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SIMULATION OF MULTISTAGE SEPARATION PROCESSES WITH MULTIPLE PHASES AND REACTIONS

by

ZHIMING HUANG

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THE UNIVERSITY OF CALGARY FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a dissertation entitled "Simulation of Multistage Separation Processes with Multiple Phases and Reactions" submitted by Zhiming Huang in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

R. Bishna

Supervisor, Dr. P. R. Bishnoi Department of Chemical and Petroleum Engineering

Dr. A. Chakma Department of Chemical and Petroleum Engineering

Richard D. Rave

Dr. R. D. Rowe Department of Mechanical Engineering

Sponan

Dr. B. B. Maini Petroleum Recovery Institute

nother 1

External Reader, Dr. D.-Y. Peng University of Saskatchewan

March 5, 1996

Date

Abstract

The steady state simulation of multi-stage separation processes is studied in this New mathematical equations are developed to simulate various separation investigation. processes which can be a two-phase separation, or a three-phase separation in which liquid phase can be split into two liquid phases or a separation process in which chemical The new proposed mathematical equations consist of the component reactions occur. mass balance equations, the phase equilibrium equations, the component summation the phase stability equations, the enthalpy balance equations (MESH equations), A new variable, equations and the implicit chemical equilibrium relationships. The component phase fraction, is introduced to formulate the new model equations. model equations are solved simultaneously for independent variables including phase fractions, phase stability factors, temperatures, component overall flow rates and reaction During the iterations, the disappearance and appearance of the second liquid extents. phase are automatically determined since the phase fractions and phase stability factors are the iterative variables of the proposed solution method

An efficient solution procedure is developed to solve the model equations. The solution procedure consists of two loops. In the inner loop, the thermodynamic properties such as K-values and enthalpy values are evaluated using the approximate thermodynamic models. With the approximate thermodynamic models, the system

model equations are solved simultaneously using the modified Powell's Dogleg method. The Powell's Dogleg method is modified to ensure the stability and efficiency for the convergence of the solution. In the outer loop, the rigorous thermodynamic models are employed to update the parameters for the approximate thermodynamic models.

The effectiveness and efficiencies of the proposed algorithm are illustrated by simulating various two-phase and three-phase separation processes. The performances of the two-phase separation process simulations are compared with some of the existing algorithms. The simulation results of the three-phase distillation columns and the reactive distillation columns are compared with results obtained from the literature. The effects of the choice of thermodynamics models on the simulation results of the three-phase column are examined. The proposed algorithm is also used to investigate the effects of ignoring the liquid phase splitting during the simulation a three-phase column.

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Dedication

70 My Parents

and

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Nomenclature

Symbols		Description
a	=	component activity
В	-	Constant in the approximate K-value model
С	=	Constant in the approximate H-value model
Ср	=	heat capacity
Df	=	function scaling factor matrix
D _x	==	variable scaling factor matrix
f	=	component fugacity
f ^{oL}	=	component standard fugacity
F	=	feed molar flow rate
g	=	steepest descent direction
G	=	Gibbs Free Energy
G(x)	=	residual function
G ^E (x)	_	energy balance residual function

$G^{M}(x)$	=	component mass balance residual function
G st (x)	=	phase stability residual function
G ^R (x)	=	chemical reaction relationship
$G^{PS}(x)$	H	phase summation residual function
h .	Π	component partial molar enthalpy
Н	П	Henry's constant
Hf	=	heat flow rate of the feed stream
∆h ^{ex}	=	molar excess enthalpy
Δh	=	molar departure enthalpy
К	=	phase equilibrium constant
KR	=	chemical equilibrium constant
J	=	Jacobian matrix
m	÷	overall component flow rate
n	=	component flow rate, or component mole number
Nc	=	number of components
Ns	=	number of stages
Nr	=	number of reactions

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Р	=	pressure
р	=	correction step in the simultaneous correction method
p _r	=	reference pressure in the activity coefficient correlation.
Qf	=	heat duty
R	=	Gas Constant
RF	=	reflux ratio
RVL		ratio between vapour distillate and liquid distillate
S(x)	=	sum of squared residual function values
T	==	temperature
v	=	molar volume
w	=	side withdraw ratio
x	=	iterative or independent variable
У	-	component mole fraction
Z	=	component mole fraction, usually for the feed stream

Greek Letter

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 α = phase fraction

β	=	component phase fraction
δ	=	reaction rate or extent
Δ	=	difference or
		radius of trust region in the Powell's method
φ	=	fugacity coefficient
γ	=	activity coefficient
η	=	combinational factor in the Powell's method
λ	=	damping factor
μ		chemical potential
ν	=	stoichiometry coefficient
π	=	number of phases within the column
θ	=	phase stability factor
ω	=	element of the diagonal matrix in the singular value decomposition

Superscript

ex	=	thermal excess property
I	=	first liquid phase
п	=	second liquid phase
ig	=	ideal gas
k	=	iteration number
m	H	iteration number
max	=	maximum

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min	=	minimum
N.	=	Newton correction step
S	=	steepest descent step
S	=	saturated liquid
Т	=	transpose
TR	=	trust region correction step
8	=	infinite solution

Subscript

b	=	base or reference
0	=	base or reference
i	=	ith component
j	=	jth stage
k	=	kth phase
m	• =	mixed property
р	=	jth phase
r	=	reference phase or rth reaction

1. Introduction

The objective of this research is to develop a better method for simulating multi-stage, multiphase separation processes, which can include two liquid phases and reactions within the column. Although a large number of successful simulation methods are available for simulation of separation processes (for example, Wu and Bishnoi, 1986, Saeger and Bishnoi, 1986, etc.). These approaches can neither account for the existence of the second liquid phase within the column, nor include the reaction processes at the stages.

The three-phase distillation process is very common in many chemical engineering processes, in which highly non-ideal mixture forms two liquid phases within the column. The formation of the second liquid phase depends on the operating conditions and the nature of feedstock. Therefore, the effective simulation of the three-phase distillation column is helpful for engineers to design and analyze the conditions under which the extent of two phase regions could be minimized, or to determine the location within the column that would be suitable for side stream withdrawal for the second liquid phase. More background information about the three phase separation process is given in the introduction section of the Chapter 2.

Many simulation methods so far have been proposed to solve the three phase distillation problems. In all these methods, it requires either a prior knowledge of the phase

pattern that indicates the location of the second liquid phase, or, more generally, the inclusion of the thermodynamic stability criterion for detecting the existence of the second liquid phase.

However, the phase stability testing, the liquid phase splitting and the phase pattern adjustment are made outside of the main solution loop. In these methods, the system equations of the column with the pre-defined phase pattern are solved first, then the existence of the second liquid phase is determined from the phase stability test on the column solution. If new occurrence of the second liquid phase is found, it returns to the main solution loop to solve the column equations again with the new phase pattern. The above iteration process continues until the phase pattern is unchanged. The convergence characteristics of solutions differ from one type of problem to another or, from one algorithm to another. A detailed review of these previously proposed methods is given in Chapter 2.

Reactive distillation column is a new separation technique in which the chemical mixtures react in the presence of catalysts, and the products are continuously separated by a fractionation process. More recently, the reactive distillation technique has received growing attention as an alternative to conventional processes, in particular, to processes in which the conversion is limited by unfavorable chemical reaction equilibrium. The reactive distillation tower has shown its advantages over the conventional separation processes, especially in the area of energy conservation, capital investments and operation costs. Chapter 5 will illustrate more details about the importance and advantages of the reactive distillation process. Most of simulation methods are based on some simplified thermodynamic

quantitative evaluations (e.g., ideal solutions), or one type of reaction processes (either chemical equilibrium control or kinetics controlled). These methods also suffer from problems of instability in convergence. Chapter 5 gives the detailed description of these previously proposed methods.

Although many methods have been developed for simulating three phase columns and reactive distillation towers, none of these methods has the capability to account for the existence of the second liquid phase in the reactive column, or to include the reaction process with the three phase column. However, in many potential reactive distillation processes, the reaction mixtures can form two partially miscible liquid phases within the column, as in the production of butyl acetate via butanol, or ethyl acetate via ethanol.

This work has developed a new algorithm for simulating multi-stage distillation with several objectives:

 The mathematical model is general so that the same model can handle very diverse separation problems, such as complex two-phase, three-phase and reactive distillation. Any specification or process constraints can be introduced to the model equations. The reaction relationship can be the implicit chemical equilibrium equations. The new algorithm is independent of the thermodynamics models. The mathematical model is able to solve the distillation problems with various types of thermodynamic models.

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- 2. The proposed method is robust under a wide variety of conditions, especially when good initial starting points are not available. Rigorous thermodynamic models are used to predict the thermodynamic properties.
- 3. Phase fractions and stability factors are determined simultaneously with other variables. Neither prior knowledge of the two-liquid phase region, nor an outer loop for phase stability testing and phase pattern adjustment are required in the new algorithm.

Chapter 3 presents the development of the new mathematical model equations for a non-reactive multi-phase separation column. In Chapter 3, it includes the description of the thermodynamic models used in this study. A new inside-out iteration approach is developed in It includes the modification of the Powell's hybrid method for Section 3 of the Chapter 3. The new computational algorithm has been used to simulate solving non-linear equations. various two-phase and three-phase distillation examples available in the literature. Chapter 4 presents the simulation results of these examples. The first section of the Chapter 4 presents The second section of the chapter the discussion of the two phase separation examples. focuses on the three phase distillation simulation results. The computational results are compared with those obtained from other existing simulation methods. The chapter also examines the effects of ignoring the liquid phase splitting, and influence of the selection of thermodynamics models and their parameters on the simulation results of the three phase columns.

The extension of the non-reactive distillation simulation to the reactive distillation is successfully developed in Chapter 6. The modified algorithm is used to simulate a reactive

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column which separates a closely boiling mixture of m-xylene and p-xylene. The results are compared with those obtained from other simulation methods in the literature.

Appendices A, B and C list the details of the column specifications and other parameters that are necessary for carrying out the column simulation. Appendix D describes how the analytical derivatives in the Jacobian matrix are evaluated.

2. Three Phase Distillation Simulation

2.1 Introduction

Three-phase distillation refers to a vapour-liquid-liquid phase separation process. Such a process is very common in chemical engineering processes where nonideal feedstocks are partially miscible, and more than one liquid phase can form within the column. For example, in the fermentation of grain to ethanol, a mixture of higher molecular weight alcohols is formed (Kirk and Othmer, 1947), which is partially miscible In a dehydration distillation column, the high molecular weight alchols in water. concentrate towards the center of the tower and form two miscible liquid phases on many stages in its stripping section. In the production of butyl acetate through esterification of butanol, the feedstock mixture can form butyl acetate - water and butyl acetate - butanol minimum boiling azeotropes. In the distillation of the ternary mixture, two immiscible liquid phases are formed within the separation column (Arrison, 1972). Azeotropic distillation is another common example of the three-phase distillation. In this process, an entrainer is added to increase the relative volatility of the components. Usually, the overhead vapour will form two immiscible liquid phases in the decanter when condensed. One typical azeotropic distillation is the dehydration of alcohol, such as ethanol and isopropanol, with entrainers such as benzene, cyclohexane and pentane (King 1980).

The presence of a second liquid phase usually generates some difficulties for designing and controlling the column. It could lead to less efficient contact among phases, uncertainty of the location of the three-phase region, cyclic build-up of the heavier phase due to its settling in the disengaging region within the column. In many distillation processes, as in the case of dehydration of alcohol mixture, the side withdrawal is necessary to remove the second liquid phase from the column. However, the location of side withdrawal of the second liquid phase depends on the operating conditions such as feed stage, feed condition and reflux ratio. Without accurate simulation methods, extensive experimentation has be to carried out to determine proper location for the side withdrawal.

For some cases, the presence of a second liquid phase can be used as an advantage in enhancing the separation. For example, in the azeotropic dehydration of alcohols, two liquid phases are expected to be formed in top decanter stage. One of two liquid phases is water rich. To enhance the removal of water from the system, the water rich phase is totally removed from the top decanter stage. The other liquid phase that is rich in the entrainer is totally refluxed back to the column in order to recover the entrainer. However, whether the two liquids will form at the top decanter stage depends on the column operating conditions.

In view of the above, it is of great importance for the design engineer to be able to predict the conditions under which the region of two liquid phases can be minimized or maximized, or to determine the location that is suitable for the side-withdrawal of the second liquid phase. The correct and efficient simulation of the three-phase distillation will be beneficial for process analysis and design under various operating conditions without the need for expensive experiments.

Although the industrial importance of three-phase distillation was perceived long time ago, there was not much attention received for simulating the three-phase distillation column until recently. The three-phase distillation is more difficult to simulate than a two-phase distillation column. The difficulty is mainly due to the following factors:

a) Uncertainty of the phase pattern within the column

The existence of the second liquid phase depends on the operating conditions such as pressure, temperature and compositions. During the calculation, it is impossible to have a prior knowledge of the two liquid phase region within the column. The second liquid phase may appear or disappear, which may lead to the instability problems in the solution method.

b) Non-ideality of feedstock mixture

In most three phase distillation applications, the feedstock usually is a non-ideal mixture, which may become partially miscible under certain conditions. The thermodynamic properties of a non-ideal mixture, such as K-values or enthalpy, become strong non-linear functions of temperature and composition. Hence, the governing equations representing such systems are very difficult to solve.

c) Lack of accurate thermodynamic representation of liquid-liquid equilibrium

Compared to vapour-liquid equilibrium studies, little effort has been made to study vapour-liquid-liquid equilibrium systems. There are few experimental data available in the literature for vapour-liquid-liquid, and liquid-liquid equilibrium. In most of thermodynamic models used for representing liquid phase behaviour, such as NRTL, UNIFAC, Equation of State, etc., the parameters are usually obtained from fitting the vapour-liquid equilibrium experimental data. When attempting to compute liquid-liquid equilibrium, the computed thermodynamic data could have great errors.

First attempt for simulating the three phase distillation process was made by Block and At that time, the liquid solution model NRTL was available to Hegner in 1976. Since then, many rigorous characterize the non-ideal liquid solution behaviour. simulation methods have been proposed, as a result of the development of better availability of better liquid solution understanding of liquid solution behaviour, and reliable solution methods for non-linear equations. thermodynamics models, the simulation methods can be grouped into the following categories: Basically, simultaneous correction, equation decoupling, hometopy and successive flashes. Within each category, the simulation methods differ from each other in the following respects:

a). mathematical model equations used and iteration variables chosen;

- b). iteration procedures employed to solve the non-linear equations;
- c). inclusion of the thermodynamic stability test for detecting the unstable liquid mixture.

A detailed literature review of those simulation models is given in the following chapter.

2.2 Review of Three-Phase Distillation Simulation Methods

Significant progress has been made in the area of simulating three-phase distillation columns in recent years. Most of these simulation methods can be grouped into the following categories: successive flash, equation decoupling, homotopy, finite element analysis, and simultaneous correction. The convergence characteristics of the methods differ from one type of problem to another, or from one algorithm to another. This chapter will concentrate on the review of previously proposed solution procedures for simulating three-phase distillation columns.

2.2.1 Successive Flash Method

2.2.1.1.1 Ferraris and Morbidelli (1981)

Ferraris and Morbidelli developed a multi-flash method to solve three-phase distillation problems. In their approach, each stage was treated as a three-phase flash unit with input streams from adjacent stages. The trial values of the unknown variables such as temperature, phase flow rate, and compositions at each stage were obtained by solving the three-phase flash problem with trial values of the corresponding variables in the adjacent stages. By applying this approach to all stages of the column, Ferraris and Morbidelli developed several input-output iterative sequences in order to approach the solution. It was noted that although this kind of approach was very stable in reaching the solution, it required many iterations, and a large amount of computation time. The convergence of the solution method also depends on the choice of the input-output iterative sequences. Thus this method was just used by the authors as an alternative to verify the phase pattern resulting from other methods used by them. The other methods proposed by the authors are the bubble point decoupling method and the Newton method. These methods required a prior knowledge of the two-liquid phase region. If the two liquid phase region is under-specified in the column, the resulting single-liquid phase solution would be false, since the single liquid phase might be unstable. The multi-flash method provided the authors with a way to analyze the stability of the proposed single liquid phase, and adjusted the phase pattern for further flash calculations.

2.2.1.1.2 Pucci, Mikitenko and Asselineau (1986)

Pucci et al. (1986) proposed a stage-to-stage approach to automatically search the On each stage, possible liquid splitting within the column. the isenthalpic MESH equations were solved simultaneously using a Newton method. To save computation time, the authors pre-specified a region in which liquid phase would be likely to split into Outside such region, only a single liquid phase was considered. two liquid phases. first, the isenthalpic vapor-liquid two phase flash Within the pre-specified region, Then the authors solved the iso-activity equations to search calculation was performed. for a possible phase-splitting of the liquid phase at the temperature, which were determined from the above vapor-liquid isenthalpic flash. To ensure the LLE equilibrium solution away from a trivial solution, Pucci et al adapted the approach of infinite dilution activity coefficients to initialize the LLE calculation. The solution of the iso-activity

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equations basically acted as a liquid phase stability test. If a liquid-liquid splitting solution was found, then the mixture was considered to be a three phase and was appropriately flashed to produce vapor-liquid-liquid compositions. If no LLE solution was found, the mixture is considered stable and previous vapor-liquid phase isenthalpic flash results were used. The calculation started first from the reboiler up to the overhead condenser, then from the top to the bottom of the column, and iterated to reach the convergence criteria. This approach was applied to simulate the separation of the rectification of butanolacetone fermentation products.

2.2.1.1.3 Guo (1986)

Guo developed a similar multi-flash approach for the water-hydrocarbon systems as that of Pucci et al. (1986), in which the isenthanlypic flash was used as a liquid phase stability test and MESH equations at each stage were solved simultaneously by a Newton-Raphson method. Guo proposed an approximate phase stability test, which was based on the assumption that the water phase was pure. The mixture was considered unstable if the vapor phase fugacity of water resulting from the flash calculation was larger than the liquid fugacity of pure liquid water.

2.2.2 Equation Decoupling Method

A model describing a three-phase distillation usually consists of a large number of non-linear and complex equations, which are very difficult to solve. One of the solution strategies is to break the set of equations into smaller subsets of equations with reduced non-linearity. The subsets of equations are used to find new values to the subsets of unknowns, with guessed or "tear" values for the remaining unknowns. This kind of solution strategy is often referred to as the equation decoupling method. The equation decoupling methods usually require less computational time and storage since it eliminates the calculation and inversion of the entire Jacobian matrix.

2.2.2.1 Bubble Point Method

One of common equation tearing methods in simulating separation processes is a so-called bubble point method. In this method, the summation and equilibrium equations are solved first to generate the stage temperature from a standard bubble point temperature calculation. Consequently the mass balance and heat balance equations are solved for the liquid phase compositions and the phase flow rates. Bubble point method has been successively applied in simulating the vapor-liquid phase separation processes.

2.2.2.1.1 Block and Hegner (1976)

The first attempt to simulate three-phase distillation column was made by Block and Hegner, whose computation procedure was based on the bubble point equation tearing method. The average compositions of the two liquid phases were considered as independent variables and the improved liquid compositions were computed from the linearized component mass balance equations. The MESH equations were decoupled into three subsets of equations that are illustrated in the algorithm of Figure 2-1. First, the iso-activity equation was solved to give equilibrium liquid phase compositions. The solution of the iso-activity equation was used to determine the stability of the liquid phase. If the solution was not found, the liquid phase was considered stable. Then the boiling temperature and vapor compositions were computed from the conventional bubble point equations, while the vapor and liquid flow rates were calculated from the energy balance equations. The independent variables, that is the average liquid phase compositions, were updated from component mass balance residuals using a Newton-Raphson method.

Block and Hegner have shown simulation results for a propanol-water-butanol system in which the butanol concentrates towards the bottom part of column to form two liquid phases, and results for a butanol-butyl_acetate-water system where the second liquid phase was formed in the upper part of the column. The significance of side withdrawal of the aqueous phase or the second liquid phase from the column was examined. It was noted that the convergence towards the solution depended on the initial estimates of the average liquid phase compositions. It was also noted that this approach was very limited to the choice of standard specified and unspecified variables, in particular, it is impossible to impose some specifications equations whose unknowns are not included in the column equations.
2.2.2.1.2 Ferraris and Morbidelli (1981)

Ferraris and Morbidelli developed a boiling point method that was similar to the one proposed by Block and Hegner. However, in Block and Hegner's approach, the average liquid composition was updated by the Newton-Raphson iterative correction method. This approach involved the numerical evaluation of the partial derivatives with respect of the average liquid composition, which took a large amount of computation time. In Ferraris and Morbidelli's method, the average liquid composition was obtained directly by solving the linear component mass balance equations in the tridiagonal form. To avoid the trivial solution for the liquid-liquid splitting calculation, the authors restricted the unknown liquid phase compositions to lie within a specified range.



Figure 2-1 Block and Hegner (1976)

2.2.2.1.3 Kinoshita, Hashimoto and Takamutsu (1983)

The simulation method proposed by Kinoshita et al. was basically the same as that of Block and Hegner. Kinoshita et al., however, modified the residual functions used to update the average liquid phase compositions. The residual functions were defined as the differences between the compositions from solving the tridiagonal component mass balance equations and the initial estimates of compositions. The authors adapted a minimisation method to examine the stability of a trivial solution of LLE calculation. If for different initial conditions, all the minimisation results converged to the trivial solution, then the mixture was considered a stable liquid phase.

2.2.2.2 Inside-Out methods

The inside-out method was first proposed by Boston and Sullivan (1974). The underlined concept of this approach is using the approximation models in an inner loop and using more accurate models in an outer loop. In an inner loop, the thermodynamic and physical properties of the fluid are computed using the approximation models. The approximation model parameters are usually assumed composition independent. In the the approximation model parameters are estimated from the rigorous outer loop. In all previously proposed inside-out methods for simulating thermodynamic models. the MESH equations in the inner-loop were solved three-phase distillation problems. Therefore, the using the equation decoupling scheme or the bubble point methods. review of inside-out methods is done under the category of equation decoupling.

2.2.2.2.1 Shah and Boston (1979)

The inside-out approach by Boston and Sullivan (1974) was extended by Boston and Shah to simulate three-phase problems. The detailed schematic of the algorithm is illustrated in Figure 2-2. In the inner loop, all parameters of approximate models were kept constant. First the tridiagonal linearized component balance equations were solved for the vapor phase compositions, with constant K values. Then, the bubble point equations were used to updated the K-values and temperatures, using the approximated The liquid-liquid flash calculation was performed at the calculated K-value equations. temperature. If no liquid-liquid splitting is found, the newly obtained splitting fraction was used to recalculate the K-values and temperature until it converged. Then the overall mass and energy balance equations were solved for the phase flow rates. The stripping factor, S-parameter, was checked, if it did not converge, it was updated using Broyden's With the new set of S-parameters, the inner loop was re-started. method. In the outside loop, the approximate thermodynamic model parameters were used as the iterative variables, along with the S-parameters. After the inner-loop converged, a stability test was carried out to determine the possibility of the second liquid phase on each stage at the new conditions. A three-phase flash calculation was used if the stability test Based on the new conditions and indicated the existence of the second liquid phase. phase pattern, the parameters for the approximate models, and the S-parameters were updated using the complex thermodynamic models. The convergence was checked for the approximate model parameters. If no convergence was reached, these parameters were updated with the application of the successive substitution method.

2.2.2.2.2 Ross and Seider (1980)

Ross and Seider (1980) proposed a three-phase simulation algorithm based on the modification of the inside-out approach of Boston and Sullivan (1974). The Murphree tray efficiency was introduced to characterize the approach to equilibrium between vapor and each liquid phase. The detailed algorithm is illustrated in Figure 2-3. In the outside loop, the Gibbs free energy minimization approach of Guatam and Seider (1979) was The authors used temperatures and used in the liquid-liquid phase splitting calculation. average liquid phase compositions as the outer-loop iterative variables instead of the parameters of the approximate thermodynamic models which was used in the original inside-out approach of Boston and Sullivan (1974). A damping factor was used in order to eliminate the oscillation in the outer loop. In the inner-loop, the temperatures were calculated directly from the approximate K-value model, instead of being calculated from the iterative bubble point temperature calculation. The inner-loop convergence criteria were tested for the liquid phase component flow rates. If not converged, the liquid flow rates were adjusted using bounded Wegstein's method, instead of quasi-Newton's method The authors noted that the new updating scheme eliminated the requirement of Broyden. of calculating the inverse of the Jacobian, which consequently saved computer storage and time.

Ross and Seider solved the three-phase distillation example of Block and Hegner (1976), with and without sidestream. The authors also examined the effects of introducing the Murphree tray efficiency. It was found that for some systems, as tray efficiency was reduced, a second liquid phase appeared in the simulation results and the assumption of the phase equilibrium became misleading. The effectiveness of the Wegstein's updating approach was illustrated by simulating both wide- and narrow boiling point two-phase systems (ethane-dodecane, and pentane-hexane systems).

2.2.2.3. Schuil and Bool (1985)

Schuil and Bool developed a mixed K-value model, which allows the existing twophase distillation simulation program to be used for three-phase systems. The mixed Kvalue was defined as the equilibrium ratio between the vapor and the average of both liquid phases. It accounts for additional equilibrium expression of a liquid-liquid-vapor system. Therefore, it eliminated the extra equilibrium equation in the MESH equations. The mixed K-value model was implemented into the Badger General Material Balance of Russell (1980). The inside-out approach of Boston and Sullivan (1974) was used for solving the system equations. The liquid-liquid equilibrium was calculated with a subroutine proposed by Prausnitz et al. (1980).



Figure 2-2 Boston and Shah (1979) algorithm



Figure 2-3 Ross and Seider's Algorithm

2.2.3 Simultaneous Correction Method

In simultaneous correction method, or commonly called Newton-Raphson method, all system equations are solved simultaneously for correcting all the iterative variables. It overcomes some difficulties associated with the equation decoupling method, such as introducing any "specification" equations. The Newton-Raphson method usually converges to the solution quadratically, provided that the initial guess of the solution is not far way the finial solution. The computation procedure proposed by Naphtali and Sandholm (1971) is a simultaneous correction method commonly used in simulating separation processes. In their approach, the MESH equations are grouped stage-bystage to give the Jacobian in a block tridiagonal matrix form.

