range of pressures around initial pressure is 11.5 atm. The details of the heuristic design at the optimum pressure is shown in Figs 5.6-5.8. The ETBE system is more sensitive to the column pressure than the column configuration. This is shown in Figs. 5.10 where the optimum column (minimum TAC) can be almost achieved from several design configuration (N_R, N_{rxn}, N_S) by varying the pressure. This pressure sensitivity may not be the case in all chemical systems. If the system is not very sensitive to the pressure, there will be no need to maneuver around the pressure originally suggested by the heuristic rule. The effect of pressure over other design parameters is shown in Fig. 5.11 and Fig. 5.12.

As a conclusion to this chapter, one can see that the optimum design of reactive distillation system is very important to generate the heuristic rules, however; it is not easy to obtain. The heuristics are very useful once they have been generated and could be used to other similar systems. This chapter clearly demonstrated how the heuristics are easy and convenient to use and to come up with a reasonable design.

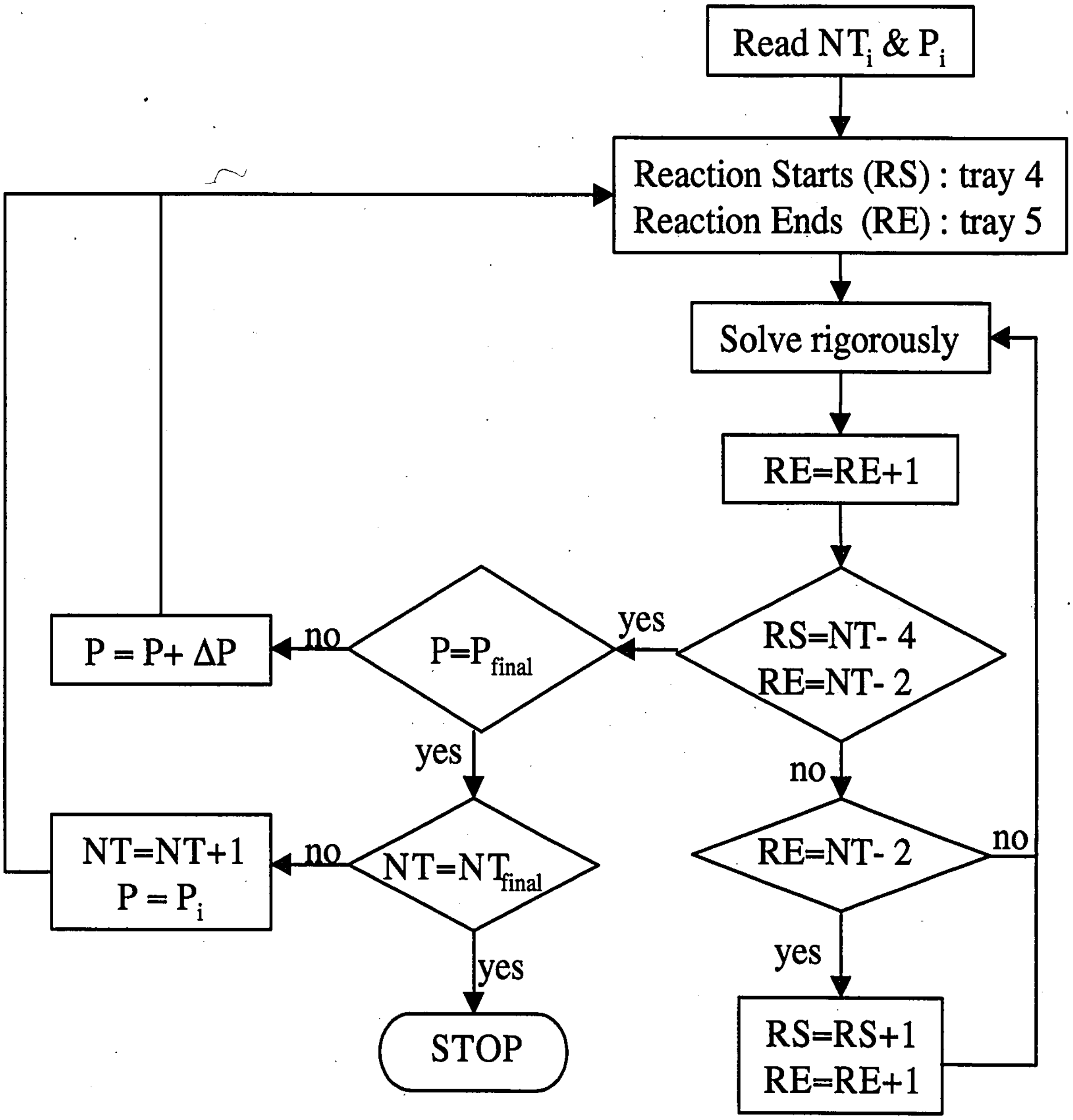

Figure 5.1: Optimization Algorithm

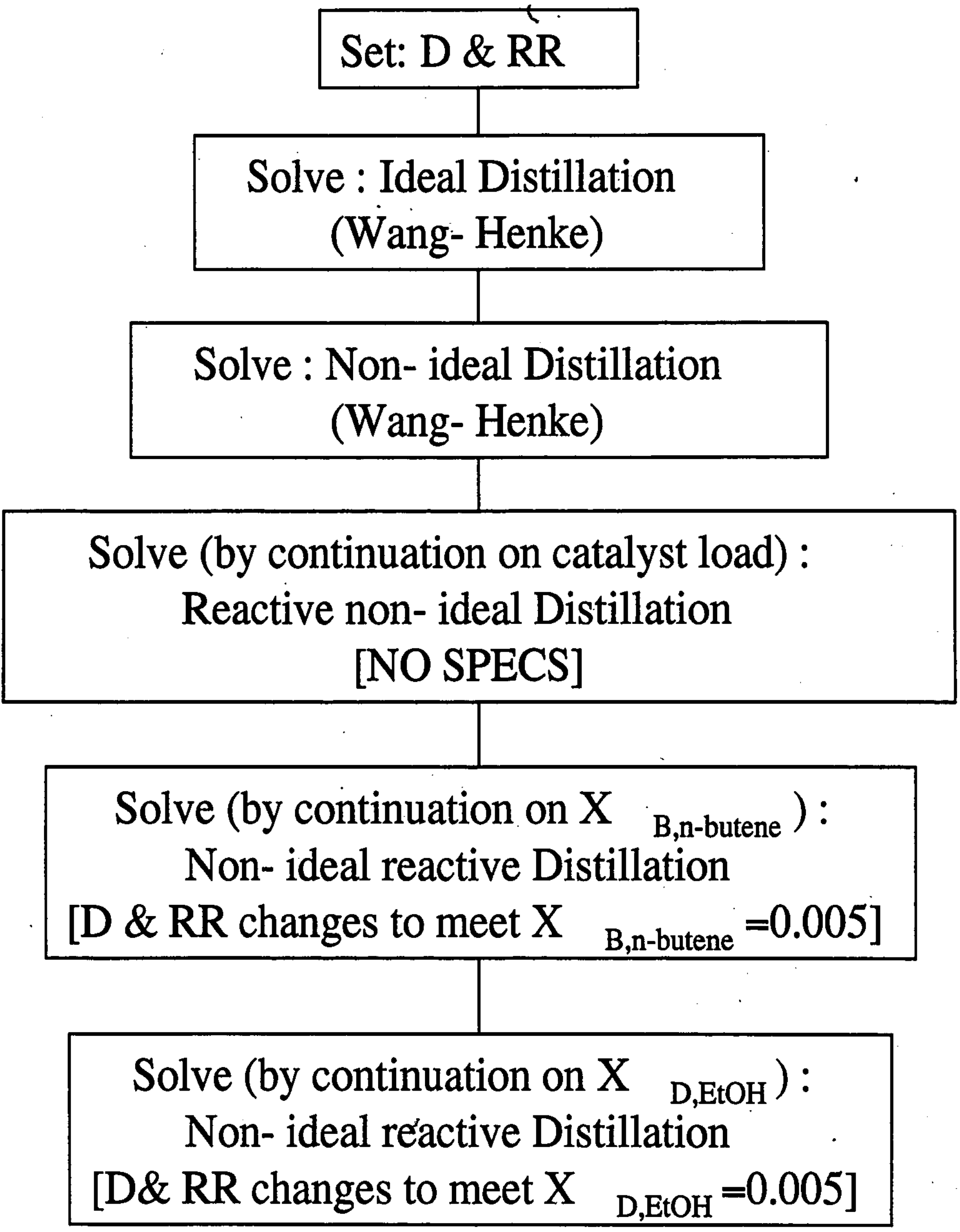

Figure 5.2: ETBE Reactive Distillation Solving Algorthim

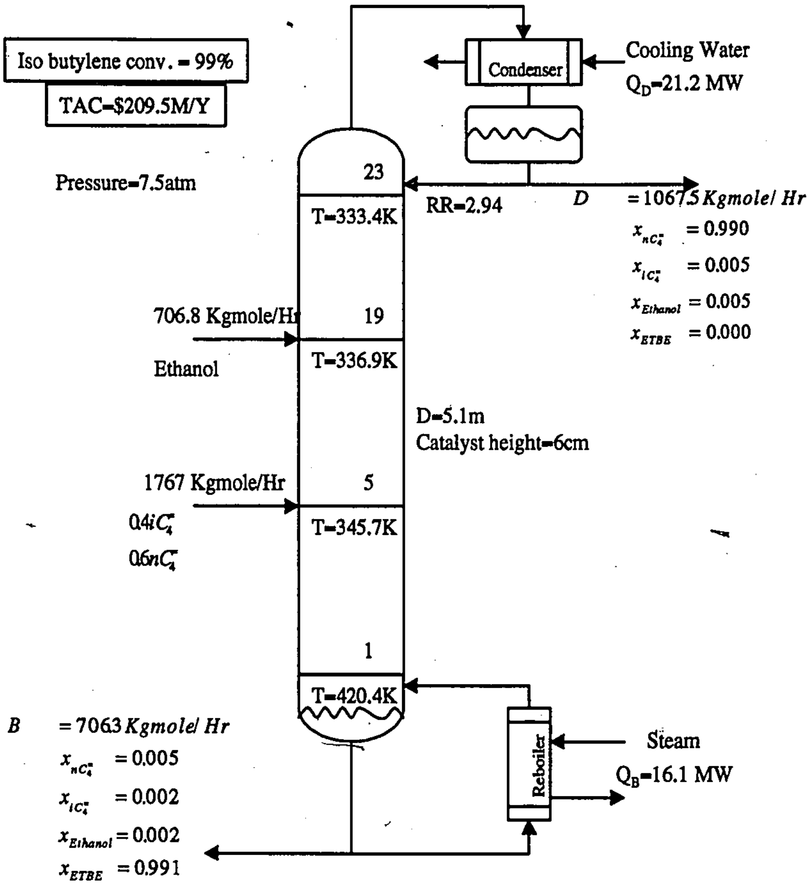

Figure 5.3: PFD of Optimum ETBE Design

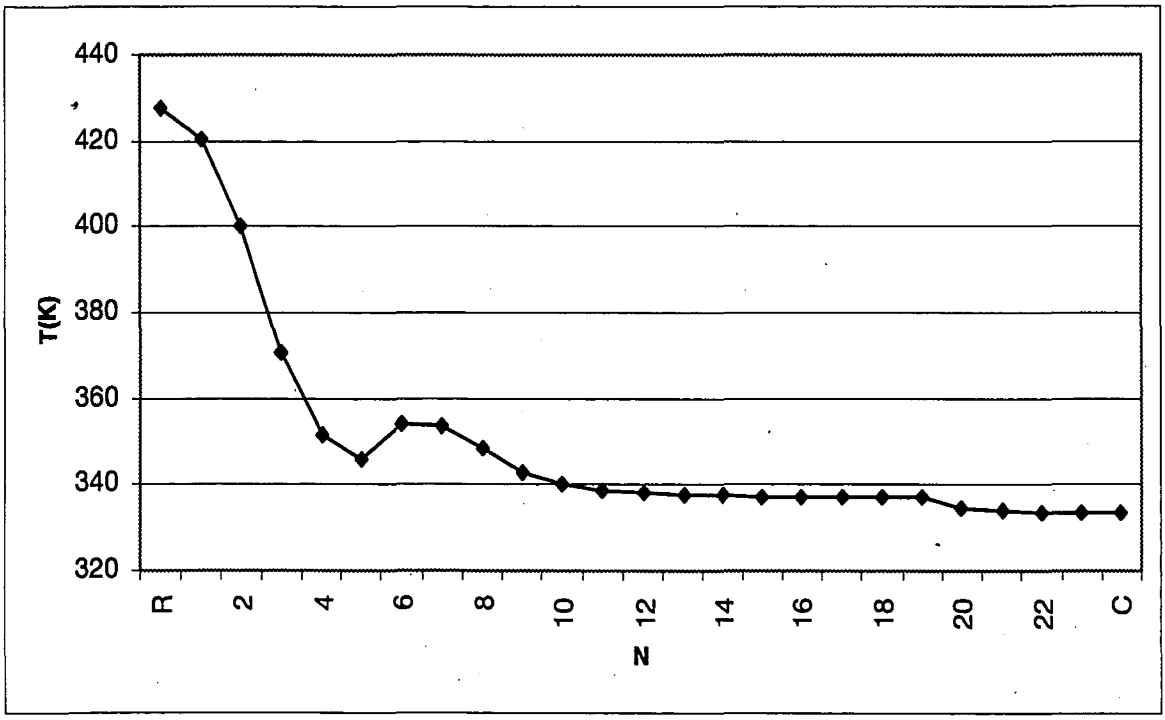

Figure 5.4: ETBE Temperature Profile (Optimum Design)

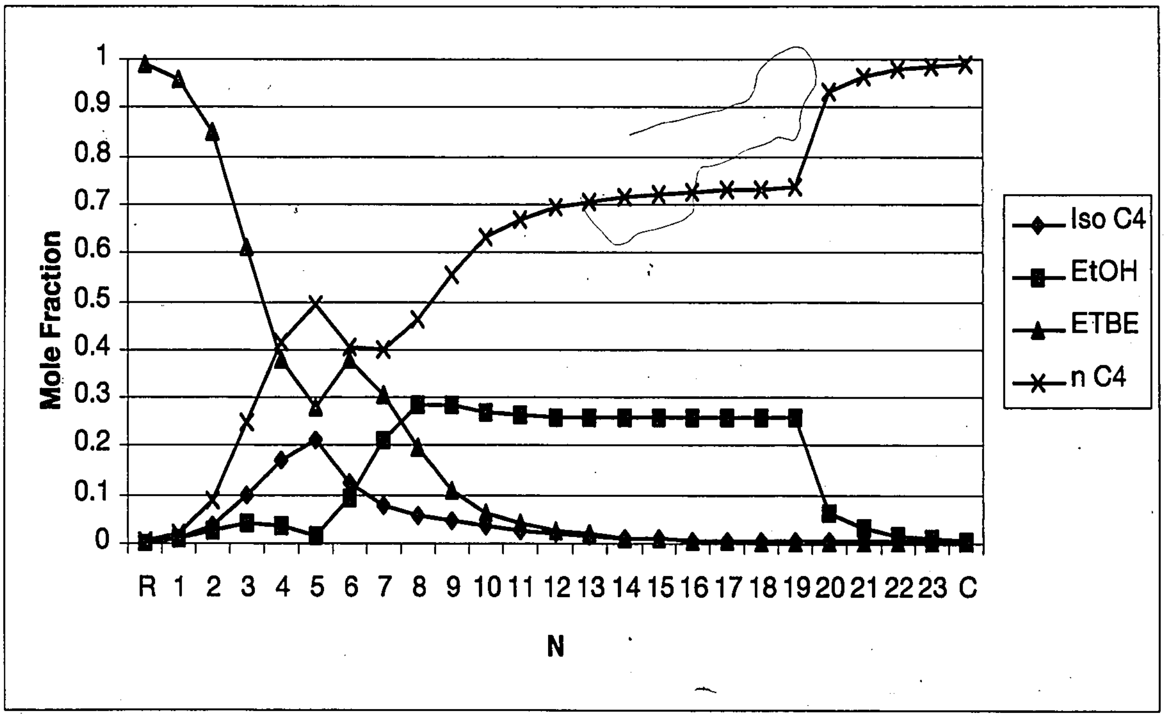

Figure 5.5: ETBE Mole Fraction Profile (Optimum Design)

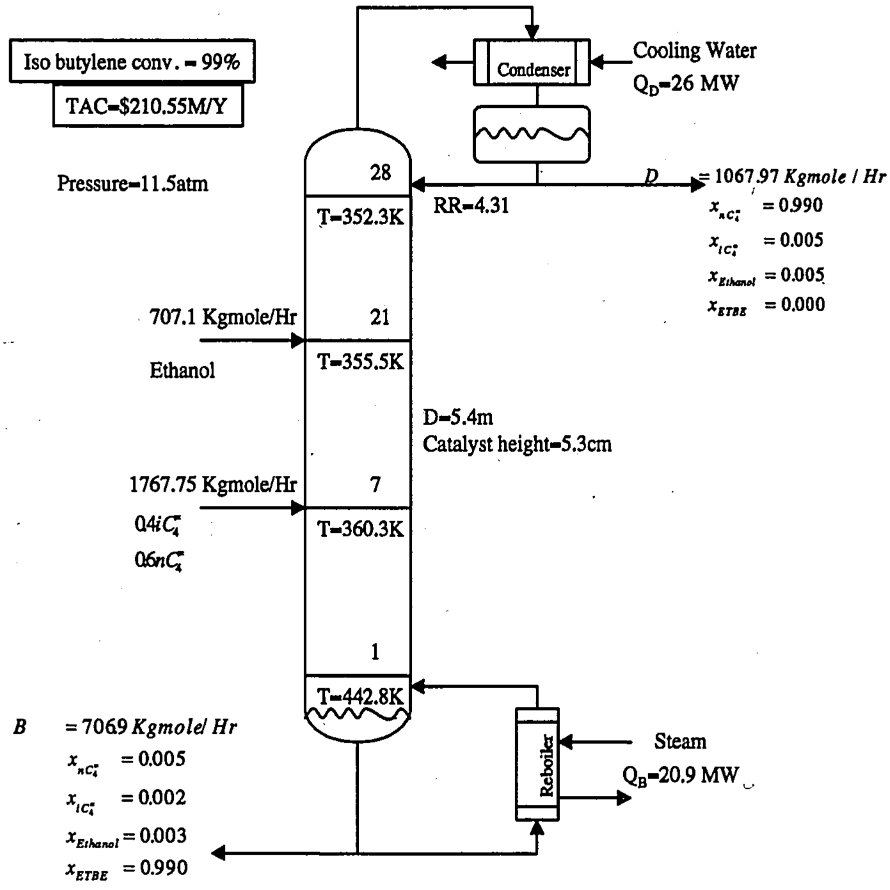

Figure 5.6: ETBE PFD (Heuristic Design)

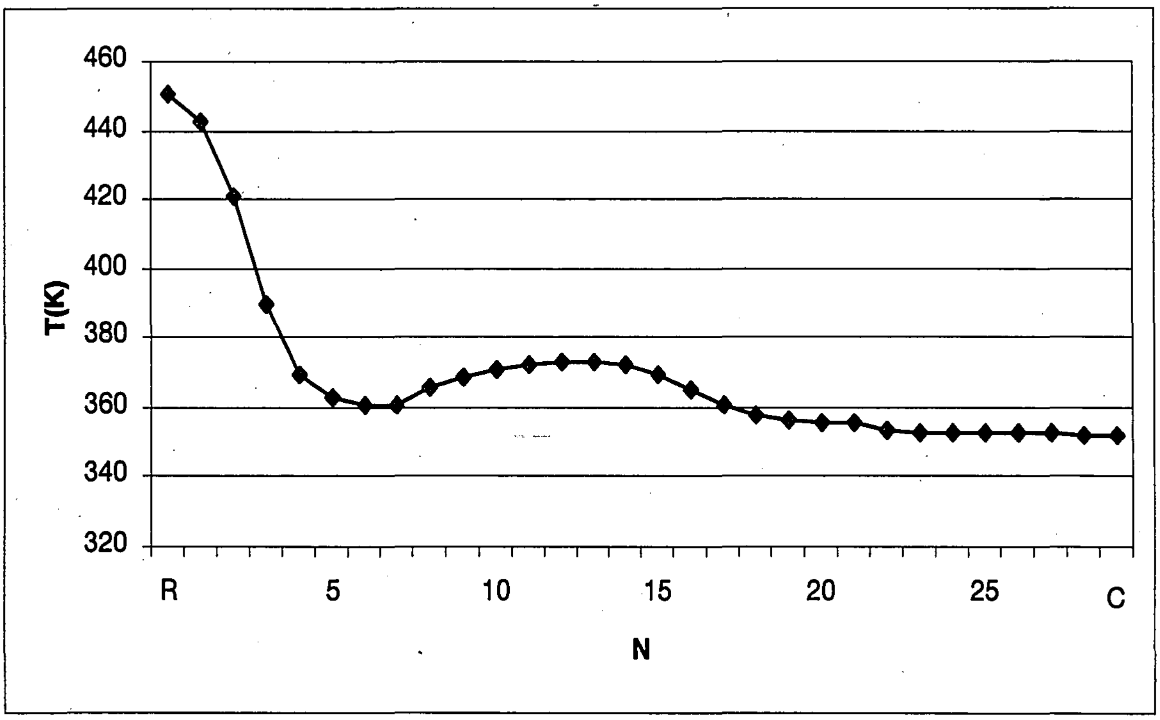

Figure 5.7: ETBE Temperature Profile (Heuristic Design)

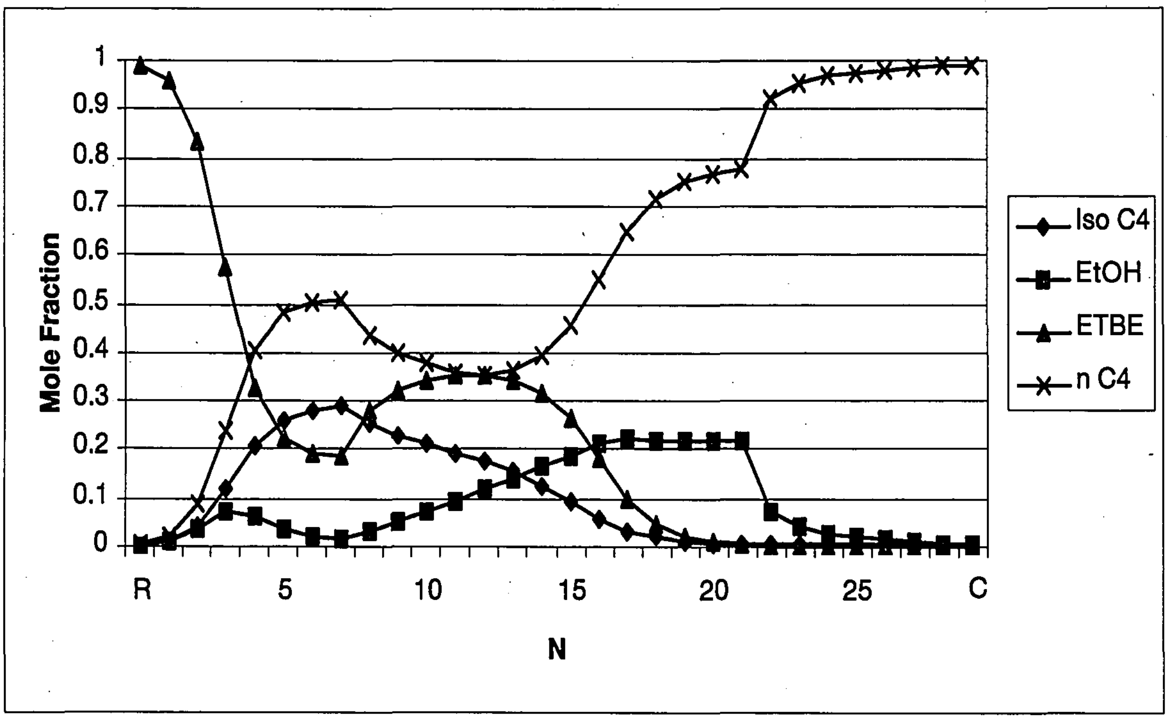

Figure 5.8: ETBE Mole Fraction Profile (Heuristic Design)