2.2.3.1.1 Ferraris and Morbidelli (1981 and 1982)

Ferraris and Morbidelli proposed a simultaneous correction approach, in which the liquid-liquid equilibrium relationship was solved with other MESH equations simultaneously. However, there was no stability test included for detecting the unstable liquid. Instead, a prior knowledge of two-liquid phase region within the column was necessary as an input of the algorithm. The authors noted that due to the high non-ideality of liquid mixtures, where phase splitting can occur, the derivatives of the equilibrium ratios with respect to the compositions and temperature can not be neglected if the convergence qualities of the Newton-Raphson method are to be preserved. In order to save computation time, those derivatives were only evaluated at few stages, and the

derivatives were estimated by linear interpolation at the intermediate stages where there was no liquid phase separation. The authors used the successive flash method to verify the obtained solution. If the multiflash method predicted the liquid phase splitting at some stages where only one liquid phase was assumed, then the whole solution has to be repeated with the starting solution obtained from the multiflash method. Later Ferraris and Morbidelli (1982) found that in many applications when liquid splitting occurs, each component is soluble almost only in one of the two immiscible liquid phase. This allows one of the liquid phase (for example, the water phase in a water-organic mixture) to be pure. It consequently simplifies the calculation procedure considerably. Ferraris and Morbidelli applied such an approximation in the Newton method and the Bubble point method.

2.2.3.2 Mixed K-value method

To eliminate the need of a prior knowledge of the three-phase region, and take advantage of the simultaneous correction method for two phase problems, a mixed or pseudo K-value concept has been introduced by many authors. This approach basically treated two liquid phases as a single liquid phase, whose thermodynamic properties were evaluated based on an appropriate averaging of the two liquid phases present. Therefore, it eliminated the restriction of having to specify two-liquid phase region, and allowed the LLE calculation to be performed outside the main Newton-Raphson equations.

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2.2.3.2.1 Niedziwiecki, Spinger and Wolfe (1981)

Niedziwiecki et al. (1981) first applied the mixed K-value method with the Newton-Raphson method to solve the three-phase distillation problems. It required the derivatives of the mixed K-values with respect to the average liquid phase composition and temperature. The paper by Niedziwiecki et al. was only very brief and did not provided detailed information about stability test and LLE calculations.

2.2.3.2.2 Baden and Michelsen (1987)

Baden and Michelsen proposed a solution procedure similar to that of Niedziwiecki (1981), which basically implements the three-phase calculation in the manner of Naphtali and Sandholm's Newton-Raphson method for two phase distillation column calculation. They modified only the liquid phase thermodynamic properties in the MESH equation calculation. The tangent plane stability analysis of Michelsen (1982) was used in outer-loop to detect the unstable liquid phase. If the liquid phase was found unstable, the LLE flash calculation was performed to determine the equilibrium phase In the Naphtali and Sandholm column calculation, the two liquid phases compositions. were treated as a pseudo-single liquid phase. The activity coefficients of two liquid phases were replaced by pseudo activity coefficients based on the overall compositions of Newton-Raphson approach was used to solve the iso-activity the two liquid phases. LLE equations to obtain the pseudo activity coefficients and their derivatives with respect to temperature and total compositions. The authors noted that in order to evaluate these derivatives, it was necessary to take into account that the equilibrium phase compositions were affected by changes in temperature and total component flows. Although this approach eliminated the requirement of a prior knowledge of phase pattern within the column, it took large amount of computer time in LLE calculation, since a large amount of "unproductive" work was spent on stability test for stable liquid phases. This, unfortunately, was the disadvantage of having the freedom of not requiring a priori specification of phase number.

2.2.4 Finite Element Collocation method

2.2.4.1.1 Swartz and Stewart (1987)

Stewart et al. (1985, 1986) developed an orthogonal collocation method for the simulation of distillation systems in which the fractionation system was represented by a series of inter-connected modules, each of which corresponds to a physical column section. The states in each module were approximated by Lagrange polynomials whose nodal values were determined by the orthogonal collocation. This method was extended by Swartz and Stewart (1987) to a multiphase system. The separate module, or finite element, was used to represent each multiphase unit. A distinction was made between physical column sections and the collocation modules, with sections that contain phase discontinuities being represented by the corresponding number of modules. The module lengths were treated as continuous variables with their sum constrained to be consistent with physical dimension of the column. The phase boundaries were included as unknown

in the system of column equations and their locations as continuous variables were calculated simultaneously with the other variables.

A general N-stage module with P liquid phases is illustrated in Figure 2-4. The liquid component flows, vapor component flows and enthalpies are approximated by polynomials with $n \le m$ M interior grids points, that is,

$$\widetilde{f}^{p}(s) = \sum W_{f_{j}}(s) \widetilde{f}^{p}(s_{j})$$

$$\widetilde{F}^{p}(s) \widetilde{h}^{p}(s) = \sum W_{f_{j}}(s) \widetilde{F}^{p}(s_{j}) \widetilde{h}^{p}(s_{j})$$

$$\widetilde{F}^{p}(s) = \sum \widetilde{f}^{p}(s_{j})$$

$$p = I, II, \dots, \pi, \quad 0 \le s \le N, \quad j = 0, 1, \dots, n$$
(2-1)
(2-1)

where f and h with tilde (\sim) denote the approximating functions of liquid or vapor component flows and enthalpies. The functions W(s) in **Equation (2-1)** are Lagrange polynomials, given

$$W(s) = \prod_{k=0, k_{j}}^{n} \frac{(s - s_{k})}{(s_{j} - s_{k})}$$
(2-2)

The collocation points s_1 , ..., s_n in a given module are calculated as the zeros of the Hahn polynomial Qn(s-1; 0, 0, N-1).

These approximating functions were substituted into MESH equations, which resulted in a corresponding set of residual functions continuous in s. The collocation equations were obtained by setting the residuals to zero at n interior grid points s_1 , ..., s_n . Therefore, the approximation functions $f(s_j)$, $h(s_j)$ at interior grid points were obtained by solving those collocation equations. The advantage of this approximating function approach was to reduce the problem of N order to a lower order (n).

Sewartz and Stewart utilized the module boundary as the multiphase boundary and included it as an independent variable. The location of multiphase boundary was defined such that the additional phase was just beginning to form or to disappear. It was required that the newly formed or vanished liquid phase at the boundary be in equilibrium with other liquid phase at that location, and be in infinitesimal amount. Therefore, the material and energy balance equations for the linkage of the modules were formulated accordingly, along with the LLE equation and the summation equation of the additional phase components.

The solution procedure (Figure 2-4) begins with solving a two-phase distillation column (one module), which provides initial breakpoints of the collocation equations. The authors applied the stability test of Fournier and Boston to the liquid phase at the collocation points, liquid entrance and exit location of each module. If the liquid mixture instability was found within the module, this module was subdivided into the indicated modules. The states at new collocation point locations were represented by interpolation, and the multiphase MESH equations were solved using a damped Newton method. The authors applied their approach to simulate the second example of Block and Hegner (1976) and the acrylonitrile-acetonitrile-water problem of Ferraris and Morbidelli (1981).



Figure 2-3 Swartz and Stewart Algorithm (1987)

2.3 Liquid-Liquid Phase Equilibrium

The fundamental equation for equilibrium between phases is the equality of chemical potential for each component in all phases, that is:

$$\mu_i^I = \mu_i^{II} \tag{2-3}$$

Since the chemical potential $\mu_i - \mu_i^o = RT \ln a_i$, the above equation can be reduced to so-called iso-activity equality equation for liquid - liquid equilibrium, that is:

$$a_i^I = a_i^{II} \tag{2-4}$$

The activity of component i can be expressed in terms of an activity coefficient in the following relationship

$$a_i = \gamma_i \ x_i \tag{2-5}$$

Therefore, Equation (2-3) becomes:

:

$$\gamma_i^I \quad \mathbf{x}_i^I = \gamma_i^{II} \quad \mathbf{x}_i^{II} \tag{2-6}$$

where the activity coefficient γ is a function of compositions and temperature, and is evaluated from appropriate thermodynamic models.

For a given liquid mixture composition (z_i) and temperature T, the equilibrium phase compositions and the fractions of the two liquid phases can be determined by solving the above liquid-liquid equilibrium equation with the mass balance equations, that is:

$$\alpha^{I} + \alpha^{II} = 1 \tag{2-7}$$

$$\gamma_i^I \quad \mathbf{x}_i^I = \gamma_i^{II} \quad \mathbf{x}_i^{II} \tag{2-8}$$

$$\alpha^{I} x_{i}^{I} + \alpha^{II} x_{i}^{II} = z_{i} \qquad (2-9)$$

$$\sum_{i=1}^{m} x_i^I = I$$
 (2-10)

However, it is more complicated to solve the above liquid-liquid flash equations than to solve the vapour-liquid flash equations. There is a possibility of multiple solutions for such a set of equations. The equilibrium liquid phase compositions and the phase fraction that satisfy **Equations** (2-7) - (2-10) could represent a system that does not exit. These phenomena can be explained by analyzing the phase stability of liquid phase.

2.3.1 Phase Stability Equation

From the classical thermodynamic analysis, the necessary and sufficient condition for a stable equilibrium is that the total Gibbs Free energy of the system attains the global minimum. In other words, for a stable system, the Gibbs free energy surface should retain the convex condition, that is mathematically:

$$\frac{\partial^2 \left(\mathbf{n} \mathbf{G} \right)}{\partial \mathbf{n}_i^2} \bigg|_{T, P, \mathbf{n}_i} \ge 0 \tag{2-11}$$

Substitution of component chemical potential gives the following condition for an intrinsically stable homogenous system:

$$\frac{\partial \boldsymbol{\mu}_i}{\partial \boldsymbol{n}_i}\Big|_{T,P,\boldsymbol{n}_i} \ge 0 \tag{2-12}$$

where n is total moles of mixture, n_i and n_j are mole numbers of ith and jth components. For a binary solution, the Equation (2-11) can be expressed in term of molar Gibbs Free energy and mixture composition, that is

$$\frac{\partial^2 \left(\mathbf{G} \right)}{\partial z_i^2} \bigg|_{T,P,n_j} \ge 0 \tag{2-13}$$

Figure 2-5 shows the molar Gibbs free energy of mixing versus composition for a binary homogenous system. The straight line AB represents the common tangent line of two points on the Gibbs free energy curve. The points C and D on the curve represent the inflection points. The inequality of **Relation** (2-13) is violated for a mixture lying between these two points. The region C-D is defined as intrinsically unstable, and mixtures with composition within this region would form another phase so as to reduce the total Gibbs free energy. The regions EAC and FBD, which satisfy the convexity **Condition** (2-13), are defined as intrinsically stable.

However, in the intrinsically stable regions (e.g., EAC and FBD in Figure 2-5), there exit metastable regions, AC and BD, within which the intrinsically stable homogenous mixture can split into two stable phases under perturbations. The phenomenon of metastable region can be illustrated in Figure 2-6. A binary homogenous mixture consists of, n_1 moles of component 1 and n_2 moles of component 2. The mixture composition of the component 1, $z = n_1/(n_1+n_2)$, is within the positively sloping range of the chemical potential curve, therefore, satisfies the criterion of **Condition** (2-13). Accordingly, z is considered intrinsically stable. If this binary solution decomposes into two phases, phase A1 and phase B1, the molar free energy of the two-phase mixture is

$$G_m = (1 - \alpha)G^{A_1} + \alpha G^{B_1}$$
 (2-14)

where α is the phase fraction of phase A1, and it can be calculated by the lever rule:

$$\alpha = \frac{n^{A_1}}{n} = \frac{z^{B_1} - z}{z^{B_1} - z^{A_1}}$$

$$1 - \alpha = \frac{n^{B_1}}{n} = \frac{z - z^{A_1}}{z^{B_1} - z^{A_1}}$$
(2-15)

So the Equation (2-14) represents the straight line passing through the two points A1 and B1 in Figure 2-6. The free energy G_m of the mixture of overall composition z is represented by the point G1 on the line A1B1. It shows that the Gibbs free energy of a two-phase mixture is lower than the one of original homogenous mixture. It illustrates that the intrinsically stable mixture can decompose into two separate phases with a lower Gibbs Free energy. Such mixture can be referred as a metastable mixture.

Metastable mixtures can exist in a stable form, for example, the supersaturated liquid solution. However, for most practical application, and specially for separation processes where mixtures are constantly subjected to macroscopic perturbation, the metastable mixtures easily become unstable. Unfortunately, solving the set of liquid-liquid equilibrium equations (Equations (2-7)-(2-10)) does not necessarily guarantee a stable equilibrium. The chemical potential equality criteria for the phase equilibrium (Equation (2-4)), which is derived from the stationary point of Gibbs free energy surface, however represents only a necessary but not sufficient condition for the stable equilibrium for the phase equilibrium. It is possible for a liquid mixture to split into two intrinsically stable phases, one of which is metastable. As shown in Figure 2-6, the Gibbs free energy of mixing could be reduced to G1, and the mixture splits into two phases A1 and

The chemical potentials of each phase are equal, which satisfy liquid-liquid B1. equilibrium criterion (Equation (2-4)). However, it does not represent a stable equilibrium state, due to the fact that the phase B1 lies in the metastable region of the The Gibbs free energy of the mixture can be further reduced to G2 Gibbs free energy. with two splitting liquid phases (A and B). Both phases have equal chemical potentials on the stable region, and G2 represents the minimum of the Gibbs free energy. The above discussion illustrates the fact that the solutions of Equation (2-7)-(2-10) only generates the equilibrium state that satisfies the stationary condition of the Gibbs free energy surface, and does not necessarily calculate stable equilibrium states. It is possible for a mixture to have multiple equilibrium states satisfying the chemical potential equality Therefore it is of importance to include the phase stability test with the phase criteria. equilibrium equation to ensure the stability of the proposed phase equilibrium, that is the Gibbs free energy of mixing is at a global minimum. It is also important for the proposed stability test algorithm to be able to identify correctly metastable region as unstable. The following section mainly reviews the stability test approaches used in the literature for the three-phase distillation simulation methods.

2.3.2 Liquid-Liquid equilibrium criteria

In many early three-phase distillation simulation works, only the chemical potential equality was used to determine the phase stability (Block and Hegner, 1976; Bril' et al., 1973; Kinoshita et al., 1983; Pucci et al., 1986). Basically, the liquid-liquid phase equilibrium equations (2-7) - (2-11) were solved for the splitting liquid phase's

compositions. If the equilibrium solution is not found, then the original mixture is considered stable. As mentioned before, such an approach could not guarantee a stable equilibrium solution, and sometimes could lead to trivial solutions.

2.3.3 Gibbs free energy minimization

Boston and Shah (1979), and Swartz and Stewart (1987) utilized the liquid stability algorithm of Shah (1980). This stability test procedure was based on the principle that the total Gibbs free energy must have its lowest value for a system of constant mass, temperature and pressure. Figure 2-7 outlines the liquid phase stability test proposed by Shah (1980). The iteration variable set λ was defined as:

$$\lambda_i = \ln(\frac{\gamma_i^I}{\gamma_i^{II}})$$
(2-16)

The initial guess of two splitting liquid phase compositions was based on the concept of infinite dilution activity coefficients. The algorithm continued until one of the conditions in Figure 2-7 was satisfied. It was noted that even though the iteration variable set, λ , may not be converged, if any of two phases was found with a lower Gibbs free energy of mixing, then this single liquid phase was unstable.

Ross and Seider (1979), Prokopakis (1981), Schuil and Bool (1985) applied the Gibbs free energy minimization approach of Gautam and Seider (1979) for the stability testing. This approach differs from the Boston and Shah (1979) stability test, as the Rand (1976) method was used to minimize the Gibbs free energy. Gautam and Seider

proposed an initialization procedure for all possible trial phase splits. Instead of using the infinite dilution activity. Gautam and Seider selected the key components based on the component's actual activity coefficient. The component with the highest activity in the single liquid phase was chosen as the first key component. The second key component was selected as the component with the highest binary activity with the first, with These two key concentrations being proportional to those in original mixture. components were allocated to two trial phases by neglecting other components and solving the binary isoactivity equation and mass balance equations. The remaining components were similarly allocated in order of decreasing binary activities with first key The algorithm was repeated for each feasible combination of trial phases component. The two trial phases with the lowest Gibbs free created by the above initialization step. energy were taken as candidates to replace their original mixture. The total Gibbs free energy of the splitting liquid phases was compared with the free energy of the original If an increase in free energy was found, then a few iterations of the mixture. minimization were performed to find a decrease. If after iterations of minimization, there was no decrease in the Gibbs free energy, the algorithm was repeated with a new trial phase with next lowest Gibbs free energy. With no decrease being found after examining all combination of trial phases, the original mixture was considered stable.

2.3.4 Tangent Plane Stability Analysis

Michelsen (1982) proposed a phase stability criterion by examining the stationary points of the vertical distance from the tangent hyperplane of the Gibbs free energy at original compositions to the Gibbs energy surface at the trial phase compositions. This is illustrated in Figure 2-8 for a binary mixture in which the original mixture z has chemical potential μ^{r}_{i} . This phase was compared with every possible trial phase having the whole range of composition y_{i} and chemical potential $\mu_{i}(y)$. If F(y) represents the vertical distance at the trial phase composition y from the Gibbs free energy curve to the tangent hyperplane originating from the original mixture z (as shown in Figure 2-8), that is defined as:

$$F(y) = \sum_{i=1}^{N_c} y_i \Big[\mu_i(y) - \mu_i^r \Big]$$
(2-17)

If, for all the trial phases at the given temperature and pressure of the system, $F(\mathbf{y}) \ge 0$, then the original mixture z is stable. In other words, if a composition y is found where the tangent at z lies above the Gibbs curve, the mixture z is unstable as shown in Figure 2-8. For a multicomponent system, the above tangent line criterion becomes a tangent plane criterion. Michelsen found that at the stationary points, **Equation** (2-17) can reduce to

$$\mu_i(y) - \mu_i^r = \sigma \qquad i = 1, \dots, N_c$$
 (2-18)

and

$$RT \ln \frac{\hat{f}_{yi}}{\hat{f}_{zi}} = \sigma$$
(2-19)

$$\ln \frac{f_{yi}}{\hat{f}_{zi}} = \frac{\sigma}{RT} = \theta, \qquad i = 1, \dots, N_c$$

The variable θ is defined as the stability factor, which can be used to identify the stability of a mixture. As noted by Michelsen (1982), the stability factor represents the vertical distance between the tangent hyperplane of the stationary point of $F(\mathbf{y})$ and the hyperplane at original mixture composition z. If the stability factor is non-negative at all stationary points, the original mixture is thus stable. If the stability factor is negative at one of stationary points, the mixture z thus is unstable. The compositions \mathbf{y} at the stationary points can be represented by using the stability factor, that is,

$$(y_i)_{sp} = z_i \left(\frac{\hat{\phi}_{zi}}{\hat{\phi}_{vi}}\right) e^{\theta} = z_i K_i e^{\theta} \qquad (2-20)$$

It has been found that if negative stability factor is detected, then the composition **y** from **Equation** (2-20) represent excellent initial estimates of the phase split. Another important feature of this tangent plane stability test is that the metastable regions are recognized as unstable. Baden and Michelsen(1987), Cairns and Furzer (1990) applied the tangent plane stability analysis to detect the unstable liquid phase and initialize the liquid-liquid flash calculations.

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Figure 2-7 Phase Stability Test of Shah (1976)





2.3.5 Simultaneous Phase Stability Testing Equation

One major problem of the above approaches is that the phase stability cannot be determined simultaneously with the solution of the MESH equations. An outer iteration loop is needed for the stability testing, phase splitting and the phase pattern adjustment. Gupta et al. (1990) developed an alternative phase stability criterion from the analysis of the minimization of the Gibbs free energy subject to mass balances. It states that for a phase at the Gibbs free energy minimum, either the phase fraction α_k or the phase stability factor, θ_k , has to be zero, mathematically that is

$$\alpha_k \theta_k = 0, \quad \alpha_k \ge 0, \text{ and } \theta_k \ge 0.$$
 (2-21)

The phase stability factor, which is derived to be the same as that defined by Michelsen (1982), is given as:

$$\theta_k = RT \ln \frac{f_{ik}}{f_{ir}} , \qquad (2-22)$$

where r stands for the reference phase. The obvious advantage of the Gupta's criterion over Michelsen's lies in the combination of the mass balance equations and the stability test analysis. The solution of **Equation** (2-21) will yield not only the mass quantity of a phase, but also the stability of the phase. If at the solution θ_k is determined as non-zero positive, the corresponding phase k is unstable. Then, the phase fraction α_k is determined as zero, which means the unstable phase does not appear. If α_k is determined as positive, the corresponding phase exits. Then θ_k becomes zero, indicating the existing phase k is stable. When the stability equation (2-21) is coupled with the MESH equations of a multiphase distillation problem, the phase stability, phase pattern and the splitting phase compositions can be determined simultaneously along with the other iterative variables. It eliminates the need for a prior knowledge of the phase pattern, or the need for the phase stability test and phase pattern adjustment after solving the MESH equations.

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2.4 The Objective of Research

Although the previously proposed methods have been used to simulate many three-phase distillation columns, there is still much improvement to be made. One of the dissatisfaction with these methods is the incorporation of the thermodynamics stability test into the solution procedure. The existence of the second liquid phase depends on the Therefore, it requires the inclusion of the phase stability criterion operating conditions, in the solution procedure to determine whether the proposed liquid phase is stable or unstable to split into two liquid phases during the calculations. In earlier methods such as bubble point methods or successive flash methods, there were no phase stability tests included. Instead, the so-called "iso-activity equation" (strictly speaking, it should be the chemical potential equality equation) was used to determine the phase stability of the proposed liquid mixture. Unfortunately, such an equation represents only the necessary but not sufficient condition for a liquid-liquid phase equilibrium. Using such criterion to determine the existence of the second liquid phase would lead a fallacious or trivial solution at which the total Gibbs free energy attains a non-minimum value. In later methods such as inside-out approach, more rigorous thermodynamics criteria such as Gibbs free energy minimization or tangent plane analysis were adapted to detect the unstable liquid phase. However, the phase stability testing was not included with system equations. Instead two-loop iteration scheme is usually used in these methods. In the inner loop, the phase pattern within the column was pre-specified, or two liquid phases were averaged into a pseudo single liquid phase. The phase stability test was carried out in outer-loop to determine the stability of the liquid mixture resulting from the inner-loop solution. Based on the stability test result, the phase pattern within the column was adjusted, or the averaging pseudo single liquid phase's thermodynamics properties were re-evaluated. The average pseudo single liquid phase approach makes it possible to solve the three-phase separation problem using the existing formulation for the two-phase separation problems. However, there are some disadvantages associated with such an approach:

• It is difficult to evaluate the derivatives of the equations with respect to the average liquid compositions.

• It is impossible to have distinctive liquid phase side withdrawals from the column since the model equations only handle the average compositions.

• It is impossible to include the constraint equations that are related to the individual liquid phase compositions such as the liquid phase composition specifications, the kinetic relationships, etc.

In this research work, a new algorithm is developed for the simulation of three phase distillation and reactive distillation columns. The specific objectives of this research include:

1. To develop a new mathematical model formulation which

• allows multiple liquid phases and reactions at each stage.

- includes the phase stability equations and determines the appearance and disappearance of a second liquid phase simultaneously with other iterative variables
- includes the implicit chemical equilibrium equations and determines the reaction extents or rates simultaneously with other iterative variables.
- 2. To develop a new solution procedure which
 - solves model equations simultaneously
 - is robust and stable to simulate various separation systems, even at unfavorable conditions.
 - has efficient and fast convergence characteristics
- 3. To apply the proposed simulation method to simulate previously attempted separation problems including two-phase, three-phase, and reactive distillation.

3. Model Development of Multiphase Non-Reactive Separation Simulation

This chapter outlines a new computational procedure for a multiphase, multicomponent and multi stage equilibrium separation column. It begins with the introduction of a general column configuration for a multistage and multiphase separation process. Then a new set of model equations is developed, based on the component mass balance , energy balance, component summation, phase equilibrium and phase stability equations. This chapter also outlines the thermodynamic properties' calculations, including evaluation of their derivatives with respect to the iterative variables, and the approximate thermodynamic model's parameters. The modification of the Powell's hybrid method for controlling step size during iterations is described. Also, an inside-out computation procedure is presented.


Figure 3-1 Schematic Figure of Multiphase distillation column

3.1 General Column Configurations and Equations

A general schematic of a multiphase, multicomponent, multi-stage equilibrium separation column is shown in Figure 3-1. The proposed column configuration and equations are general and applicable to all the specific column configurations such as distillation, absorption, stripping, reboiled absorption, extraction and extractive distillation.

For distillation the stage N is a reboiler and the stage 1 is a combination of a condenser and a decanter. In the case of absorption and stripping columns, stages 1 and N represent the top and bottom trays. For reboiled absorption, it is similar to the absorption, except that the stage N is a reboiler. The proposed column also allows the existence of multiple liquid phases within the column. There are one vapor phase stream, and $(\pi - 1)$ liquid phase streams leaving each stage. For each leaving stream, there is a side stream withdrawal. On each stage, there is a feed stream and an energy input stream. The mass and energy flow streams for the jth stage are shown in the Figure 3-1.

The following assumptions are made to develop the mathematical equations for simulating this general separation process:

1. It is a steady state problem, therefore, there is no time variation in any of the model equations.

- 2. Each stage is treated as an equilibrium (or "theoretical") stage, and all phase streams leaving from a stage are related by an equilibrium relationship.
- 3. Perfect mixing occurs for the liquid phase of each stage. The withdrawal streams have the same composition and condition as the inter-stage stream from which they are drawn.
- 4. The two liquid phases are completely separated on each stage.
- 5. The liquid feed mixes perfectly with the liquid phase below its entry points, the vapor feed stream mixes perfectly with the vapor rising from the stage below and then to enter the stage above.

Based on the above assumptions, the mathematical equations that describe the operations for the jth stage are given below:

Component Mass Balance Equations:

$$G_{ij}^{m} = -\sum_{k=1}^{\pi} n_{ijk} + F_{ij} + (1 - w_{j+1,1}) n_{ij+1,1} + \sum_{k=2}^{\pi} (1 - w_{j-1,k}) n_{ij-1,k}$$
(3-1)

where n_{ijk} refers to the number of moles of component i in phase k at the stage j, while w_{jk} represents the side withdrawal ratio of kth phase stream leaving from stage j. The vapour phase is represented by k = 1.

Energy Balance Equations:

$$G_{j}^{E} = -\sum_{k=1}^{\pi} \sum_{i=1}^{N_{c}} n_{ijk} h_{ijk} + \sum_{i=1}^{N_{c}} (1 - w_{j+1,1}) n_{ij+1,1} h_{ij+1,1} + \sum_{k=2}^{\pi} \sum_{i=1}^{N_{c}} (1 - w_{j-1k}) n_{ij-1k} h_{ij-1k} + Hf_{j} + Qf_{j}$$
(3-2)

where h_{ijk} is partial molar enthalpy for component i in phase k. Hf_j is the total enthalpy of feed stream entering stage j, and Qf_j is the enthalpy values of the energy input stream.

Component Summation Equations:

$$G_{jk}^{s} = \sum_{i=1}^{N_{c}} (y_{ijk} - y_{ijr})$$
(3-3)

where, y_{ijk} is defined as the mole fraction of component i in phase k and y_{ijr} is the mole fraction of the component in the reference phase. The vapour phase is used as the reference phase in this study.

Phase Summation Equations

$$G_{j}^{ps} = \sum_{k=1}^{\Pi} \alpha_{jk} - 1$$
 (3-4)

where α_{jk} is the phase fraction of the kth phase at the jth stage.

Phase stability Equations:

$$G_{jk}^{st} = \frac{\alpha_{jk} \theta_{jk}}{\alpha_{jk} + \theta_{jk}}$$
(3-5)

 α_{jk} and θ_{jk} represent the phase fraction and stability factor of phase k at stage j, respectively. Equation (3-5) is the modified form as suggested by Gupta et al.(1990) of equation (2.21).

Phase Equilibrium Relationship:

From the stability factor,

$$\theta_{jk} = \ln \frac{\hat{f}_{ijk}}{\hat{f}_{ijr}} , \qquad (3-6)$$

and the equilibrium ratios

$$K_{ijk} = \frac{\hat{\phi}_{ijr}}{\hat{\phi}_{iik}} = \frac{y_{ijk}f_{ijr}}{y_{ijr}f_{ijk}} = \frac{y_{ijk}}{y_{ijr}}e^{-\theta_{jk}}$$
(3-7)

the following relationship is written for a phase which may be stable or unstable

$$y_{ijk} = y_{ijr} \quad K_{ijk} \quad e^{\theta_{\mathcal{A}}}$$
(3-8)

It is noted from equation (3-8) that when the phase k is stable with a zero value of the phase stability factor, the equation is reduced to the conventional equilibrium relationship. When phase k is unstable with non-zero positive value of the phase stability factor, equation (3-8) is used to calculate the composition of the unstable phase. Thus for an unstable phase, equation (3-8) can be viewed as a "quasi-equilibrium" relationship. It is because of this important feature that it is possible to allow the disappearance and appearance of a phase during the iterations.

To simplify the model equations describing the column and their derivatives, we introduce a new variable β , which is defined as follows:

$$\beta_{ijk} = \frac{n_{ijk}}{\sum_{k=1}^{\pi} n_{ijk}} = \frac{n_{ijk}}{m_{ij}}$$
(3-9)

where m_{ij} refers to the overall flow rate of the ith component leaving stage j. The variable β may be called as the component phase fraction, and represents the distribution of the component i in phase k on the stage j. The composition and the flow rate of the component i in phase k are related to β by the following equation:

$$n_{ijk} = \beta_{ijk} m_{ij}, \text{ and } y_{ijk} = \frac{n_{ijk}}{\sum_{l=1}^{N_e} n_{ijk}} = \frac{\beta_{ijk} m_{ij}}{\alpha_{jk} \sum_{i=1}^{N_e} m_{ij}} \quad (3-10)$$

Substitution of Equation (3-10) into all the model equations (3-1)-(3-5) generates a set of new model equations in term of variables α , β , θ and m, that is:

Component Mass Balance Equations:

$$G_{ij}^{m} = -m_{ij} + F_{ij} + (1 - w_{j+1,1})\beta_{ij+1,1}m_{ij+1} + \sum_{k=2}^{\pi} (1 - w_{j-1k})\beta_{ij-1k}m_{ij-1}$$
(3-11)

Energy Balance Equations:

$$G_{j}^{E} = -\sum_{k=1}^{\pi} \sum_{i=1}^{N_{c}} \beta_{ijk} h_{ijk} m_{ij} + \sum_{i=1}^{N_{c}} (1 - w_{j+1,1}) \beta_{ij+1,1} h_{ij+1,1} m_{ij+1} + \sum_{k=2}^{\pi} \sum_{i=1}^{N_{c}} (1 - w_{j-1k}) \beta_{ij-1k} m_{ij-1} + Hf_{j} + Qf_{j}$$
(3-12)

Component Summation Equations:

$$G_{jk}^{s} = \sum_{i=1}^{N_{c}} \left(\frac{\beta_{ijk}}{\alpha_{jk}} - \frac{\beta_{ijr}}{\alpha_{jr}} \right) m_{ij}$$
(3-13)

Phase Summation Equations:

$$G_{j}^{ps} = \sum_{k=1}^{\Pi} \alpha_{jk} - 1$$
 (3-14)

Phase stability Equations:

$$G_{jk}^{ST} = \frac{\alpha_{jk} \theta_{jk}}{\alpha_{ik} + \theta_{ik}}$$
(3-15)

Rearranging equation (3-10) and substituting (3-8) gives,

$$n_{ijk} = y_{ijk} \alpha_{jk} \sum_{i=1}^{N_c} m_{ij} = y_{ijr} \alpha_{jk} e^{\theta_{jk}} K_{ijk} \sum_{i=1}^{N_c} m_{ij} \quad .$$
(3-16)

Substituting equation (3-16) into equation (3-9) and manipulating we obtain,

$$\beta_{ijk} = \frac{\alpha_{jk} e^{\theta_{jk}} K_{ijk}}{\sum_{p=1}^{\pi} \alpha_{jp} e^{\theta_{jp}} K_{ijp}}.$$
(3-17)

Thus, equation (3-17) for the variable β implicitly incorporates the equilibrium relation given by equation (3-8). Equations (3-11) through (3-15) and (3-17) are governing equations for the steady-state simulation of a multistage, multicomponent and multiphase separation column. They are referred as MESH equations. The equations are solved to drive the residual functions G^M , G^E , G^S , G^{ST} , and G^{PS} to zero. The above mentioned equations are $N_s(1+N_c+2\pi+N_c\pi)$ in number (**Table 3-1**).

The variables which are necessary to describe the process are pressure P_j (N_s), temperature T_j (N_s), overall component stage flow rate, m_{ij} (N_s N_c), phase fraction α_{jk} (N_s π), phase stability factor θ_{jk} (N_s π), component phase fraction β_{ijk} (N_s N_c π), component phase flow rate n_{ijk} (N_sN_c π), phase composition y_{ijk} (N_sN_c π), feed stream component flow rate F_{ij} (N_sN_c), feed stream thermal condition Tf_j and Pf_j (2N_s), feed stream enthalpy Hf_j (N_s), stage heat input Qf_j (N_s), and side withdrawal ratio w_j (N_s π). Thus a total of N_s(6 + 2N_c + 3 π + 3N_c π) variables are required to describe the process).

The variables y_{ijk} and n_{ijk} can be determined from equation(3-10), and therefore, can be viewed as dependent variables. Also the feed stream enthalpies, Hf_j, can be determined using an enthalpy function based on the feed stream component flow rates (F_{ij}) and feed thermal conditions (Tf_j and Pf_j). Thus, there are now N_s(5 + 2N_c + 3 π + N_c π) independent system variables and N_s(1+N_c+2 π +N_c π) equations, resulting in N_s(4+N_c+ π) degrees of freedom or design variables to be specified.

3.1.1 Iterative Variables

The iterative variables for the system equations can be chosen as temperature T_j (N_s), phase stability factor θ_{jk} (N_s π), phase fraction α_{jk} (N_s π), component overall flow rate m_{ij} (N_sN_c), and component phase fraction β_{ijk} (N_s N_c π). The fugacity coefficients and K-values are directly related to the inverse of the temperature, whereas, enthalpy is related directly to the temperature. The fugacity coefficients and K-values, however, appear more often in the model equations than the enthalpy. Also, the non-linearity associated with the fugacity coefficients and K-factors is implicit in nature and more difficult to handle than that associated with enthalpy. It therefore may be expected that their partial derivatives with respect to the inverse temperature. Good first order approximations in the Jacobian matrix are very important to ensure the convergence of Newton-like methods. Thus the inverse stage temperature, instead of the normal temperature, is used as the iterative variable in this work. The advantage of using the phase fraction and phase stability factor as independent variables is determine the phase pattern simultaneously with the other variables. The simultaneous adjustment of phase pattern is important when dealing with the appearance and disappearance of a phase during the iterations.

3.1.2 Specification Variables

Typical specifications include feed stream component flow rates (N_sN_c) , feed stream thermal conditions $(2N_s)$, stage heat input (N_s) , pressure profile (N_s) , and side withdrawal ratios $(N_s\pi)$. However, the above list of specifications can flexibly be substituted by other specifications. In certain cases, the alternate specifications can be more convenient, depending on the nature of a particular problem to be solved. The following sections illustrate the choice of the specifications for each configuration treated in the present study.

3.1.3 Configuration with Condenser (and Decanter)

It is usually more convenient to allow the condenser heat input duty (Qf_1) to be determined, instead of being specified. The alternative specification can be the ratio of vapor distillate flow rate to the total liquid distillate rate (RVL). Then, the additional specification is written as,

$$G_{condenser}^{E} = RVL \sum_{k=2}^{\pi} w_{1k} \alpha_{1k} - \alpha_{11} = 0 \quad .$$
(3-18)

It is noted that for a total condenser, the ratio of vapor distillate to total liquid distillate (RVL) is specified as zero. In this case, the above equation for the total condenser becomes:

$$G_{\text{condenser}}^{E} = \alpha_{11} = 0 \tag{3-19}$$

The condenser specification equations (3-18) or (3-19) is used to replace the energy balance equation (3-12) for the top condenser stage. The energy balance equation for the top condenser stage is then used to calculate the heat duty of Qf₁.

$$Qf_{j} = \sum_{k=1}^{\pi} \sum_{i=1}^{N_{c}} \beta_{ijk} h_{ijk} m_{ij} - \sum_{i=1}^{N_{c}} (1 - w_{j+1,1}) \beta_{ij+1,1} h_{ij+1,1} m_{ij+1} - Hf_{j} \quad (j = 1) \quad (3-20)$$

At the top stage, the side withdrawal ratio for the vapor phase flow is always specified as unity, since the vapor distillate flow can be viewed as a total withdrawal from the condenser. The liquid phase side-stream ratio is usually less than unity, so as to allow some fraction of liquid phase reflux back to the column. However, if there are two liquid phases at the top stage, it is possible to specify that one of the liquid phases has a total side-withdrawal. In addition, it is possible to have one of the liquid phases with no withdrawal, in other words, it is completely refluxed back to the column.

In the case of vapour-liquid two phase distillation problems, the reflux ratio, RF, which is defined as the ratio of liquid reflux to the total distillate flow, usually can

substitute the side-withdrawal ratio of liquid phase as the specifications. In such a case the liquid phase side-withdrawal ratio can be determined from the following relationships:

$$w_{12} = \frac{l_d}{l_d + l_r} = \frac{l_d}{l_d + RF(l_d + v_d)}$$
$$= \frac{1}{RF + 1 + \frac{v_d}{l_d}} = \frac{1}{RF + 1 + RVL}$$
(3-21)

However, it is difficult to specify the reflux ratio for the three-phase system, since the relationship between the liquid phase side-stream ratio and the reflux ratio is not straightforward as in the two-phase system. Instead, the side-withdrawal ratio is an implicit function of the phase fractions, and has to be evaluated iteratively during the calculation. Another drawback of using reflux ratio of liquid phase as a specification is the difficulty to specify the reflux ratio of the liquid phase that is the completely refluxed. In this case, the reflux ratio is basically an infinite value. Therefore, for the three phase separation problem, the side draw ratio of each distillate stream at the decanter is used as the specification in this study.

3.1.4 Configuration with Reboiler

Similar to the above situation, It is usually not convenient to specify the reboiler heat input duty (Qf_{Ns}) . In this case, the bottom product rate is specified, and the heat duty of a reboiler is determined from the energy balance equation for the bottom stage.

$$Qf_{j} = \sum_{k=1}^{\pi} \sum_{i=1}^{N_{c}} \beta_{ijk} h_{ijk} m_{ij} - \sum_{k=2}^{\pi} \sum_{i=1}^{N_{c}} (1 - w_{j-1k}) \beta_{ij-1k} h_{ij-1k} m_{ij-1} - Hf_{j}$$

$$(j = Ns)$$
(3-22)

In the iterative scheme then, the energy balance equation for the bottom stage is replace by the following specification equation, that is,

$$G_{N_s}^E = G_{reboiler}^E = \sum_{k=2}^{\pi} \sum_{i=1}^{N_c} \beta_{i_{N_s}k} m_{i_{N_s}} - BF = 0 \qquad (3-23)$$

where BF is the specified bottom product rate and should be equal to the calculated liquid flow rate leaving from the bottom stage. Since,

$$\sum_{k=1}^{\pi} \beta_{ijk} = 1, \quad and \quad \sum_{k=1}^{\pi} \sum_{i=1}^{N_c} \beta_{ijk} m_{ij} = \sum_{i=1}^{N_c} m_{ij} \quad , \quad (3-24)$$

the equation (3-23) becomes :

$$G_{N_s}^E = G_{reboiler}^E = \sum_{i=1}^{N_c} (1 - \beta_{iN_s i}) m_{iN_s} - BF = 0 \qquad (3-25)$$

Equation Type	Equation Number	Number of Equations
Component Mass Balance Equation	(3-1) or (3-11)	$N_c N_s$
Energy Balance Equation	(3-2) or (3-12)	N_s
Component Summation Equation	(3-3) or (3-13)	(π-1) N _s
Phase Summation Equation	(3-4) or (3-14)	N_s
Phase Stability Equation	(3-5) or (3-15)	$N_s \pi$
Component Phase Fraction Equation	(3-17)	$N_c N_s \pi$
Total		$N_{s}(1+N_{c}+2\pi+N_{c}\pi)$

Table 3-1Summary of Independent Constraining Equations

.

Variable type	Number of Variables
Temperature, T	Ns
Pressure, P	Ns
Overall Component Phase Flow Rates, m	$N_s N_c$
Phase Fraction, α	. $N_s \pi$
Phase Stability Factor, θ	$\mathrm{N_s}\pi$
Component Phase Fraction, β	$N_s N_c \pi$
Component Phase Flow Rates, n	$N_s N_c \pi$
Component Phase Compositions, y	$N_s N_c \pi$
Feed Stream Component Flow Rate, F	$N_s N_c$
Feed Stream Thermal Condition, Tf, Pf	2 N _s
Feed Stream Enthalpy, Hf	Ns
Heat Input Stream Enthalpy, Qf	Ns
Side withdrawal Ratio, w	$N_s \pi$
Total	$N_{s}(6+2N_{c}+3\pi+3N_{c}\pi)$

Table 3-2Summary of Independent System Variables

3.2 Thermodynamic Properties Calculation and Data Structure

The simulation results of separation process depend on the accuracy of the thermodynamic models that are used to evaluate the thermodynamic properties of the In this work, an efficient thermodynamic data structure is implemented so that system. it is possible to evaluate effects of selection of thermodynamic models and their The data structure is organized in the form of parameters on the simulation results. inheritance using the object-oriented programming language. Figure 3-2 outlines the The data structure not only provides values of details of the data structure. thermodynamic properties such as fugacity coefficient, partial molar enthalpy, it also calculates the analytical partial derivatives of these properties. The physical and thermodynamic properties data bank, which includes critical properties, heat capacities, acentric factors etc., are archived from the book by Reid et al. (1988) . The choice of thermodynamic models for each phase is given as the input of the algorithm. The following sections give details of calculation of thermodynamic properties.



Figure 3-2 Thermodynamic Properties Data Structure

.

3.2.1.1 Evaluation of K-values and their derivatives

As mentioned in Section 3.1, the equilibrium ratio, K-values, is defined as the ratio of the fugacity coefficient of a component in a phase k and reference r, that is,

$$K_{ik} = \frac{\hat{\phi}_{ir}}{\hat{\phi}_{ik}}, \qquad k = 1...\pi, \quad k \neq r \qquad (3-26)$$

The fugacity coefficient of a component in the vapor phase (k=1) is usually determined using an equation of state. This work has implemented the Peng-Robinson (PR) Equation of State (1976), Soave-Redlich-Kwong (SRK) Equation of State (1972) and the Virial Equation of State. The binary interaction coefficients of the components for both the equations of state are supplied by the user. Since the vapor phase is normally close to an ideal solution at low pressure conditions, the vapour phase can also be modeled by the ideal gas law.

The fugacity coefficient of the component in the liquid phase $(k=2,..\pi)$ can also be calculated by the equation of state approach. However, for a liquid phase with a strong molecular interaction, it usually has a large deviation from ideal solutions, especially in the case of the multi-liquid phase equilibria solution. In this case, liquid solution models, or activity coefficient models are used here to describe the liquid phase behavior. The

activity coefficient models which have been implemented in this work include NRTL, UNIQAC, UNIFAC, Wilson models.

In the activity coefficient model, the component fugacity can be represented by:

$$f_{ik} = y_{ik} \gamma_{ik} f_{i}^{oL} \qquad (k = 2...\pi)$$

$$= y_{ik} \gamma_{ik}^{(P_r)} f_{i}^{oL} \left(\exp \left(\int_{P_r}^{P} \frac{-L}{RT} dp \right) \right)$$
(3-27)

where p_r is an arbitrary reference pressure which is used to correct the pressure influence on the activity coefficients, and f_i^{oL} represents the standard fugacity of the component. The reference pressure p_r was taken as zero for all the components in this work. The corresponding fugacity coefficient of a component in liquid phase is given by:

$$\hat{\phi}_{ik} = \frac{\hat{f}_{ik}}{y_{ik}P} = \frac{\gamma_{ik}^{(p_r)}f_i^{oL}}{P} \int_{p_r}^{P} \exp\left(\frac{-L}{RT}\right) dp$$
(3-28)

The definition of the activity coefficient in the above equations depends on the definition of the standard fugacity, f_i^{oL} . For a condensable component, the standard fugacity is defined as the fugacity of the pure liquid i at the temperature of the solution and at the reference pressure, based on the symmetric normalization, that is,

$$\gamma_i^{(p_r)} \rightarrow 1, \quad as \quad y_i \rightarrow 1 \tag{3-29}$$

The standard fugacity f_{ik}^{ol} for a condensable component can be given by

$$f_i^{oL} = p_i^s \phi_i^s \left(\exp \int_{p_i^s}^{p_r} \frac{v_i^L}{RT} dp \right)$$
(3-30)

where p^s stands for the saturation pressure of pure liquid i at the temperature T, while ϕ^s represents the fugacity coefficient of pure saturated vapour i at the temperature T and the pressure p^s . The values of p^s and ϕ^s are obtained from vapor pressure equations (such as Antoine Equation) and the equation of state respectively. It assumes that both these partial molar volume \overline{v}_i^L and molar volume v_i^L are functions only of temperature, not of pressure and composition. This implies that \overline{v}_i^L can be approximately equal to v_i^L for the same temperature. In this study, this molar volume is calculated using Rackett's equation (Prausnitz et al., 1980).

For a liquid phase containing a noncondensable, or a supercritical component, however, the above normalization cannot be applied since a liquid is a physical impossibility in the supercritical state. Instead, the following unsymmetric normalization equation is employed

$$\gamma_i^{(p_r)} \to 1 \text{ as } y_i \to 0 \tag{3-31}$$

Therefore, the standard-state fugacity for a uncondensable component is the Henry's constant evaluated at the system temperature T and pressure $P_{r,}$. It can be represented by

$$H_i^{(p_r)} \equiv \lim_{y_i \to \theta} \left(\frac{f_i^L}{y_i} \right) = H_i^{(p_i^r)} \exp \int_{p_i^r}^{p_r -\infty} \frac{1}{RT} dp \qquad (3-32)$$

where ∞ denotes the infinite dilution. Since the solubility of a noncondensable component in the liquid solution is very small, the noncondensable component fugacity can be simplified as

$$\hat{f}_{ik} = \gamma_i^{(p_r)} y_{ik} H_i^{(p_r)} \int_{p_r}^{p} \left(\frac{-L}{N} \right) dp = y_{ik} H_i^{(p_r)} \approx y_{ik} H_i^{(p_r')}$$
(3-33)

In this work, the noncondensable component Henry's constant, H_i , is assumed being independent of the temperature and its value is supplied by the user.

Prausnitz et al. (1980) proposed a polynomial equation for evaluating the standard fugacity, that is,

$$\ln f_i^{oL} = C_{1i} + C_{2i}/T + C_{3i} T + C_{4i} \ln T + C_{5i} T^2 \qquad (3-34)$$

where the C's are constants which are obtained by fitting the experimental saturation equilibrium data. The above correlation is used as the default method for calculating the standard fugacity for the activity model in this work. The C's constants are taken from the book by Prausniz et at. (1980). When C's constants are not available for a component, the standard fugacity is calculated using the equations (3-30) and (3-33).

3.2.1.2 Enthalpy Calculation

The partial molar enthalpy of a component is computed based on the ideal gas enthalpies and the correction of enthalpy for the temperature and pressure, that is,

$$h_{ik} = h_i^{ig} + \Delta h_{ik} \qquad (3-35)$$

The ideal gas enthalpy is calculated using the heat capacity of an ideal gas,

$$h_i^{ig}(T) = h_i^{ig}(T_o) + \int_{T_o}^T C p_i^{ig} dT$$
 (3-36)

where

$$Cp_{i}^{ig} = C_{1i} + C_{2i}/T + C_{3i}T + C_{4i}\ln T$$
 (3-37)

The coefficients C are empirical constants from the data bank of Reid et al (1980). Enthalpy $h^{ig}_{i}(T_{o})$ is the ideal gas enthalpy value at the reference temperature $T_{o}(298.15K)$. The values of $h^{ig}_{i}(T_{o})$ are obtained from the physical property data bank (Reid, et al. 1980).

The Δh_{ik} represents the partial molar enthalpy departure function, and it can be evaluated from thermodynamic model equations using the following relationship:

$$\frac{\Delta h_{ik}}{R} = \frac{\partial (\ln \hat{\phi}_{ik})}{\partial (\frac{1}{T})}$$
(3-38)

For liquid phase whose phase behavior is described by the activity coefficient models (3-28), and (3-33), the excess enthalpy of the component is used to calculate the partial molar enthalpy :

$$h_{ik} = h_i^L + \Delta h_{ik}^{ex}$$

$$\Delta h_{ik}^{ex} = R \left(\frac{\partial \ln \gamma_{ik}}{\partial \frac{1}{T}} \right)_{p,x}$$
(3-39)

The pure liquid component enthalpy is calculated by:

$$\boldsymbol{h}_{i}^{L} = \boldsymbol{h}_{i}^{ig}(T) + R \left(\frac{\partial \ln \phi^{sat}}{\partial \frac{1}{T}} \right)_{pure \ liquid, T, P^{sat}}$$
(3-40)

3.2.1.3 Approximate Thermodyanmics Models

The equilibrium ratio K-values, and the enthalpies are functions of temperature and composition. The composition dependence of those thermodynamic properties becomes very complicated when dealing with non-ideal mixtures. An "inside-out" approach is adopted to approximate the composition effects on K-values and enthalpies ' evaluations

in the inner loop similar to that of Boston and Sullivan (1974). In the inner loop, the K-values and the enthalpies can be presented as follows:

$$\ln K_{ik}(T) = \ln K_{ik}(T_b) - B_{ik}(\frac{1}{T} - \frac{1}{T_b})$$
(3-41)

$$h_{ik}(T) = h_i^{ig}(T_o) + \int_{T_o}^{T_o} c p_i^{ig} dT + \Delta h_{ik}(T)$$
 (3-42)

and

$$\Delta h_{ik}(T) = \Delta h_{ik}(T_b) + C_{ik}(T - T_b) \qquad (3-43)$$

To determine the parameters B_{ik} and C_{ik} in the above equations, equations, (3-41) (3-42) and (3-43) are differentiated to give:

$$B_{ik} = -\left(\frac{\partial \ln K_{ik}}{\partial (\frac{1}{T})}\right)_{T=T_{b}} = \left(\frac{\partial \ln \phi_{ik}}{\partial (\frac{1}{T})}\right)_{T=T_{b}} - \left(\frac{\partial \ln \phi_{ir}}{\partial (\frac{1}{T})}\right)_{T=T_{b}}$$
(3-44)

$$C_{ik} = \left(\frac{\partial(\Delta h_{ik})}{\partial(T)}\right)_{T=T_{b}} = R\left(\frac{\partial}{\partial T}\left(\frac{\partial(\ln \phi_{ik})}{\partial(\frac{1}{T})}\right)\right)_{T=T_{b}}$$
(3-45)

The derivatives of fugacity coefficients are evaluated analytically from the rigorous thermodynamic models at the trial stage temperature (T_b) in the outer loop, and are kept constant within the inner loop.

3.3 Solution Procedure

The solution procedure, which consists of two loops, is summarized in Figure 3-3. In the inner loop, the K-values and enthalpies are approximated as only functions of temperature, and the equations (3.11) through (3.15) are solved simultaneously using the modified Powell's method (Powell, 1970). In the outer loop, the component compositions are updated using equation (3.10), and rigorous thermodynamic models are used to evaluate the thermodynamic properties and the parameters of the approximation models. The detailed descriptions of the solution procedure will be given in the following sections.