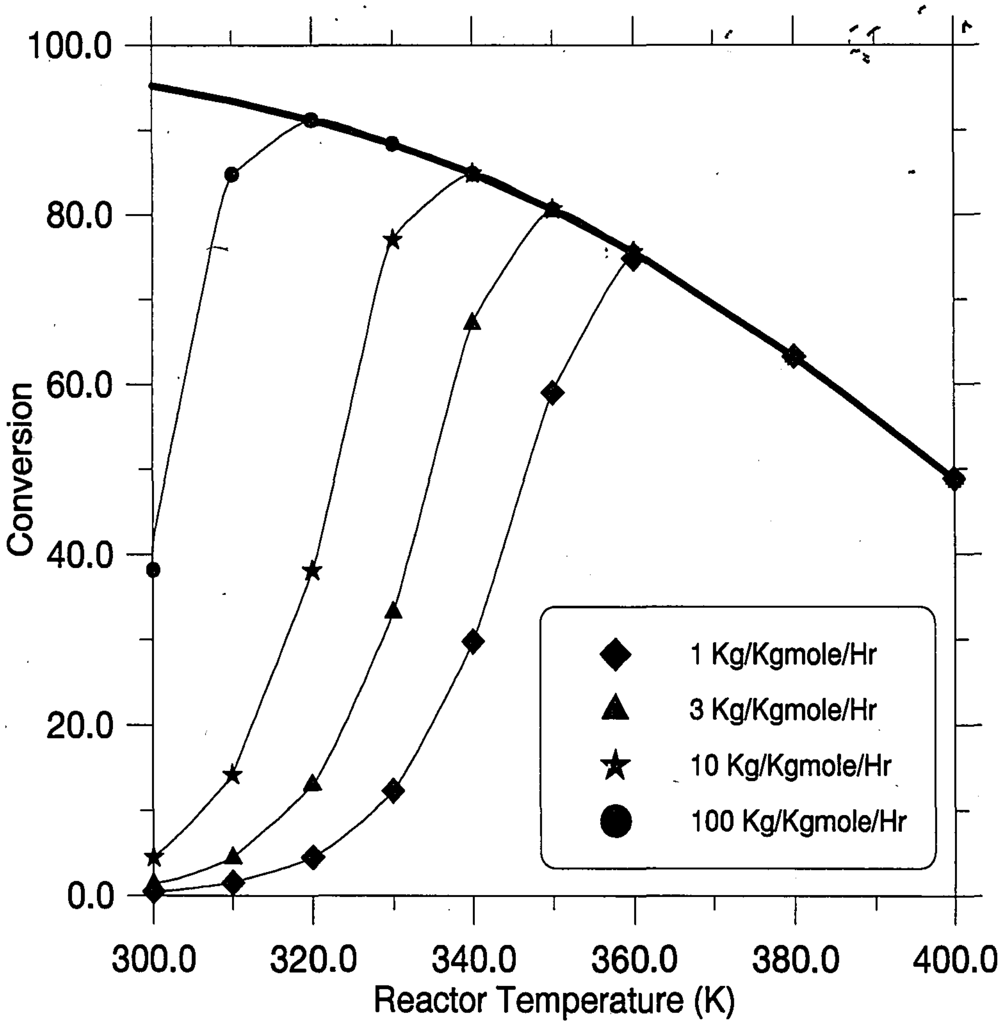

Figure 5.9: ETBE CTD

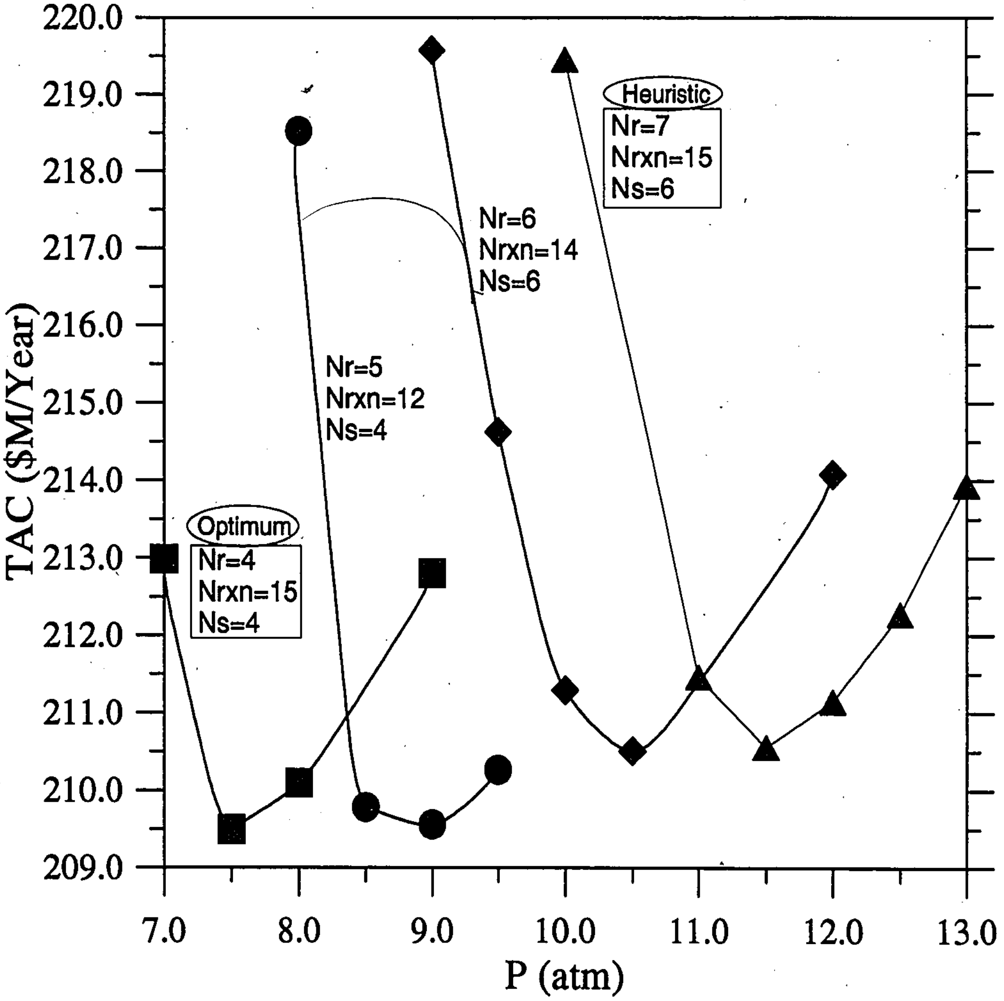

Figure 5.10: Pressure Effect on TAC for Four Column Configurations

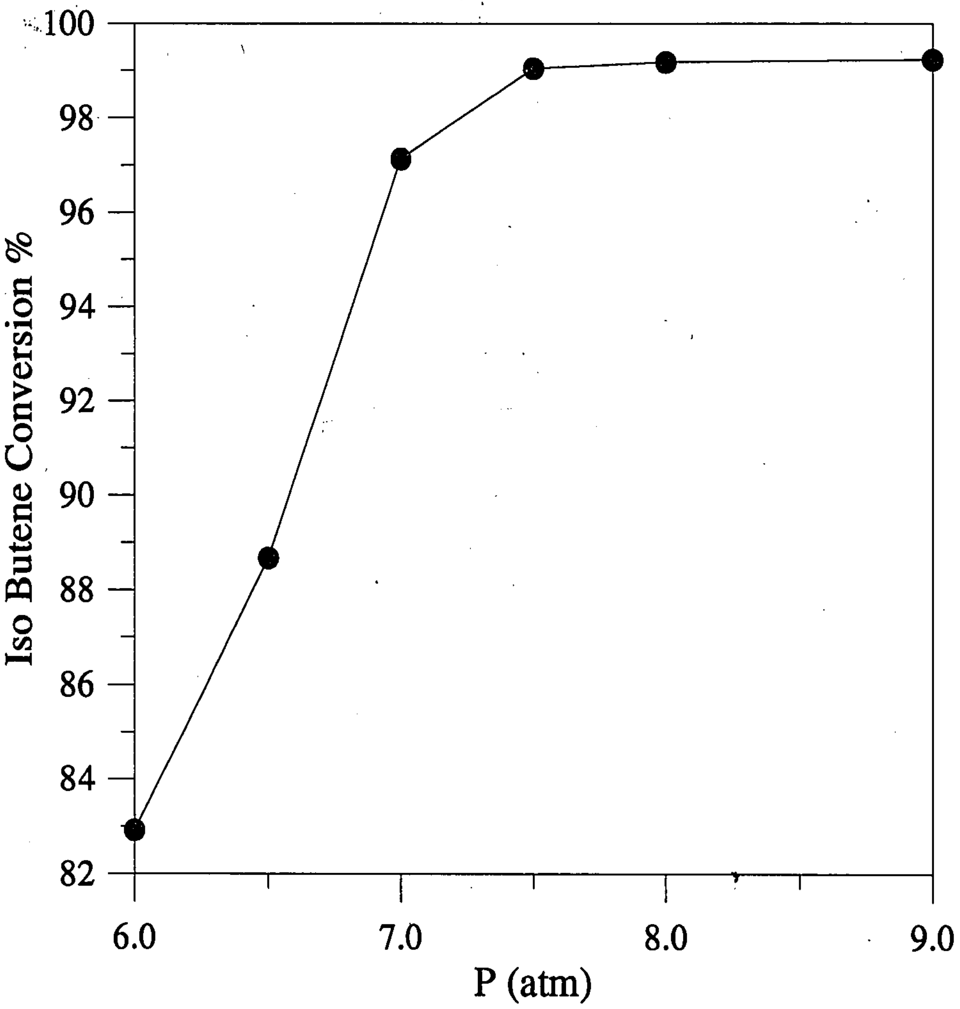

Figure 5.11: Pressure Effect on Conversion - Optimum Design

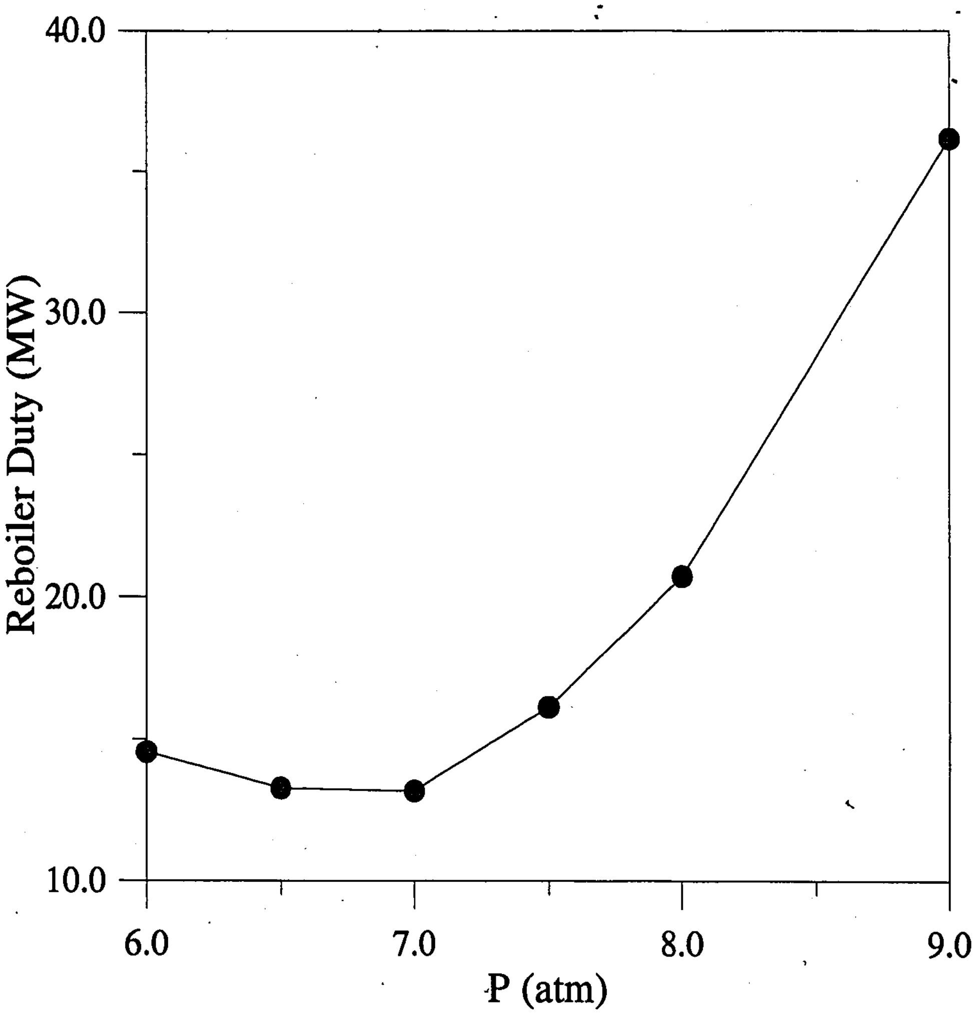

Figure 5.12: Pressure Effect on Reboiler Duty - Optimum Case

Chapter 6

Design of Methyl Acetate Reactive Distillation Column

6.1 The Methyl Acetate Process

6.1.1 Introduction

The production of methyl acetate is a good candidate for reactive distillation due to its reaction equilibrium limitation and favorable volatilities. Conventional manufacture of high purity methyl acetate is very difficult due to reaction equilibrium limitations and the formation of methyl acetate-methanol and methyl acetate-water minimum-boiling azeotropes. A complex separation/ reaction/ recycle system is required.

Reactive distillation provides a much more effective way to produce a high purity methyl acetate ([53], [30]). Traditional problems are overcame because of the continuous separation while reaction is going on. In their development process of the methyl acetate reactive distillation, Agreda and co-workers went through bench-scale experiments and pilot plant testing. A full scale plant was designed based on the experimental work and computer simulation of the process.

6.1.2 The Reaction Kinetics

Methyl acetate ($MeOAc$) can be made by the liquid-phase reaction of acetic acid ($HOAc$) and methanol ($MeOH$) catalyzed by sulfuric acid or a sulfonic acid ion-exchange resin in the temperature range of 310-325 K and at a pressure of 1 atm. The reaction is

$$HOAc + MeOH \rightleftharpoons MeOAc + H_2O \tag{6.1}$$

Kinetic rate expressions used in reactive distillation models are best written in terms of activities as opposed to the more familiar concentration-based rate expression. For the methyl acetate system the rate expression in terms of activities is strongly preferred because the high polarity of water and methanol compared to methyl acetate leads to strongly non-ideal solution behavior. Earlier works on the kinetics of this system have reported pre-exponential and the activation energies for the concentration-based rate expressions for the esterification kinetics of different alcohols [25]. A new activity-based model that utilized the Langmuir-Hinshelwood/ Hougen-Watson (LHHW) isotherm was developed recently [1]. The new reaction rate was able to predict the experimental data very well.

The reaction rate expression and constants are:

$$r_{MeOAc} = \frac{M_{cat}\, k_1 \left(a_{HOAc}\, a_{MeOH} - \frac{a_{MeOAc}\, a_{H_2O}}{K_{eq}}\right)}{\left(1 + K_{HOAc}\, a_{HOAc} + K_{MeOH}\, a_{MeOH} + K_{MeOAc}\, a_{MeOAc} + K_{H_2O}\, a_{H_2O}\right)^2} \tag{6.2}$$

$$k_1 = 6.942 \times 10^9 \exp\left(\frac{-6287.7}{T}\right) \tag{6.3}$$

$$K_{eq} = 2.32 \exp\left(\frac{782.98}{T}\right) \tag{6.4}$$

$$K_{HOAc} = 3.18 \tag{6.5}$$

$$K_{MeOH} = 4.95 \tag{6.6}$$

$$K_{MeOAc} = 0.82 \tag{6.7}$$

$$K_{H_2O} = 10.5 \tag{6.8}$$

where a_i (the activity) = γ_i (liquid activity coefficient) × x_i (liquid mole fraction), k_1 is the reaction rate constant (mole/(g cat. Hr)), M_{cat} is the mass of the catalyst (g) and T is the temperature (K).

An increase in pressure leads to an increase in the boiling points of the components and hence the operating temperature of the reactive distillation. This leads to higher rates of reaction and smaller equipment, leading to a saving of investment costs. An increase in temperature has a little effect on the equilibrium constant (and hence the equilibrium conversion). However, temperature increase could potentially trigger unwanted side reactions such as the methanol dehydration reaction. In that side reaction, methanol dehydrate to dimethyl ether (DME) and water: $2MeOH \rightleftharpoons DME + H_2O$. It appears that most studies ignore this side reaction, so we have not considered it.

6.1.3 Vapor-Liquid Equilibrium

Accurate prediction of the VLE of the methyl acetate system is vital to the simulation and design of the process. To correlate the VLE in mixtures containing a vapor-phase associating substance such as acetic acid, Mark's method (See Appendix A.1) in combination with liquid activity coefficient model is usually used. At present, there are many types of correlations for the prediction of activity coefficients in chemical systems. The most comprehensive comparison of five of the methods (Van Laar, Margules, Wilson, NRTL, and UNIQUAC) was made in the DECHEMA Vapor Liquid Equilibrium Data Collection. From this statistical analysis, the Wilson equation was found to be the best, and Van Laar and UNIQUAC tied for last. Most of the literature dealing with methyl acetate reactive distillation uses the Wilson model for activity coefficients. Therefore, the Wilson model and Mark's method were used to correlate the VLE in our research. Figs. C.6 to C.11 in the appendix show the binary vapor-liquid equilibrium for all components.

6.2 Eastman Chemical Co. Design

The Eastman Chemical Co. design is published in the literature ([30], [53]). The reactive distillation has 4 parts: the rectifying section, extractive section, reactive section, and stripping section as shown in Fig. 6.1. In their design, acetic acid is fed in top of the reactive zone to extract the water from the mixture and therefore this purifies methyl acetate in the top as the methyl acetate-water azeotrope is no longer encountered. The catalyst in their process is liquid sulfuric acid and is fed into the top reactive tray. The developers of the Eastman reactive distillation column suggest that the reactive section should have about 30-45 trays and every other section should have about 10 trays. Therefore, the minimum recommended number of trays is 60. In their process, methyl acetate was produced with a purity up to 95% mole fraction (99.5% wt. fraction). The temperature and composition profiles can be found in their published paper.

The extractive section used in the Eastman process is a special case for this specific reaction and cannot be generalized for every reactive distillation column. Our design approach aims at producing a general method that should be good for many reactive distillation column. Therefore, we ignore the extractive section. Our design method suggests an operating pressure, total number of trays, number of trays in each one of the three sections (rectifying, reactive, and stripping) and a catalyst load.

In order to compare our findings with the Eastman design, two assumptions were made. The first assumption involved tray efficiency and the second one involved catalyst and kinetics. The design given in the Eastman paper shows actual trays. We assumed an average tray efficiency of 50%. Therefore the theoretical tray design used for comparison purposes has half the number of trays in each zone.

They used sulfuric acid as their catalyst. The kinetics for this catalyst are not available in the open literature. The kinetic model we used was proposed by Doherty *et. al.* [1]. Unlike the Eastman kinetic model, this model uses solid catalyst. A correction factor was needed to correlate our kinetics to the Eastman kinetics. Different correction factors were examined in order to produce the same methyl acetate purity (95%) achieved in the Eastman design. A factor of 2.5 was found to achieve the desired methyl acetate purity. The column specifications are 0.002% impurity of acetic acid in the top and 0.002% impurity of methanol in the bottom. The modified Eastman design that we came up with is shown in Figs. 6.2-6.5.

6.3 Heuristic Design of the Methyl Acetate Process

Since the reaction equilibrium constant is not a strong function of temperature, the methyl acetate case can be classified as Case II. In this case, we know that the distillate is going to be almost methyl acetate. The heuristic design rule to select the pressure for Case II systems suggests that the pressure of the column be the saturation pressure of methyl acetate at temperature around 330 K in order to use cooling water in the condenser. To design the reactive zone, the CTD and MCTD are needed. The two key components in the stripping section are as in typical cases: the methanol (which is the light reactant) and water (which is the heavy product). The methanol impurity specification in the bottom is 0.02%. The key components in the rectifying section had also been selected according to the typical configuration, i. e. acetic acid (heavy reactant) and methyl acetate (light product).

To obtain a short-cut design for this reactive system we have to follow the steps given in Section 4.5 which are:

Step 1: Methyl acetate saturation pressure at 330 K is around 1 atm. Therefore, the operating pressure of the column is set be equal to 1 atm

Step 2: The CTD is shown in Fig. 6.6 and the MCTD is shown in Fig. 6.7: At conversion ration of 93%, $(M_{cat})_{min} = 1800\,Kg$ and $T_R = 336.54K$

Step 3: From PFR calculation at 336.54K and 1800Kg catalyst: $\{x_{OHAc} = 0.1611;$ $x_{MeOH} = 0.1611;$ $x_{MeOAc} = 0.3389;$ $x_{H2O} = 0.3389\}$

Step 4: $M_{cat} = 7\,(M_{cat})_{min} = 12,600\,Kg$

Step 5: $V_{max} = 2\cdot$ total feed $= 2\cdot(300Kgmole\,MeOH/Hr + 300Kgmole\,OHAc/Hr)$ $= 1200Kgmole/Hr$. Using $T_R = 336.54K,\ P = 1\ atm$ and average molecular weight $= \frac{60.05+32.04+74.08+18.02}{4} = 46$ on Eqn. 3.28 results in $D_c = 4.3m$

Step 6: Calculate catalyst per tray $= \rho_{cat}\frac{\pi D_c^2}{4}(0.075)(0.8) \simeq 700Kg$. Therefore, $N_{Reactive} = \frac{M_{cat}}{\text{cat per tary}} = 18$

Step 7: The pseudo binary mole fraction in the bottom of the rectifying zone is $\left(\tilde{x}_{OHAc}\right)_{BottomRectifying} = \frac{0.1611}{0.1611+0.3389} = 0.3222$ and $\left(\tilde{x}_{MeOAc}\right)_{BottomRectifying} = 1 - 0.3222 = 0.6778$ and the pseudo binary mole fraction specification at the top of the column is $\left(\tilde{x}_{OHAc}\right)_{D} = 0.0002$ and $\left(\tilde{x}_{MeOAc}\right)_{D} = 0.9998$

Step 8: The relative volatility between methyl acetate and acetic acid at 1 atm at the top of the column is 25.39 and at the bottom of the rectifying zone is 6.21. The geometric average relative volatility = 12.56

Step 9: $N_R = 2\left(N_R\right)_{min} = 2\left[\ln\left(\frac{0.9998}{0.0002}/\frac{0.6778}{0.3222}\right) \div \ln 12.56\right] = 6$

Step 10: Following steps 8-10 for the stripping section gives:

- The pseudo binary mole fraction in the top of the stripping zone is $\left(\tilde{x}_{MeOH}\right)_{TopStripping} = \frac{0.1611}{0.1611+0.3389} = 0.3222$ and $\left(\tilde{x}_{H2O}\right)_{TopStripping} = 1 - 0.3222 = 0.6778$ and the pseudo binary mole fraction specification at the bottom of the column is $\left(\tilde{x}_{MeOH}\right)_{B} = 0.0002$ and $\left(\tilde{x}_{H2O}\right)_{B} = 1 - 0.0002 = 0.9998$
- The relative volatility between methanol and water at 1 atm at the bottom of the column is 7.31 and at the top of the stripping zone is 4.37. The geometric average relative volatility = 5.65
- $N_S = 2\left(N_R\right)_{min} = 2\left[\ln\left(\frac{0.3222}{0.6778}/\frac{0.0002}{0.9998}\right) \div \ln 5.65\right] = 9$

6.3.1 Design Details

The details of the design is shown in Fig. 6.8 -6.11.