3.3.1 Outer loop Iteration

3.3.1.1 Initialization

In dealing with two-phase distillation problems, the initial temperature profile is obtained from the linear interpolation of temperatures at the condenser and the reboiler. The initial temperatures of the condenser and the reboiler are determined from the dew and bubble point calculations at the average composite feed condition. The initial estimates of the phase fractions are obtained from solving total mass balance, with the assumption of the constant mole overflow. K-values are initialized at the average composition of feed streams, stage temperature and pressure. Then the component mass balance and equilibrium equations are solved to give component overall flow rates. The vapour and liquid phase compositions are calculated directly from equation (3.10) and are

used to evaluate the thermodynamic properties such as K values and enthalpies using the vigorous thermodynamic models. The schematic of the initialization procedure is shown in Figure 3-4.

The three-phase distillation calculation is initialized by performing a few iterations of two-phase distillation calculation. On each stage, the three-phase equilibrium and stability equations are solved for the overall composition generated from the two-phase solution. The solution gives the initial estimates of phase fractions, phase stability factor, and the compositions of two liquid phases. The compositions of the two liquid phases are used to calculate the parameters for the simple thermodynamic models.



Figure 3-3 Inside - Out Solution Algorithm



Figure 3-4 Two Phase Distillation Initialization Procedure

3.3.1.2 Check Convergence for the Outer Loop Variables

In the original "inside-out" approach of Boston and Sullivan (1974) the convergence of the outer loop was tested by examining the changes in the coefficients of the approximated thermodynamic models. However, such approach makes it difficult to distinguish between convergence and the effects due to the damping. Therefore, the changes in the temperature and the compositions during the iterations are used as the convergence test for the outer loop in this study. Such tests for the convergence are unaffected by the damping, as the conditions at the end of the inner loop are purely a function of the compositions and temperatures at which the parameters for the approximated thermodynamic models.

The component phase compositions are computed from the conditions that are converged in the inner loop, that is,

$$y_{ijk} = \frac{\beta_{ijk} m_{ij}}{\alpha_{jk} \sum_{i=1}^{n_c} m_{ij}} = \frac{K_{ijk} e^{\theta_{jk}} m_{ij}}{\left(\sum_{p=1}^{\Pi} \alpha_{jp} K_{ijp} e^{\theta_{jk}}\right) \left(\sum_{i=1}^{n_c} m_{ij}\right)}$$
(3-46)

The relative tolerances of 1.0E-16 for the inverse temperatures and 1.0E-8 for the compositions are specified as the convergence criteria of the outer loop. Within such relative tolerances, the thermodynamic properties and the system residual functions do not change by perturbations in temperatures and compositions. If these criteria are not

satisfied, the temperatures and the compositions are updated by the successive substitution method.

Based on these newly obtained temperatures and compositions, the rigorous thermodynamic models then are used to compute the fugacity coefficients, enthalpies and their derivatives with respect to the temperatures. The parameters of the approximated thermodynamic models are updated from the calculated thermodynamic properties. Then, the inner loop is restarted with a new set of parameters and column conditions. The iteration continues until the outer loop convergence criteria are satisfied.

3.3.2 Inner Loop Iteration

In the inner loop, the set of linearized equations are solved simultaneously using the Newton Raphson approach, that is,

$$J\Delta x^{N} = -G(x) \tag{3-47}$$

where the independent variables are temperature, composition, phase fraction, phase stability factor and component flow rates. The Jacobian matrix contains the first order partial derivatives of all the residual functions with respect to the independent variables. The derivatives are analytically computed using the approximated thermodynamic models, in which the K-values and enthalpies are independent of the effects of compositions. Since the variables are arranged stage by stage, the Jacobian matrix is in the form of a block tridiagonal matrix. The Thomas tridiagonal matrix solution method was modified for solving the linearized set of equations to get the Newton correction step, Δx^N , and to update the iterative variables x

$$x^{m+1} = x^m + \Delta x^N$$
 (3-48)

The Newton's iterative scheme converges quadratically towards the solutions provided the initial estimates of the variables are near the final solution. However, if the initial estimate is far away from the final solution, the iterative scheme may converge slowly, oscillate or diverge. To stabilize or control the correction step size within the trust region from which the Newton's method will converge to the desired solution, the Powell's dogleg method (Chen and Stadtherr, 1981) was modified to use in this work. Figure 3-5 illustrates the outline of the inner loop iteration. The details of the modified Powell's dogleg method and its implementation in this work, is discussed in the following section.

3.3.3 Modified Block-Tri-Diagonal Thomas Algorithm

The linearized equations generated by the Newton method are in the form of block tri-diagonal matrix, that is:

$$\begin{pmatrix} B_{1} & C_{1} & & & \\ A_{2} & B_{2} & C_{2} & & \\ & \ddots & \ddots & \ddots & \\ & & A_{N-1} & B_{N-1} & C_{N-1} \\ & & & & A_{N} & B_{N} \end{pmatrix} \bullet \begin{pmatrix} \Delta x_{1} \\ \Delta x_{2} \\ \vdots \\ \vdots \\ \Delta x_{N-1} \\ \Delta x_{N} \end{pmatrix} = \begin{pmatrix} D_{1} \\ D_{2} \\ \vdots \\ D_{N-1} \\ D_{N} \end{pmatrix}$$
(3-49)

which are solved by the direct application of the Thomas algorithm. It starts with the forward elimination of the lower diagonal block elements, so that the equations are reduced to the following form:

$$\begin{pmatrix} I_1 & C_1^{\star} & & & \\ & I_2 & C_2^{\star} & & \\ & & \ddots & \ddots & \\ & & & I_{N-1} & C_{N-1}^{\star} \\ & & & & I_N \end{pmatrix} \bullet \begin{pmatrix} \Delta x_1 \\ \Delta x_2 \\ \vdots \\ \vdots \\ \Delta x_{N-1} \\ \Delta x_N \end{pmatrix} = \begin{pmatrix} D_1^{\star} \\ D_2^{\star} \\ \vdots \\ D_{N-1}^{\star} \\ D_N^{\star} \end{pmatrix}$$
(3-50)

where I is unity matrix, for stage 1,

$$B_{1}^{*} = B_{1}$$

$$C_{1}^{*} = (B_{1}^{*})^{-1}C_{1}$$

$$D_{1}^{*} = (B_{1}^{*})^{-1}D_{1}$$
(3-51)

and for stage j (j=2, ... NS),

$$B_{j}^{*} = B_{j} - A_{j}C_{j-1}^{*}$$

$$C_{j}^{*} = (B_{j}^{*})^{-1}C_{j}$$

$$D_{j}^{*} = (B_{j}^{*})^{-1}(D_{j} - A_{j}D_{j-1}^{*})$$
(3-52)

The solution for the equations at stage N is easily obtained from the above form, that is:

$$\Delta X_N = D_N^* \tag{3-53}$$

The backwards substitution of Δx_N into the equations at N-1 stage yield:

$$\Delta X_{N-1} = D_{N-1}^{*} - C_{N-1}^{*} \Delta X_{N}$$
 (3-54)

The procedure is repeated for stages (N-2, 1) to give :

$$\Delta X_{j} = D_{j}^{*} - C_{j}^{*} \Delta X_{j+1}, \quad j = N - 2, \dots, 1$$
(3-55)

The inverse of the matrix B_j^* is computed using LU decomposition procedure. However, there are cases when the matrix B is either singular or numerically close to singular, the LU decomposition method fails to give satisfactory inverse results. This can result in the failure of the final solution of the set equations. To avoid this situation, the technique, known as the singular value decomposition or SVD, is used in this work as an alternative for computing the inverse of the matrix B. For any square matrix B, it can be always decomposed into the following form:

$$\begin{pmatrix} B \\ B \\ \end{pmatrix} = \begin{pmatrix} U \\ U \\ \end{pmatrix} \bullet \begin{pmatrix} \omega_1 & & & \\ & \omega_2 & & \\ & & \ddots & & \\ & & & \ddots & \\ & & & & \omega_{N-1} & \\ & & & & & \omega_N \end{pmatrix} \bullet \begin{pmatrix} V^T \\ V \\ V \end{pmatrix}$$
(3-56)

The matrix U and V are each orthogonal, and the middle matrix is diagonal square matrix with non-negative values. The inverse of matrix B can be easily obtained as follow:



When one of ω_j is zero or very small, the matrix becomes singular or illconditioned. In such cases, the inverse of the matrix B is computed from equation (3-57) by replacing $1/\omega_j$ by zero if $\omega_j=0$ or very small. It basically throws away a combination of equations that is so corrupted by roundoff error as to be at best useless. It is noted that the computed inverse matrix is not necessarily the "exact" inverse. However, it is a "better" inverse in the sense of the compounded roundoff errors being reduced and the residual | B B⁻¹ - I | being smaller. The SVD routine is based on the approach of Forsythe et al. (1977), which has been proved very stable. There is a tradeoff in term of the performance and the stability of the matrix inversion. The singular value decomposition takes more computation time than the LU decomposition does. However using the singular value decomposition provides a more stable solution.

3.3.4 Modification of Powell's Dogleg Method

The Newton iteration for solving a system of nonlinear equations

$$G(x) \equiv 0 \tag{3-58}$$

replaces an estimate x^(k) of the solution by the estimate

$$x^{(k+1)} = x^{(k)} + p^{N(k)}$$
(3-59)

where the Newton correction step $p^{N(k)}$ is obtained by solving the linear equations

$$J \bullet P^{N(k)} = -G(x^{(k)})$$
 (3-60)

The coefficient matrix J, called Jacobian matrix, contains the partial derivative information of the functions. The Newton's method provides a very good approximation to the functions provided that the initial estimate of the vector x is close to the actual solution. A common approach to increase the size of the region in which the Newton method will converge to the desired solution is the use of a damped step size. Such an approach retains the direction, but restricts the length of the step predicted by the Newton method. That is, equation (3-59) is replaced by

$$\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \lambda^{(k)} \mathbf{p}^{N(k)}$$
(3-61)

The value of the parameter $\lambda^{(k)}$, or called damping factor, is calculated by a search process, which tries to make the estimate x^{k+1} better than the estimate x^k ,

$$S(x^{(k+1)}) < S(x^{(k)})$$
 (3-62)

S(x) is the sum of squares of residuals

$$S(x) = \|D_f G(x)\|^2 = \|\overline{G}(x)\|^2$$
 (3-63)
where D_f is a diagonal scaling matrix with positive diagonal elements and $\| \|$ stands for the Euclidean norm. One of the techniques to search this damping factor $\lambda^{(k)}$ is to transform the nonlinear equations into a nonlinear least square problem of finding a minimum, that is,

$$\min_{p} S(x + \lambda p)$$
(3-64)

One of well-tested approach for numerical solution of least square problem is the Levernberg-Marquardt (L-M) method (1963). According to the L-M method, if we find a correction step p that minimizes,

$$\Phi(p) = S(x+p) = \|D_f G(x+p)\|^2 = \|\overline{G}(x+p)\|^2$$
(3-65)

then x+p would be the desired solution. The linearization of the above function gives the following linear least square problem:

$$\min_{p} Q(p) = \min_{p} \|D_{f}(G(x) + Jp)\|^{2}$$
(3-66)

Since this linearization is not valid for all values of p, the size of p shall be restricted within a region. This region is usually defined as the trust region, Δ , within which the linearization can be trusted. Therefore the minimization problem of equation (3-66) is subject to the following constraint

$$\| D_x p \| = \| p \| \leq \Delta \tag{3-67}$$

where D_x is a diagonal scaling matrix with positive diagonal elements. The solution of (3-66) gives

$$p(\lambda) = -(J^T D_f^2 J + \lambda D_x^2)^{-1} J^T D_f^2 G$$
 (3-68)

where the L-M parameter λ must satisfy one of the following conditions:

$$\lambda = 0 \text{ and } \| D_x p(0) \| \le \Delta$$
$$\lambda > 0 \text{ and } \| D_x p(\lambda) \| = \Delta$$
(3-69)

The L-M parameter λ cannot be determined analytically. It implies that the linear system equation (3-68) has to be solved many times in each iteration. To overcome this searching complexity problem, Powell (1970) developed an approximated L-M method for the step-search. It is noted that if $\lambda = 0$, then equation (3-68) becomes

$$p(0) = -(J^T D_f^2 J)^{-1} J^T D_f^2 G = -J^{-1} G \equiv p^N$$
(3.70)

which is identical to the correction step determined by the Newton-Raphson method, and when λ is very large, equation (3-68) reduces to

$$p(\lambda) = -\lambda^{-1} D_{x}^{-2} J^{T} D_{f}^{2} G = -\lambda^{-1} D_{x}^{-1} \overline{J}^{T} \overline{G} = \lambda^{-1} D_{x}^{-1} g$$
(3-71)

where g is the steepest descent direction of Q(p). Based on these special features of the L-M method, Powell (1970) developed an alternative approach for the step search. In his approach, the L-M method search step was approximated by the combination of the Newton correction step and the steepest descent step, that is

$$\overline{p} = \overline{p}^{N}, \qquad \text{if } \|\overline{p}^{N}\| \leq \Delta$$

$$\overline{p} = \eta \overline{p}^{N} + (1 - \eta) \overline{p}^{S}, \qquad \text{if } \|\overline{p}^{N}\| > \Delta > \|\overline{p}^{S}\| \qquad (3-72)$$

$$\overline{p}^{S} = \frac{\Delta}{\|\overline{g}\|} \overline{g}, \qquad \text{if } \|\overline{p}^{S}\| \geq \Delta$$

The scaled Newton correction step, p^N , and the steepest descent step, p^S , are calculated through the following equations

$$\overline{p}^{N} \equiv D_{x} p^{N} = -\overline{J}^{1} \overline{f}$$
(3-73)

$$\overline{p}^{S} \equiv D_{x} p^{S} = -\frac{\left\|\overline{g}\right\|^{2}}{\left\|\overline{J} \,\overline{g}\right\|^{2}} \overline{g}$$
(3-74)

and

$$\overline{g} = D_x g = -\overline{J}^T \overline{G}$$
(3-75)

$$\overline{G} = D_f G(x); \quad \overline{J} = D_f J D_x^{-1} \qquad (3-76)$$

The combinational factor η is determined by satisfying that the correction step size is equal to the size of the trust region

$$\|\overline{p}\| = \Delta \tag{3-77}$$

which gives

The search step in equation (3-72) retains the most important feature of L-M method, which is that if the length of the correction step must be small, its direction is biased towards the steepest descent direction of G(x). For example when the Jacobian matrix J is nearly singular, then usually the Newton correction step is unacceptably large. In this case, it will result in the divergence of the Newton iteration. In such a situation, equation (3-72) tends to take steps along the steepest descent step. The steepest descent iteration usually is very stable on convergence of the solution. However it tends to Since within the proximity of the become very slow when approaching the solution. solution, the equation (3-72) tends to take steps biased towards the Newton correction The convergence becomes very fast since Newton iteration is a quadrically step. convergence process when nearing the solution. Therefore, the Powell's hybrid method ensures a rapid yet stable convergence to the solution. By combining the stability of the steepest descent method with the rapidity of the Newton-Raphson method, the iteration will be kept within a "trust" region, and converge to the solution easily without encountering the difficulties of employing these methods separately. The Powell's hybrid method has been adapted and modified successfully by Chen and Stadtherr (1981) for solving problems with chemical engineering applications.

Several modifications have been made in this work in order to apply the Powell's hybrid method for solving multiphase separation problems. The modifications are described below.

3.3.4.1 Enforcement of the variable constraints

It is known *a priori* that some iterative variables must be non-negative or within certain limits to be physically feasible (such as temperature and composition). However, during the iteration process it is possible that some variables' estimates become negative or violate the limits. In many cases, this can cause the iteration to converge to an unfeasible solution or to diverge because function G(x) becomes undefined for these negative iterative variables.

In this work, an enforcement is provided to ensure the iteration variable within the pre-defined bounds. For an iteration variable x_i , it has

$$x_i^{\min} \leq x_i \leq x_i^{\max} \tag{3-79}$$

where x_i^{min} and x_i^{max} are pre-defined constraints for variable x (eg $x^{min} = 0$ and $x^{max} = 1$ for composition variables). If the new estimate $x_i + p_i$ violates constraints (3-79), we define d_i as the distance from the current point to the violated constraint for variable x_i

$$d_{i} = \begin{cases} x_{i}^{\min} - x_{i} & \text{if } p_{i} + x_{i} \leq x_{i}^{\min} \\ x_{i}^{\max} - x_{i} & \text{if } p_{i} + x_{i} \geq x_{i}^{\max} \end{cases}$$
(3-80)

Then the correction step, p, is replaced by the following

$$p_{i} = \begin{cases} 0.95d_{i} & \text{if } \left|\frac{p_{i}}{d_{i}}\right| \ge 2.0\\ 0.425d_{i} & \text{if } 1.0 \le \left|\frac{p_{i}}{d_{i}}\right| < 2.0 \end{cases}$$
(3-81)

3.3.4.2 Modified Trust Region Updating

The size of the trust region depends on the goodness of the linearization of the function. Smaller the trust region, the better the linearization is. However the trust region can not be too small, because it would require small steps to decrease the sum of the squares S(x) in every iteration. Usually the trust region is adjusted as large as possible, subject to the condition that each Jacobian matrix provides a good prediction of the difference G(x+p) - G(x).

When J is a new Jacobian matrix and $S(x+p) \ge S(x)$, the optimal step-size policy of Kalogerakis and Luus (1983) is used to reduce the trust region,

$$\Delta = \|\overline{p}\| \max \{ 0.1, \lambda_{opt} \}$$
(3-82)

where λ_{opt} is obtained from the minimization of the following function

$$\min_{\lambda} S(x + \lambda p) = \min_{\lambda} (a \lambda^2 + b\lambda + c)$$
 (3-83)

The goodness of the linearization around x is measured by comparing the reduction in the sum of the squares (S(x) - S(x + p)) with the predicted reduction (S(x) - Q(x+p))

$$\zeta = \{S(x) - S(x+p)\} - 0.1 \{S(x) - Q(x+p)\}$$
(3-84)

when $\xi < 0.1$, which implies poor linearization, then the trust region is reduced by half. If $\xi \ge 0.1$, the trust region is either maintained or increased, using Powell's updating formula (1970).

The schematic of the modified Powell's hybrid method is illustrated in Figure 3-5. The initial value of trust region is set to where DMAX is specified to an estimate of the "distance" of the solution from the initial guess, and R is a user-provided number.

$$\Delta = \min \{ DMAX, R m \max \{ \| D_x x \|, 10.0 \} \}$$
 (3-85)

The convergence criteria for Powell's method is

$$\left\| \overline{p}^{N} \right\| \leq \delta \max \left\{ \left\| D_{x} x \right\|, 1.0 \right\}$$
and
$$\left\| G(x+p) \right\| \leq \sqrt{\delta}$$
(3-86)

where δ is specified accuracy of the solution.

3.3.4.3 Function and Variable Scaling

Both the function and variable scaling matrices (D_f and D_x) are diagonal scaling matrices. The diagonal elements of these matrices are positive values. There are two options available in this work for calculating these two scaling matrices:

1. Maximum scaling factors

In this option, the diagonal element of the function scaling matrix Df is the inverse of the absolute value of the element whose absolute value is maximum in the corresponding row in the Jacobian matrix. The diagonal element of the variable scaling matrix is the inverse of the maximum absolute value of the elements in the corresponding column in the Jacobian matrix.

1. Specific scaling factors

In this option, the scaling factors are computed based on specific equations and variables. For component mass balance equation, the scaling factor is the maximum feed flow rate. The scaling factor for the energy balance equation is the maximum heat flow rates. The maximum heat flow rate can be either the heat flow associated with the feed or the specified column duty flow. The scaling factor for the inverse temperature variable is 1/298 K. For the overall mass component flow rate variable, the scaling factor is the maximum feed flow rates. The diagonal elements of the functions and variables scaling matrices are the inverse of the above scaling factors' absolute values.



Figure 3-5 Modified Powell's Dogleg method diagram

4. Results and Discussion of Two and Three Phase Non-Reactive Separation Processes

In this section, a variety of examples representing very diverse two-phase and three-phase separation applications are presented to illustrate the efficiency and the reliability of this new algorithm. The program was executed on a NeXT Station computer at the University of Calgary. The relative tolerances of 1.0×10^{-16} for inverse temperature and 1.0×10^{-8} for composition were specified as the Convergence criteria for the outer loop iteration.

4.1 Two-phase separation systems

Examples of two-phase separation processes from the work of Shah (1977), Saeger (1985), Saeger and Bishnoi (1986) and Wu and Bishnoi (1986) have been studied using the proposed method. These examples represent major types of two-phase separation processes, including simple distillation, azeotropic distillation, extractive distillation, absorption and reboiled absorption. The details of the column configurations and the specifications for each example are listed in Table 4-5. The necessary input parameters for executing the proposed solution algorithm are listed in the Appendix A.

4.1.1 Comparison with Shah's Simulation Results

First two examples shown in Table 4-5 are two-phase separation columns that are taken from Shah (1977), First is a reboiled demethanizer absorber used in an ethane

recovery plant, and the second is a debutanizer distillation column operating at Petrogas Soave-Redich-Kwong (SRK) and Peng-Robinson (PR) Canada Limited Calgary. equations of state (Soave, 1972; Peng and Robinson 1976) were used to calculate the thermodynamics properties of both vapor and liquid phases. Both columns use feed stocks consisting of wide boiling point components, and are found very difficult to simulate (Shah, 1977). In order to achieve the convergence of the solution, good initial estimates of temperature and flow rate profiles that are close to finial solutions were provided (Figure 4-1 and Figure 4-2). However in this new proposed method, no initial guess of temperatures and flow rates are needed as input. The initial estimates of stage temperatures and flow rates are automatically generated based on the average feed stage conditions and the assumption of the constant molar overflow condition. As shown in Figure 4-1 and Figure 4-2, the initial temperature profiles estimated from this method are far away from the finial solutions. In spite of these poor initial guesses, the new method has shown its stability and efficiency to reach the final solution. It took a total of 10 outer loop iterations for Example 1, and 6 outer loop iterations for Example 2 to converge. Table 4-1 is the comparison of calculation results with the plant data of the debutanizer Table 4-2 shows the comparison of calculation results for the column (Shah, 1977). The same thermodynamic models (PR and SRK demethanizer column (Shah, 1977). EOS) are used this work to simulate these two columns.

Figure 4-3 demonstrates the convergence characteristics of the inner loop iterations during the first iteration in the outer loop for Example 1. The sum of squares of the residual functions obtained for the iteration variable, x, are shown in the figure as S(x). The sum obtained with the Powell hybrid step, x+p, is shown as S(x+p). Initially, the guess of iterative variables was far from the finial solution that resulted in a very large Newton correction step-size. The sum, S(x+p), was much larger than the original sum S(x). Therefore, the trust region radius, to which the Powell's hybrid step-size is equal, was reduced. The process of reduction was continued till a successful point was found, where S(x+p) was lower than S(x). Once S(x+p) was less than S(x), the trust region size was expanded till it was equal to the Newton correction step-size. The iteration then converged quadarically to the final solution. Once the inner loop was converged for the first outer loop iteration, the subsequent inner loop iterations converged using the direct Figure 4-4 shows the convergence characteristics of outer loop Newton step-size. One line represents the sum of square of difference in iterations for Example. 1. component mole fraction between two iterations, and other line indicates the sum of square of difference for the inverse temperatures between two iterations. In the case of other two phase distillation examples, most of first inner loop iteration is within 10 to 15 iterations, and outer loop iteration's number varies from 6 to 15. The Powell's Hybrid approach has been proven to be very effective in stabilizing the convergence when the outer loop guess is far from the solution.



Figure 4-1 Initial and Final Temperature Profile (Example #1)



Figure 4-2 Initial and Final Temperature Profile (Example #2)



Figure 4-3 Characteristics of Convergence of inner loop iterations using Powell's Hybrid method



Figure 4-4 Convergence characteristics of consequent outer loops

	Result (T	his work)	Shah's	work	Plant Data
	SRK	PR	SRK	PR	
Number of	31	31	31 .	31	38
stages					
Reflux ratio	1.7235	1.7235	1.7235	1.7235	1.7235
Temperature, °C					
Top stage	60.5	61.0	59.3	58.8	54.4
Bottom stage	128.5	129.2	132.4	131.7	122.2
Top Product	mole	mole	mole	mole	mole
Composition	fraction	fraction	fraction	fraction	fraction
C ₂	0.00 <u>3</u> 7	0.0037	0.0024	0.0024	0.0021
C ₃	0.0168	0.0168	0.012	0.012	0.0121
i-C4	0.4568	0.4565	0.4294	0.4294	0.4295
C 4	0.5222	0.5225	0.5554	0.5553	0.5563
i-C₅	0.0006	0.0006	0.0008	0.0008	0 ·
C5	2.957E-5	3.095E-5	2.000E-5	2.000E-5	0
C ₆	6.481E-11	9.554E-11	0	0	0
C ₈	2.426E-22	6.487E-22	0 0		0

Table 4-1 Comparison of Simulation Results and Plant data (Example#2)

	This work	Shah's work
	PR	PR
Number of stages	13	13
Temperature, °C		
Top stage	-120	-117.88
Bottom stage	-33.4	-32.86
Top Product	mole fraction	mole fraction
Composition		
Cı	0.9596	0.9562
C ₂	0.0019	0.0084
C ₃	0	1.1E-5
i-C4	0	0
C ₄	0	0
i-C₅	0	0
C ₆	.0	0
N_2	0.0339	0.0339
CO ₂	0.0046	0.0015

4.1.2 Comparison with Wu and Bishnoi, Saeger and Bishnoi's work

In both inside-outside approaches proposed by Wu and Bishnoi (1986) and Saeger and Bishnoi (1986), the K-values were partitioned into a temperature dependent function (Kb) and the composition dependent function (γ) to account for the non-ideality of the In Saeger and Bishnoi's method, the activity coefficient of a component is mixture. approximated as a linear function of its component composition. It has been found that the introduction of the composition dependence in the approximated K-value model has improved the convergence of the solution, especially for highly non ideal systems (Wu and Bishnoi, 1986, Saeger 1985, Saeger and Bishnoi 1986). The disadvantage of these approaches lies in the evaluation of the partial derivatives of activity coefficient with respect to the compositions. It usually consumed lots of computation time and storage. This disadvantage becomes more obvious when the separation system consists of strongly non-ideal mixtures. It is due to the fact that the activity coefficient is a highly non-linear function of compositions for a strong non-ideal mixture In this proposed algorithm, the K-value is assumed as only a function of temperature in the inner loop. It eliminates the evaluation of the partial derivatives of the K-value with respect to the composition, which results in saving CPU time and computer storage. In spite of the assumption that Kvalue is independent of composition in the inner loop, the proposed algorithm has proven to be very efficient and stable for solving strongly non-ideal separation examples. These examples are listed in Table 4-5 and taken from the works of Wu and Bishnoi (1986), Saeger (1985) and Saeger and Bishnoi (1986). The same thermodynamic models of the Wu et al. and Saeger et al. are used in this work for simulating these examples. Table 4-4 shows that using Powell's hybrid method give fewer iterations to achieve convergence than using Wu and Bishnoi's method. It is noted in Table 4-3 that the tighter tolerances were employed in this work than in Wu and Bishnoi's work. In the examples of the extractive distillation of non-ideal mixture of acetone-methanol-water and distillation of acetone-methanol-chloroform, the solution method of Saeger et al. failed to converge to the final solution if the activity coefficient is assumed to be independent of the By using the composition dependent model, the algorithm of Saeger and composition. Bishnoi was able to converge towards the final solutions of the above examples. However it takes lots of computational time (~278 CPU seconds) to achieve finial convergence of relative error 1.0E-5 in Saeger's work (Saeger 1985). Using the new method only takes few iterations to converge to the final solution.(Table 4-5) For Saeger (1985) had encountered poor convergence for extractive distillation examples, the hydrocarbon-solvent systems. In examples of methylcyclohexane-toluene-phenol and n-octane-ethylcyclohexane-ethylbenzene-phenol, in which phenol was used as solvent, it failed to converge to the solutions even using the linearized approximated activity However such difficulty has not been encountered coefficient model (Saeger, 1985). Both examples of phenol solvent extractive columns are when using this new method. converged within few iterations using the new approach (Table 4-5).

In summary, the new proposed algorithm with modified Powell's hybrid solution method has shown advantage over the existing methods (Shah 1977, Saeger and Bishnoi, 1986, Wu and Bishnoi, 1986) in solving various two-phase separation problems. It is very stable and efficient to reach the solution, especially for system that requires good initial guess of the solution or for system that consists of highly non-ideal mixtures.

	CPU unit	Outer Loop Tolerance	Inner Loop Tolerance
Wu &	Honeywell DPS		
Bishnoi	8/70M mainframe	$\left \Delta \mathbf{x}^{\text{out}} \right \le 0.001$	$\left \Delta \mathbf{G}(\mathbf{x}) \right \leq 0.001$
(1986)	computer		
This	Next 2.0 workstation	$ \Delta \mathbf{y}^{out} \le 10^{-8}$ and	$\left \Delta \mathbf{x}^{\text{inner}}\right \leq 10^{-5}$ and
Work			
	,	$ \Delta \mathbf{T}^{\text{out}} \leq 10^{-16}$	$ \mathbf{G}(\mathbf{x}) \leq 10^{-12}$
		x - refer to iterative	
		variables	G(x) - refer to the
		y - refer to	residual error
		composition variables	function
		T - refer to the	
		inverse temperature	
		variable	

Table 4-3Convergence comparison of This work with Wu's work

•	Example#3		Example#4		Example#5	
	Wu & This		Wu & This		Wu &	This
	Bishnoi	Work	Bishnoi	Work	Bishnoi	Work
	(1986)		(1986)		(1986)	
CPU Time						
(S)	16.41	10.6	40.8	9.7	71.3	22.5
Total Inner		• •				······································
Loop Iterations	29	20	N/A	12	N/A	25
Outer-Loop						
Loop Iterations	7	5	N/A	4	N/A	6

Table 4-4 Comparison of this and Wu and Bishnoi's simulation results

Note: For Example #3, both Wu's program and this work are executed at the same Next Computer Machine. So the CPU times for example #3 are compared based on the same computer execution time.

No	Components	No. of Stages	Feed Condition	Bottom Rates	Reflux Ratio	Pressure	No of Outer loop Iterations
	C ₁ (1),		F1=17986.0 L	4404.7	R = 0.0	P1 = 931	
1	C ₂ (2),	29	P = 930.KPa		(Reboiled	KPa	10
	C3(4),		T = -118.61C		Absorber)		
	iC4(5),		y1=0.9281,				
	nC5(6),		y2=0.0294			P2 = 1085	
	iC5(7),		y3=0.0006,			KPa	
	C6(8),		y9=0.0398		•		
	N2(9),						
	CO2(10)		F3=7874.7, L				
			P =1034.3 KPa				
			T = -108.06C				
			y1=0.4946,				
i i			y2=0.4030				
			y3=0.0066,				
			y4=0.0041				
			y5=0.0066,				
			y6=0.0017				
			y7=0.0018,				
			y8=0.0030				
			y9=0.0015,				
			y10=0.0084				
			Q5 = 6.6469 GJ;				
			G9 = 6.6469 GJ;				

Table 4-5 Two-phase distillation examples

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2	C2(1), C3(2), iC4(3), C4(4), iC5(5), C5(6), C6(7), C8(8)	31	F15 = 6657, L $P = 758.42 KPa$ $T = 65.56 C$ $y = 0.0012,$ $0.0068, 0.2408,$ $0.3152, 0.1217,$ $0.1024, 0.1316,$ 0.0804	2925.0	R = 1.724	P1 = 710 KPa P31 = 812 KPa	6
3	n-hexane, ethanol, methyl- cyclohexane, benzene	10	F10=100, SL. y =0.3, 0.1, 0.3, 0.3	50	R = 2.0	P1 = 0.1 MPa P10= 0.1 MPa	5
4	methanol, ethanol, water	22	F12=100, SL. y =0.1, 0.2, 0.7	50	R = 3.0	P1 =0.1 MPa P22 = 0.1 MPa	4
5	acetone, chloroform, methanol	10	F5=100, SL. y =0.45, 0.33, 0.22	40	R = 3.0	P1 =0.1 MPa P10=0.1 . MPa	6
6	methanol, ethanol, water, n-propanol	20	F10=100,.SL y =0.25, 0.25, 0.25, 0.25	55	R = 2.5	P1 = 0.1 MPa P20 = 0.1 MPa	12

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7	acetone, methanol, water	33	F9 = 150, L. P = 0.1MPa T = 50 C	175	R = 4.0	P1 =0.1 MPa	7
			y =0.0, 0.0, 1.0 F21 = 100, L. P = 0.1MPa T = 56 C			P33=0.1 MPa	
8	methyl- cyclohexane,	21	y =0.5, 0.5, 0.0 F10 = 76.74SL y =0.0, 0.0, 1.0	87.76	R = 8.1	P1 = 1 atm	6
	toluene, phenol		F15 = 23.26SL y =0.5, 0.5, 0.0			P21= 1 atm	
9	n-octane, ethyl- cyclohexane, ethylbenezene,	30	F11 = 300, SL y =0.0, 0.0, 0.0, 1.0	330	R = 8.0	P1 = 1 atm P30= 1 atm	10
	phenol		F16 = 100, SL y =0.2, 0.4, 0.4, 0.0				
10	toluene, 2-butanone, n-heptane	17	F8 = 197, SL y =0.228, 0.492,0.280 F12 = 97 S.L. y =0.0, 1.0, 0.0	45	R = 1.5	P1 =0.1 MPa P17=0.1 MPa	7
11	C2, iC4, C4, C6	13	F1 = 50, SL y =0.93, 0 04, 0.028, 0.002 F3 = 300, S.L. y =0.80, 0.12, 0.07, 0.01	60	R = 0 (Reboiler Absorber)	P1 = 1.7 MPa P13= 1.7 MPa	6

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12	C2,	12	F1 = 100, L	$\mathbf{R} = 0$	P1 = 1	
	C3,		P = 1 MPa	(Absorber)	MPa	7
	C4,		T = -53 C			
	С6,		y =0.0, 0.05,		P12= 1	
	C10		0.20, 0.75		MPa	
			F12 = 680, SV y =0.882, 0.074, 0.044, 0.0			

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4.2 Three-Phase Separation

The proposed algorithm has been successfully used to simulate most of the threephase distillation examples available in the literature (Cairns and Furzer, 1990) (Appendix B). The definitions of the examples are given in Appendix B. These examples are discussed in the following sections. It may be noted that the new proposed method has the capability of dealing with the disappearance and appearance of a second liquid phase within a column.

4.2.1 N-Butanol - Water- n-Propanol Ternary Separation

The most refereed three phase example is the separation of the n-propanol, nbutanol and water (Block and Hegner, 1976). This ternary system consists of two substances that are partially soluble: water and n-butanol. At atmospheric pressure, water and n-butanol will form a binary azeotrope (boiling point temperature 93°C). Component n-propanol is completely soluble in both water and n-butanol, forms a binary azerotrope with water (boiling point temperature 80.4°C). A mixture of butanol, water, and propanol is fed in the middle of a distillation column. Two immiscible liquid phases are formed in the bottom stages of the column as butanol concentrates towards the reboiler. The detailed column configuration of this example is listed in Appendix B. It was first simulated by Block and Hegner (1976), then tested as a benchmark example by Ferraris and Morbidelli (1981), Ross and Seider (1980), Kinoshita et al (1983), Schuil and Bool (1985), Swart and Stewart (1987) and Cairns and Furzer (1990). To test the proposed method, the NRTL activity model was used to calculate the activity coefficients of the liquid phases. Block and Hegner had also used the NRTL model. The interaction parameters for the NRTL equation were taken from Block and Hegner (1976). The coefficients for the standard fugacity equation were taken from Prausnitz et al. (1980). The computations are started with the initialization procedure discussed in Chapter 3. It takes 8 outer loop iterations to converge to the final solution. Figure 4-5 shows the converged profiles of the two liquid phase fractions and the phase stability factor of the second liquid in the column. The liquid I is the stable, while the liquid II could appear or disappear in the column. In Figure 4-5, for the stages the liquid II has positive values of the stability factors and zero values of the phase fractions, the liquid is unstable and The figure shows the stable second liquid phases would not be present at equilibrium. exist from stage 8 to the bottom stage. The calculated mole fractions, stage temperatures and phase fractions compared well with the results of Block and Hegner as shown in It is noted from Figure 4-7 that Block and Figure 4-6, Figure 4-7 and Figure 4-8. Hegner calculated the compositions of the second liquid phase only at the stages at which the second liquid phase is present. However in the proposed method, the compositions and the thermodynamic properties of the unstable (absent) second liquid phase (from stage 1 to stage 7), are calculated during each iteration. These calculations are possible because of the proposed algorithm that allows the appearance and disappearance of the proposed liquid phase during the iterations. The phase fraction and compositions of the absent unstable liquid phase are iterated along with other system variables. If during the iteration, the phase fraction of this absent liquid phase becomes non-zero positive, it

implies that this absent unstable phase switches to a stable liquid phase and the liquid can coexist with other phases. Consequently the calculated compositions of the second liquid phase become compositions of a stable second liquid phase. Thus, the unstable liquid phase is smoothly transformed into a stable liquid phase during iteration without initialization and reconstructing the model equation. Similar transition occurs when a stable liquid phase when it turns into an unstable liquid phase during an iteration. Therefore, for any given phase, the compositions and its thermodynamics properties are always evaluated at every iteration. It eliminates the need for a separate outer loop of initialization, liquid stability test, and liquid splitting calculation for generating a second liquid composition whenever a second liquid phase is detected. Indeed, the phase can switch from a stable phase to an unstable phase simultaneously with other valuables during the iteration. The drawback of this approach is that it needs extra storage space to hold information for unstable liquid phases. It also increases the size of the model equations, consequently the size of the Jacobian matrix.

In Figure 4-9 and Figure 4-10, the phase fraction and the phase stability factor of the second liquid, which is rich in water, are plotted as functions of outer loop iterations. In the first iteration, the phase fraction of the water rich liquid phase was non-zero, and its phase stability factor was zero value on all the stages. This implies that all stages are assumed to have two liquid phases. At second iteration, the phase fraction of the second liquid phase at stage 2 becomes zero and the stability factor becomes non-zero. So the second liquid phase at stage 2 switches to an unstable liquid phase. The phase fraction of

117 water rich liquid phase at stages 1 and 6 become zero at 4^{th} iteration, and switch to Subsequently the water rich phase at stage 3, 4 and 7 become unstable liquid phases. unstable at 5^{th} , 6^{th} and 7^{th} iterations respectively



Figure 4-5 Converged profile of both liquid phase fractions and stability factors



Figure 4-6 Comparison of liquid phase I composition (butanol-water-propanol)



Figure 4-7 Comparison of liquid II composition (butanol-water-propanol)



Figure 4-8 Comparison of temperature profiles (butanol-water-propanol)



Figure 4-9 Second liquid phase fractions as function of outer loop iterations(butanol-water-propanol)



Figure 4-10 Second liquid phase stability factors as function of outer loop iterations(butanol-water-propanol)
4.2.2 N-Butanol - Butyl_Acetate - Water Ternary Separation

Another example, discussed here, is the dehydration of the saturated butanol and butyl acetate mixture, also taken from Block and Hegner (1976). Different from the first example, the second liquid phase is formed at top stages of column as the water concentrates towards to overhead. At the top decanter, the water rich liquid phase is totally withdrawn, and the organic liquid phase is completely refluxed to the column. The purpose of the separation is to remove water from organic components. The bottom product contains butyl butanol and butyl acetate with small amounts of water. To enhance the separation of alcohol from water, it is necessary to withdraw water from the column as much Therefore, usually at the top decanter, the water rich liquid phase is totally as possible. withdrawn, and the organic liquid phase is completely refluxed to the column. In such cases, the new algorithm allows to specify the side-withdrawal ratio of water phase from the decanter as one, and the side-withdrawal ratio of organic phase as zero. The thermodynamic model is NRTL and its interaction parameters are taken from Block and Hegner (1976). The column specifications are given in the Appendix B.

The computations are started with the initialization procedure discussed in Chapter 3. It takes 13 iterations in the outer loop to reach the convergence. Figure 4-11 shows the initial estimates of the temperature for the pseudo-two phase column. After one or two iterations of the pseudo-two phase column calculation, the resulting temperatures (Figure 411) and compositions on each stage are used to generate the initial guesses of the compositions of the three phases on each stage. The initialized compositions of the two liquids are shown in Figure 4-12. The liquid I denotes the butyl_acetate rich liquid phase, while the liquid II represents the water rich liquid phase. The liquid II (water rich phase) is only formed at the top-decanter stage and is totally withdrawn as a top product. Figure 4-13 shows phase fractions and phase stability factors at final solution. Figure 4-14 shows profiles of the two liquid phases' compositions. The converged temperature profile is shown in Figure 4-11.



Figure 4-11 Initial profiles of temperatures and liquid compositions (butanol-water-butyl_acetate)



Figure 4-12 Initial profile of liquid phases compositions



Figure 4-13 Converged profile of liquid phase fractions and stability factors



Figure 4-14 Converged profile of liquid phase compositions

4.2.3 Azeotropic Separation of Ethanol-Water-Benzene

Heterogeneous azeotropic distillation is another common example of three-phase distillation. In such processes, an entrainer is added to increase the relative volatility of the components. Usually, the overhead vapor forms two immiscible liquid phases in the One extensively studied example of the heterogeneous decanter when condensed. azeotropic distillation is ethanol dehydration using benzene as entrainer. Most of the previous work simulated such process without considering vapor-liquid-liquid coexistence within the column (Magnussen, et al. 1979, Wu and Bishnoi 1986, Kovach and Seider, Baden and Michelsen (1987), Cairns and Furzer (1990) simulated this separation 1987). process by considering the splitting of the liquid phase in the column. In the work of Baden and Michelsen (1987), Cairns and Furzer(1990), the concept of pseudo-mixed The detailed review of these single liquid phase was used in the MESH equation. With the pseudo-mixed single liquid phase model, methods can be found in Chapter 3. it is very difficult to specify distillates of both liquid phases and the corresponding reflux ratio as the column specification. The difficulty is due to the fact that the distribution of the two liquid phases was determined from the liquid-liquid flash calculation of the pseudo-mixed single liquid phase. It probably needs another outer loop to converge the distillates' specification. Another problem is that the mixed liquid composition is used for the reflux stream for the MESH equation. However, in most azeotropic distillation, the reflux stream usually consists of only the entrainer-rich liquid, while the water rich phase is completely withdrawn from the condenser. These two flow streams have total different compositions. The mixed liquid composition would misrepresent the true reflux stream in the MESH calculation. In order to overcome such difficulties, the modified column configuration shown in Figure 4-15 was used by most authors. In the formulation based on this configuration, the decanter, in which two liquid phases form, was excluded from the MESH equations. A portion of the overhead vapor after the condenser, (which in reality consists of two liquid phases), was refluxed directly back to the column. The other portion of the vapor is fed in the decanter. Then the organic phase from decanter stage was specified as the feed stream of the column. The decanter is solved separately to determine the amount of the organic phase and the aqueous phase. The specified organic phase feed composition does not necessarily match the composition generated from the decanter's solution.

The configuration is quite different with a realistic one as illustrated in Figure 4-16 from King (1980). In King's configuration, the overhead vapor stream that condenses into two liquid phases is sent to the decanter. The organic liquid phase from the decanter is completely refluxed, while the aqueous liquid phase is totally withdrawn and is fed to the top tray of the benzene recovery tower.

Since the second liquid phase is determined simultaneously during the iterations in this work, the two-liquid phase decanter can be easily included in the MESH equation.. The new algorithm was used to simulate a 20 stage azeotropic column using the configuration shown in Figure 4-16 which includes the condenser-decanter and reboiler. An ethanol-water azeotropic stream is fed to the column, along with a benzene-rich stream recycled from the top stage of the benzene recovery column. The side-withdrawal ratio of water phase from decanter was specified as one, while the side-withdrawal ratio of organic phase was given as zero. Other specifications are listed in Appendix B. The UNIFAC model was used to calculate the liquid phase thermodynamic properties, with its parameters taken from Gmehling et al. (1982). The simulation results are illustrated in Figure 4-17, in which 98 mole percent ethanol is withdrawn from the bottom, and the two liquid phases are formed only on the decanter.

In Figure 4-17, it may be noted that for stage 3-20 two liquid phase compositions are almost identical. This implies one of the proposed liquid phase becomes trivial phase. In such case, the MESH equations become undefined, which leads to a singular Jacobian matrix. A heuristic approach was implemented to overcome the problem of "trivial phase". In the inner loop, if two identical liquid phases are found at the stage, the stage's summation equations are switched from

$$G_{k}^{s} = \sum_{i=1}^{Nc} x_{ik} - \sum_{i=1}^{Nc} x_{ir} \quad k = 1...\pi, \ k \neq r$$

to

$$G_k^s = \sum_{i=1}^{Nc} x_{ik} - 1 \quad k = 1...\pi, k \neq r$$

The singular value decomposition, discussed in Chapter 3, is also used to calculate the inverse of the Jacobian matrix, if two liquid phases are close to be identical. The K-

values are updated in the outside the inner loop. The updated K-values are checked whether two liquid phase's K values are close to be equal. If two liquid phases are identical, then the two liquid phases are combined into as single liquid phase, and the phase number for such stage is redefined as two. During the outer loop iteration, the stability test is used to examine the stability of single liquid phase. If the liquid phase is founded unstable, then second liquid phase compositions are initiated using stability test result, and the phase number of stage is redefined as three.



Figure 4-15 The typical column configuration for modeling the azeotropic distillation



Figure 4-16 Azeotropic distillation configuration (King, 1980)



Figure 4-17 Converged profile of both liquid phases compositions (ethanol-water-benzene)

4.2.4 Other Three-Phase Examples

This new algorithm has been also applied to simulate many other three-phase distillation examples which are reported in the literature. These examples' specifications are listed in Appendix B.

Figure 4-18 is the simulation result for separation of acetone, water and chloroform (Cairns and Furzer, 1990). The two liquid phases are formed throughout the whole column. The results compared well with the results by Cairns and Furzer (1990).

The example of Figure 4-19 is taken from the work of Ross and Seider (1980). This example is similar to the example of n-butanol, water and n-propanol given by Block and Hegner (1976), except for the n-propanol being replaced by ethanol. The two liquid phase region exists within bottom two stages.

For example of ethanol-water-ethyl_acetate, it is found that all stages are within the single phase region. No liquid splitting is found throughout the whole column. Figure 4-20 shows simulation result for the example of 2-propanol-water-benzene (Bril' et al., 1973), which only forms two liquid phases on the top decanter. The UNIFAC model is used for calculating liquid phase thermodynamic properties in both examples.

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In the example of separation for propylene-benzene-hexane-water (Boston and Shah 1979, and Cairns and Furzer 1990), the liquid phase splits into two liquid phases on bottom two stages as water concentrates towards to the bottom stages (Figure 4-21 and Figure 4-22). It compares well with the results from Cairns and Furzer (1990), who used UNIFAC model and found two liquid phases formed on bottom two stages. The same UNIFAC model was used in this work. However, Boston and Shah (1979) used Marqules model for activity coefficient calculation and found two liquid phases formed on all stages except the top stage.



Figure 4-18 Simulation Results of acetone, chloroform and water



Figure 4-19 Simulation result of ethanol-water-n-butanol system

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Figure 4-20 Simulation results of 2-propanol-water-benzene system



Figure 4-21 Simulation Results of Liquid Phase Fractions and Stability Factors (propylene-benzene-hexane-water)



Figure 4-22 Simulation Results of Liquid Composition - propylene-benzene-hexane-water System

4.2.5 The Effects of Ignoring Liquid Phase Splitting

It is always possible that two phase solution exist for a distillation problem which may in fact be satisfied by a three phase solution. In many cases, the two phase solution may differ significantly from the actual three phase solution.

To illustrate the difference between a three-phase solution and a solution that two liquid phases from the three phase solution are ignores the liquid phase splitting. The mixed single liquid phase compositions are combined into a single liquid phase. compared with the single liquid phase composition resulted from the two phase solution. Figure 4-23 show the comparison of the temperatures from the two phase and the three phase solutions for the separation of n-butanol, water and butyl acetate. The difference in the temperature profile is significant, especially towards the bottom stage where the Figure 4-24 shows the difference in liquid composition second liquid phase is formed. The water content at the separation column bottom is higher in the two phase profile. solution than that in the three phase solution. It indicates the two phase solution predict poorer separation of water from n-butanol and butyl acetate mixture. The difference of the composition profiles for separation of n-butanol, water and n-propanol mixture is not However, there is a significant difference in significant as shown in Figure 4-25. In the two phase solution, designing the top stage of the column. the high water concentrated top product is refluxed back to the column. However in the three phase solution, the top product can be separated into two liquid phases (water rich phase and alcohol rich phase) in the decanter. The water rich phase is total withdrawal from the column and the low water content phase is refluxed back to the column. As result, more water are removed from the column in the three phase solution. Therefore the three-phase solution is of importance in helping engineers to design a proper decanter to remove water rich phase so as to enhance the dehydration efficiency.



Figure 4-23 Temperature profiles of the three-phase and two-phase solutions



Figure 4-24 Liquid Composition of three-phase and two-phase solutions (n-butanol-water-butyl_acetate)



Figure 4-25 Liquid Composition of three-phase and two-phase solutions (butanol-water-propanol)

4.2.6 Effects of Thermodynamic Models

The simulation results for separation processes highly depend on the accuracy of thermodynamic models' predictions under separation operation conditions. The parameters of the thermodynamic model are usually obtained by fitting model's prediction to the experimental data. Although the overall error of the prediction is acceptable, in some specific region of data the prediction may be relatively poor. The problem for three phase distillation is further complicated because of the limited VLLE experimental data. Most of LLE or VLLE are predicted from thermodynamic models whose parameters are derived from experimentally determined VLE data. Therefore, it inevitably introduces errors in simulation results for three phase distillation problems, especially in determining the liquid phase splitting region.

To illustrate the effects of thermodynamic models on the three phase distillation simulation results, the example of n-Propanol-Water-n-Butanol (Block and Hegner, 1976) is solved using various thermodynamic models including UNIFAC-VLE1, UNIFAC-VLE2 (Gmehling et al., 1982) UNIFAC-LLE (Magnussen et al. 1981) and NRTL (Block and Hegner, 1976). In UNIFAC-VLE2, the OH group is used for the alcohol components, instead of the CH2CH2OH group in UNIFAC-VLE1. The NRTL parameters are obtained from Block and Hegner (1976). Figure 4-26, Figure 4-27 and Figure 4-28 show the differences in the temperature and composition profiles of the three phase column as predicted using all these thermodynamic models. The temperature profiles predicted by UNIFAC-VLE1, UNIFAC-VLE2 are very close. However, NRTL and UNIFAC-LLE models predict much higher stage temperature than the other models. The predicted second liquid phase fractions by all models are shown in Figure 4-29. It illustrates that the thermodynamic model's choice has more significant effect on predicting the liquid phase splitting. The UNIFAC-VLE1 and UNIFAC-VLE2 predict more stages of the column having two liquid phase than NRTL and UNIFAC-LLE do. The second liquid phase fractions calculated using UNIFAC-VLE1 and UNIFAC-VLE2 are also much higher than those predicted by other models.