6.4 Comparison Between the Two Designs

The heuristic design method produces a reactive distillation column that is quite similar to the Eastman design. We can observe the following:

1. TAC (which does not include the cost of the raw materials) for both cases is very close.
2. The conversion is very close for both cases.

From the above observations we can see that the heuristic method did a good job in giving a good starting design. The heuristic design underestimated the number of rectifying and stripping trays. This might suggest that the Eastman design could be overestimating the separation trays needed or that the 50% tray efficiency assumed in our calculations is too high.

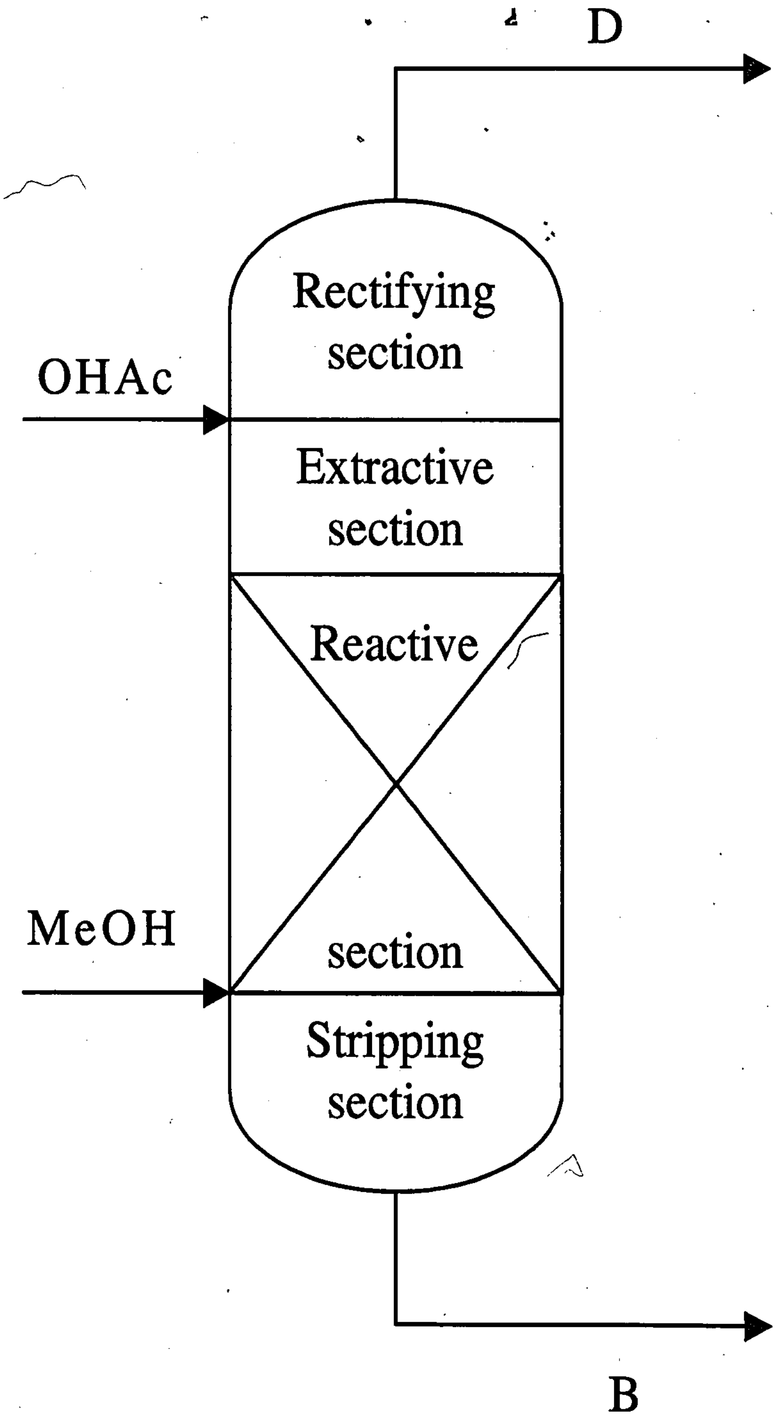

Figure 6.1: Eastman Chemical Co. Reactive Distillation Column

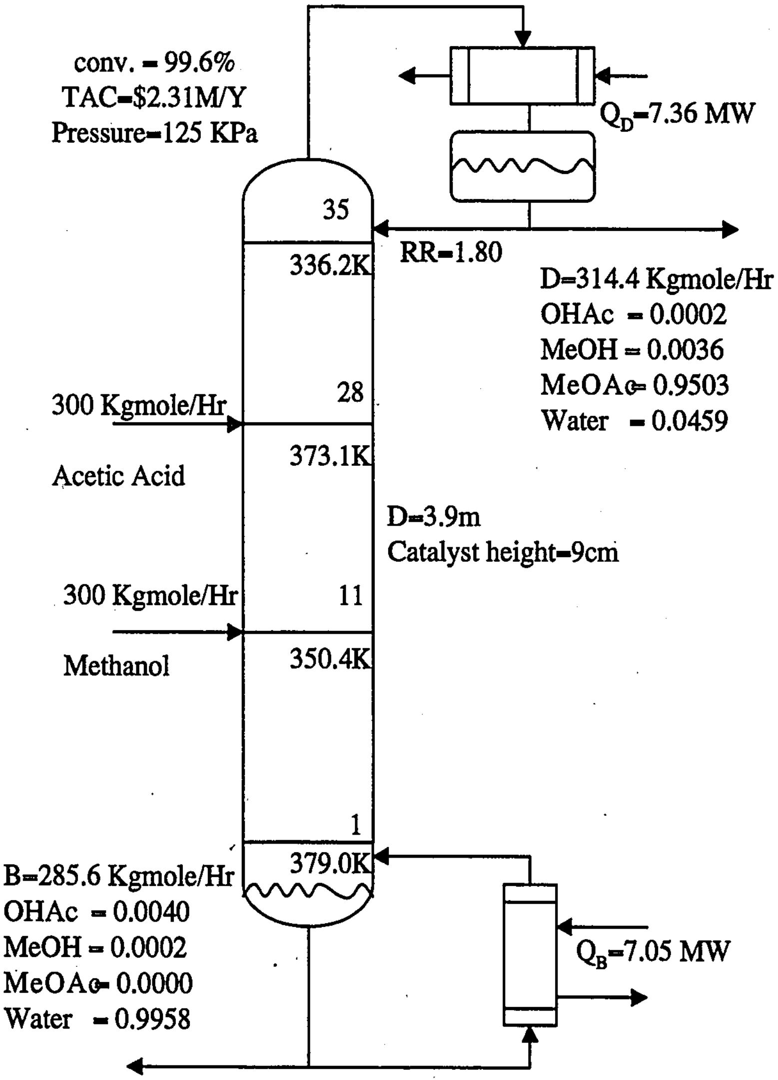

Figure 6.2: Modified Eastman MeOAc PFD

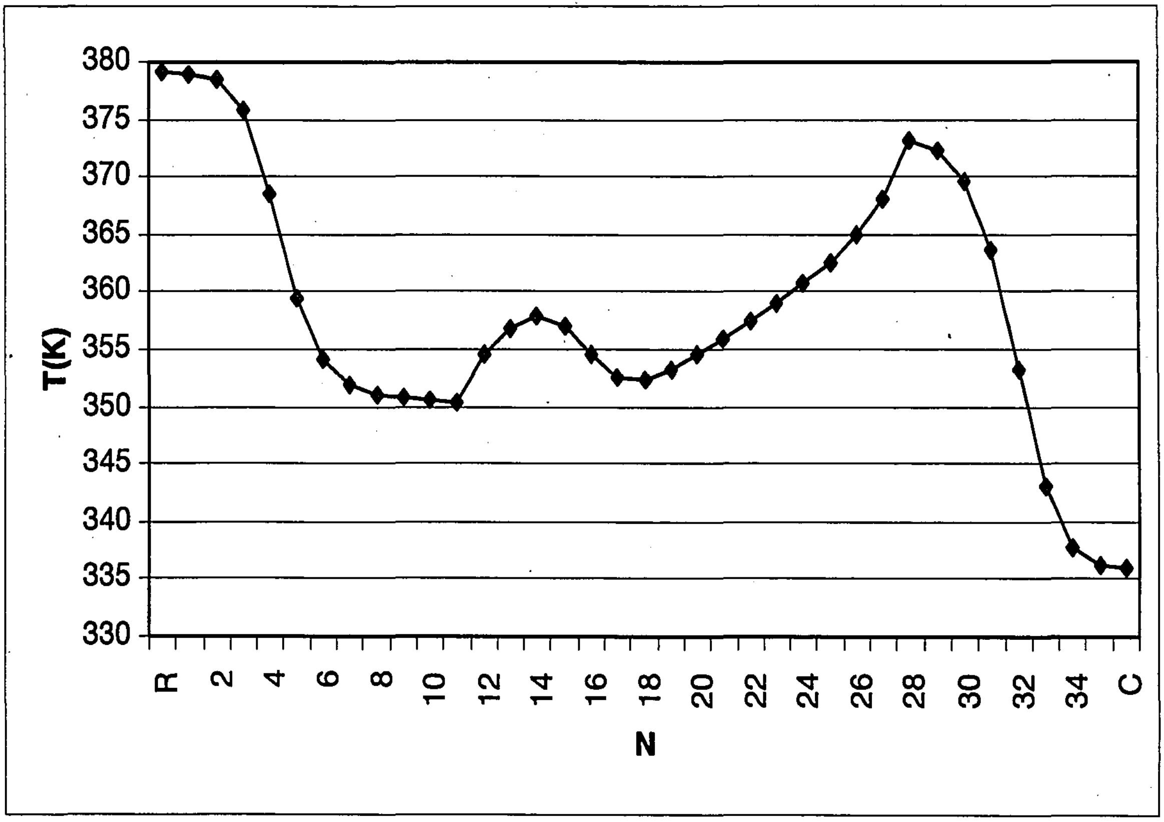

Figure 6.3: Modified Eastman MeOAc Temperature Profile

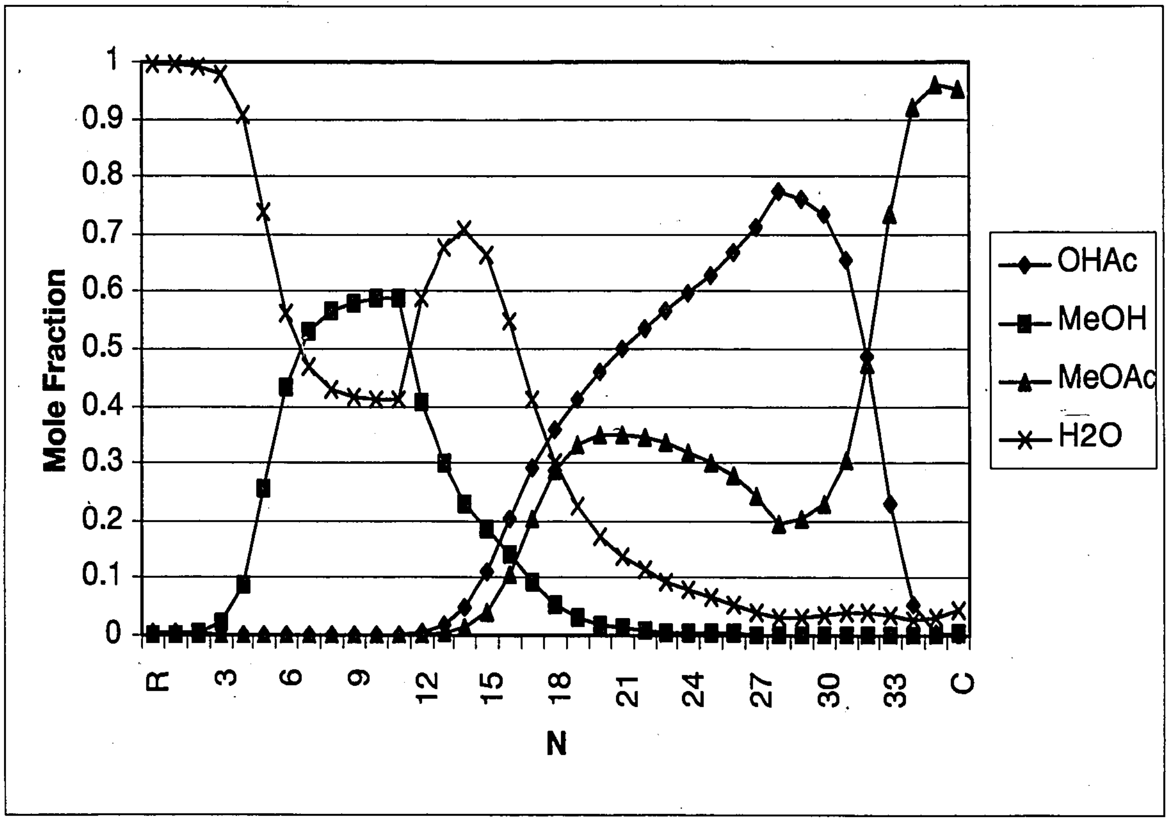

Figure 6.4: Modified Eastman MeOAc Mole Fraction Profile

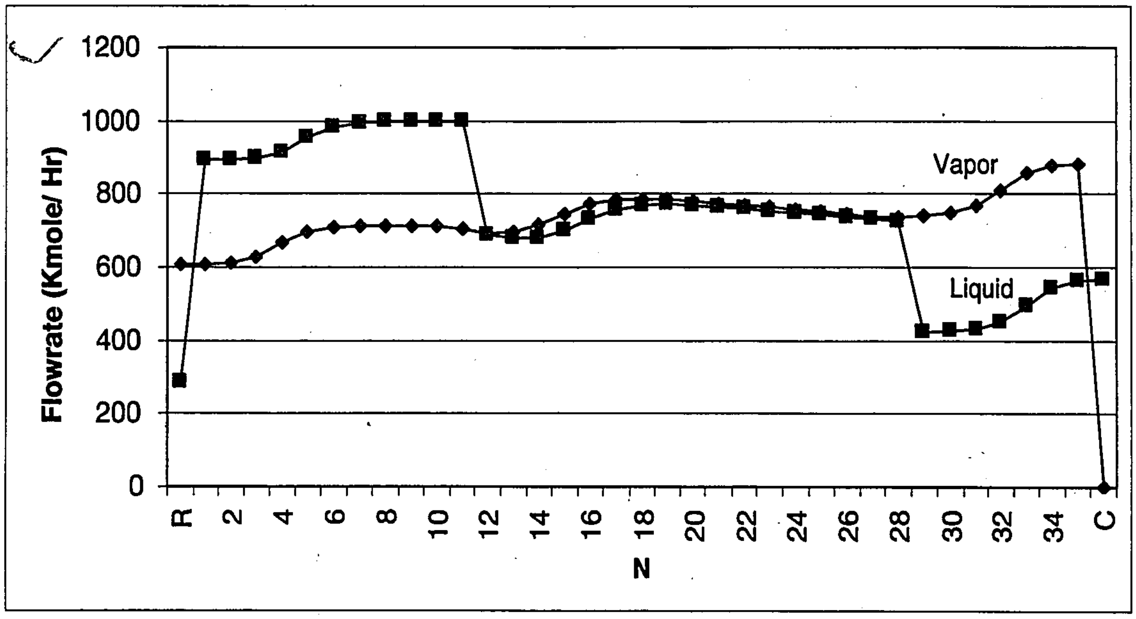

Figure 6.5: Modified Eastman MeOAc Flowrate Profile

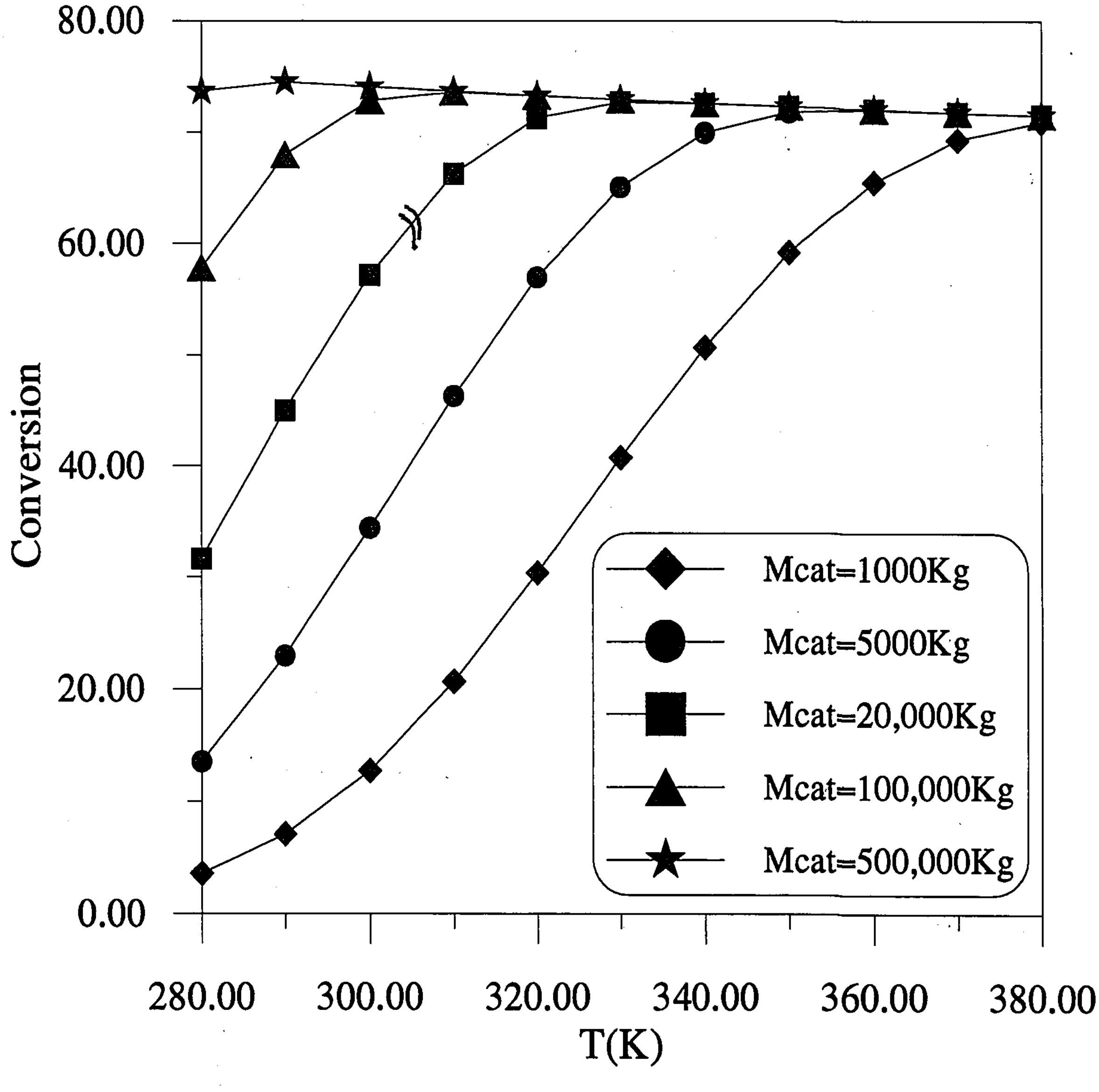

Figure 6.6: Methyl Acetate CTD

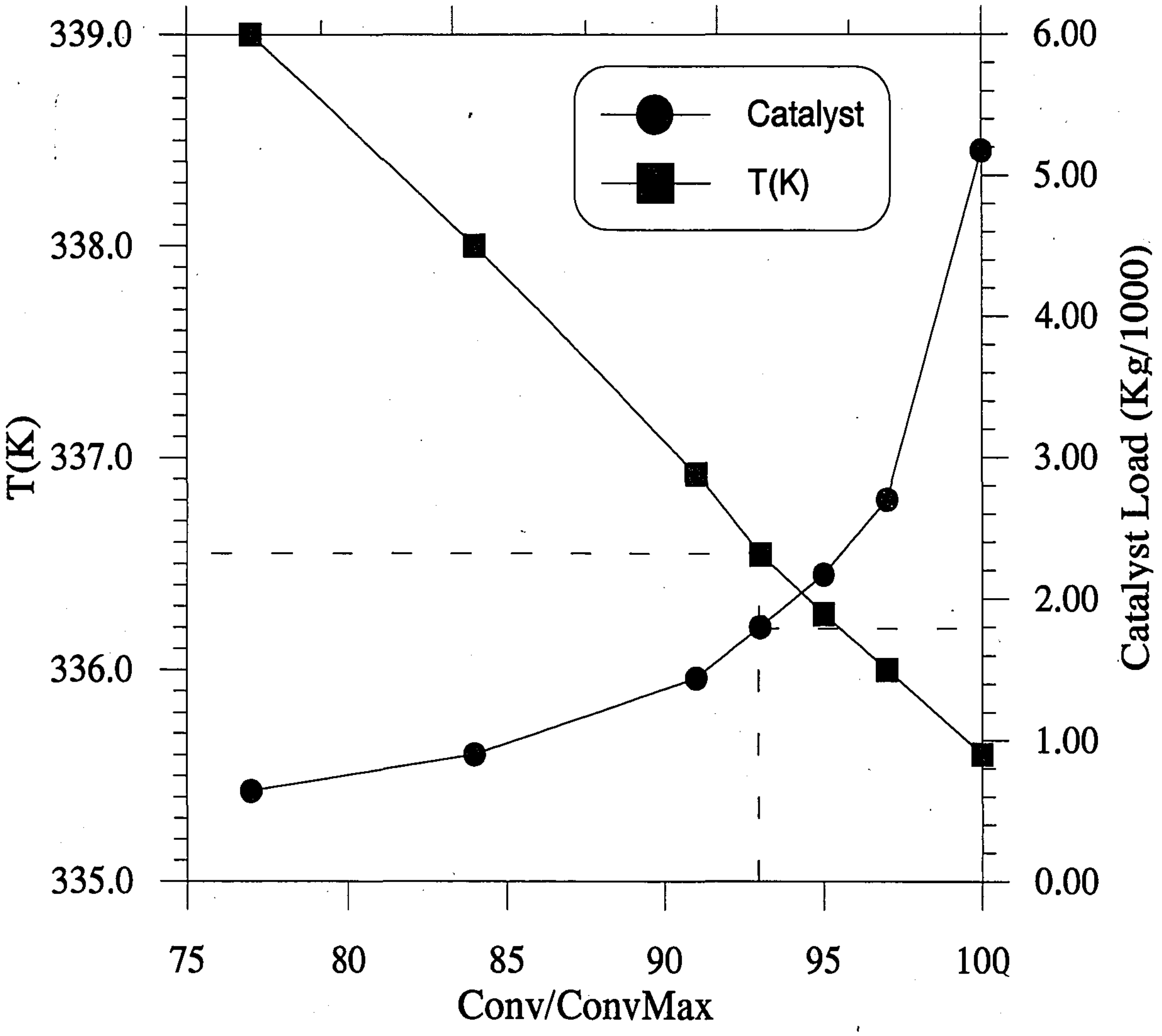

Figure 6.7: Methyl Acetate MCTD

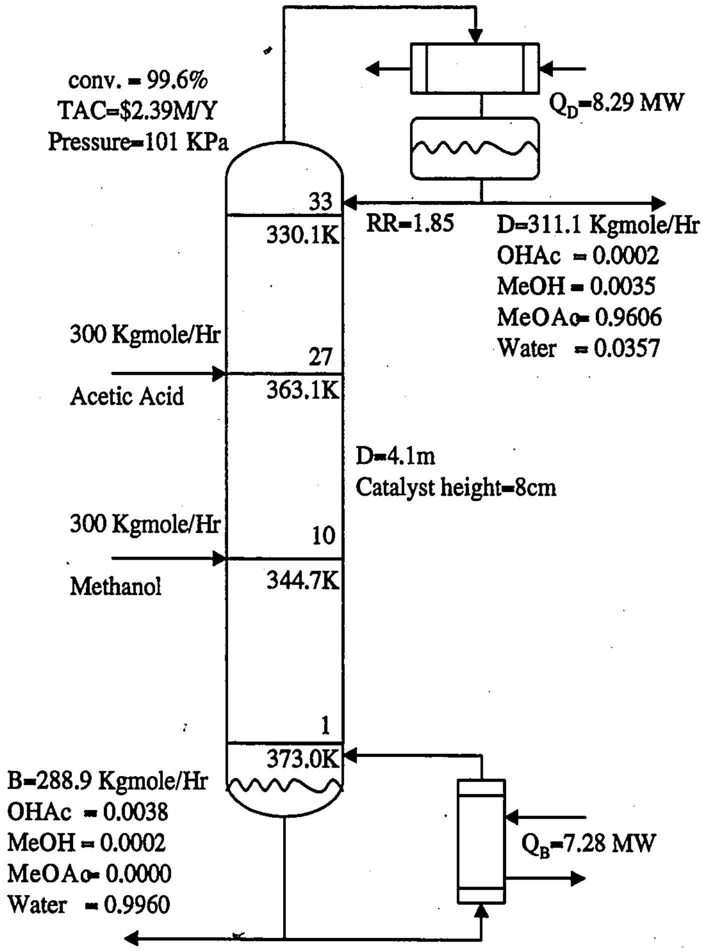

Figure 6.8: MeOAc PFD (Heuristic Design)

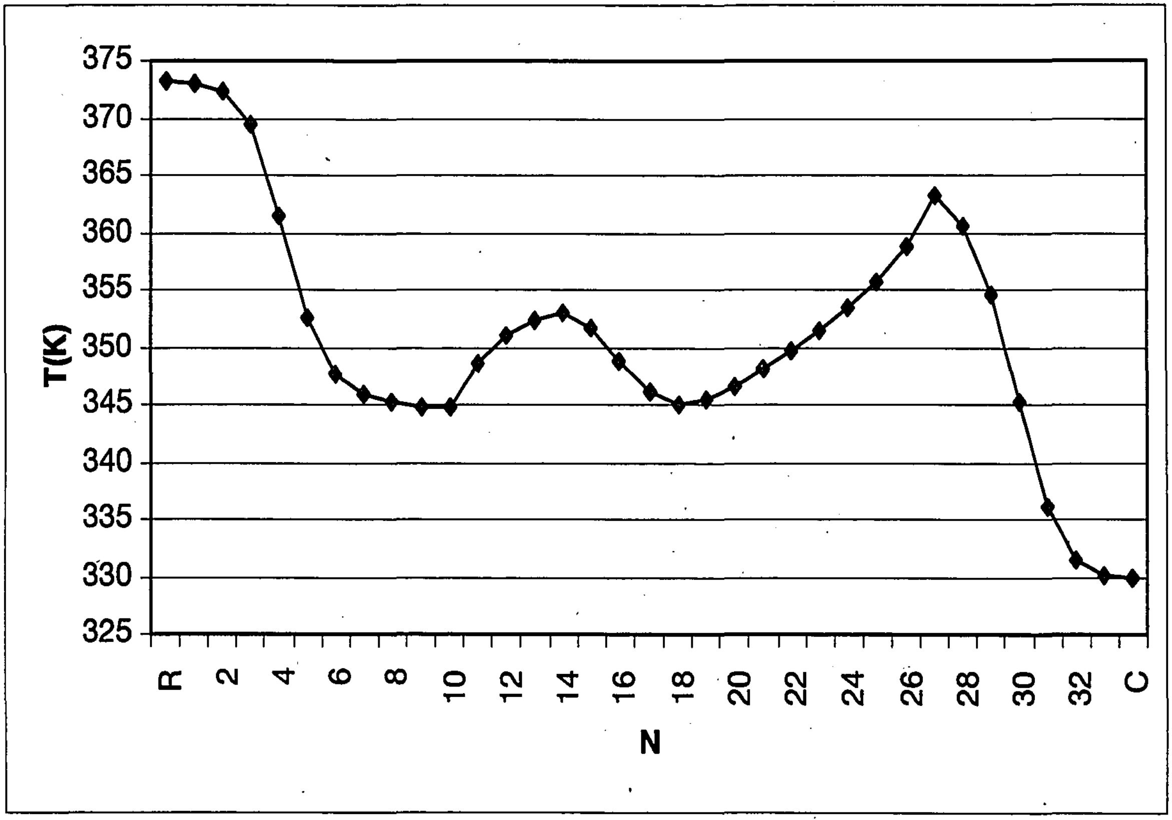

Figure 6.9: MeOAc Temperature Profile (Heuristic Design)

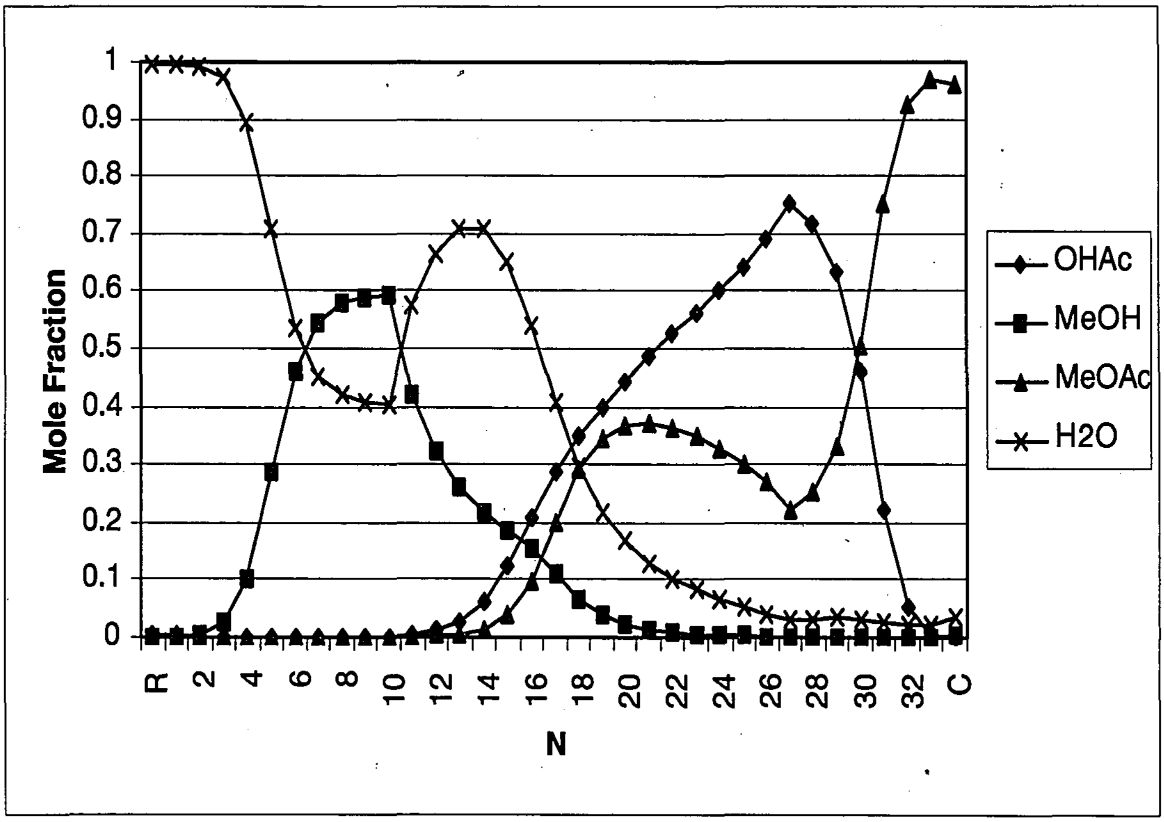

Figure 6.10: MeOAc Mole Fraction Profile (Heuristic Design)

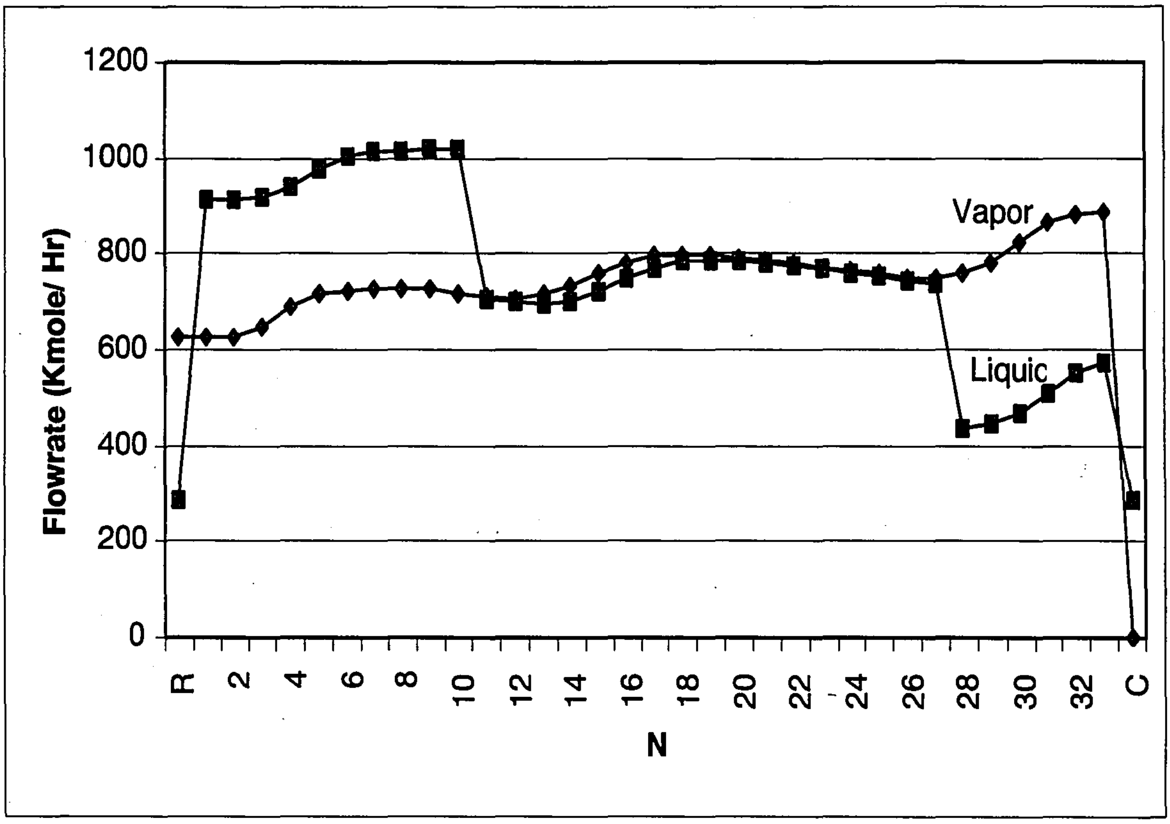

Figure 6.11: MeOAc Flowrate Profile (Heuristic Design)

Chapter 7

Other Reactive Distillation Systems

7.1 Introduction

In this section we discuss briefly our preliminary work with the TAME and TAA systems. TAME production reaction is a highly exothermic reaction ($\Delta H^{\circ}_{rxn} \simeq -75\, Kj/mole$). TAA reaction is considered as well to be highly exothermic ($\Delta H^{\circ}_{rxn} \simeq -46\, Kj/mole$). Based on the heat of reactions both systems are considered to fall in Case I category. Both reactions need a lot of excess of one of the reactants to obtain high conversion. Unfortunately, our present heuristic method does not address the design in case of an excess of one reactants. The application of the heuristic method to these systems require and is the subject of future research.

7.2 TAME System

The TAME is produced by reacting 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) with methanol. The reaction is equilibrium limited and the equilibrium conversion at $60°C$ is 56%. The three main reactions are:

$$2M1B + MeOH \rightleftharpoons TAME \tag{7.1}$$

$$2M2B + MeOH \rightleftharpoons TAME \tag{7.2}$$

$$2M1B \rightleftharpoons 2M2B \tag{7.3}$$

The etherification reactions are exothermic and thus the equilibrium conversion will decrease as temperature increases. The first etherification reaction which uses 2M1B is preferred over the second one because the first one is faster than the second reaction.

Subawalla [18] considered this system as an example to test his design heuristics. He used the kinetics proposed by [16]. Recently, better kinetic parameters were obtained by the same author. This will affect Subawalla's findings which were based on the old parameters. We used the old parameters that Subawalla used for comparison purposes. Later when a design is to be made, the new kinetic parameters should be used instead. The typical stream that is fed to react with methanol to produce the TAME is obtained from a catalytic cracker which consists of i-pentane, n-pentane, 1-pentene, 2-pentene, 2M1B and 2M2B. UNIFAC is used to predict the liquid activity coefficients.

The Subawalla design used a pre-reactor with a 25% excess methanol. The pre-reactor products were fed to the reactive distillation with another methanol feed which makes the overall methanol excess about 100%. The CTD of the system where the three reactions are considered and a stoichiometric ratio of methanol to 2M1B is fed is shown in Fig. 7.1. This shows that our method suggests that the system requires a huge amount of catalyst when a stoichiometric reactants are fed. This CTD explains why Subawalla used a pre-reactor and a large methanol excess.

Our method does not handle the cases where a pre-reactor or a huge excess of one reactants is need. However, we tried to improve our method in order to be able to handle such cases. A new diagram which shows the amount of catalyst at 80% conversion as a function of methanol excess was generated. In that diagram, the amount of catalyst at 80% conversion will drop as we increase the methanol excess until it reaches a steady-state point where no matter how much excess methanol is used the amount of catalyst will not decrease. This diagram is shown in Fig. 7.2. The idea was to pick that excess of methanol and the amount of catalyst and use them directly in the reactive distillation without the pre-reactor. However, the amount of catalyst obtained from that diagram (about 200 Kg Catalyst/ Kgmole/ Hr) is still large, but our original method suggests 7 times that amount. Subawalla used about 115 Kg of catalyst/Kgmole of isoamylene which is about double the amount we obtained in Fig. 7.2. This suggests that we may modify our method for cases similar to this case such that we consider the catalyst at 80% conversion to be the required total amount of catalyst.

Our method suggests a refrigeration in the condenser. In most cases this is not justified. Therefore, the other alternative is to set the pressure in the column such that cooling water is used instead. By doing that we are losing on the conversion as we are limited by the chemical equilibrium constrain. Using the top product composition from Subawalla's column, the pressure which enables us to use cooling water in condenser is 2.79 atm. Since the pressure was selected similar to Case II, the other procedure for Case II should be followed. Following that procedure by obtaining the MCTD and 93% of the conversion ratio, this path does not yield a design close to Subawalla's design. The MCTD for the case of 100% excess methanol is shown in Fig. 7.3. This system is subject for a future research and improvements.

7.3 TAA System

TAA is formed by isoamylenes hydration. The reactions are chemical equilibrium limited to 50% olefin conversion. The three reactions are :

$$2M1B + H2O \rightleftharpoons TAA \tag{7.4}$$

$$2M2B + H2O \rightleftharpoons TAA \tag{7.5}$$

$$2M1B \rightleftharpoons 2M2B \tag{7.6}$$

Gonzalez *et. al.* [4] studied the reactive distillation of this system experimentally. They developed a kinetic expression which considers only the reaction of 2M2B due to its excess presence in the feed. The reaction rate expression is:

$$r_{TAA} = \frac{4.9 \cdot [1.01 \times 10^{14} exp(-8359/T(K)) a_{2M2B} \cdot a_W^{3.64} - 7.6 \times 10^{15} exp(-10448/T(K)) a_{TAA}]}{\left(1 + 26.2 \cdot a_W^{3.64}\right)^2} \tag{7.7}$$

Where a_i is the activity which is $x_i \times \gamma_i$. The activity coefficient (γ) is calculated by UNIFAC.

In their experimental work, they used a packed bed reactive column. Acetone was used as a solvent because the reactants are mutually insoluble. Subawalla *et. al.* [5] used a rate based model to verify the experimental results. The water in the feed he used was about 250% excess. This system needs a large excess of one reactant to achieve high conversion and therefore we expected that our method will overestimate the total amount of catalyst needed. For example, for about 250% excess water Subawalla used about 115 Kg catalyst/ Kgmole 2M2B/Hr while our method suggests a value more than 500 times bigger than that.

If Case II design procedure is followed, a pressure around 1.87 atm will enable us to use cooling water in the column. However, the procedure did not predict the amount of catalyst correctly. The MCTD for the case of 150% excess water is shown in Fig. 7.4. This shows that our method needs to be modified to handle cases where large excess is needed. This motivates us to proceed with the ideas we have about modifying our method for such case.

7.4 Ethylene Glycol

Ethylene glycol (EG) is produced from an irreversible liquid reaction of water (H_2O) and ethylene oxide (EO):

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2$$

Ethylene glycol reacts further with ethylene oxide to produce an unwanted by-product diethylene glycol (DEG) :

$$C_2H_4O + C_2H_6O \rightarrow C_4H_{10}O_3$$

The two reactions are exothermic. Ciric and Gu [7] applied a mixed integer nonlinear programming (MINLP) model to synthesize a reactive distillation column. This method is considered as a rigorous method to find the optimum solution. In their design, the pressure was not a design parameter. The holdup in their method was allowed to vary as much as needed to achieve the desired selectivity and conversion. The liquid height on the trays was as high as 42 inches which is impractical.

Although we believe that our method is applicable to homogeneous as well as heterogeneous reactions, none of the cases which were examined was a homogeneous reaction. The parralel reactions system that is taking place in this system was not investegated in the other systems. Therefore, this system will be of an interest in the future work.