These difference can be explained by examining the accuracy of models' prediction of vapour-liquid and vapour-liquid-liquid equilibrium. Figure 4-30, Figure 4-31 and Figure 4-32 show the predicted bubble temperatures and vapour composition profiles by all these models. It illustrates that UNIFAC-VLE1, UNIFAC-VLE2 have good prediction for VLE equilibrium. It is mainly because that those model's parameters are obtained from experimental VLE data. However, models UNIFAC-LLE and NRTL have predicted poorly the bubble point temperatures. Such derivation is expected for UNIFAC-LLE and NRTL models due to fact that the parameters of these models are obtained from LLE data. The higher bubble point temperature predictions using UNIFAC-LLE and NRTL are the cause of the higher prediction of the column temperature profiles as shown in Figure 4-26

Figure 4-34 shows comparison of the experimental LLE binodal curve with the The experimental LLE binodal curve are taken calculated binodal curves by all models. from the measurements of Newsham and Vahdat (1977). All models have very good predictions for the right-side liquid phase, which is approximately a pure water phase. However, the predictions of left-side n-butanol rich liquid phase by all models are far It consequently expand the concentration region which outside the experimental curve. Among those models, UNIFAC-VLE1, liquid phase would split into two liquid phases. UNIFAC-VLE2 predict much larger two-liquid phase region than UNIFAC-LLE and For a given mixture point, A, within the two-liquid region, the UNIFAC-NRTL-LLE. LLE and NRTL-LLE would produce less amount of right-side liquid phase (water rich) than other models, according to the LEVER-Rule. These facts correspond with the results shown in Figure 4-29, in which UNIFAC-LLE and NRTL models predict fewer stages of two-liquid phase and less amount of water rich liquid phase.

It can be seen from the above discussion that the simulation results of separation process highly depends on the selection of thermodynamic model and its parameters, especially for three phase problems. The chosen thermodynamic model and its parameters should provide not only a good estimation of vapour-liquid equilibrium, also correct prediction of liquid-liquid equilibrium. Otherwise, the simulation results of number of two-liquid phase stages, and two liquid phase distribution become meaningless. Unfortunately, there is very limit vapour-liquid-liquid equilibrium data in the literature. Almost all thermodynamic models are derived from either VLE or LLE data.



Figure 4-26 Temperature profile various thermodynamic models



Figure 4-27 Liquid I compositions profiles by various thermodynamic models



Figure 4-28 Liquid II compositions profiles by various thermodynamic models

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Figure 4-29 Liquid phase fractions profiles by various thermodynamic models



Figure 4-30 n-butanol vapour composition prediction's deviation by various thermodynamic models



Figure 4-31 water vapour composition prediction's deviation by various thermodynamic models



Figure 4-32 n-propanol vapour composition prediction's deviation by various thermodynamic models


Figure 4-33 Deviation of bubble point temperature prediction by various thermodynamic models



Figure 4-34 Liquid-Liquid Equilibrium Binodal Curve (n-butanol, water, n-propanol)

No	Components	Stages	Feed Condition	Bottom Rates	Side Draw Ratio	Pressure
1	n-butanol, water, 1-propanol	12	F1=50, L. P = 101.3.KPa T = 90.0 C y = 0.13, 0.65, 0.22	21.0	SL1 = 0.25 SL2 = 0.25	P1 = 101Kpa P12= 101Kpa
2	n-butanol, water, n-butyl_acetate	7	F2 = 50, S.L. P = 101.3 KPa y = 0.24, 0.30, 0.46	38.84	SL1 = 0.0 SL2 = 1.0	P1 = 101 KPa P7 = 101 KPa
3	ethanol, benzene, water	10	F1 = 82.101, L. P = 101.3 KPa T = 25.0 C y =0.01, 0.9, 0.11 F3 = 100.0, S.L. P = 101.3 KPa	65	SL1 = 0.0 SL2 =1.0	P1 =101 KPa P10=101 KPa
4	acetone, chloroform, water .	10	F3 = 50, S.V. $P = 101.3 KPa$ $y = 0.167, 0.333,$ 0.500 $F4 = 100 S.L.$ $P = 101.3 KPa$ $y = 0.60, 0.20, 0.20$	110	SL1 = 0.285 SL2 = 0.285	P1 = 1 atm P10= 1 atm

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Table 4-6 List of Three Phase Distillation Examples

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5	n-butanol, water, ethanol	11	F7 = 0.5, L. P = 101.3 KPa T = 52 C y = 0.03, 0.75, 0.22	0.36	SL1 = 0.25 SL2 = 0.25	P1 = 1 atm P11= 1 atm
6	propylene, benzene, n-hexane, water	5	F3 = 200, S.L. $P = 101.3 KPa$ $y = 0.45, 0.30,$ $0.20, 0.05$	130.0	SL1= 0.2857 SL2= 0.2857	P1 = 1 atm P5 = 1 atm
	2-propanol, water, benzene	10	F5 = 100, S.L. P = 101.3 KPa y =0.743, 0.248, 0.009 F1= 35, S.L. P = 101.3 KPa y=0.24, 0.46, 0.5	40	SL1 = 0.1 SL2 = 0.9	P1 = 1 atm P30= 1 atm

5. Reactive Distillation Simulation

5.1 Introduction

The catalytic distillation or reactive distillation is an innovative process in which chemical mixtures can be reacted in the presence of catalysts, and products are continuously separated by fractionation. This unique feature gives reactive distillation technical and economical advantages over the conventional distillation processes. This new technology can save substantial capital investment because it is simpler and requires less capital equipment.

5.1.1 High Conversion and High Selectivity

Many reactions of commercial interest are limited to their desirable extents of conversion by unfavorable chemical equilibrium. For example in the production of methyl acetate via esterification reaction,



It has been found that the production of high-purity methyl acetate via the above reaction is very difficult and expensive, because of the reaction equilibrium limitation. Conventional process has to use many reactors with large excess of one reactant to achieve the high conversion of the other reactant. The separation of the reaction mixture is also complicated by the azeotrope formation (methyl acetate - methanol and methyl acetate - water minimum boiling azeotrope). However this reaction can be enhanced significantly towards completion in a reactive distillation process, in which the volatile product is continuously removed from the reaction zone. Therefore, high-purity of acetate product is taken off as the top product while pure water is taken off as the bottom product. Both reactants are completely converted within the reactive zone in the column. It can be seen that the reactive distillation process can have substantial capital benefits by eliminating ancillary reaction mixture separation units. It also saves large recycle costs for the excess reactants.

Since the reaction products are being removed from the reaction zone, further reaction to byproducts is also minimized. The reaction in the reactive distillation usually can achieve very high selectivity. The other reason is that the reaction is completed by the sum of numerous "low conversion" stages, and selectivity is normally high for the low conversion chemistry.

5.1.2 Temperature Control and Energy Conservation

In reactive distillation columns, the reaction usually occurs in the liquid phase in the presence of solid catalysts. Since the stage temperature of the column is the boiling point of the component mixture and is easily controlled by the system pressure, the "hot spots" problem of conventional reactors can be easily eliminated. The most important feature of reactive distillation processes is their lower demand in energy consumption than conventional processes. It is primarily because the heat of exothermic reactions can be fully recovered as

the boil-up for fractionation, the needed energy consuming recycle stream is eliminated, and fewer distillation units are required than for a conventional process.

5.1.3 Separation of Closely Boiling Mixtures

In many important chemical processes, there is need to separate closely boiling, usually isomeric mixtures (e.g., C_8 aromatics). The conventional distillation usually takes large number of stages and high reflux ratio to separate these mixtures. The alternative technique for separating closely boiling mixture is the extractive distillation. However it is not effective in separating isomer mixtures due to their similar chemical nature. The entrainer has almost the same effect on each of the isomers and therefore does not change their relative volatility. For example, Berg et al. (1966) investigated 40 entrainer for the separation of *m*-xylene and *p*-xylene and found that their relative volatility of 1.02 could be increased to a mere 1.029. In these cases, the reactive distillation processes prove to be very effective by introducing reactive entrainers. The reactive entrainer reacts preferentially with one of the isomers (usually the heavy one) in a reversible reaction. The reaction product is less volatile. Therefore the lighter isomer will leave as the top product, while the other isomer, reactive entrainer and reaction product become the bottom product. The heavy isomer and reactive entrainer are recovered from another reactive distillation column, in which the reverse reactions take places.

The concept of distillation with reaction was recognized a long time ago. The technique was first applied in the 1920's to esterification processes using homogeneous

Later many works have been carried out in developing this catalysts (Backhaus 1921). technique for various applications (Keves 1932, Logntin and Randall 1942, Leves and Othmer 1945, Berman et al. 1948, Belck 1955, Corrigan and Ferris 1969, and Satio et al. 1971). However only recently, the reactive distillation technique has received attentions from Many commercial plants have been designed and built. chemical process industry. The catalytic distillation technology has been demonstrated successfully in many commercial scale The Chemical Research and Licensing Company (CR&L) (Jones and petrochemical plants. Smith, 1989) developed a catalytic distillation process for the production of MTBE, which is the world's fastest growing chemical as a clean-burning octane enhancer. This process has been used by almost all new MTBE plants. Other commercial processes developed by CR&L include isobutylene recovery, ethylbenzene and cumene production. Eastman Chemical Company developed a reactive distillation process for the production of high-purity methyl acetate (Agreda et al., 1990). The Eastman Chemical process has potential for other esterification reactions and nitrations, and the hydrolysis of methyl acetate. Since the successful commercialization of the reactive distillation technology, many other potential applications are being developed and evaluated as a part of the research and development work at most of the major oil and chemical companies. These potential applications cover a wide range of petrochemical processes such as alkylation of aromatics, dimerization of olefins, hydrolysis, esterification, removal of acid gases, and waste water treatment.

5.2 Literature Review of Reactive Distillation Simulation

As any novel technology, the catalytic distillation not only revolutionizes the refinery and petrochemical industries, but also opens up a new frontier of scientific research - coupled multicomponent mass and energy transport with catalytic reaction. One of the important research areas is the simulation of the catalytic distillation columns. The simulation work is of great importance for process engineers, because it will not only provide a better understanding of the catalytic distillation process, but also supply an efficient tool to design and scale-up potential catalytic distillation processes.

The first attempt was made by Othmer and Belck using manual plate-to-plate calculations with very rough approximations for V-L equilibrium and reaction rate relations. Hofmann (1958) proposed a graphical technique which he applied to the production of furfural from xylose. In recent years, several computational methods have been proposed to solve the problem (Saito et al. 1971, Nelson, 1971; Suzuki et al. 1971; Jelinek et, 1976; Komatsu, 1977; Komatsu and Holland 1977; Tierney et al. 1982, Simandl, 1988, and Alejski et al. 1988, Venkataraman et al. 1990). These methods can be classified into:

- 1) equation decoupling methods;
- 2) Newton-Raphson based methods;
- 3) simulation methods used for dynamic processes;
- 4) minimization methods.

The review of these methods is given in the following section.

5.2.1 Equation Decoupling Methods (Saito et al., 1971, Suzuki et al., 1977, Tierney et al., 1982)

The equation decoupling method is similar to the equation decoupling approach for non-reactive separation problems. First the component mass balance equations were linearized and solved for liquid phase compositions by assuming temperature and reaction rates. The k-values were assumed to be only dependent on the temperature and pressure.

In Suzuki's work (1977), the ideal gas was assumed for the vapor, and liquid phase was assumed an ideal solution. The modified Muller's method was used to update temperatures from the summation equations. The reaction rate was calculated from the reaction rate equation, while the vapor phase flow rate was computed from the energy balance equation.

However Tierney and Riquelme (1982) applied the Newton-Raphson method to update temperatures, reaction rates and vapor compositions by solving the summation equation, equilibrium relation, heat balance equation and reaction rate equations together.

With a new set of temperatures, reaction rates and vapor phase flow rates, the linearized component mass balance equations were solved again until the desired accuracy was attained.

An example of esterification of acetic acid was used to demonstrate the Suzuki's method. Tierney and Riquelme applied their method to simulate the separation of meta-xylene and para-xylene, which has equilibrium limited reactions.

The equation decoupling methods are very efficient in storage. However this algorithm depends on the initial estimation of the starting points. They usually suffer from poor convergence property when dealing with strongly non-ideal mixtures. These methods also expose limitation on the design specifications.

5.2.2 Relaxation Method (Jelinek et al. 1976; Komatsu, 1977; Komatsu and Holland, 1977; Bogacki et al. 1989)

Relaxation method is based on the method of false transients, or false unsteady state. It has been utilized to simulate numerous non-reactive distillation problems. The method offers stability and convergence. Jelinek et al. (1976), Komatsu (1977) and Bogacki et al. (1989) had successfully extended the relaxation approach to solve the reacting distillation problems. In Komatsu's work, the explicit forward approximation is employed for approximating the unsteady state partial differential equations. Some very rough simplifications have been made such as ideal behavior for both vapor and liquid mixtures, and constant phase flows thus neglecting the heat balance equation. Jelinek (1976), however, used an implicit backwards approximation approach to improve the stability of the solution. Later Bogacki et al. (1989) applied the Adams-Moulton formula to solve the partial differential equations. Jelinek et al. (1976), Komatsu (1977) and Bogacki et al. (1989) have illustrated the capability of their relaxation methods by solving highly non-linear systems such as esterification of acetic acid. It shows that relaxation method is a very stable to converge but slow. The convergence of iterations is usually controlled by the choice of the relaxation factors.

5.2.3 Minimization Method (Alejski, et al. 1988)

A computational procedure based on the minimization of error functions was proposed by Alejski (1988). The error functions contain mass balance, equilibrium and reaction equations, and all the parameters together with their constraints. The energy equations were excluded from the error functions and were solved in an outer iteration loop. The vapor phase flow rates were corrected from the energy balance equations.

The application of the minimization method was demonstrated by solving the esterification of acetic acid with ethanol. It has shown that even with poor estimates of start points, the proposed minimization method always gives good solution. However, the method takes very long time to approach the solution. The proposed method seems very useful for providing rough estimates of starting points for other means of solution methods such as Newton-Raphson methods.

5.2.4 Newton-Raphson Based Methods (Nelson, 1971; Simandl, 1988, Venkataraman, 1990)

In Nelson's work, the system equations are grouped into two sets of linearized equations. These are linearized component mass balance equations with respect to the liquid composition, and energy balance and summation equations with respect to temperature and vapor flow rates. The Newton iteration approach was applied on two levels: in the inner loop, the component mass balance equations were solved for compositions; in the outer loop the heat and summation balance equations were solved for temperature and phase flow rates. The extent of reactions was expressed explicitly as a function of the compositions and the temperature. The method of damped least squares was employed to control the correction step towards the final solution. No details of the reactive distillation example were reported in Nelson's work.

Simandl (1988) developed a similar simultaneous correction method, in which the temperature, vapor flow rates and compositions were determined simultaneously from the component mass balance, heat balance and summation equations. The reaction rates were directly calculated from kinetic rate expressions. In order to damp out large excursions and stabilize the iteration, Simandl (1988) introduced a weighting factor, which is determined by a sequential testing approach.

Simandl (1988) also extended an inside-out approach to solve the reactive distillation column. The computational procedure was almost the same as the original inside-out

approach of Boston (1978), except for the inclusion of reaction rates calculations from the explicit kinetics function. The application of the simultaneous correction and inside-outside methods of Simandl (1988) has been illustrated by simulation of esterification of ethyl acetate and a commercial reactive separation process.

It is noted that both Simandl and Nelson simulation methods can be only applied to kinetic controlled reaction process. Both methods need explicit reaction rate expressions to calculate the reaction rates directly, instead of solving reaction rates with other iterative variables simultaneously. Such approaches would be difficult to be applied to solve the reactive column which has implicit reaction relationship, such as the chemical equilibrium reaction.

Venkataraman et al. (1990) developed a new inside-out approach for simulating reactive distillation. In the inner loop, the MESH equations coupled with the reaction relationships were solved simultaneously using Newton iteration method. The reaction relationship can be either kinetics rate expression or the chemical equilibrium conditions, along with electrolytic reactions. The new approach of Venkataraman et al. has been successfully applied to simulate different reactive distillation problems including the separation of *para*-xylene and *meta*-xylene, the esterification production of ethyl acetate, a sour water stripper and a nitric acid absorption tower.

So far, all these previously proposed algorithms are very specific for the reactive distillation process. None of these methods includes the capability for handling the liquid

phase splitting. However, in many potential reactive distillation processes, reaction mixtures can form two partially immiscible liquid phases within the column, as in the case of production of butyl acetate via butanol (Arrison, 1972) or ethyl acetate via ethanol. It is because of the formation of ethyl(butyl) acetate - ethanol (butanol) and ethyl(butyl) acetate - water minimum boiling azeotropes. In this study, the non-reactive multi-phase distillation simulation procedure described in the previous chapters will be modified to include chemical reactions. Therefore the new computational algorithm not only solves complicated two and three phase separation processes, but also can solve the reactive distillation problems.

6. Model Development of Reactive Distillation

In this chapter, a new computational procedure for reactive distillation processes will be developed. The chapter begins with a new mathematical model that allows the reactive model equation to be easily incorporated in the approach that is described in Chapter 3. The reaction relationship is taken into account for the mass and energy balance calculation.

6.1 Mathematical Model

A schematic representation of a tray in a reactive column is shown in Figure 6-1. Multi-tray columns consist of a sequence of such stages. It is noted the schematic of reactive column is similar to the one shown in Figure 3-1, except for reactions on each stage. The following assumptions are made to develop the mathematical equations for simulating this general separation process:

- 1. It is a steady state problem, therefore, there is no time variation in any of the model equations.
- Each stage is treated as an equilibrium stage, and all phase flow streams leaving from a stage are in complete thermal, phase and chemical equilibrium.
- 3. Chemical reactions can occur in either vapor phase or liquid phase.

4. Perfect mixing occurs for the liquid phase at each stage. The withdrawal streams have the same compositions and conditions as the interstage stream from which they are drawn.

Based on these assumptions, a set of mathematical equations which describe these operations consists of the followings:

Chemical Reaction Stoichiometry:

$$\sum_{i=1}^{N_c} \boldsymbol{v}_{ir} \boldsymbol{A}_i = 0 \qquad \boldsymbol{r} = 1...N\boldsymbol{r}$$
(6-1)

where the A_i represents the ith component and the v_{ir} is the stoichiometric coefficient of the component in the rth reaction. The stoichiometric coefficients are taken postive for products and negative for reactants.

Chemical Equilibrium Relationship:

$$G_{rj}^{R} = KR_{rj} \prod_{\substack{i=1\\v_{k}<0}}^{N_{c}} a_{ijp}^{v_{k}} - \prod_{\substack{i=1\\v_{k}>0}}^{N_{c}} a_{ijp}^{v_{k}}$$
(6-2)

 KR_{ij} is the chemical equilibrium constant for the rth reaction and stage j. Its value is evaluated from the Gibbs free energies. a_{ijp} denotes for the activity of the ith component in the pth phase at the j stage, and is given by,

$$a_{ijp} = \frac{\hat{f}_{ijp}}{f_{ijp}^{o}} = \frac{\hat{\phi}_{ijp} P_{j}}{f_{ijp}^{o}} y_{ijp}$$
(6-3)

where the subscript p is the index for the phase in which the reaction occurs. y_{ijk} is the mole fraction of component i in phase p at the stage j.

Component Mass Balance Equations:

$$G_{ij}^{m} = -\sum_{k=1}^{\pi} n_{ijk} + F_{ij} + (1 - w_{j+1,1}) n_{ij+1,1} + \sum_{k=2}^{\pi} (1 - w_{j-1,k}) n_{ij-1,k} + \sum_{r=1}^{Nr} v_{ir} \delta_{jr} \quad (6-4)$$

where n_{ijk} refers to the number of moles of component i in phase k at the stage j, while w_{jk} represents the side withdrawal ratio of kth phase stream leaving from stage j.

Energy Balance Equations:

$$G_{j}^{E} = -\sum_{ki=1}^{\pi} \sum_{i=1}^{N_{c}} n_{ijk} h_{ijk} + \sum_{i=1}^{N_{c}} (1 - w_{j+1,1}) n_{ij+1,1} h_{ij+1,1} + \sum_{k=2}^{\pi} \sum_{i=1}^{N_{c}} (1 - w_{j-1k}) n_{ij-1k} h_{ij-1k} + Hf_{j} + Qf_{j}$$
(6-5)

where h_{ijk} is partial molar enthalpy for component i in phase k. Hf_j is the total enthalpy of feed stream entering stage j, and Qf_j is the enthalpy values of the energy input stream. Since the elemental reference state is used for evaluating the enthalpies, the heat of reaction is not included for the energy balance equation.

Component Summation Equations:

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$$G_{jk}^{s} = \sum_{i=1}^{N_{e}} (y_{ijk} - y_{ijr})$$
(6-6)

where, y_{ijk} is defined as the mole fraction of component i in phase k and y_{ijr} is the mole fraction of the component in the reference phase.

Phase Summation Equations

$$G_{j}^{ps} = \sum_{k=1}^{\Pi} \alpha_{jk} - 1$$
 (6-7)

where α_{jk} is the phase fraction of the kth phase at the jth stage.

Phase stability Equations:

$$G_{jk}^{st} = \frac{\alpha_{jk} \theta_{jk}}{\alpha_{jk} + \theta_{jk}}$$
(6-8)

 α_{jk} and θ_{jk} represent the phase fraction and stability factor of phase k at stage j, respectively.

To simplify the model equations describing the column and their derivatives, the same variable, β , as discussed in Chapter 3 is used here, that is:

$$\beta_{ijk} = \frac{n_{ijk}}{\sum_{k=1}^{\pi} n_{ijk}} = \frac{n_{ijk}}{m_{ij}}$$
(6-9)

The explanation of β variable is given in Chapter 3. The composition and the flow rate of the component i in phase k are related to β by the following equation:

$$n_{ijk} = \beta_{ijk} m_{ij}, \quad and \quad y_{ijk} = \frac{n_{ijk}}{\sum_{l=1}^{N_c} n_{ijk}} = \frac{\beta_{ijk} m_{ij}}{\alpha_{jk} \sum_{i=1}^{N_c} m_{ij}} \quad . \quad (6-10)$$

Substitution of Equation (6-10) into all the model equations (6-4)-(6-8) and (6-2) generates a set of new model equations in term of variables α , β , θ and m and δ , that is:

Chemical Equilibrium Relationship:

$$G_{ij}^{R} = KR_{ij} \prod_{\substack{i=1\\\nu_{\nu}<0}}^{N_{c}} a_{ijp}^{\nu_{\nu}} - \prod_{\substack{i=1\\\nu_{\nu}>0}}^{N_{c}} a_{ijp}^{\nu_{\nu}}$$
(6-11)

and

$$a_{ijp} = \frac{\hat{f}_{ijp}}{f^{o}_{ijp}} = \frac{\hat{\phi}_{ijp} P_j}{f^{o}_{ijp}} x_{ijp} = \frac{\hat{\phi}_{ijp} P_j}{f^{o}_{ijp}} \frac{\beta_{ijp} m_{ij}}{\alpha_{jp} \sum_{i=1}^{N_c} m_{ij}}$$
(6-12)

Component Mass Balance Equations:

$$G_{ij}^{m} = -m_{ij} + F_{ij} + (1 - w_{j+1,1}) \beta_{ij+1,1} m_{ij+1} + \sum_{k=2}^{\pi} (1 - w_{j-1k}) \beta_{ij-1k} m_{ij-1} + \sum_{r=1}^{Nr} v_{ir} \delta_{jr} (6-13)$$

Energy Balance Equations:

$$G_{j}^{E} = (6-14)$$

$$-\sum_{k=1}^{\pi} \sum_{i=1}^{N_{e}} \beta_{ijk} h_{ijk} m_{ij} + \sum_{i=1}^{N_{e}} (1 - w_{j+1,1}) \beta_{ij+1,1} h_{ij+1,1} m_{ij+1}$$

$$+ \sum_{k=2}^{\pi} \sum_{i=1}^{N_{e}} (1 - w_{j-1k}) \beta_{ij-1k} h_{ij-1k} m_{ij-1} + Hf_{j} + Qf_{j}$$

Component Summation Equations:

$$G_{jk}^{s} = \sum_{i=1}^{n_{c}} \left(\frac{\beta_{ijk}}{\alpha_{jk}} - \frac{\beta_{ijr}}{\alpha_{jr}} \right) m_{ij}$$
(6-15)

Phase Summation Equations:

$$G_j^{ps} = \sum_{k=1}^{\Pi} \alpha_{jk} - 1$$
 (6-16)

Phase stability Equations:

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$$G_{jk}^{st} = \frac{\alpha_{jk} \theta_{jk}}{\alpha_{jk} + \theta_{jk}}$$
(6-17)

and

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$$\beta_{ijk} = \frac{\alpha_{jk} e^{\theta_{jk}} K_{ijk}}{\sum_{p=1}^{\pi} \alpha_{jp} e^{\theta_{jp}} K_{ijp}}$$
(6-18)

The above system equations (6-11)-(6-18) are referred as the MESHR equations, where R stands for the reaction relationship. It is noted that Equations (6-13)- (6-18) are exactly the same as the ones in the Chapter 3. Additional system equations are the chemical equilibrium relationships (6-11) for all reactions (N_sN_r). The iteration variables include the extent of each reaction, δ_{jr} (N_sN_r), together with other variables described in developing nonreactive separation model equations (Chapter 3). The same approach in Chapter 3 is used for selecting the specification equations. It is noted that when there is no reaction occurring within the stage, the above system equations and variables reduce to the equations described in Chapter 3.

6.2 Development of Solution Procedure

The inside-outside approach described in **Chapter 3** is extended to solve the reactive distillation model equations. Approximate evaluations of thermodynamic properties are made in the inner loop. Parameters of the approximate models are updated using rigorous thermodynamic models in the outer loop. The governing model equations are then solved simultaneously using the modified Powell's hybrid method. The details of the new algorithm is illustrated in Figure 6-2

6.2.1 Initialization of reactive distillation column calculation

The initialization procedure is basically similar to the one developed for non-reactive separation column calculation. The initial temperature profile is based on the estimate of the

dew and bubble point temperatures of the averaged composite feed. The initial estimates of the phase fractions are obtained by assuming the constant molar overflow. Then the component mass balance and equilibrium equations are solved to give component overall flow rates. The initial estimates of reaction extents are computed by performing a simplified chemical equilibrium calculation on each stage, instead of complicated chemical and thermodynamics equilibrium (or reactive flash) calculation.

The simplified chemical equilibrium calculation consists of solving the following equations:

Mass balance equation:

$$n_{ijp} = n_{ijp}^{o} + \sum_{r=1}^{N_r} v_{ir} \delta_{jr}$$
 (6-19)

where n°_{ijp} is the initial estimate of component phase flow rate, and p is the phase index in which reactions occur.