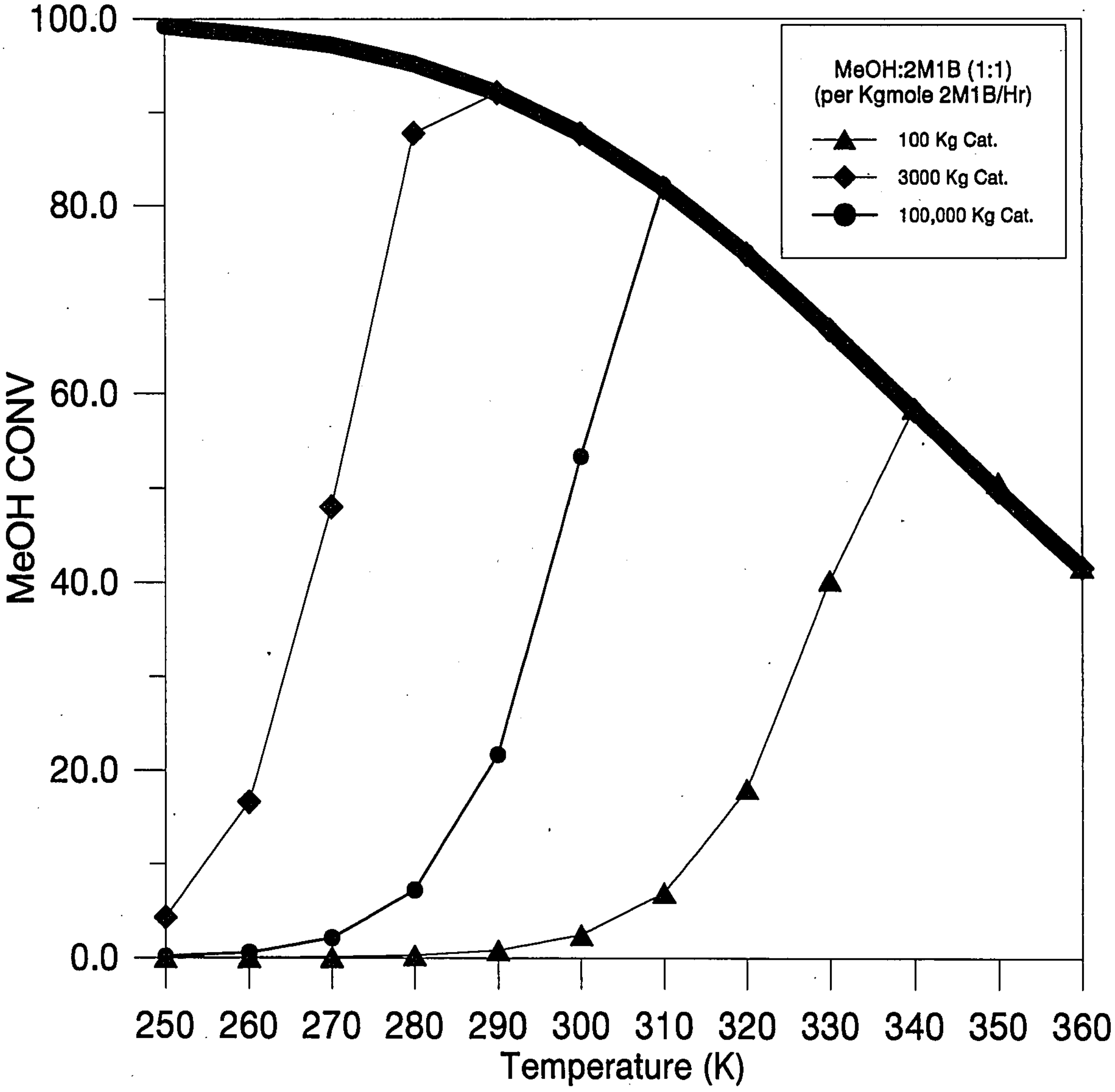

Figure 7.1: TAME CTD

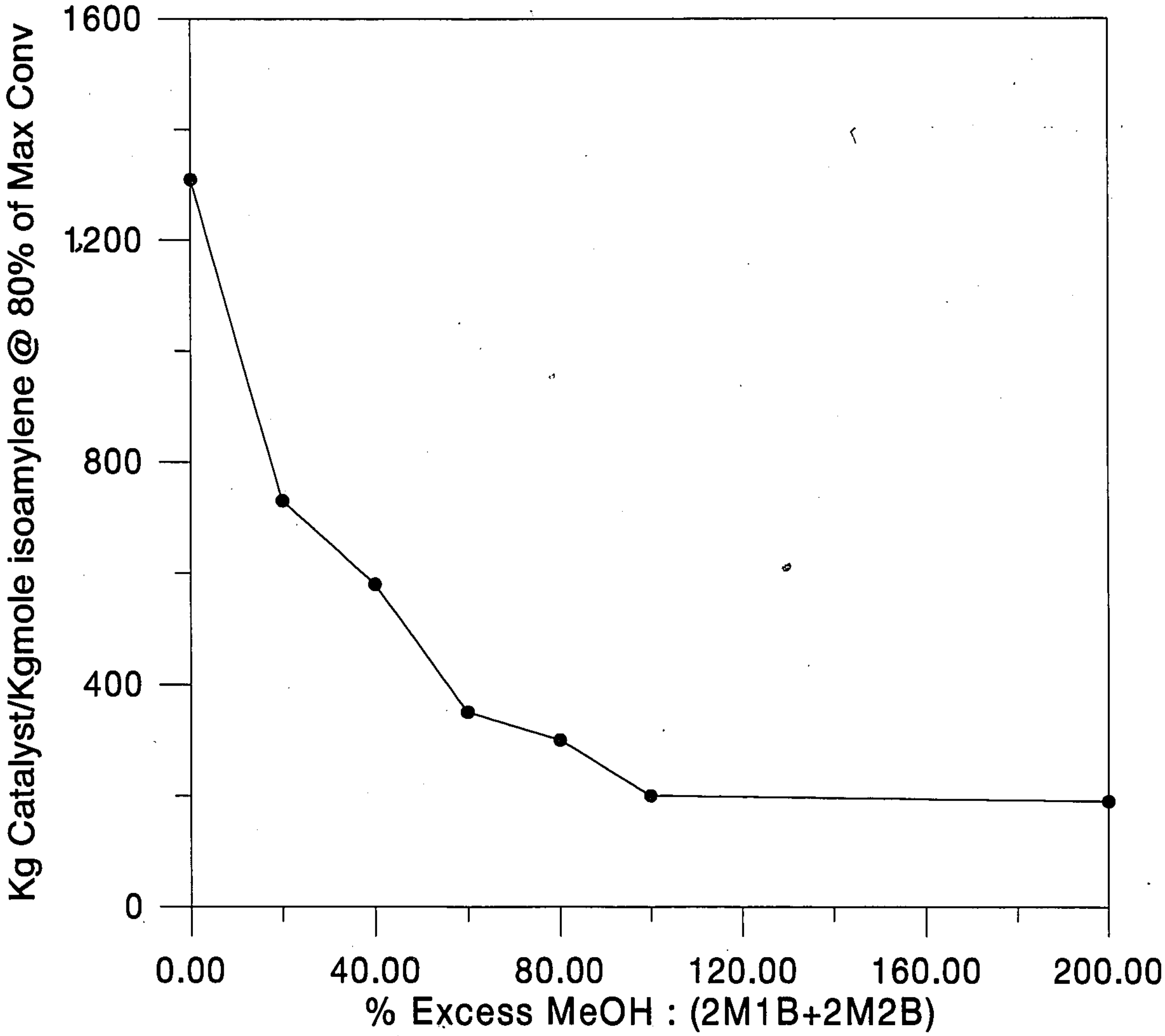

Figure 7.2: Effect of Methanol Excess

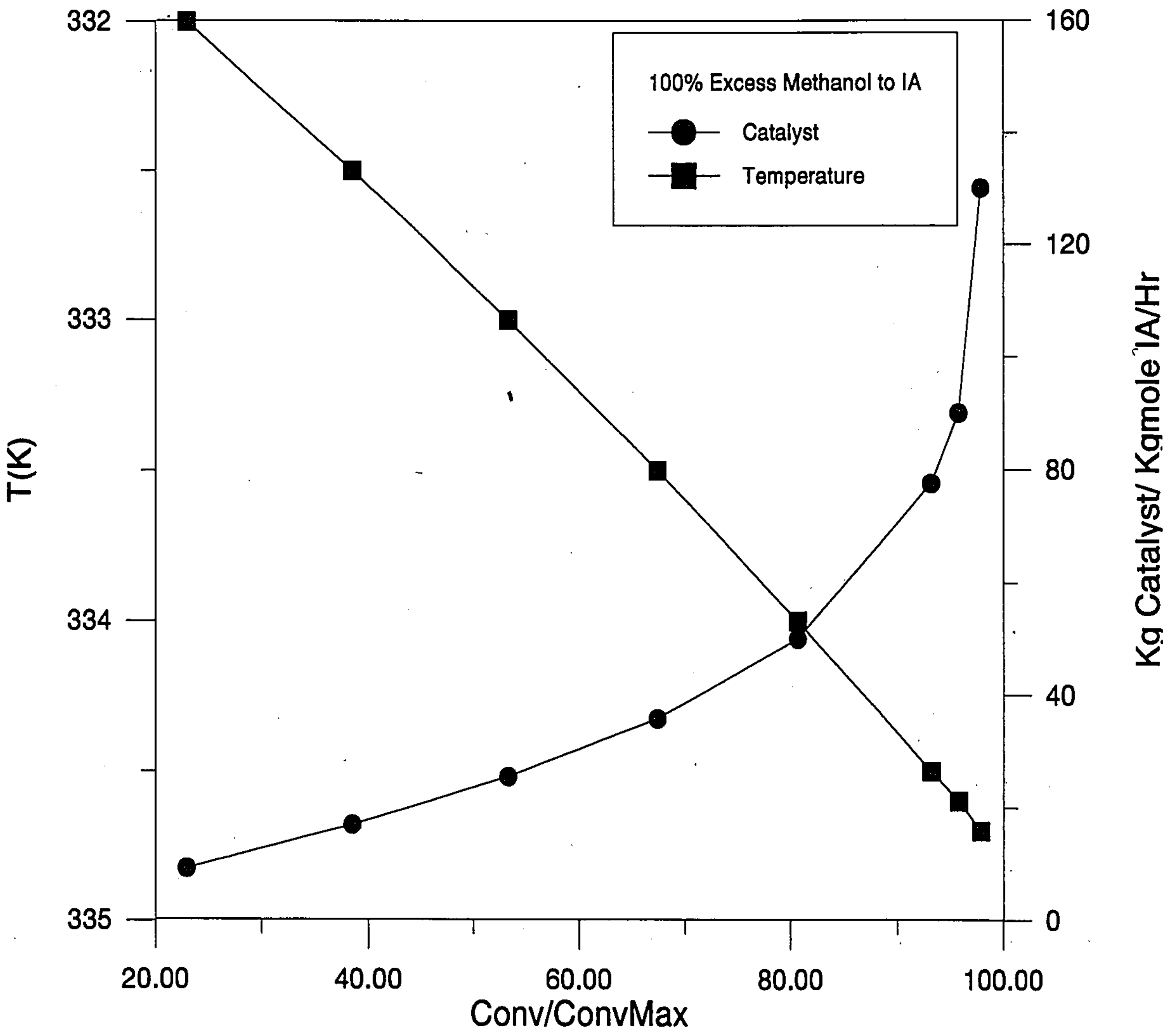

Figure 7.3: TAME MCTD

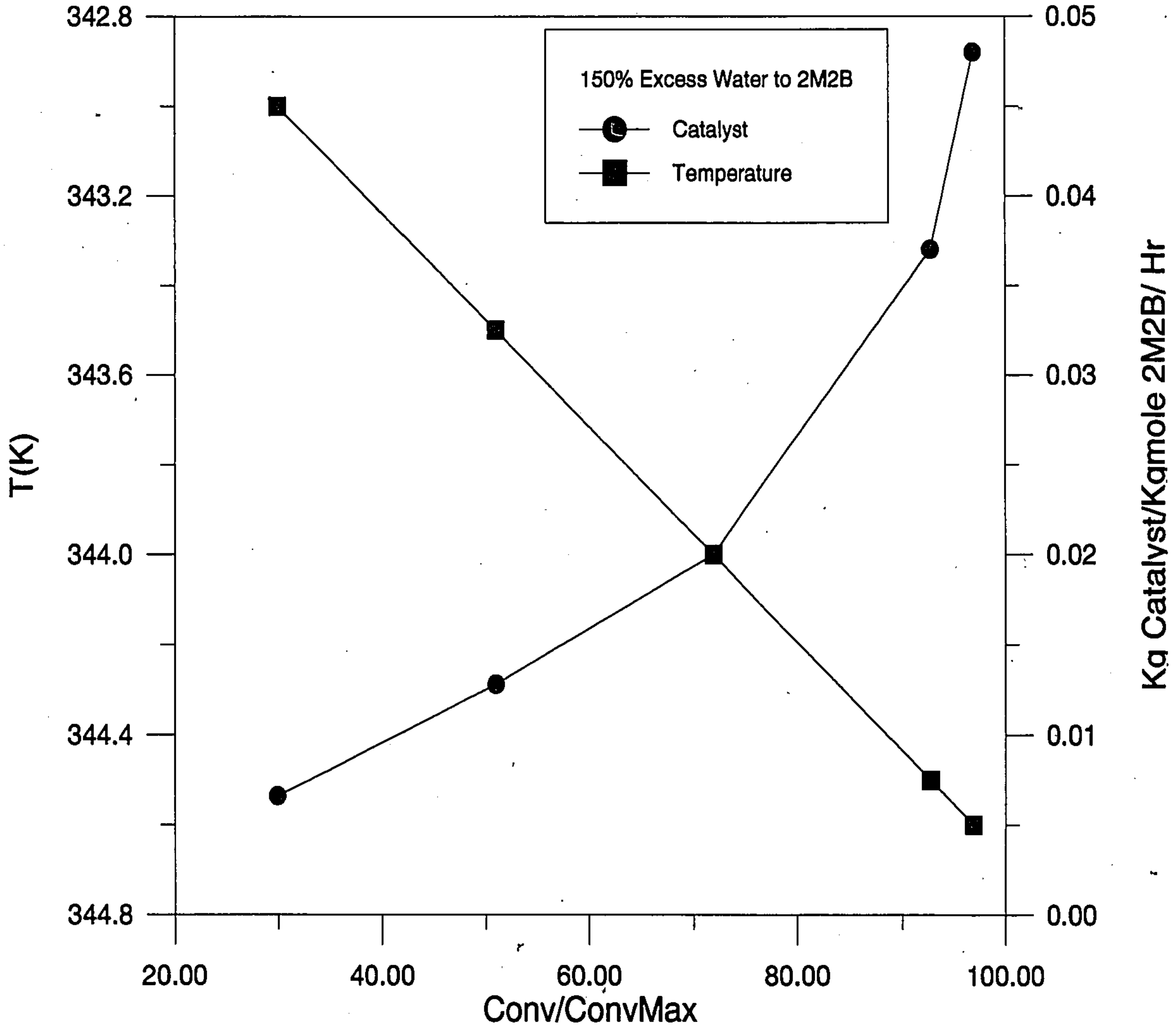

Figure 7.4: TAA MCTD

Chapter 8

Future Work and Conclusion

There is a great need for a simple heuristic approximation design proceedure for reactive distillation. The development of such a method would be quite useful. The method developed in this work is based on two cases. It can be extended to cover more cases but additional data are required. Although this method is not applicable to all the systems, it covers a wide range of applications. The more systems become available in the literature, the more we can extend this method to a bigger applicability range. The importance of pursing this work and developing this method relies on the fact that it is a simple and a good way to start designing this important process. This work is an initial exploration that we hope will be investigated more to refine and extend it.

Reactive distillation, like any other process, behaves in a certain fashion depending on certain parameters. Therefore, we think that one can categorize reactive distillation systems into different groups where each group behaves the same. For each group there should be short-cut rules that one can apply to obtain a good starting design. The determining factor in categorizing those groups will be the reaction(s) that take place inside the column.

A potential area of research is to do more work in studying reactive distillation systems that are available in the literature and to work out an index or set of indices to categorize these processes. Some of the things that need to be considered in categorizing the reactive distillation systems are: do we need a pre-reactor? and if yes where should most of the reaction(s) be carried out? Does any of the reactants need to be fed in excess? and how big is that excess? Do we have more than one reaction? What type of reactions are they? Is the reaction(s) exothermic or endothermic? Is the reaction(s) reversible or irreversible? How temperature dependent is the equilibrium constant? Is the reaction(s) homogeneous or heterogeneous reaction(s)? Do we need to recycle from the column? After categorizing all the available reactive systems, it is hoped that one can develop a comprehensive short-cut method.

Adding trays is the common practice to come up with a *conservative* design. This concept was assumed through out our work. However, a recent literature paper has suggested that adding additional trays in the stripping and rectifying sections of a reactive distillation column can result in a degradation in performance. This effect, if true, is interesting and counter-intuitive, and at the same time, very disturbing. It suggests that the design of reactive distillation columns cannot use *conservative* estimates of tray numbers, i. e. we cannot simply add excess trays. The problem is compounded by the large uncertainty in estimating tray efficiencies even if we know the optimum number of theoretical trays required. The implication of this is that the design of reactive distillation systems would require extensive experimental work at the pilot-plant and plant stages to find the numbers of column stages that provide the best performance. Such a scenario would mean long and expensive development programs. Studying and examining this effect is of great interest in the future research.

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Appendix A

Mathematical Models

A.1 Vapor-Liquid Equilibrium

In VLE there are three main categories: the ideal system, the ideal vapor system and the real system. In the ideal system both the vapor and the liquid phases are ideal, whereas in the ideal vapor system only the vapor is ideal while the liquid is not. The real system is the one where both the vapor and liquid are not ideal.

An ideal gas is a model gas comprised of imaginary molecules of zero volume that do not interact. Each chemical species in an ideal-gas mixture therefore has its own private properties, uninfluenced by the presence of other species. The partial pressure of component k in the ideal gas is therefore:

$$p_k = y_k P \tag{A.1}$$

where y_k is the vapor mole fraction of component k and P is the total pressure. The vapor property M of an ideal gas can then be expressed mathematically as:

$$M^{ig}(T, p_k) = \sum y_k M_k^{ig}(T, p_k) \tag{A.2}$$

An ideal solution is one in which molecules are of the same size and all forces between them (like and unlike) are equal. Ideal solution behavior is often approximated by solutions comprised of molecules that are not too different in size and of the same chemical nature. Combining the ideal gas and the ideal solution models of phase behavior produces a simple and useful equation known as Raoult's law, which can be expressed as follows:

$$y_k P = x_k P_k^{sat} \tag{A.3}$$

where x_k is the liquid mole fraction of component k and P_k^{sat} is the vapor pressure of component k. According to Eq. A.3, the left-hand side is the partial pressure of species k in the vapor phase, equal here to the product of the liquid-phase mole fraction of species k and its vapor pressure at temperature T. Vapor pressure is function of temperature only and can be found using the Antoine equation.

The equilibrium constant, K, is defined as:

$$K(x, y, T, P) = \frac{y}{x} \tag{A.4}$$

By using both Eq. A.3 and Eq. A.4, the equilibrium constant for the ideal system becomes:

$$K_k(T) = \frac{P_k^{sat}}{P} \tag{A.5}$$

Although the ideal system representation is useful and simple to implement, it is not accurate especially in representing the liquid phase behavior. Therefore, several corrections have been developed to more accurately capture the vapor-liquid equilibrium behavior. Fugacity coefficient, ϕ, and activity coefficient, γ, are used to correct vapor-phase and liquid-phase non-ideality respectively. For many applications, specially at low to moderate pressure, the vapor phase can be assumed to follow ideal behavior and therefore the fugacity coefficient is set to unity. Liquid phase non-ideality, however, can only rarely be ignored. There are many correlations to predict the liquid phase non-ideality via activity coefficients. Two of those correlations have been used in our research: Wilson and UNIFAC.

For a multicomponent system, the Wilson model to predict the activity coefficient is:

$$\ln \gamma_i = 1 - \ln\left(\sum_{j=1}^{C} x_j \Lambda_{ij}\right) - \sum_{k=1}^{C}\left[\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{C} x_j \Lambda_{kj}}\right] \tag{A.6}$$

Where

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left(\frac{-A_{ij}}{RT}\right) \tag{A.7}$$

V_j = Molar volume, $A_{ij} \equiv$ Wilson parameters and R is the universal gas constant.

The Wilson correlation predicts the liquid phase non-ideality based on local-composition theory. In several cases Wilson correlation cannot accurately predict the activity coefficient of the multicomponent system. The most recent correlation that is claimed to be more applicable than any other single correlation method is UNIFAC, which is based on the UNIQUAC correlation. UNIQUAC stands for UNIversal QUAsi-Chemical. UNIFAC, on the other hand, stands for UNIquac Functional group Activity Coefficients. The UNIFAC method for evaluation of activity coefficients depends on the concept that a liquid mixture may be considered a solution of the structural units from which the molecules are formed rather than a solution of the molecules themselves. The structural units are called subgroups. An identifying number, represented by k, is associated with each group. The relative volume R_k and relative surface area Q_k are properties of the subgroup. The great advantage of the UNIFAC method is that a relatively small number of subgroups combine to form a very large number of molecules. Activity coefficients depend not only on the subgroup properties R_k and Q_k, but also on interactions between subgroups.

The UNIFAC method is based on the UNIQUAC equation, for which the activity coefficients are given by:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{A.8}$$

But the combinatorial part $\ln \gamma_i^C$ and the residual part $\ln \gamma_i^R$ are calculated in UNIFAC as follows:

$$\begin{aligned} \ln \gamma_i^C &= 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) && \text{(A.9)} \\ \ln \gamma_i^R &= q_i \left(1 - \ln L_i\right) - \sum \left(\theta_k \frac{s_{ki}}{\eta_k} - G_{ki} \ln \frac{s_{ki}}{\eta_k}\right) && \text{(A.10)} \end{aligned}$$

The quantities J_i and L_i are given by:

$$\begin{aligned} J_i &= \frac{r_i}{\sum_j r_j x_j} && \text{(A.11)} \\ L_i &= \frac{q_i}{\sum_j q_j x_j} && \text{(A.12)} \end{aligned}$$

In addition, the following definitions apply:

$$\begin{aligned} r_i &= \sum_k \nu_k^{(i)} R_k && \text{(A.13)} \\ q_i &= \sum_k \nu_k^{(i)} Q_k && \text{(A.14)} \\ G_{ki} &= \nu_k^{(i)} Q_k && \text{(A.15)} \\ \theta_k &= \sum_k G_{ki}\, x_i && \text{(A.16)} \\ s_{ki} &= \sum_m G_{mi} \tau_{mk} && \text{(A.17)} \\ \eta_k &= \sum_i s_{ki}\, x_i && \text{(A.18)} \end{aligned}$$

and

$$\tau_{mk} = \exp\left(\frac{-a_{mk}}{T}\right) \qquad \text{(A.19)}$$

Subscript i identifies species, and j is a dummy index running over all species. Subscript k identifies subgroups, and m is a dummy index running over all subgroups. The quantity $\nu_k^{(i)}$ is the number of subgroups of type k in a molecule of species i. Values of the subgroup parameter R_k and Q_k and of the group interaction parameters a_{mk} come from tabulations in the literature [22].

In some chemicals even if the pressure is low and the vapor phase can safely be assumed ideal, there should be another correction to take care about the specific non ideality in that specific chemical. Acetic Acid is one of the chemicals that is considered an associating component and when present in a mixture of component the vapor phase has to be corrected to take care of that problem. Mark and Standart (1954) and Mark (1955) developed a model to correlate the vapor-liquid equilibrium data for a mixture containing an associating component. For the associating component A

$$P y_A \xi_A = p_{AC}\, x_A\, \gamma_A \qquad \text{(A.20)}$$

where

$$\xi_A = \frac{\sqrt{1 + 4\Gamma P\, y_a\,(2 - y_A)} - 1}{2\Gamma P\, y_A\,(2 - y_A)} \qquad \text{(A.21)}$$

$$p_{AC} = \frac{\sqrt{1+4k_A P_A^{sat}}-1}{2k_A} \tag{A.22}$$

For the non-associating component B

$$P\, y_B\, \xi_B Z_B = P_B^{sat} x_B \gamma_B \tag{A.23}$$

where

$$\xi_B = \frac{2\left(1-y_A+\sqrt{1+4\Gamma P\, y_A\,(2-y_A)}\right)}{(2-y_A)\left(1+\sqrt{1+4\Gamma P\, y_A\,(2-y_A)}\right)} \tag{A.24}$$

The factors ξ_A and ξ_B; which express the influence of the vapor phase association of A, may be evaluated from a knowledge of its association constant Γ. The equation for the factor Z_B is a correlation for the non-ideality in the vapor phase and may be evaluated from any equation of state (See Section A.2); however, at low to moderate pressure this compressibility factor can be assumed unity.

The corrected vapor pressure of the association component, p_{AC}, may be determined from the association constant of pure associating component (e.g. acetic acid) k_A, and its vapor pressure, P_A^{sat}. The correlation between k_A and P_A^{sat} and temperature have been given by Mark (1955) for several components.

A.2 Equation of State

There are many EOS models available in the literature. No single model is best for all systems. In our research the Peng-Robinson (PR) equation of state was used to estimate the needed properties such as the enthalpy and the density by using the concept of the departure function and the compressibility factor.

The Peng-Robinson equation of state is

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{A.25}$$

where

$$b_i = 0.077796\frac{RT_{ci}}{P_{ci}} \tag{A.26}$$

$$m_i = 0.37646 + 1.54226\omega_i - 0.26992\omega_i^2 \tag{A.27}$$

$$a_{ci} = 0.457235\frac{(RT_{ci})^2}{P_{ci}} \tag{A.28}$$

$$\alpha_i = \left[1 + m_i\left(1 - \sqrt{\frac{T}{T_{ci}}}\right)\right]^2 \tag{A.29}$$

$$a_i = a_{ci}\,\alpha_i \tag{A.30}$$

$$\frac{da_i}{dT} = -m_i a_{ci}\sqrt{\frac{\alpha_i}{T T_{ci}}} \tag{A.31}$$

$$b = \sum_i x_i b_i \tag{A.32}$$

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i\, a_j} \tag{A.33}$$

$$\frac{da}{dT} = \frac{1}{2}\frac{x_i x_j}{\sqrt{a_i a_j}}\left(a_i\frac{da_j}{dT} + a_j\frac{da_i}{dT}\right) \tag{A.34}$$

$$A = \frac{aP}{(RT)^2} \tag{A.35}$$

$$B = \frac{bP}{RT} \tag{A.36}$$

The $T_{c,i}$, $P_{c,i}$, and ω_i are the critical temperature, critical pressure and the acentricity factor, respectively, of component i. x_i is the liquid mole fraction if a liquid property, such as the liquid enthalpy, is to be found and is equal to vapor mole fraction if a vapor property, such as the vapor enthalpy, is to be found. The compressibility factor can be calculated using the PR EOS as:

$$Z^3 - (1 - B)\,Z^2 + \left(A - 2B - 3B^2\right)Z - \left(AB - B^2 - B^3\right) = 0 \tag{A.37}$$

There are three roots for Eq. A.37. The smallest one corresponds to the liquid compressibility factor Z^L and the largest one corresponds to the vapor compressibility factor Z^V. The middle root has no meaning.

Departure function is defined as the difference between the property in the real state and an ideal gas state at the same temperature. The enthalpy departure function using PR EOS is:

$$H(T,P) - H^{ig}(T,P) = RT\,(Z-1) + \frac{T\left(\frac{da}{dT}\right) - a}{2\sqrt{2}b}\ln\left[\frac{Z + \left(1+\sqrt{2}\right)B}{Z + \left(1-\sqrt{2}\right)B}\right] \tag{A.38}$$

The vapor enthalpy will be found if Z^V is used in Eq. A.38 and the liquid enthalpy will be found if Z^L is used in the same equation. The ideal gas vapor enthalpy is calculated as follows:

$$\begin{aligned} H_i^{ig}(T) &= H_i^{ig}(T^o) + \int_{T^o}^{T} C_{p,i}(T)\,dT && \text{(A.39)} \\ H^{ig}(T) &= \sum_i^C y_i H_i^{ig}(T) && \text{(A.40)} \end{aligned}$$

The liquid density can be evaluated using PR EOS as well as follows:

$$\rho_L = \frac{PM_w}{Z^L RT} \tag{A.41}$$

A.3 Conventional Distillation Model

As discussed earlier in Section 2.1, we used a MESH model in our research. MESH model is commonly used in modeling conventional distillation processes and it is reasonably accurate. A schematic diagram of an equilibrium tray is shown in Fig. A.1.

Referring to Fig. A.1, the governing equations are:

Total material balance

Total column

$$\sum_{j=1}^{NT} F_j = \sum_{j=1}^{NT} (U_j + W_j) + D + B \tag{A.42}$$

Total condenser

$$V_{NT} = D(1 + RR) \tag{A.43}$$

Tray j

$$V_{j-1} + L_{j+1} + F_j = (L_j + U_j) + (V_j + W_j) \tag{A.44}$$

Reboiler

$$L_1 = B + V_B \tag{A.45}$$

Component material balance

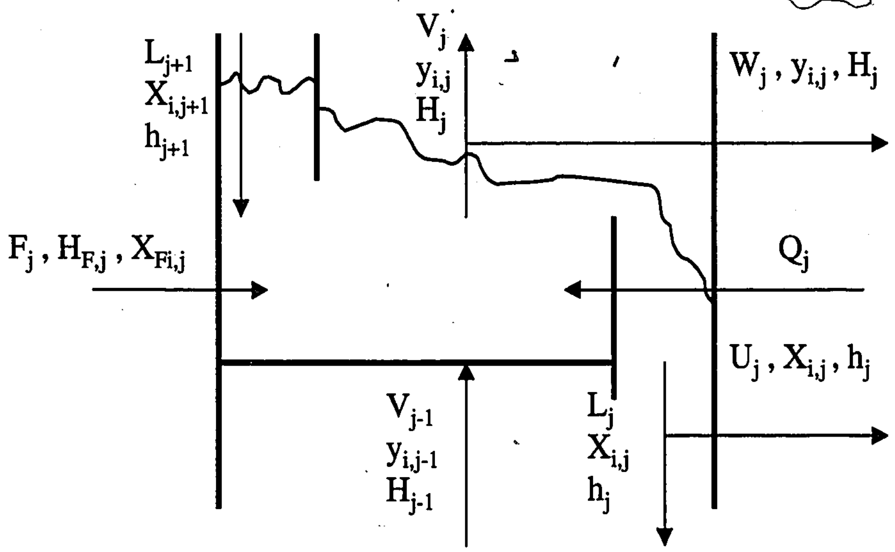

Figure A.1: Equilibrium Tray

Total condenser

$$V_{NT}\, y_{i,NT} = D(1+RR)x_{i,D} \tag{A.46}$$

Tray j

$$V_{j-1}y_{i,j-1} + L_{j+1}x_{i,j+1} + F_{i,j} = (L_j + U_j)x_{i,j} + (V_j + W_j)y_{i,j} \tag{A.47}$$

Reboiler

$$L_1 x_{i,1} = Bx_{i,B} + V_B\, y_{i,B} \tag{A.48}$$

Total heat balance

Total condenser

$$V_{NT}\, H_{NT} = D(1+RR)\, h_D + Q_D \tag{A.49}$$

Tray j

$$V_{j-1}H_{j-1} + L_{j+1}h_{j+1} + F_j H_j^F + Q_j = (L_j + U_j)\, h_j + (V_j + W_j)\, H_j \tag{A.50}$$

Reboiler

$$L_1 h_1 + Q_B = B\, h_B + V_B\, H_B \tag{A.51}$$

Equilibrium equation

$$y_{i,j} = K_{i,j}\, x_{i,j} = \frac{\gamma_{i,j}\, P^{sat}_{i,j}}{P}\, x_{i,j} \tag{A.52}$$

Summation equation

$$\sum_i y_{i,j} = 1.0 \tag{A.53}$$

$$\sum_i x_{i,j} = 1.0 \tag{A.54}$$

where L, V, F ,U ,W, x_i, y_i, $x_{F,i}$, h, H, H^F, Q, γ_i, P_i^{sat}, P are the liquid flowrate, the vapor flowrate, the feed flowrate, the liquid side stream flowrate, the vapor side stream flow rate, the liquid mole fraction of component i, the vapor mole fraction of component i, the feed mole fraction of component i, the liquid enthalpy, the vapor enthalpy, the feed enthalpy, the side heating or cooling rate, the activity coefficient of component i, the vapor pressure of component i, and the pressure respectively on their respective stages.

Appendix B

Numerical Methods

B.1 Muller Method

The Muller method uses a quadratic equation to estimate the solution. The idea is illustrated in Fig. B.1. Three values of the unknown x variable are guessed: x_1, x_2,and x_3. The function is evaluated at these three values of x, giving f_1, f_2, and f_3. A quadratic curve is drawn through these points.

$$g(x) = a_0 + a_1 x + a_2 x^2 \tag{B.1}$$

Then the equation $g(x) = 0$ is solved for the two roots, and the appropriate one is selected for the next guess of $x\,(x_4)$. In Fig. B.1 the appropriate root is the one between x_1 and x_2.

The Muller method converges more quickly than Newton-Raphson method when the function have more curvature. However, it is more complex to program and more susceptible to numerical divergence problems.

B.2 The Newton-Raphson Method

The Newton-Raphson method is one of the most effective methods to solve nonlinear algebraic equations. The method is very powerful; but it has the disadvantage that the derivative is needed. This can be a problem when one deals with complex coupled nonlinear algebraic equation, for example, the reactive distillation model. To circumvent this problem, one can estimate the derivative

$$\frac{dF(x)}{dx} \approx \frac{F(x+\Delta x)-F(x)}{\Delta x} \tag{B.2}$$

For system of equations, the Newton-Raphson can be implemented iteratively to find the new solution as follows:

$$\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} - \mathbf{J}^{-1}\left(\mathbf{x}^{(k)}\right) \cdot \mathbf{F}\left(\mathbf{x}^{(k)}\right) \tag{B.3}$$

where **J** is the Jacobian matrix and it is defined as:

$$J(x) = \begin{bmatrix} \frac{\partial F_1}{\partial x_1} & \frac{\partial F_1}{\partial x_2} & \vdots & \frac{\partial F_1}{\partial x_n} \\ \frac{\partial F_2}{\partial x_1} & \frac{\partial F_2}{\partial x_2} & \vdots & \frac{\partial F_2}{\partial x_n} \\ \cdots & \cdots & & \cdots \\ \frac{\partial F_n}{\partial x_1} & \frac{\partial F_n}{\partial x_2} & \vdots & \frac{\partial F_n}{\partial x_n} \end{bmatrix} \tag{B.4}$$

With an initial guess close to the exact solution, Newton's method is expected to give a quadratic convergence, provided of course that the Jacobian **J** exists. Moreover, the Newton-Raphson method can experience divergence problems if the initial guess is not close to the exact solution. Therefore, having a good initial guess is the key for the Newton-Raphson method to work. Obtaining a good initial guess can be very tricky and tedious. The model can be simplified to obtain a good guess. For example, ideal VLE can be assumed first to get a solution that then can be used as an initial guess to find the non-ideal VLE solution. A good initial guess can also be obtained using the relaxation method. Figure B.2 shows the Newton-Raphson method graphically.P. C. Wankat, *Equilibrium Staged Separations*, PTR Prentice Hall, Englewood Cliffs, New Jersey, 1988.

B.3 Wang Henke Method

Wang and Henke (Wang and Henke,1966) developed a new iterative method for solving problems of multicomponent distillation in complex columns. This method employs the tridiagonal matrix algorithm for the solution of the linearized material balance equations, and uses Muller's method for the convergence of column temperature profile. The material balance is solved simultaneously for each component, and therefore no matching is required. The computational procedure is simple and fast. This method is best suited for narrow-boiling point mixtures.

The mathematical model is based on a theoretical stage model (Fig. A.1). Each tray can accept up to one feed stream and can produce up to one vapor sidestream and one liquid sidestream. Heat may be transferred to or from any tray. The governing equations for each tray were giving in Section A.3. Thus, for each equilibrium stage, with the feed,the heat transfer, the liquid, and/or vapor sidestream flowrates specified, there exist $3 + 2C$ equations, where C equals the number of chemical species. The $3 + 2C$ unknowns, at a given column pressure, are:

$$\begin{aligned} x_{i,j},\ \text{equilibrium liquid mole fractions} &= C\ \textit{unknowns} \\ y_{i,j},\ \text{equilibrium vapor mole fractions} &= C\ \textit{unknowns} \\ L_j,\ \text{liquid flow rate from one tray to ajacent tray} &= 1\ \textit{unknowns} \\ V_j,\ \text{vapor flow rate from one tray to ajacent tray} &= 1\ \textit{unknowns} \\ T_j,\ \text{tray equilibrium temperature} &= 1\ \textit{unknowns} \end{aligned}$$

Eq. A.47 and Eq. A.52 can be combined and L_j is expressed as function of V_j by an overall material balance (Eq. A.42) of all equilibrium stages from the top of the column to the jth tray

$$L_j = V_{j-1} + \sum_{k=j}^{NT} (F_k - W_k - U_k) - D \tag{B.5}$$

$$1 \leqslant j \leqslant NT$$

Eq. A.47 can then reduced to a tridiagonal matrix form,

$$B_D x_{i,D} + C_D x_{i,NT} = D_D \tag{B.6}$$

$$A_j x_{i,j-1} + B_j x_{i,j} + C_j x_{i,j+1} = D_j \tag{B.7}$$

$$1 \leqslant j \leqslant NT$$

$$A_B x_{i,1} + B_B x_{i,B} = D_B \tag{B.8}$$

or in a matrix form

$$\begin{bmatrix} B_D & C_D & & & & & & \\ A_{NT} & B_{NT} & C_{NT} & & & & & \\ & \cdots & \cdots & \cdots & & & & \\ & & A_j & B_j & C_j & & & \\ & & & \cdots & \cdots & \cdots & & \\ & & & & A_1 & B_1 & C_1 \\ & & & & & A_B & B_B \end{bmatrix} \begin{bmatrix} x_{i,D} \\ x_{i,NT} \\ \vdots \\ x_{i,j} \\ \vdots \\ x_{i,1} \\ x_{i,B} \end{bmatrix} = \begin{bmatrix} D_D \\ D_{NT} \\ \vdots \\ D_j \\ \vdots \\ D_1 \\ D_B \end{bmatrix} \tag{B.9}$$

where,

$$\begin{aligned} B_D &= -V_{NT} \\ C_D &= V_{NT} K_{i,NT} \\ D_D &= 0 \\ A_j &= L_{j+1} = V_j + \sum_{k=j}^{NT} (F_k - W_k - U_k) - D \\ B_j &= -\left[(V_j + W_j) K_{i,j} + V_{j-1} + \sum_{k=j}^{NT} (F_k - W_k - U_k) - D + U_j \right] \\ C_j &= V_{j-1} K_{i,j-1} \\ D_j &= -F_j x_{i,j}^F \\ A_B &= V_B + B \\ B_B &= -(V_B K_{i,B} + B) \\ D_B &= 0 \end{aligned}$$

Eq. B.9 is linearized by the use of assumed values of V_j and T_j and then solved for the liquid mole fraction, $x_{i,j}$ by means of Thomas algorithm. In general, the calculated liquid mole fraction $x_{i,j}$ for a given stage do not sum to 1.0 and, their sum must be normalized. A new set of stage temperature, T_j, is then computed from the component equilibrium relationships in the form of bubble-point equations. This

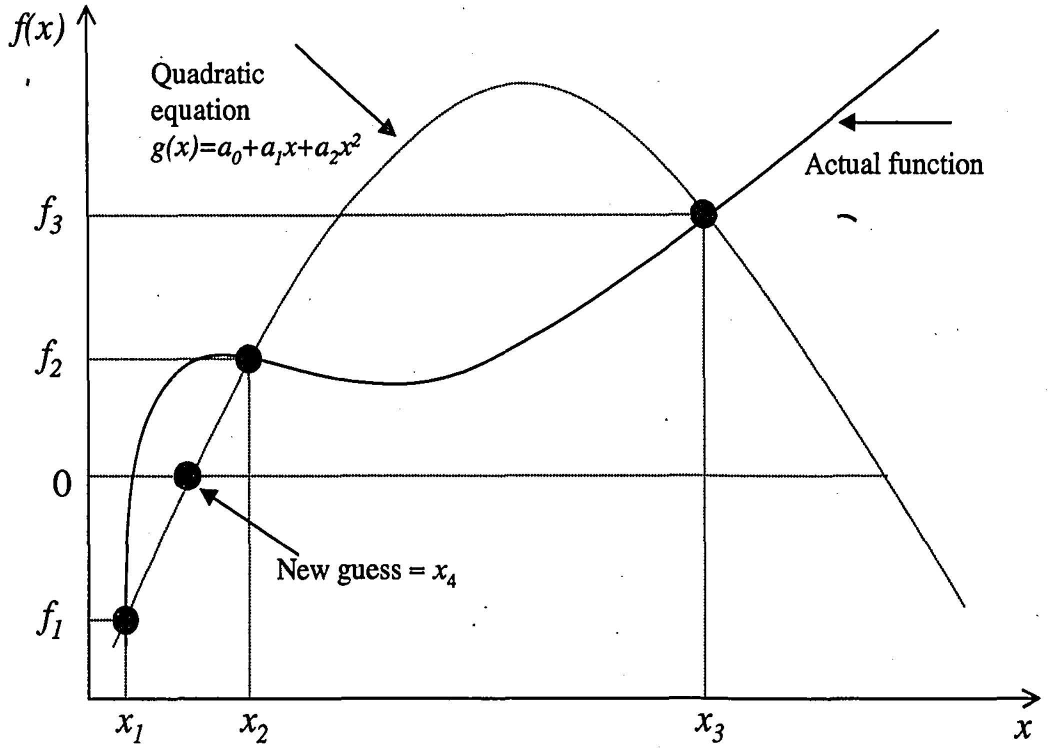

Figure B.1: Muller Method

iterative calculation utilizes Muller's method. A new set of vapor flow rate, V_j, is then computed from the heat balance equations. The entire calculation procedure for the distillation column is repeated until the differences between successive sets of computed stage temperatures satisfy the overall convergence criterion.

The algorithm that was used in our research follows Wang-Henke procedure. However, there were modifications to account for the non-ideality in the vapor-liquid equilibrium. Our algorithm is shown in Fig. B.3.

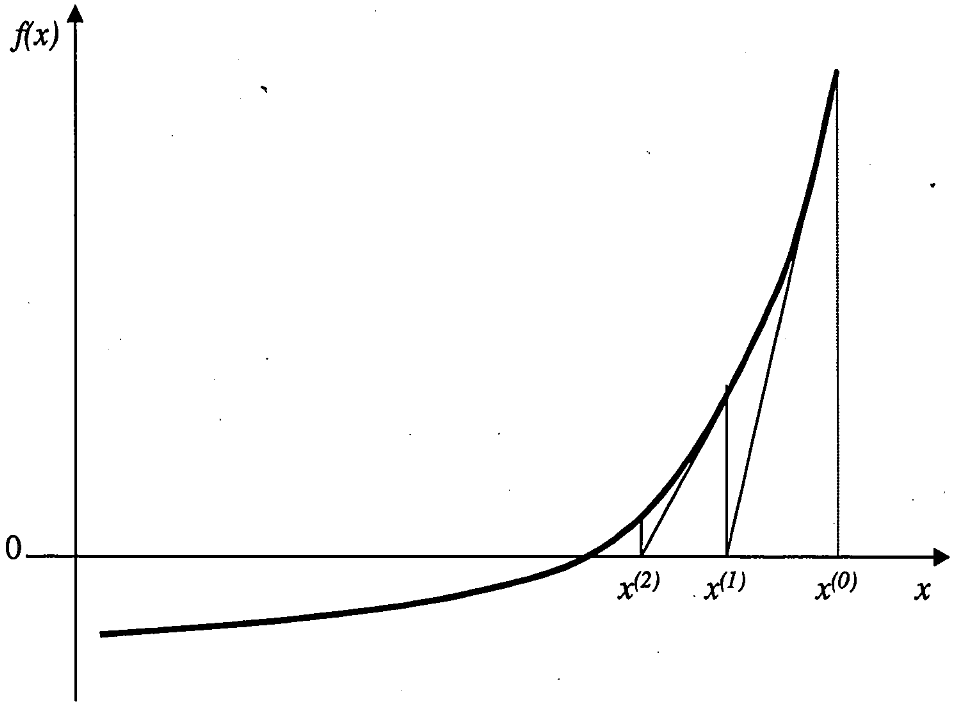

Figure B.2: Newton- Raphson Method

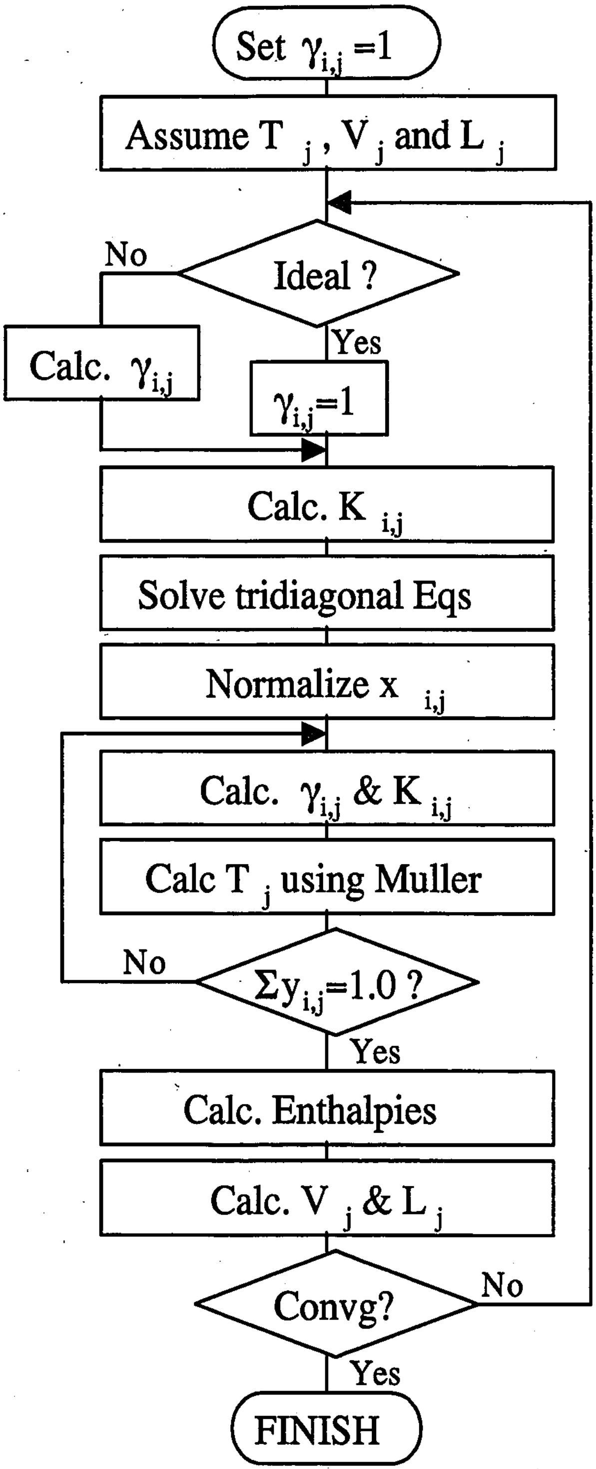

Figure B.3: Modified Wang- Henke Algorithm

Appendix C

Physical Properties

C.1 ETBE System Physical Properties

The physical properties were obtained from HYSYS [24] and they are tabulated in Table C.1-C.4.

The vapor and liquid enthalpies are calculated using the departure function. Peng-Robenson EOS was used. The vapor enthalpy is calculated from Eqs. A.38, A.39, and A.40 and the final form is:

$$H(T,P) = \sum_{i}^{C} y_i \left(H_i^{ig}(T^o) + \int_{T^o}^{T} C_{p,i}^{V}(T)\, dT \right) + RT\left(Z^V - 1\right) +$$

$$\frac{T\left(\frac{da}{dT}\right) - a}{2\sqrt{2}b} \ln \left[\frac{Z^V + \left(1+\sqrt{2}\right)B}{Z^V + \left(1-\sqrt{2}\right)B} \right] \tag{C.1}$$

Table C.1: ETBE System Vapor Pressure

$\ln P = A + \frac{B}{T+C} + D\ln T + ET^F$, T in K and P in Pa						
	A	B	C	D	E	F
$nC_4^=$	72.3277	-4488	0.00	-8.018	1.131×10^{-5}	2.0
$iC_4^=$	64.7977	-4236	0.00	-6.810	9.399×10^{-6}	2.0
Ethanol	93.3977	-7931	0.00	-10.25	6.389×10^{-6}	2.0
ETBE	82.2977	-6226	0.00	-9.192	7.938×10^{-6}	2.0

Table C.2: ETBE System Vapor Heat Capacity

$C_p^V = A + BT + CT^2 + DT^3$, T in K and C_p^V in Joule/mole/K

	A	B	C	D
$nC_4^=$	14.55	0.2804	-1.010×10^{-4}	9.098×10^{-9}
$iC_4^=$	14.55	0.2804	-1.010×10^{-4}	9.098×10^{-9}
Ethanol	19.80	0.2040	-8.450×10^{-5}	1.373×10^{-9}
ETBE	7.505	0.6293	-3.690×10^{-4}	7.072×10^{-9}

Table C.3: ETBE System Liquid Heat Capacity

$C_p^L = A + BT + CT^2 + DT^3$, T in K and C_p^L in Joule/mole/K

	A	B	C	D
$nC_4^=$	135.9	-0.4774	2.1840×10^{-3}	-2.223×10^{-6}
$iC_4^=$	35.44	0.8020	-3.120×10^{-3}	5.0450×10^{-6}
Ethanol	29.01	0.2697	-5.658×10^{-4}	2.0790×10^{-6}
ETBE	40.41	0.7532	-1.053×10^{-3}	1.8066×10^{-6}

Table C.4: ETBE System Critical Properties

	P_c (Pa)	T_c (K)	ω	$H_{std}^{vap}(T = 298.15)$ in Joule/mole	$H_{std}^{form}(T = 298.15)$ in Joule/mole
$nC_4^=$	4023×10^3	419.6	0.1870	20.22×10^3	-20.5×10^3
$iC_4^=$	4002×10^3	417.9	0.1900	20.60×10^3	-37.7×10^3
Ethanol	6147×10^3	513.9	0.6444	42.56×10^3	-277.51×10^3
ETBE	3114×10^3	517.1	0.2917	41.00×10^3	-357.50×10^3

Table C.5: MeOAc System Vapor Pressure

$\ln P = A + \frac{B}{T+C} + D \ln T + E T^F$, T in K and P in Pa

	A	B	C	D	E	F
$OHAc$	68.2477	-6769.0	0.0	-6.727	4.843×10^{-6}	2.0
$MeOH$	66.7477	-6283.0	0.0	-6.379	4.617×10^{-6}	2.0
$MeOAc$	103.4277	-7050.0	0.0	-12.38	1.137×10^{-5}	2.0
H_2O	72.8377	-7228.0	0.0	-7.177	4.031×10^{-6}	2.0

where $H_i^{ig}(T^o)$ is the standard heat of vaporization and Z^V is the largest root found from Eq. A.37. All the other terms are as the ones explained in Section A.2. In order to calculate the above equation correctly, the vapor mole fraction has to be used in Eqs. A.32 to A.37. The liquid enthalpy is calculated the same way except that $H_i^{ig}(T^o)$ is set equal to zero and the liquid mole fraction is used in Eqs. A.32 to A.37. Z^L is the smallest root found from Eq. A.37, the liquid enthalpy equation is:

$$h(T,P) = \sum_i^C x_i \left(\int_{T^o}^{T} C_{p,i}^V(T)\, dT \right) + RT\left(Z^L - 1\right) + \frac{T\left(\frac{da}{dT}\right) - a}{2\sqrt{2}b} \ln \left[\frac{Z^L + \left(1+\sqrt{2}\right) B}{Z^L + \left(1-\sqrt{2}\right) B} \right] \tag{C.2}$$

The heat of reaction is found from the following equation:

$$H^R(T) = \sum_i^C \nu_i \left(H_i^{form}(T^o) + \int_{T^o}^{T} C_{p,i}^L(T)\, dT \right) \tag{C.3}$$

where ν_i is the stoichiometric coefficient of component i in the reaction.