Chemical Reaction Equilibrium equation:

$$G_{rj}^{R} = KR_{rj} \prod_{\substack{i=1\\v_{k}<0}}^{N_{c}} a_{ijp}^{-v_{lr}} - \prod_{\substack{i=1\\v_{k}>0}}^{N_{c}} a_{ijp}^{v_{lr}} \qquad (6-20)$$

where the activity of the ith component in the pth phase is defined as follow

$$a_{ijp} = \frac{\hat{f}_{ijp}}{f_{ijp}^{o}} = \frac{\hat{\phi}_{ijp} P}{f_{ijp}^{o}} x_{ijp}$$
 (6-21)

$$x_{ijp} = \frac{n_{ijp}}{\sum_{i=1}^{Nc} n_{ijp}}$$
(6-22)

The above mass balance and chemical equilibrium equations are solved simultaneously for generating initial estimates of reaction extents. Compared to the rigorous reactive flash calculation, this simplified chemical equilibrium calculation eliminates the calculation of thermodynamic equilibrium. It consequently saves computation time. Such calculation is good enough for the purpose of the initialization.

6.3 Results and Discussion of Reactive Distillation Simulation

To illustrate the performance of the new algorithm, a reactive separation example of para- and meta-xylene is simulated. Because of the close boiling and isomer nature of paraxylene (boiling point: -139.3 °C) and meta-xylene (boiling point: -138.5 °C), it is extremely difficult to separate them by a conventional distillation. The extractive distillation cannot be successfully applied to the separation of this mixture since the entrainer has almost same effect on both xylene components, therefore does not change their relative volatility. The alternative industrial practice uses a fractional crystallization process, due to the difference in the melting Another separation alternative is the reactive points of para-xylene and meta-xylene. distillation process, which can employ chemical reaction differences (i.e. selectivity) between the isomers with other components (i.e., solvent or reactive entrainer). It has been ditertiary preferentially with that meta-xylene can be reacted determined.

butyl_benzene(DTBB), tertiary butylbenzene(TBB) to produce tertiary butyl_meta-xylene (TBMX) and benzene(BZ), that is



The butylated product (TBMX) is less volatile and is easily separated from para-xylene. Therefore benzene and para-xylene will be taken off as distillate, while the heavier m-xylene, butylated products will be taken off as bottom products. A second column can then be used to separate the bottoms into pure m-xylene and solvents (DTBB and TBB) because of the favorable reverse reaction conditions within the second column. These transalkylation reactions usually rapidly attain equilibrium over a constantly circulated solid catalyst (such as aluminum chloride). Saito et al. (1971) first proposed a distillation scheme based on the above reactions. Saito et al. also presented the experimental result of this reactive separation process. Saito et al. (1971), and later Tierney and Riquelme (1982), Venkataraman et al. (1990)

presented different solution methods for simulating such column. The simulation results qualitatively agreed with the experimental data.

The column specifications are listed in Appendix C. The close-boiling mixture of para- and meta- xylene is fed through the reboiler, while the transakylation agents (TBB and DTBB) are fed to the top of the column. The reactions are assumed to reach equilibrium on all stages except the condenser where reactions are assumed not to occur due to the absence of the catalyst. It takes six iterations to converge to a relative tolerance 1.0E-8 for compositions and reaction extents and 1.0E-16 for inverse temperatures. The simulation results are shown As the result of complete reaction of meta-xylene, top in Figure 6-3 and Figure 6-4. product consists of mixture of para-xylene, benzene, and TBB. High purity para-xylene can be easily separated from this top product mixture by a simple distillation. The comparison of these simulation results with the ones from Venkataraman et al. (1990) shows a good agreement (Figures 6-5, 6-6, 6-7 and Figure 6-8). In Venkataraman's work, the constant molar overflow is assumed. Such assumption is not made in this simulation work. However, Figure 6-8 shows the constant molar overflow assumption is very close to the actual overflow The negative values of reaction extents in Figure 6-7 indicate the reverse reaction profile. extents instead of the forward reaction values. The reverse direction of the second reaction at stage 2 is mainly caused by large excess of benzene from the top stage reflux.

6.4 Conclusion

The non-reactive, multi-phase separation simulation procedure has been successfully extended for the simulation of reactive distillation columns. The numerical example illustrates that the algorithm is efficient and stable in solving reactive distillation problems.







Figure 6-2 Outline of Reactive Column simulation algorithm







Figure 6-4 Vapour Phase Composition (xylene separation)



Figure 6-5 Comparison of Liquid Phase Composition Profile (xylene separation)



Figure 6-6 Comparison of Temperature Profile (xylene separation)



Figure 6-7 Comparison of Reaction extents (xylene separation)



Figure 6-8 Comparison of Vapour Phase Fraction (xylene separation)

7. Conclusions and Recommendations

7.1 Conclusions

- A mathematical model has been developed for simulating various multi-stage, and 1. A new variable, defined as the component multi-phase separation problems. phase fraction, is used to simplify the formulation of the model equations. The phase stability testing equation and the liquid-liquid phase splitting calculation are coupled with MESH equations, and are solved simultaneously for phase fractions, phase stability factors, temperatures and component overall flows. The appearance and disappearance of the second liquid phase are determined It either eliminates the simultaneously with other variables during iterations. requirement of prior knowledge of the two-liquid phase region, or removes the extra outer loop for the phase stability testing and liquid phase splitting calculations.
- 2. An effective inside-out approach has been implemented to solve the non-linear system equations of multi-stage and multi-phase separation processes. In the inner loop, the thermodynamic properties such as K-values and enthalpies are assumed independent of compositional effects. The system equations are solved simultaneously in the inner loop. The parameters of approximate thermodynamic models of inner loop are updated in an outer loop.
- 3. An initialization procedure based on the pseudo-two phase distillation has been proposed to generate the initial guess of the second liquid phase compositions and phase fractions in the three-phase distillation process.
- 4. An effective strategy has been implemented to calculated the inverse of the matrix when it is close to singular while using the Thomas method.
- 5. The Powell's hybrid, which combine the minimization and the Newton method, has been modified and implemented to increase the size of convergence or the size of region from which the algorithm will converge to the desired solutions. The modified Powell's method has shown its stability and rapidity of convergence over various types of separation problems. There is no need for good estimates of conditions as the starting points of the solutions. A strategy is also implemented so as to prevent the variables from violating their physical feasible bound.
- 6. The new algorithm has been tested for a variety of non-ideal systems and for a variety of two phase separation operations including simple distillation, azeotropic and extractive distillation, absorption, and reboiled absorption. The simulation

convergence characteristics have been compared favorably with those obtained other existing programs, even with very poor initial starting points.

- 7. Most of three-phase distillation examples available in the literature have been used to test the new algorithm's capability of handling the existence of the second liquid phase. The simulation results compared well with those available in the literature. The effects of ignoring the possibility of the liquid splitting have been examined. It shows that significant difference in the designing operation conditions and column configuration could be resulted if the true three-phase column is assumed as a two phase column. The comparison of simulation results using various thermodynamic models shows that the prediction of two liquid phase regions, and separation conditions not only depends on the model's accuracy of predicting vapor-liquid equilibrium, but also relies on the precision of liquid-liquid equilibrium prediction.
- 8. The simulation algorithm for non-reactive distillation columns has been successfully extended to simulate the reactive distillation columns. The implicit chemical equilibrium reaction constraints are incorporated in the MESH equation to account for the reaction extents. The same inside-out approach is used to simulate the reactive separation problem. An effective initialization procedure has been implemented for generating the initial estimates of reaction extent. In the

inner loop, the MESH equations together with the chemical equilibrium relationships are solved simultaneously for phase fractions, phase stability factors, temperatures, component overall flows and the reaction extents.

7.2 Recommendations

The proposed algorithm has be proved to an effective and successful methods for simulating multi-stage, multi-liquid phase separation with chemical reactions. There are still some improvements need to be made so that the algorithm could be more general and efficient:

Improvement on the solution method of linear system equations:

The current Jacobian matrix of the model equations is in the form of the tri-diagonal block matrix. The modified Thomas's method is used to computer the inverse of the matrix. However, when modeling a separation process which has a multi-columns configuration or more general specifications, the Jacobian matrix can be in the form of the tri-diagonal block matrix with some off-diagonal blocks. The Thomas's approach can't be applied in this case. A more general linear system equation solution method is needed to implement for solving such matrix. The general solution method should make use of the sparsity of the Jacobian matrix so as to save storage and computation time.

Improvement on calculating the inverse of the Jacobian matrix:

The inverse of the Jacobian matrix is evaluated at every iteration to compute the Newton correction step size. However, computing the inverse of the Jacobian matrix is very expensive in term of the computation time, especially for the large separation system. In order to speed up the computation, a strategy is needed for approximating the inverse of the Jacobian matrix between the iteration. Such strategy could be Schubert's update, or Brent's update or a application of the hybrid method (Venkatarman and Lucia, 1986)

• Implementation of the kinetic controlled chemical reaction relationships

The proposed algorithm has been successfully applied to simulate the reactive column where the reaction relationships are the implicit chemical equilibrium constraints. For the kinetic controlled reactive distillation column, the reaction relationships will be kinetic rate expressions which are explicit functions of the temperature and compositions of mixture.

• Inclusion of electrolyte thermodynamic model

There are many separation processes which are associated with electrolyte chemical equilibrium. Such processes include azerotrope distillation with salts as the entrainers, sour water stripper, acid absorption tower and etc. The proposed algorithm can be extended to solve these separation problems by using the appropriate

chemical equilibrium equations and thermodynamic models that can describe the electrolyte equilibrium behavior.

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Appendix A

Two Phase Separation Examples

How many number of component 10 methane ethane propane toluene ethvlene hydrogen (equilibrium) benzene o-xylene cyclopropane ethylcvclohexane ****** * 1. Wilson Model 2. UNIFAC 3.NRTL * 11. Virial 12. Trebble-Bishnoi 14. Soave-RK 15.Ideal Gas * 13. PengRobinson Choice of thermodynamic model for vapor phase.... 14 Choice of thermodynamic model for liquid phase.... 14 Choice of thermodynamic model for liquid phase.... 14 Number of Stage: 20 Minimum Temperature at Distillation Tower ...(K) 200.000000(K) 300.000000 Maximum Temperature at Distillation Pressure at Distillation Tower Top......(Kpa) 3204.000000 3204.000000 Pressure at Distillation Bottom(Kpa) 2 Number of Feed Stream Stage Number of FEED position 17 Feed Flow rate 866.029000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Saturated Vapor Pressure(Kpa): 283.000000 The Saturated Vapor Pressure(Kpa): 3204.000000 flow rate(mole/time) or composition(%) component 127.920000 methane: 278.870000 ethane: propane: 1.279000 0.000000 toluene: 0.000000 ethylene: hydrogen (equilibrium): 457.960000 benzene: 0.000000

o-xylene:	0.00000	00			
cyclopropane:	0.0000	00			
ethylcyclohexane:	0.00000	00	•		
Stage Number of FEED posit	ion	1			
Feed Flow rate 1975.6	10000				
Feed Thermal Specification:					
(1) S.L (2) S.V (3) Superhea	ted∙Vap	or (4) S	Subcooled Liquid	4	
The Saturated Vapor Pressure	e(Kpa):	258.00			
The Saturated Liquid Pressure(Kpa): 3204.200000					
component	flow rat	te(mole	/time) or composition	(%)	
methane:	0.0000	00			
ethane:	0.0000	00	,		
propane:	0.0000	00			
toluene:	70.980	000			
ethylene:	792.61	0000			
hydrogen_(equilibrium):		0.0000	00		
benzene:	792.61	0000			
o-xylene:	23.660	000			
cyclopropane:	59.150	000			
ethylcyclohexane:	236.60	0000			
Maximum Number of Phases	in the T	ower	2		
Number of Heat Input 2					
Stage Number of heat input position 4					
heat input rate (J/time) -0.886300					
Stage Number of heat input p	osition	7			
heat input rate (J/time)	-1.1553	300			
0 NON-Condenser(defa	ult)	1	Total Condenser	2. Parti	al
Condenser					
Condenser_INDEX: 0					
Reflex ratio: 0.000000					
0 NON-REBOLIER(de	fault)	1	REBOILER		
REBOILER_INDEX: 1	_		· · · · · · · · · · · · · · · · · · ·		
The Specified Bottom flow rate for Reboiler: 2199.439000					
The Number of Stage which has side-withdrawal 0					
Choices of Initial Temperature Procedure					
1. Automatic Initialization					
2. Terminal Input Initialization (in C)					
Choice of Initial Temperature Procedure 1					

,

How many number of component 8 ethane propane isobutane n-butane 2-methyl butane n-pentane n-hexane n-octane ***** 1. Wilson Model 2. UNIFAC 3.NRTL * 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 14. Soave-RK 15.Ideal Gas ***** Choice of thermodynamic model for vapor phase.... 14 Choice of thermodynamic model for vapor phase.... 14 Choice of thermodynamic model for vapor phase.... 14 Number of Stage: 31 Minimum Temperature at Distillation Tower ...(K) 200.000000 Maximum Temperature at Distillation 500.000000(K) Pressure at Distillation Tower Top......(Kpa) 758.420000 758,420000 Pressure at Distillation Bottom(Kpa) Number of Feed Stream 1 15 Stage Number of FEED position Feed Flow rate 6657.000000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Subcooled Liquid Temperature(K): 338.560000 758.420000 The Subcooled Liquid Pressure(Kpa): flow rate(mole/time) or composition(%) component 8.000000 ethane: 45.000000 propane: 1603.000000 isobutane: 2098.000000 n-butane: 2-methyl butane: 810.000000 682,000000 n-pentane: 876,000000 n-hexane: 535.000000 n-octane: Maximum Number of Phases in the Tower 2 Number of Heat Input 0

0 NON-Condenser(default) 1 **Total Condenser** 2. Partial Condenser Condenser_INDEX: 2 The vapor distillate rate: 3.732000 Reflex ratio: 1.724000 NON-REBOLIER(default) 0 1 REBOILER REBOILER_INDEX: 1 Bottom Rate: 2925.0 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1

4 How many number of component n-hexane ethanol methylcyclohexane benzene ***** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi 14. Soave-RK 15.Ideal Gas 13. PengRobinson Choice of thermodynamic model for vapor phase... 15 Choice of thermodynamic model for liquid phase.... 2 5 Total Sub_group For component n-hexane-(1): Total sub group: 2 sub.No Group No. Rk Qk main.No sub main 0.9011 CH3 1 2 0.8480 CH2 1 0.6744 0.5400 2 4 CH₂ CH₂ 1 For component ethanol-(2): Total sub group: 1 Qk sub.No Group No. Rk main.No sub main 1.9720 2.1055 17 1 CCOH 5 CH3CH2OH For component methylcyclohexane-(3): Total sub group: 3 main.No sub sub.No Group No. Rk Ok main 1 0.9011 0.8480 CH3 1 CH₂ 1 2 5 0.6744 0.5400 CH2 CH2 1 1 0.4469 0.2280 1 CH 3 CH₂ For component benzene-(4): Total sub group: 1 sub.No Group No. Rk Qk main.No sub main 0.4000 9 6 0.5313 3 ACH ACH ******UNIFAC INTERACTION PARAMETER******* 0.000000e+00 7.375000e+02 6.113000e+01 CH2 1 -8.793000e+01 0.000000e+00 -6.413000e+01 CCOH 5 -1.112000e+01 4.770000e+02 0.000000e+00 ACH 3 Choice of Standard State Fugacity Calculation 1. Empirical Equation by J. Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3. Henry's Constants (noncondensable)

n-hexane 1 3.3183e+03 -2.0259e-01 6.8498e+01 8.8924e-05 -3.5052e+0270 n-hexane 2.6350e-01 ethanol 1 -9.0910e+01 -3.4659e+03 -6.2301e-02 2.0486e+01 2.0664e-05 25 ethanol 2.5200e-01 methylcyclohexane 1 74 methylcyclohexane 1.4687e+02 -8.3627e+03 4.1169e-02 -2.3246e+01 -1.6077e-05 2.6990e-01 1 benzene 1.9082e-02 -1.4212e+01 -6.7182e-06 9.7209e+01 -6.9761e+03 60 benzene 2.6960e-01 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 10 Minimum Temperature at Distillation Tower ...(K) 100.000000 700.000000 Maximum Temperature at Distillation(K) Pressure at Distillation Tower Top......(Kpa)100.000000 Pressure at Distillation Bottom......(Kpa) 100.000000 Number of Feed Stream 1 Stage Number of FEED position 10 100.000000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 100.000000 flow rate(mole/time) or composition() component n-hexane: 0.300000 ethanol: 0.100000 0.300000 methylcyclohexane: 0.300000 benzene: Maximum Number of Phases in the Tower 2 Number of Heat Input 0 NON-Condenser(default) **Total Condenser** Partial 2. 0 1 Condenser Condenser INDEX: 2 The ratio of vapor distillate to liquid distillate: 1000.000000 Reflex ratio:(For Two-Phase Distillation Calculation) 2.000000 NON-REBOLIER(default) 1 REBOILER 0 **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 50.000000 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure..., 1

3 How many number of component methanol ethanol water ****** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi * 14. Soave-RK 15.Ideal Gas 13. PengRobinson Choice of thermodynamic model for vapor phase.... 13 ethanol water methanol 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 Choice of thermodynamic model for liquid phase.... 2 Total Sub group 3 For component methanol-(1): Total sub group: 1 Ok main.No sub sub.No Group No. Rk main 19 1 1.4311 1.4320 CH3OH 6 CH3OH For component ethanol-(2): Total sub group: 1 Ok main.No sub sub.No Group No. Rk main 5 CH3CH2OH 17 1 2.1055 1.9720 CCOH For component water-(3): Total sub group: 1 main.No sub sub.No Group No. Rk Qk main 20 0.9200 1.4000 H2O 7 H20 1 ******UNIFAC INTERACTION PARAMETER****** 0.000000e+00 -8.078000e+01 -1.810000e+02 CH3OH 6 5 1.274000e+02 0.000000e+00 2.854000e+02 CCOH 7 2.896000e+02 -1.485000e+02 0.000000e+00 H2O Choice of Standard State Fugacity Calculation 1.Empirical Equation by J.Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) methanol 1 3.3387e+02 -1.2679e+04 1.3761e-01 -5.7722e+01 -5.9496e-05 12 methanol 2.3180e-01 ethanol1

-9.0910e+01 -3.4659e+03 -6.2301e-02 2.0486e+01 2.0664e-05 25 ethanol 2.5200e-01 water 1 3.5888e-03 -6.6689e+00 -8.5054e-07 86 water 5.7042e+01 -7.0048e+03 2.3800e-01 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 22 Minimum Temperature at Distillation Tower ...(K) 100.000000 Maximum Temperature at Distillation(K) 600.000000 Pressure at Distillation Tower Top......(Kpa) 100.000000 Pressure at Distillation Bottom...... (Kpa) 100.000000 Number of Feed Stream 1 Stage Number of FEED position 12 100.000000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 100.000000 flow rate(mole/time) or composition() component methanol: 0.100000 0.200000 ethanol: 0.700000 water: Maximum Number of Phases in the Tower 2 Number of Heat Input 0 **Total Condenser** 2. Partial NON-Condenser(default) 1 0 Condenser Condenser INDEX: 1 Reflex ratio: (For Two-Phase Distillation Calculation) 3.000000 NON-REBOLIER(default) 1 REBOILER 0 **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 50.000000 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1

How many number of component 3 acetone chloroform methanol ***** ********* 1. Wilson Model 2. UNIFAC 3 NRTL 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 15.Ideal Gas 14. Soave-RK ***** Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 2 Total Sub group 4 For component acetone-(1): Total sub group: 2 sub.No Group No. Rk Qk main.No sub main 1.4880 22 1 1.6724 9 CH3CO CH₂CO 1 0.9011 0.8480 1 CH₂ 1 CH3 For component chloroform-(2): Total sub group: 1 main main.No sub sub.No Group No. Rk Ok 2.4100 48 1 2.8700 CCL3 20 CHCL3 For component methanol-(3): Total sub group: 1 main.No sub sub.No Group No. Rk Qk main 1.4320 CH3OH 19 1 1.4311 CH3OH 6 ******UNIFAC INTERACTION PARAMETER****** 0.000000e+00 2.676000e+01 -3.546000e+02 1.087000e+02 9 CH₂CO 4.764000e+02 0.000000e+00 2.490000e+01 6.972000e+02 1 CH2 5.521000e+02 3.670000e+01 0.000000e+00 6.491000e+02 CCL3 20 2.339000e+01 1.651000e+01 -1.394000e+02 0.000000e+00 CH3OH 6 Choice of Standard State Fugacity Calculation 1.Empirical Equation by J.Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) acetone 1 6.8603e+02 -1.4358e-01 4.6384e+01 6.3961e-05 -2.3066e+02 29 acetone 2.4700e-01 chloroform 1 6.5975e-02 -2.9011e+01 -3.0001e-05 8 chloroform 1.7424e+02 -8.1400e+03 2.7480e-01

methanol 1 3.3387e+02 -1.2679e+04 1.3761e-01 -5.7722e+01 -5.9496e-05 12 methanol 2.3180e-01 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 10 Minimum Temperature at Distillation Tower ...(K) 100.000000 Maximum Temperature at Distillation 500.000000 **(K)** Pressure at Distillation Tower Top......(Kpa) 100.000000 100.000000 Pressure at Distillation Bottom...... (Kpa) Number of Feed Stream 1 Stage Number of FEED position 5 Feed Flow rate 100.000000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 2 The Saturated Vapor Pressure(Kpa): 100.000000 flow rate(mole/time) or composition() component 0.450000 acetone: 0.330000 chloroform: methanol: 0.220000 Maximum Number of Phases in the Tower 2 Number of Heat Input 0 Partial NON-Condenser(default) **Total Condenser** 2. 1 0 Condenser Condenser INDEX: 2 The liquid distillate rate: 60.000000 The vapor distillate rate: 0.000010 Reflex ratio: 3.00000 NON-REBOLIER(default) REBOILER 0 1 **REBOILER INDEX: 1** The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1

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How many number of component 4 methanol ethanol water 1-propanol ***** 1. Wilson Model 2. UNIFAC 3.NRTL * * 11. Virial 12. Trebble-Bishnoi * 13. PengRobinson 14. Soave-RK 15.Ideal Gas ***** Choice of thermodynamic model for vapor phase... 15 Choice of thermodynamic model for liquid phase.... 2 Total Sub group 5 For component methanol-(1): Total sub group: 1 main.No sub sub.No Group No. Rk Ok main 1.4320 19 1 1.4311 6 CH3OH CH3OH For component ethanol-(2): Total sub group: 1 Qk main.No sub sub.No Group No. Rk main 2.1055 1.9720 17 1 CCOH 5 CH3CH2OH For component water-(3): Total sub group: 1 sub.No Group No. Rk Ok main main.No sub 0.9200 1.4000 H2O 20 1 H20 7 For component 1-propanol-(4): Total sub group: 2 main main.No sub sub.No Group No. Rk Qk 0.8480 1 0.9011 CH3 1 CH₂ 1 1.6640 CH2CH2OH 14 1 1.8788 5 CCOH ******UNIFAC INTERACTION PARAMETER******* 0.000000e+00 -8.078000e+01 -1.810000e+02 1.651000e+01 6 CH3OH 1.274000e+02 0.000000e+00 2.854000e+02 -8.793000e+01 5 CCOH 2.896000e+02 -1.485000e+02 0.000000e+00 5.806000e+02 7 H20 6.972000e+02 7.375000e+02 1.318000e+03 0.000000e+00 CH₂ 1 Choice of Standard State Fugacity Calculation 1. Empirical Equation by J. Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) methanol 1

12 methanol 3.3387e+02 -1.2679e+04 1.3761e-01 -5.7722e+01 -5.9496e-05 2.3180e-01 ethanol 1 2.0664e-05 25 ethanol -9.0910e+01 -3.4659e+03 -6.2301e-02 2.0486e+01 2.5200e-01 water 1 -7.0048e+03 3.5888e-03 -6.6689e+00 -8.5054e-07 86 water 5.7042e+01 2.3800e-01 1-propanol 1 35 1-propanol -1.0789e+03 1.8583e+04 -5.3858e-01 2.0250e+02 2.2251e-04 2.4850e-01 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 20 100.000000 Minimum Temperature at Distillation Tower ...(K) Maximum Temperature at Distillation (K) 600.000000 Pressure at Distillation Tower Top......(Kpa) 100.000000 Pressure at Distillation Bottom...... (Kpa) 100,000000 Number of Feed Stream 1 Stage Number of FEED position 10 100.000000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 100.000000 flow rate(mole/time) or composition() component methanol: 0.250000 ethanol: 0.250000 0.250000 water: 1-propanol: 0.250000 Maximum Number of Phases in the Tower 2 Number of Heat Input 0 Partial NON-Condenser(default) 1 Total Condenser 2. 0 Condenser Condenser INDEX: 1 2.500000 Reflex ratio: (For Two-Phase Distillation Calculation) NON-REBOLIER(default) REBOILER 1 0 **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 55.000000 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1

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How many number of component 3 acetone methanol water 1. Wilson Model 2. UNIFAC 3.NRTL * 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 14. Soave-RK 15.Ideal Gas Choice of thermodynamic model for vapor phase... 15 Choice of thermodynamic model for liquid phase.... 2 Total Sub group 4 For component acetone-(1): Total sub group: 2 sub.No Group No. Rk Ok main.No sub main 1.4880 CH2CO 9 CH3CO 22 1 1.6724 1 CH3 1 1 0.9011 0.8480 CH₂ For component methanol-(2): Total sub group: 1 sub.No Group No. Rk Qk main.No sub main CH3OH 6 CH3OH 19 1 1.4311 1.4320 For component water-(3): Total sub group: 1 Ok main main.No sub sub.No Group No. Rk H2O 20 1 0.9200 1.4000 H2O 7 ******UNIFAC INTERACTION PARAMETER****** 0.000000e+00 2.676000e+01 1.087000e+02 6.056000e+02 9 CH2CO 4.764000e+02 0.000000e+00 6.972000e+02 1.318000e+03 CH₂ 1 2.339000e+01 1.651000e+01 0.000000e+00 -1.810000e+02 CH3OH 6 -2.808000e+02 5.806000e+02 2.896000e+02 0.000000e+00 H2O 7 Choice of Standard State Fugacity Calculation 1. Empirical Equation by J. Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) acetone 1 6.3961e-05 -2.3066e+026.8603e+02 -1.4358e-01 4.6384e+01 29 acetone 2.4700e-01 methanol 1 3.3387e+02 -1.2679e+04 1.3761e-01 -5.7722e+01 -5.9496e-05 12 methanol 2.3180e-01 water 1