C.2 Methyl Acetate System Physical Properties

The physical properties were obtained from HYSYS [24] and they are tabulated in Table C.5-Table C.8.

The vapor and liquid enthalpies and the heat of reaction are calculated in the same way those enthalpies were calculated in the ETBE process which was discussed in appendix ??.

Table C.6: MeOAc System Vapor Heat Capacity

$C_p^V = A + BT + CT^2 + DT^3 + ET^4$, T in K and C_p^V in Joule/mole/K

	A	B	C	D	E
OHAc	34.28	0.041460	2.756×10^{-4}	-3.021×10^{-7}	9.129×10^{-11}
MeOH	31.49	0.013490	1.431×10^{-4}	-1.356×10^{-7}	3.751×10^{-11}
MeOAc	17.94	0.238700	-3.077×10^{-5}	-6.904×10^{-8}	2.648×10^{-11}
H_2O	33.65	-0.005723	2.316×10^{-5}	-1.172×10^{-8}	1.877×10^{-12}

Table C.7: MeOAc System Liquid Heat Capacity

$C_p^L = A + BT + CT^2 + DT^3 + ET^4$, T in K and C_p^L in Joule/mole/K

	A	B	C	D	E
OHAc	139.6	-0.3208	8.985×10^{-4}	0.0	0.0
MeOH	105.8	-0.3622	9.379×10^{-4}	0.0	0.0
MeOAc	61.26	0.2709	0.0	0.0	0.0
H_2O	276.4	-2.0900	8.125×10^{-3}	-1.412×10^{-5}	9.370×10^{-9}

Table C.8: MeOAc System Critical Properties

	P_c (Pa)	T_c (K)	ω	$H_{std}^{vap}(T = 298.15)$in Joule/mole	$H_{std}^{form}(T = 298.15)$ in Joule/mole
OHAc	5770×10^3	592.7	0.447	23.31×10^3	-435.1×10^3
MeOH	7376×10^3	512.6	0.557	38.01×10^3	-201.3×10^3
MeOAc	4690×10^3	506.8	0.326	32.39×10^3	-409.7×10^3
H_2O	2212×10^4	647.3	0.344	43.87×10^3	-241.0×10^3

Table C.9: MeOAc System Wilson Binary Parameters and Molar Volumes

	$OHAc$	$MeOH$	$MeOAc$	H_2O	molar volume $\left(\frac{m^3}{mole}\right)$
$OHAc$	0.0	2535.2019	1123.1444	237.5248	57.54
$MeOH$	-547.5248	0.0	0831.1843	107.3832	44.44
$MeOAc$	-696.5031	-31.1932	0.0	645.7225	79.84
H_2O	0658.0266	0469.5509	1918.323	0.0	18.07

The Wilson binary parameters and the molar volumes that were used are [1] found in Table C.9.

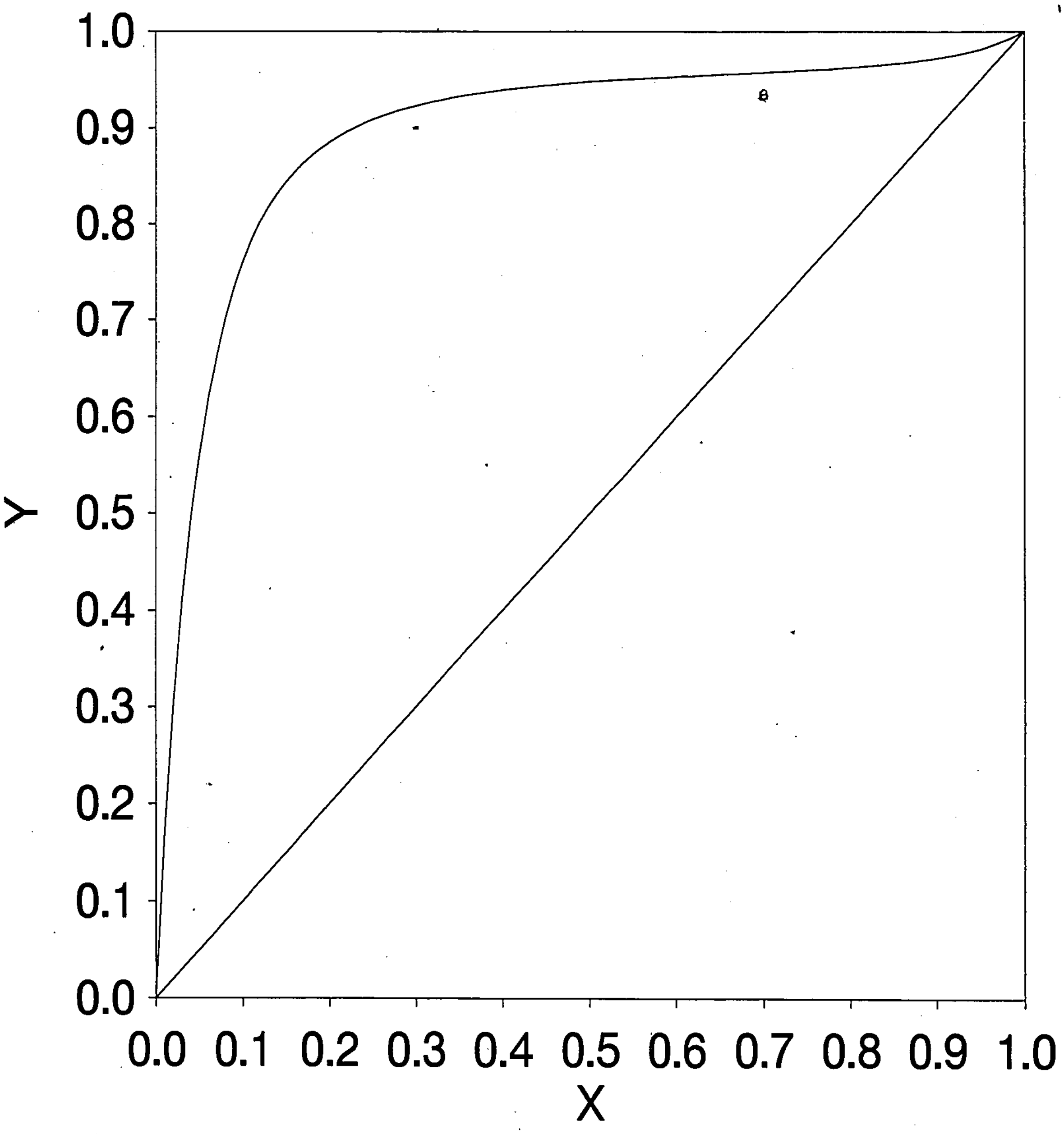

Figure C.1: $iC_4^{=}$ – *Ethanol* VLE at 7.77 atm

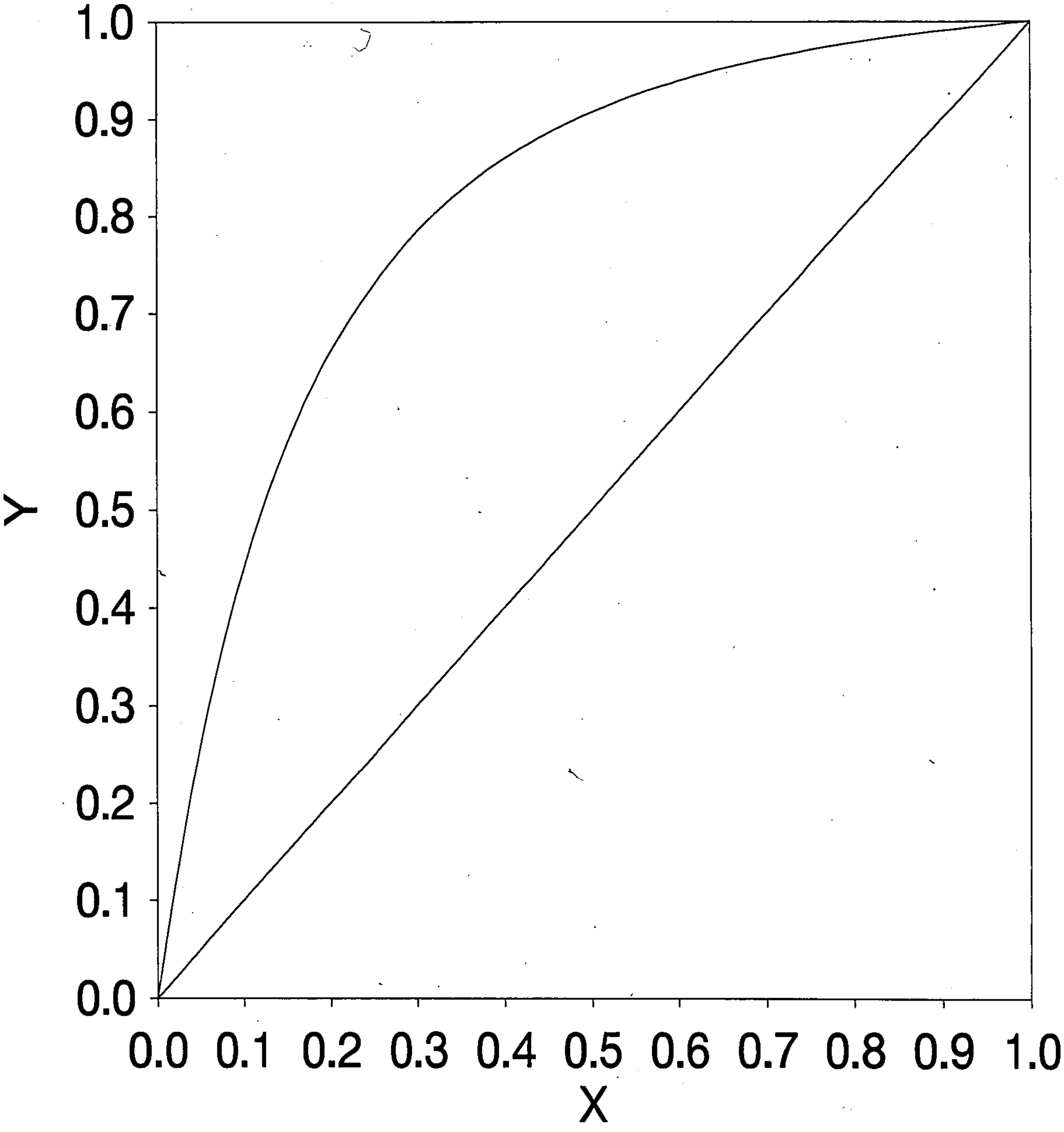

Figure C.2: $iC_4^= - ETBE$ VLE at 7.77 atm

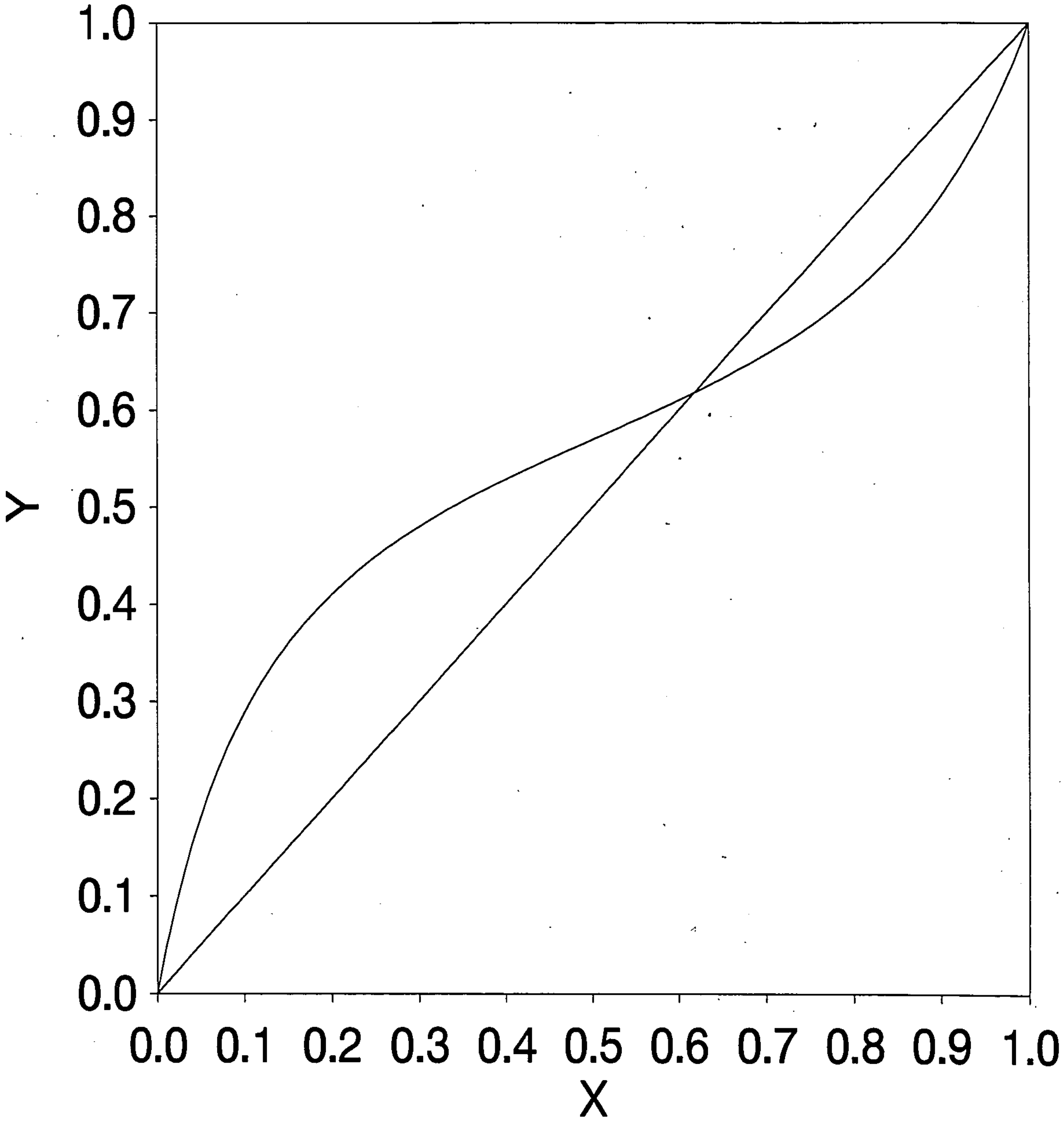

Figure C.3: *Ethanol* – *ETBE* VLE at 7.77 atm

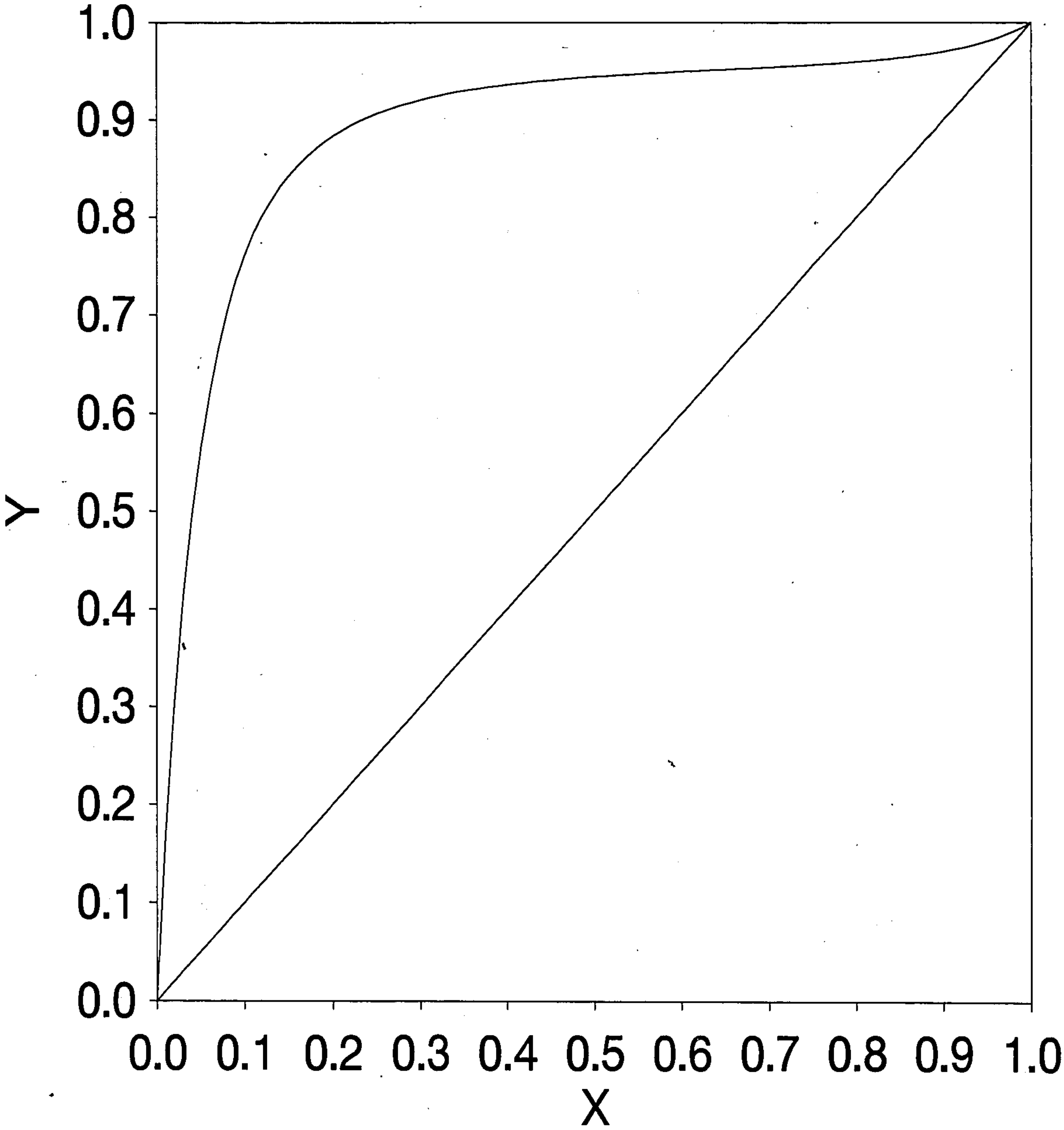

Figure C.4: $nC_4^{=} - Ethanol$ VLE at 7.77 atm

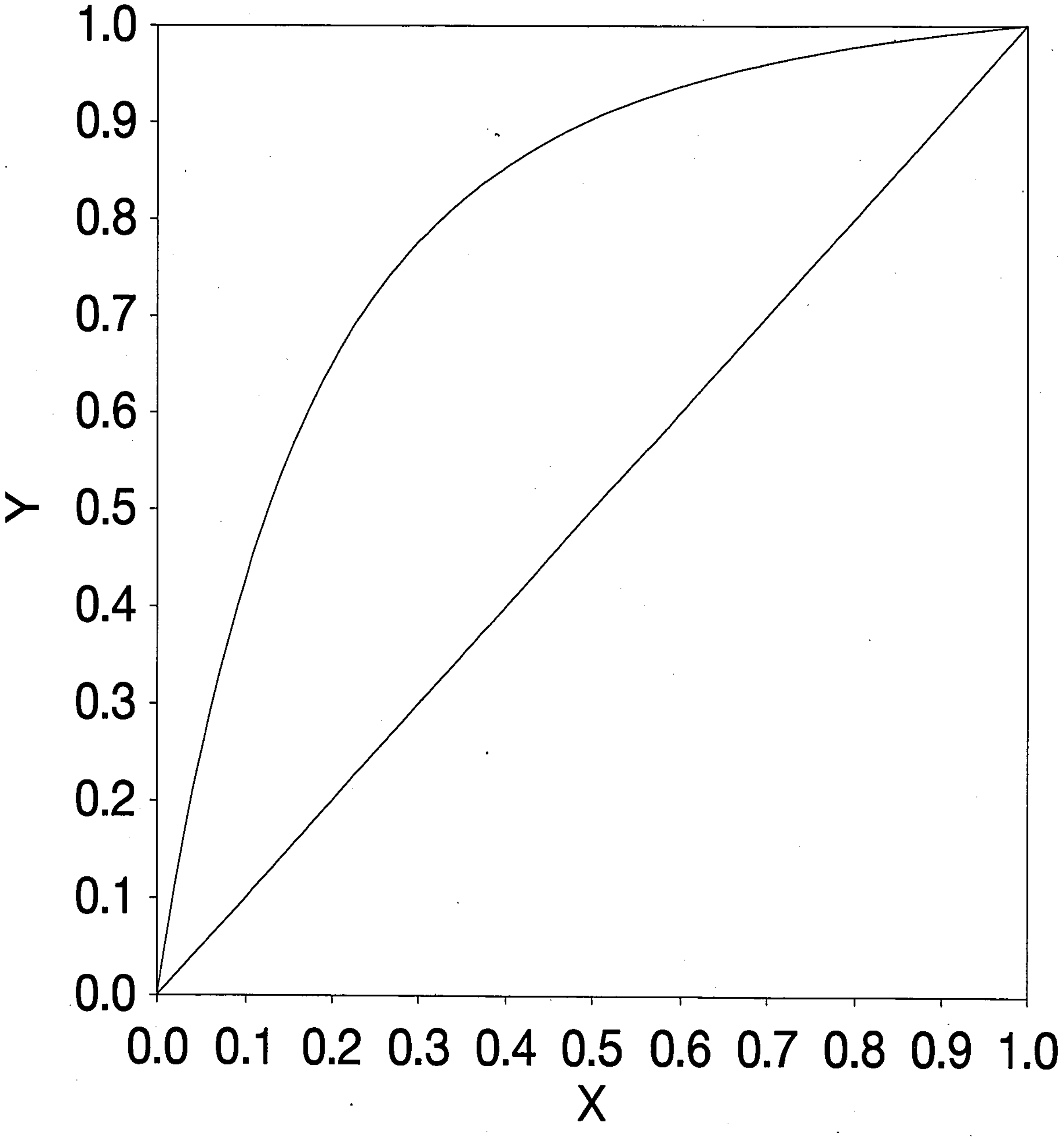

Figure C.5: $nC_4^= - ETBE$ VLE at 7.77 atm

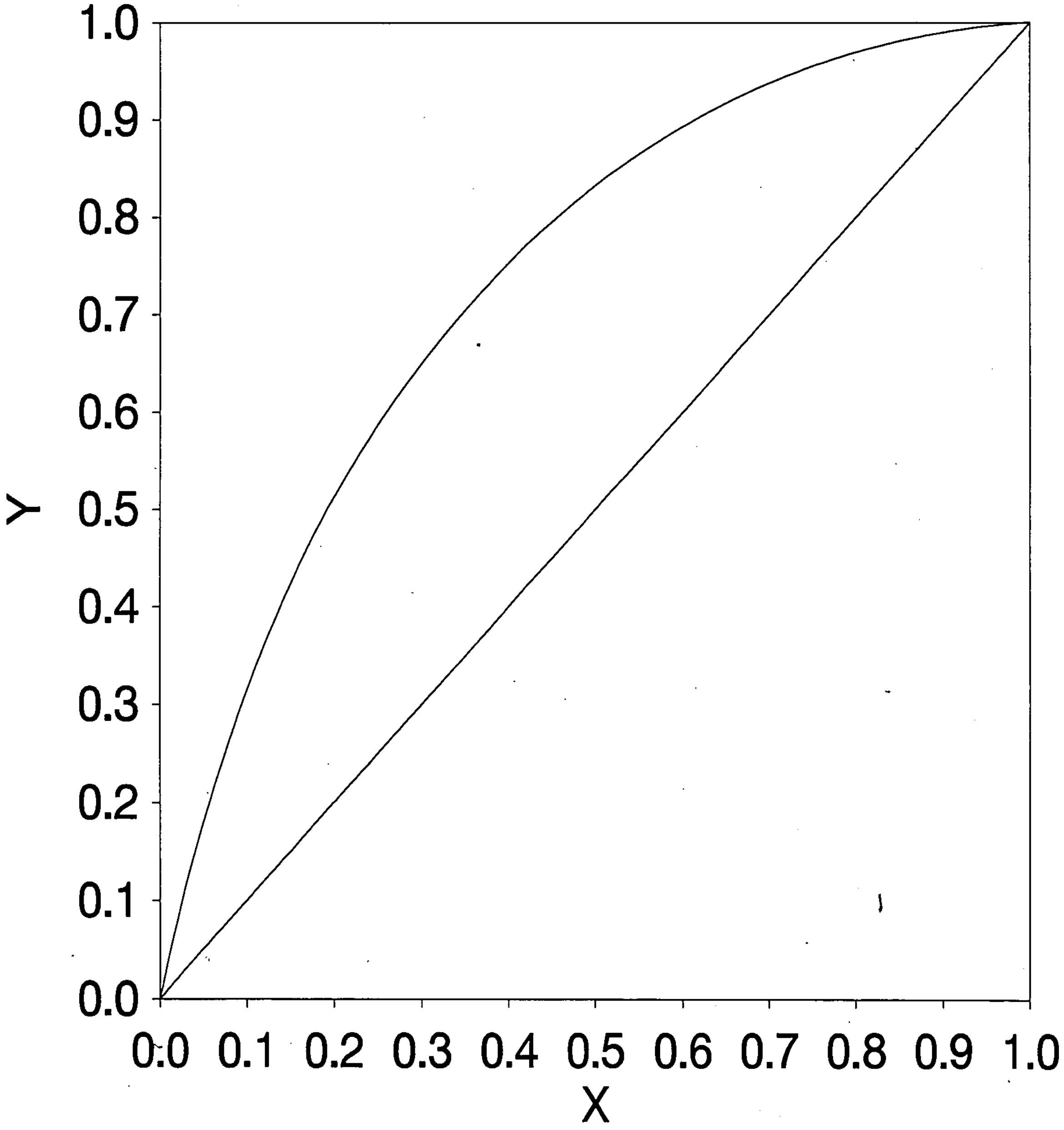

Figure C.6: $MeOAc - OHAc$ VLE at 1 atm

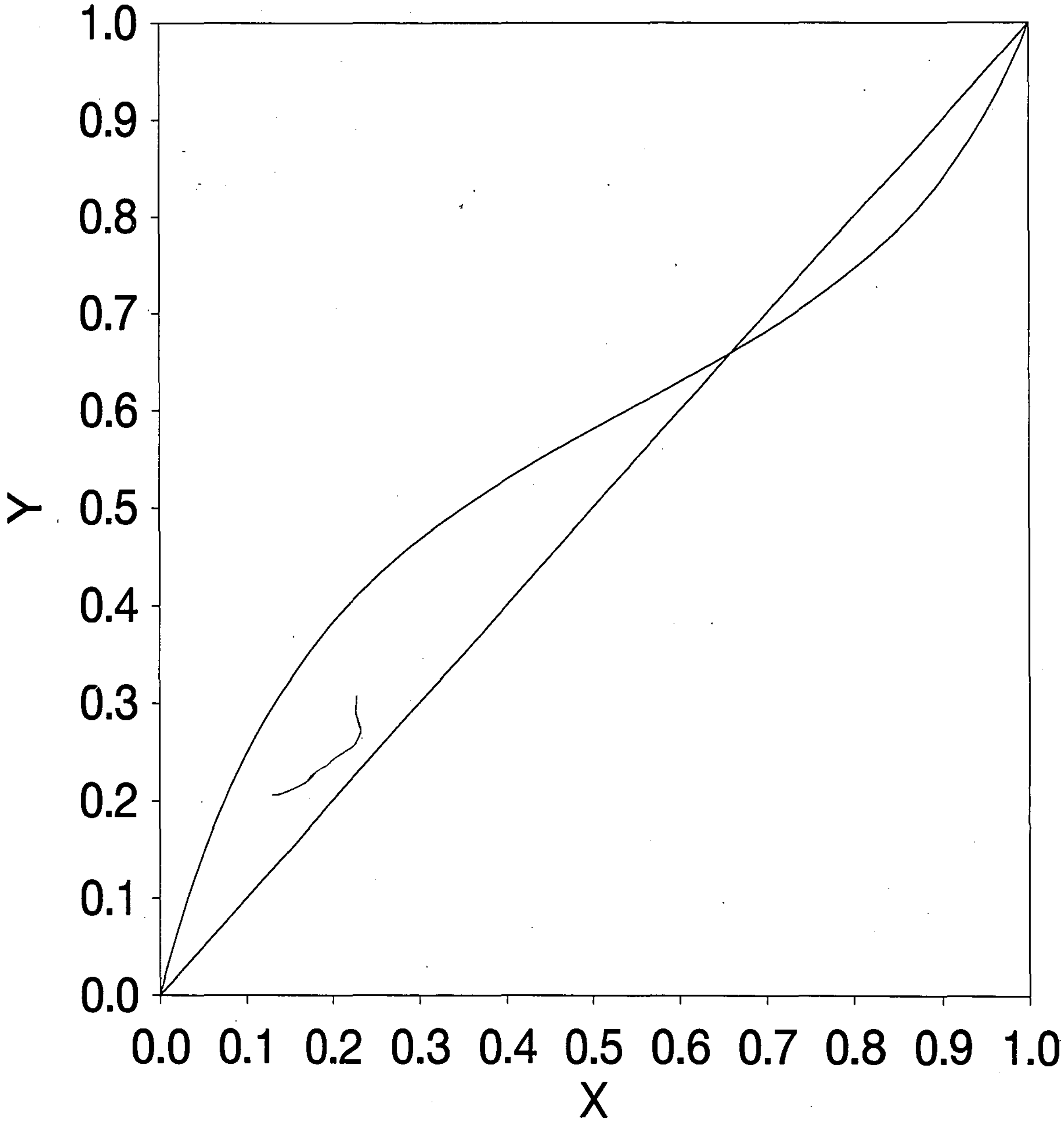

Figure C.7: $MeOAc - MeOH$ VLE at 1 atm

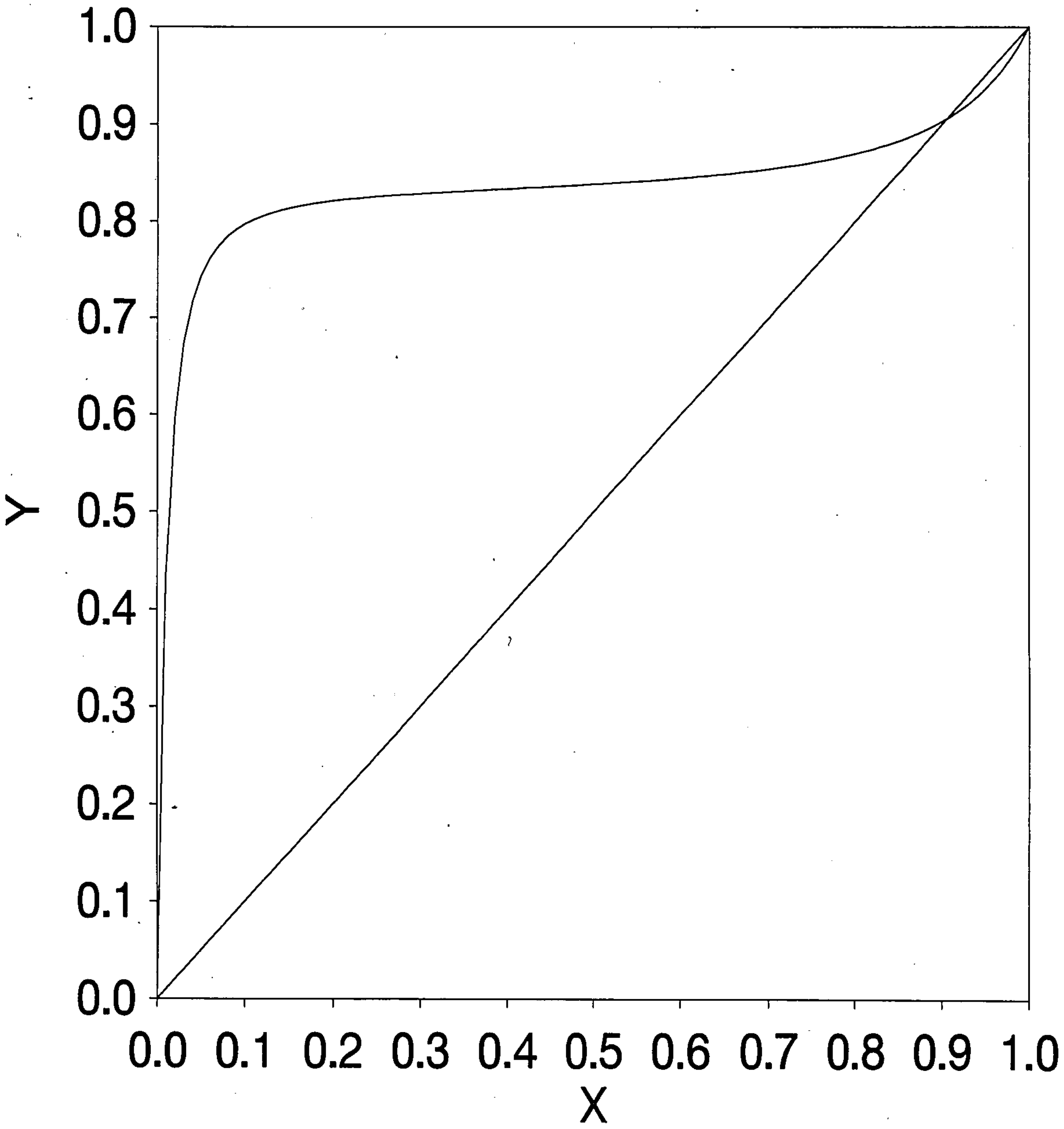

Figure C.8: $MeOAc - H_2O$ VLE at 1 atm

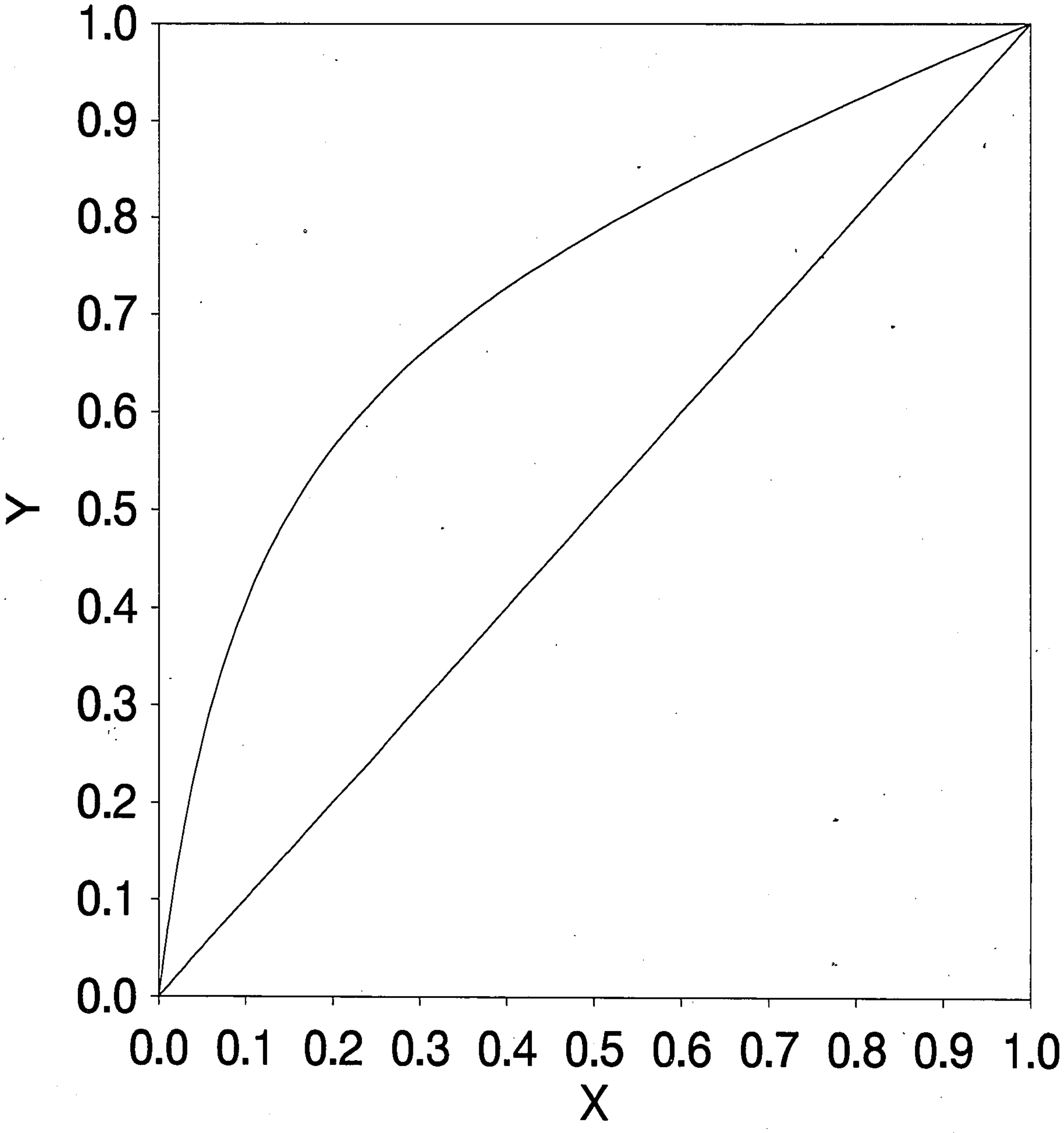

Figure C.9: $MeOH - H_2O$ VLE at 1 atm

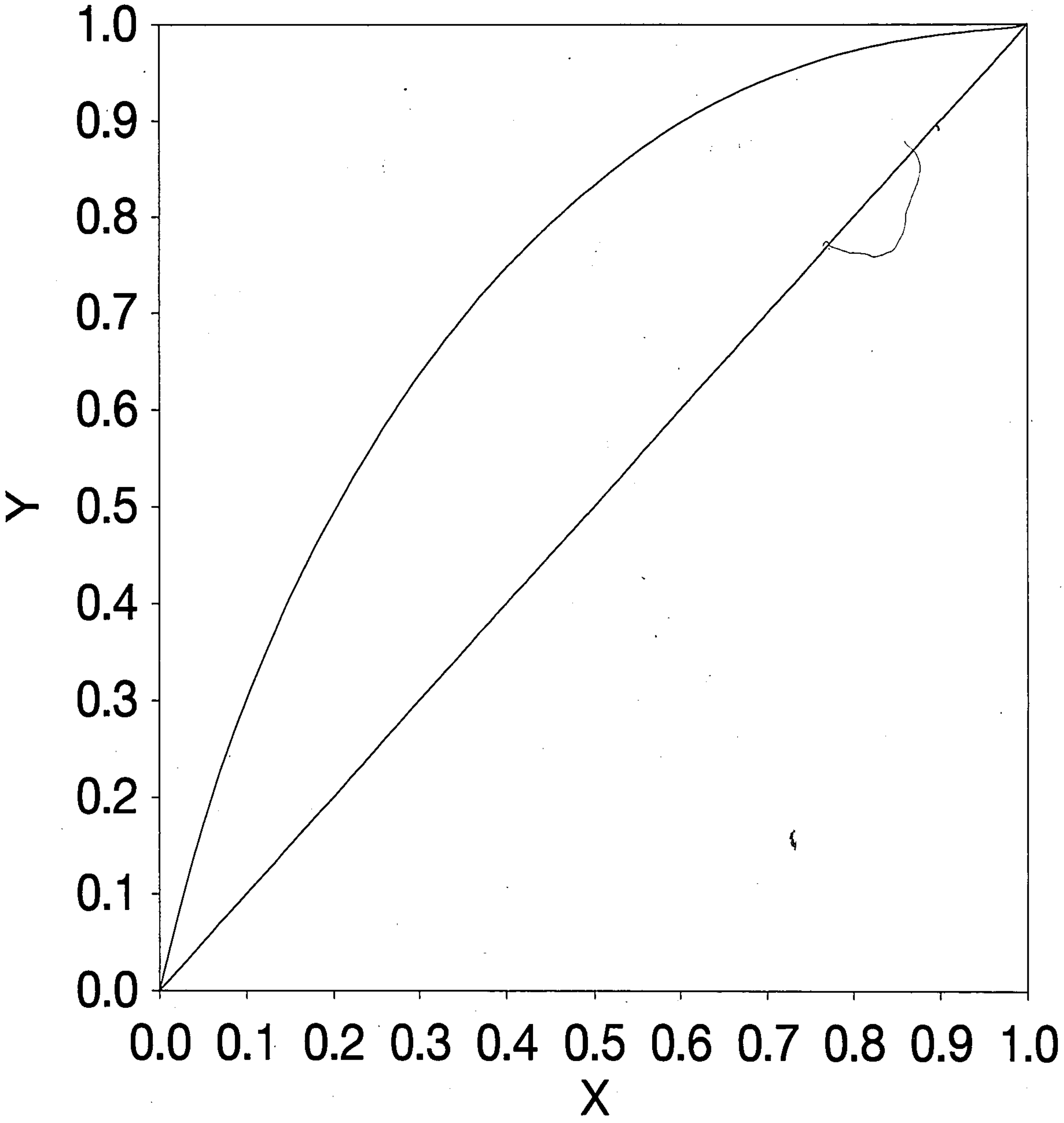

Figure C.10: $MeOH - OHAc$ VLE at 1 atm

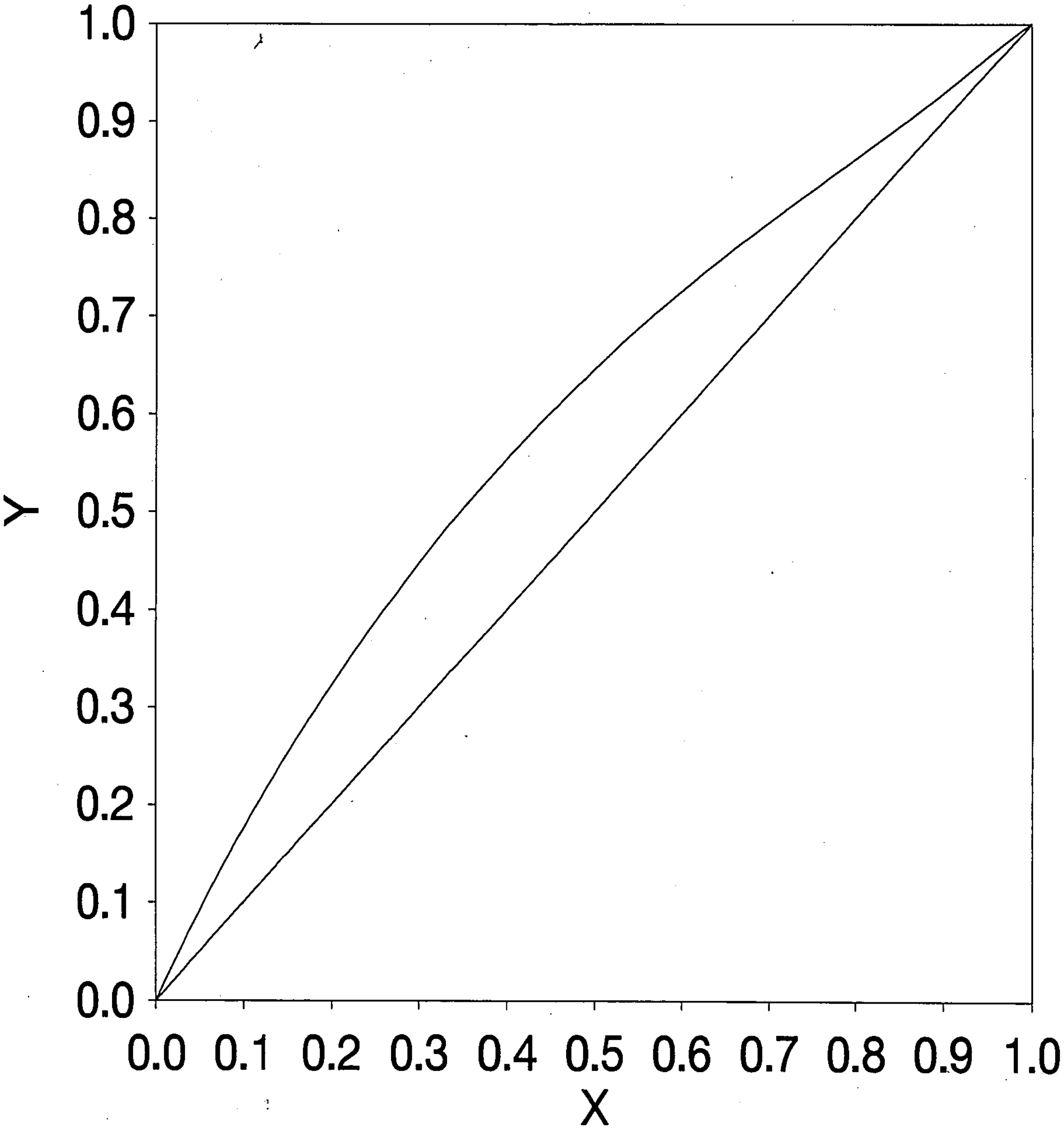

Figure C.11: $H_2O - OHAc$ VLE at 1 atm

Vita

Personal

Place of Birth: Dhahran, Saudi Arabia

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Interests: Travel, reading, multimedia production

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