86 water 5.7042e+01 -7.0048e+03 3.5888e-03 -6.6689e+00 -8.5054e-07 2.3800e-01 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 33 Minimum Temperature at Distillation Tower ...(K) 120.000000 Maximum Temperature at Distillation (K) 500.000000 Pressure at Distillation Tower Top......(Kpa) 100.000000 Pressure at Distillation Bottom...... (Kpa) 100.000000 Number of Feed Stream 2 Stage Number of FEED position 9 150.000000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Subcooled Liquid Temperature(K): 323.000000 The Subcooled Liquid Pressure(Kpa): 100.000000 flow rate(mole/time) or composition() component 0.000000 acetone: 0.000000 methanol: 1.000000 water: Stage Number of FEED position 21 Feed Flow rate 100.000000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Subcooled Liquid Temperature(K): 329,000000 The Subcooled Liquid Pressure(Kpa): 100.000000 flow rate(mole/time) or composition() component 0.500000 acetone: 0.500000 methanol: 0.000000 water: Maximum Number of Phases in the Tower 2 Number of Heat Input 0 Partial NON-Condenser(default) 1 Total Condenser 2. 0 Condenser Condenser INDEX: 2 The ratio of vapor distillate to liquid distillate: 0.000001 Reflex ratio:(For Two-Phase Distillation Calculation) 4.000000 0 NON-REBOLIER(default) 1 REBOILER **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 200.000000 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1

How many number of component 3 n-heptane toluene methyl ethyl ketone **** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi * 14. Soave-RK 15.Ideal Gas 13. PengRobinson ***** Choice of thermodynamic model for vapor phase.... 14 toluenemethyl ethyl ketone n-heptane 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 Choice of thermodynamic model for liquid phase.... 2 Total Sub group 5 For component n-heptane-(1): Total sub group: 2 sub.No Group No. Rk Qk main.No sub main CH2 1 CH3 1 2 0.9011 0.8480 0.5400 2 5 0.6744 CH2 1 CH₂ For component toluene-(2): Total sub group: 2 main.No sub sub.No Group No. Rk Qk main 0.5313 0.4000 ACH 3 ACH 9 5 11 1.2663 0.9680 4 ACCH3 1 ACCH2 For component methyl ethyl ketone-(3): Total_sub_group: 3 main main.No sub sub.No Group No. Rk Qk 0.8480 1 1 0.9011 CH₂ 1 CH3 2 1 0.6744 0.5400 CH₂ CH₂ 1 9 CH3CO 22 1 1.6724 1.4880 CH2CO ******UNIFAC INTERACTION PARAMETER*** 0.000000e+00 6.113000e+01 7.650000e+01 4.764000e+02 CH2 1 -1.112000e+01 0.000000e+00 1.670000e+02 2.577000e+01 ACH 3 4 -6.970000e+01 -1.468000e+02 0.000000e+00 -5.210000e+01 ACCH2 2.676000e+01 1.401000e+02 3.658000e+02 0.000000e+00 CH₂CO 9 Choice of Standard State Fugacity Calculation 1.Empirical Equation by J.Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable)

3.Henry's Constants (noncondensable) 2 n-heptane 1 -1.7613e+01 -4.6698e+03 6.9580e+00 1.4503e-05 75 n-heptane -3.5093e-02 2.6110e-01 toluene 1 7.1440e-02 1.1510e-05 73 toluene 2.0899e+01 -5.7902e+03 -2.0741e-02 2.6460e-01 methyl ethyl ketone 1 3.6725e+01 39 methyl ethyl ketone -1.8254e+02 -1.8187e+02 -1.0790e-01 4.5490e-05 2.5100e-01 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 17 Minimum Temperature at Distillation Tower ...(K) 100.000000 Maximum Temperature at Distillation 700.000000 **(K)** Pressure at Distillation Tower Top......(Kpa) 101.300000 Pressure at Distillation Bottom...... (Kpa) 101.300000 Number of Feed Stream 2 Stage Number of FEED position 6 197.000000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 101.300000 flow rate(mole/time) or composition() component 0.279200 n-heptane: toluene: 0.228400 0.492400 methyl ethyl ketone: Stage Number of FEED position 11 97.000000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 101.300000 flow rate(mole/time) or composition() component n-heptane: 0.000000 toluene: 0.000000 1.000000 methyl ethyl ketone: Maximum Number of Phases in the Tower 2 Number of Heat Input 0 Partial Total Condenser 2. NON-Condenser(default) 0 1 Condenser Condenser INDEX: 2 The ratio of vapor distillate to liquid distillate: 000010.0 Reflex ratio: 1.500000 NON-REBOLIER(default) REBOILER 0 1 **REBOILER INDEX: 1**

The Specified Bottom flow rate for Reboiler: 45.000000 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure...

1. Automatic Initialization

2. Terminal Input Initialization (in C)

Choice of Initial Temperature Procedure.... 1

How many number of component 3 methylcyclohexane toluene phenol ***** ж 1. Wilson Model 2. UNIFAC 3.NRTL * * 11. Virial 12. Trebble-Bishnoi * 13. PengRobinson 14. Soave-RK 15.Ideal Gas ·********** ***** Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 2 Total Sub group 6 For component methylcyclohexane-(1): Total sub group: 3 sub.No Group No. Rk Qk main.No sub main 1 0.9011 0.8480 CH₂ CH3 1 1 2 5 0.6744 0.5400 CH₂ 1 CH2 3 1 0.4469 0.2280 CH2 1 CH For component toluene-(2): Total sub group: 2 sub.No Group No. Rk Ok main main.No sub 0.9680 ACCH3 11 1 1.2663 4 ACCH2 5 0.4000 3 9 0.5313 ACH ACH For component phenol-(3): Total sub group: 2 Qk main.No sub sub.No Group No. Rk main 0.4000 ACH 3 ACH 9 5 0.5313 21 1 0.8952 0.6800 8 ACOH ACOH ******UNIFAC INTERACTION PARAMETER****** 0.000000e+00 7.650000e+01 6.113000e+01 2.789000e+03 CH2 1 -6.970000e+01 0.000000e+00 -1.468000e+02 7.263000e+02 4 ACCH2 -1.112000e+01 1.670000e+02 0.000000e+00 1.397000e+03 ACH 3 3.110000e+02 6.245000e+03 2.043000e+03 0.000000e+00 ACOH 8 Choice of Standard State Fugacity Calculation **1.Empirical Equation by J.Prausnitz** 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) methylcvclohexane 1 74 methylcyclohexane 1.4687e+02 -8.3627e+03 4.1169e-02 -2.3246e+01 -1.6077e-05 2.6990e-01

toluene1 7.1440e-02 -5.7902e+03 -2.0741e-02 1.1510e-05 73 toluene 2.0899e+01 2.6460e-01 phenol 1 8.7395e-02 -7.4933e+01 -9.3166e-06 61 phenol 4.7203e+02 -2.3326e+04 2.7800e-01 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 21 Minimum Temperature at Distillation Tower ...(K) 200.000000 Maximum Temperature at Distillation 500,000000 (K) 101.300000 Pressure at Distillation Tower Top......(Kpa) Pressure at Distillation Bottom...... (Kpa) 101.300000 Number of Feed Stream 2 Stage Number of FEED position 10 Feed Flow rate 76,740000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 323,000000 The Subcooled Liquid Temperature(K): The Subcooled Liquid Pressure(Kpa): 100.000000 component flow rate(mole/time) or composition() methylcyclohexane: 0.000000 0.000000 toluene: 1.000000 phenol: Stage Number of FEED position 15 23.260000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Subcooled Liquid Temperature(K): 333.000000 The Subcooled Liquid Pressure(Kpa): 101.300000 flow rate(mole/time) or composition() component methylcyclohexane: 0.500000 toluene: 0.500000 phenol: 0.000000 Maximum Number of Phases in the Tower 2 Number of Heat Input 0 Partial NON-Condenser(default) **Total Condenser** 2. 1 0 Condenser Condenser INDEX: 2 The ratio of vapor distillate to liquid distillate: 100000.0 Reflex ratio:(For Two-Phase Distillation Calculation) 8.100000 NON-REBOLIER(default) REBOILER 0 1 **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 87.600000 The Number of Stage which has side-withdrawal 0

Choices of Initial Temperature Procedure... 1. Automatic Initialization

2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1
How many number of component 4 n-octane ethylcyclohexane ethylbenzene phenol ****** 1. Wilson Model 2. UNIFAC 3.NRTL * 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 14. Soave-RK 15.Ideal Gas Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 2 Total Sub group 6 For component n-octane-(1): Total sub group: 2 sub.No Group No. Rk Ok main main.No sub CH2 CH3 1 2 0.9011 0.8480 1 0.6744 0.5400 2 8 CH₂ 1 CH2 For component ethylcyclohexane-(2): Total sub group: 3 sub.No Group No. Rk Ok main main.No sub 1 1 0.9011 0.8480 CH₂ 1 CH3 1 CH₂ 2 6 0.6744 0.5400 CH₂ CH₂ . 1 CH 3 1 0.4469 0.2280 For component ethylbenzene-(3): Total sub group: 3 sub.No Group No. Rk main.No sub Ok main 0.9011 0.8480 CH2 1 CH3 1 1 9 5 0.4000 3 0.5313 ACH ACH 0.6600 ACCH2 12 1 1.0396 ACCH2 4 For component phenol-(4): Total sub group: 2 sub.No Group No. Rk Qk main main.No sub 9 5 0.5313 0.4000 ACH ACH 3 21 0.8952 0.6800 ACOH 8 ACOH 1 ******UNIFAC INTERACTION PARAMETER******* 0.000000e+00 6.113000e+01 7.650000e+01 2.789000e+03 CH2 1 -1.112000e+01 0.000000e+00 1.670000e+02 1.397000e+03 ACH 3 -6.970000e+01 -1.468000e+02 0.000000e+00 7.263000e+02 ACCH2 4 3.110000e+02 2.043000e+03 6.245000e+03 0.000000e+00 ACOH 8

Choice of Standard State Fugacity Calculation 1.Empirical Equation by J.Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) n-octane 2 2 ethylcyclohexane ethylbenzene 2 phenol 2 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 30 100.000000 Minimum Temperature at Distillation Tower ...(K) Maximum Temperature at Distillation(K) 500.000000 100.000000 Pressure at Distillation Tower Top......(Kpa) Pressure at Distillation Bottom(Kpa) 100.000000 Number of Feed Stream 2 11 Stage Number of FEED position Feed Flow rate 300.000000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Subcooled Liquid Temperature(K): 323.150000 100.000000 The Subcooled Liquid Pressure(Kpa): flow rate(mole/time) or composition() component 0.000000 n-octane: ethylcyclohexane: 0.000000 ethylbenzene: 0.000000 phenol: 1.000000 Stage Number of FEED position 16 100.000000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Subcooled Liquid Temperature(K): 343.150000 100.000000 The Subcooled Liquid Pressure(Kpa): flow rate(mole/time) or composition() component n-octane: 2.000000 4,000000 ethylcvclohexane: ethylbenzene: 4.000000 phenol: 0.000000 Maximum Number of Phases in the Tower 2 Number of Heat Input 0 NON-Condenser(default) 1 **Total Condenser** 2. Partial 0 Condenser Condenser INDEX: 1 Reflex ratio:(For Two-Phase Distillation Calculation) 8.000000 NON-REBOLIER(default) REBOILER 0 1

REBOILER INDEX: 1

The Specified Bottom flow rate for Reboiler: 300.000000 The Number of Stage which has side-withdrawal 0. Choices of Initial Temperature Procedure...

1. Automatic Initialization

2. Terminal Input Initialization (in C)

Choice of Initial Temperature Procedure.... 1

How many number of component 4 ethane isobutane n-butane . n-hexane ***** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 14. Soave-RK 15.Ideal Gas Choice of thermodynamic model for vapor phase.... 14 ethane propane propane methane 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 0.000000 Choice of thermodynamic model for liquid phase.... 14 Choice of thermodynamic model for liquid phase.... 14 Number of Stage: 13 Minimum Temperature at Distillation Tower ...(K) 250.000000 Maximum Temperature at Distillation 400.000000(K) 1700.000000 Pressure at Distillation Tower Top......(Kpa) Pressure at Distillation Bottom(Kpa) 1700.000000 Number of Feed Stream 2 Stage Number of FEED position 1 50.000000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 1700.000000 flow rate(mole/time) or composition(%) component 0.930000 ethane: 0.040000 isobutane: 0.028000 n-butane: 0.002000 n-hexane: Stage Number of FEED position 3 Feed Flow rate 300.000000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 1700.000000 flow rate(mole/time) or composition(%) component 0.800000 ethane:

isobutane: 0.120000				
n-butane: 0.070000				
n-hexane: 0.010000	•			
Maximum Number of Phases in the Tower	2			
Number of Heat Input 0				
0 NON-Condenser(default) 1	Total Condenser	2.	Partial	
Condenser				
Condenser INDEX: 0	•			
Reflex ratio: 0.000000				
0 NON-REBOLIER(default) 1	REBOILER		•	
REBOILER_INDEX: 1				
spcified bottom flow rate for reboiler:	60.0			
The Number of Stage which has side-withd	rawal 0			
Choices of Initial Temperature Procedure				
1. Automatic Initialization				
2. Terminal Input Initialization (in C)				
Choice of Initial Temperature Procedure	1			

Appendix B

Three Phase Separation Examples

How many number of component 3 n-butanol water n-butyl acetate ***** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi 14. Soave-RK 15.Ideal Gas * 13. PengRobinson Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 3 water n-butyl acetate n-butanol 403.0625 0.0000 315.1645 1229.575 0.000000 1766.282 0.0000 615.0095 -687.336 ********* The INTER-BINARY NRTL ALPHA VALUE ****** 0.000000e+00 4.800000e-01 3.000000e-01 4.800000e-01 0.000000e+00 3.40000e-01 3.00000e-01 3.40000e-01 0.000000e+00 Choice of Standard State Fugacity Calculation 1. Empirical Equation by J. Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) n-butanol 1 1.4677e+00 8.9569e-06 45 n-butanol 2.1605e+01 -8.0399e+03 -2.8619e-02 2.5900e-01 1 water 3.5888e-03 -6.6689e+00 -8.5054e-07 5.7042e+01 -7.0048e+03 86 water 2.3800e-01 n-butyl acetate 1 1.7741e+02 -1.0002e+04 5.7383e-02 -2.8568e+01 -2.5981e-69 n-butyl acetate 05 2.5700e-01 Choice of thermodynamic model for liquid phase.... 3 Number of Stage: 7 Minimum Temperature at Distillation Tower ...(K) 250,000000 Maximum Temperature at Distillation(K) 500.000000 Pressure at Distillation Tower Top......(Kpa) 101.300000 Pressure at Distillation Bottom(Kpa) 101.300000 1 Number of Feed Stream

Stage Number of FEED position 2 Feed Flow rate 50.000000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 101.300000 flow rate(mole/time) or composition() component 0.240000 n-butanol: 0.300000 water: n-butyl acetate: 0.460000 Maximum Number of Phases in the Tower 3 The second liquid phase rich component (water) index: 2 Number of Heat Input 0 NON-Condenser(default) 1 **Total Condenser** 2. Partial 0 Condenser Condenser INDEX: 2 15.600000 The liquid distillate rate: The vapor distillate rate: 0.001000 Reflex ratio: 0.910000 The sidewithdraw ratio for water non-rich (1st)liquid phase 0.01 The sidewithdraw ratio for water rich (2nd)liquid phase 0.9999 REBOILER NON-REBOLIER(default) 1 0 **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 38.840000 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1

How many number of component 3 n-butanol water 1-propanol ****** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 14. Soave-RK 15.Ideal Gas ***** Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 3 1-propanol n-butanol water 0.000 273.9 260.0532 0.000 995.528 1275.24 -25.95 0.000 -222.370********* The INTER-BINARY NRTL ALPHA VALUE ****** 0.000000e+00 4.800000e-01 3.00000e-01 0.000000e+00 4.80000e-01 3.00000e-01 3.00000e-01 0.000000e+00 3.00000e-01 Choice of Standard State Fugacity Calculation 1.Empirical Equation by J.Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) n-butanol 1 1.4677e+00 8.9569e-06 45 n-butanol 2.1605e+01 -8.0399e+03 -2.8619e-02 2.5900e-01 water 1 5.7042e+01 -7.0048e+03 3.5888e-03 -6.6689e+00 -8.5054e-07 86 water 2.3800e-01 1-propanol 1 1.8583e+04 -5.3858e-01 2.0250e+02 2.2251e-04 35 1-propanol -1.0789e+032.4850e-01 Choice of thermodynamic model for liquid phase.... 3 Number of Stage: 12 Minimum Temperature at Distillation Tower ...(K) 300.000000 Maximum Temperature at Distillation 400.000000(K) Pressure at Distillation Tower Top......(Kpa) 101.300000 Pressure at Distillation Bottom(Kpa) 101.300000 Number of Feed Stream 1 4 Stage Number of FEED position 50.000000 Feed Flow rate Feed Thermal Specification:

(1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Subcooled Liquid Temperature(K): 363.000000 The Subcooled Liquid Pressure(Kpa): 101.300000 flow rate(mole/time) or composition() component 0.130000 n-butanol: 0.650000 water: 1-propanol: 0.220000 Maximum Number of Phases in the Tower 3 The second liquid phase rich component (water) index: 2 Number of Heat Input 0 2. Partial NON-Condenser(default) 1 **Total Condenser** 0 Condenser Condenser INDEX: 2 The liquid distillate rate: 29.000000 The vapor distillate rate: 0.001000 Reflex ratio: 3.000000 The sidewithdraw ratio for water non-rich (1st)liquid phase 0.25 The sidewithdraw ratio for water rich (2nd)liquid phase 0.25 NON-REBOLIER(default) 1 REBOILER 0 **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 21.000000 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1

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3 How many number of component ethanol benzene water ***** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 14. Soave-RK 15.Ideal Gas ***** Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 3 benzene ethanol water 0.000000e+00 -0.596620e+02 -5.779150e+01 1.028266e+03 0.000000e+00 -4.211670e+02 6.926060e+02 2.287489e+03 0.000000e+00 ********* The INTER-BINARY NRTL ALPHA VALUE ****** 2.983000e-01 0.000000e+00 2.960000e-01 0.000000e+00 6.400000e-02 2.960000e-01 2.930000e-01 6.400000e-02 0.000000e+00 Choice of Standard State Fugacity Calculation 1.Empirical Equation by J.Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) ethanol1 2.0664e-05 25 ethanol -9.0910e+01 -3.4659e+03 -6.2301e-02 2.0486e+012.5200e-01 1 ' benzene 1.9082e-02 -1.4212e+01 -6.7182e-06 9.7209e+01 -6.9761e+03 60 benzene 2.6960e-01 water 1 5.7042e+01 -7.0048e+03 3.5888e-03 -6.6689e+00 -8.5054e-07 86 water 2.3800e-01 Choice of thermodynamic model for liquid phase.... 3 Number of Stage: 20^{-1} Minimum Temperature at Distillation Tower ...(K) 330.000000 Maximum Temperature at Distillation(K) 360.000000 Pressure at Distillation Tower Top......(Kpa) 101.300000 Pressure at Distillation Bottom(Kpa) 101.300000 Number of Feed Stream 2 Stage Number of FEED position 1 Feed Flow rate 82.101000

Feed Thermal Specification:	
(1) S.L (2) S.V (3) Superhea	ated Vapor (4) Subcooled Liquid 4
The Saturated Liquid Pressur	re(Kpa): 298.0
The Saturated Liquid Pressur	re(Kpa): 101.300000
component	flow rate(mole/time) or composition(%)
ethanol:	0.01
benzene:	0.9
water:	0.11
Stage Number of FEED posit	tion 4
Feed Flow rate 100.00	00000
Feed Thermal Specification:	
(1) S.L (2) S.V (3) Superhea	ated Vapor (4) Subcooled Liquid 1
The Saturated Liquid Pressur	re(Kpa): 101.3
component	flow rate(mole/time) or composition(%)
ethanol:	0.90000
benzene:	0.000000
water:	0.10000
Maximum Number of Phases	s in the Tower 3
The Dich component H2O in	ndex is 3
The Mon component 120 m	
Number of Heat Input 0	
Number of Heat Input 0 0 NON-Condenser(defa	ault) 1 Total Condenser 2. Partial
Number of Heat Input 0 0 NON-Condenser(defa Condenser	ault) 1 Total Condenser 2. Partial
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2	ault) 1 Total Condenser 2. Partial
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate:	ault) 1 Total Condenser 2. Partial
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate:	ault) 1 Total Condenser 2. Partial 117.1 0.001
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate: Reflex ratio: 10.470000	ault) 1 Total Condenser 2. Partial 117.1 0.001
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate: Reflex ratio: 10.470000 The sidewithdraw ratio for w	ault) 1 Total Condenser 2. Partial 117.1 0.001 vater non-rich liquid phase 0.00001
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate: Reflex ratio: 10.470000 The sidewithdraw ratio for w The sidewithdraw ratio for w	ault) 1 Total Condenser 2. Partial 117.1 0.001 vater non-rich liquid phase 0.00001 vater rich liquid phase 0.99999
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate: Reflex ratio: 10.470000 The sidewithdraw ratio for w 0 NON-REBOLIER(defa)	Yault) 1 Total Condenser 2. Partial 117.1 0.001 vater non-rich liquid phase 0.00001 vater rich liquid phase 0.99999 efault) 1 REBOILER
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate: Reflex ratio: 10.470000 The sidewithdraw ratio for w 0 NON-REBOLIER(def REBOILER_INDEX: 1	NumberITotal Condenser2.Partial117.10.001vater non-rich liquid phase0.00001vater rich liquid phase0.99999efault)1REBOILER
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate: Reflex ratio: 10.470000 The sidewithdraw ratio for w 0 NON-REBOLIER(defa REBOILER_INDEX: 1 The Specified Bottom flow r	Yault) 1 Total Condenser 2. Partial 117.1 0.001 vater non-rich liquid phase 0.00001 vater rich liquid phase 0.99999 efault) 1 REBOILER rate for Reboiler: 65.000000
Number of Heat Input 00NON-Condenser(defaCondenserCondenserCondenser_INDEX: 2The liquid distillate rate:The liquid distillate rate:Reflex ratio: 10.470000The sidewithdraw ratio for w0NON-REBOLIER(defaREBOILER_INDEX: 1The Specified Bottom flow rThe Number of Stage which	Autor isITotal Condenser2.Partial117.1 0.0011117.1 0.0011000000000000000000000000000000000000
Number of Heat Input 00NON-Condenser(defaCondenserCondenser_INDEX: 2The liquid distillate rate:The liquid distillate rate:Reflex ratio: 10.470000The sidewithdraw ratio for w0NON-REBOLIER(deREBOILER_INDEX: 1The Specified Bottom flow rThe Number of Stage whichChoices of Initial Temperatu	Yault) 1 Total Condenser 2. Partial 117.1 0.001 vater non-rich liquid phase 0.00001 vater rich liquid phase 0.99999 efault) 1 REBOILER rate for Reboiler: 65.0000000 has side-withdrawal 0 ure Procedure
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate: Reflex ratio: 10.470000 The sidewithdraw ratio for w 0 NON-REBOLIER(defa REBOILER_INDEX: 1 The Specified Bottom flow r The Number of Stage which Choices of Initial Temperatu 1. Automatic Initialization	Yault) 1 Total Condenser 2. Partial 117.1 0.001 vater non-rich liquid phase 0.00001 vater rich liquid phase 0.99999 efault) 1 REBOILER rate for Reboiler: 65.000000 has side-withdrawal 0 ure Procedure
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The liquid distillate rate: Reflex ratio: 10.470000 The sidewithdraw ratio for w 0 NON-REBOLIER(def REBOILER_INDEX: 1 The Specified Bottom flow r The Number of Stage which Choices of Initial Temperatu 1. Automatic Initialization 1. Automatic Initialization	Norm of the second s

How many number of component 3 acetone chloroform water ***** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 14. Soave-RK 15. Ideal Gas ***** Choice of thermodynamic model for vapor phase... 15 Choice of thermodynamic model for liquid phase.... 3 chloroform water acetone 0.000000e+00 -2.544100e+02 4.282200e+02 -3.695000e+01 0.000000e+00 1.009000e+03 1.503600e+03 0.000000e+00 3.225600e+02 ********* The INTER-BINARY NRTL ALPHA VALUE ****** 4.594000e-01 0.000000e+00 3.069000e-01 2.00000e-01 0.000000e+00 3.069000e-01 0.00000e+00 2.000000e-01 4.594000e-01 Choice of Standard State Fugacity Calculation 1. Empirical Equation by J. Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3. Henry's Constants (noncondensable) acetone 1 6.3961e-05 29 acetone -2.3066e+026.8603e+02 -1.4358e-01 4.6384e+01 2.4700e-01 chloroform 1 1.7424e+02 -8.1400e+03 6.5975e-02 -2.9011e+01 -3.0001e-05 8 chloroform 2.7480e-01 water 1 5.7042e+01 -7.0048e+03 3.5888e-03 -6.6689e+00 -8.5054e-07 86 water 2.3800e-01 Choice of thermodynamic model for liquid phase.... 3 Number of Stage: 10 Minimum Temperature at Distillation Tower ...(K) 250.000000 Maximum Temperature at Distillation 500.000000(K) Pressure at Distillation Tower Top......(Kpa) 101.300000 Pressure at Distillation Bottom(Kpa) 101.300000 Number of Feed Stream 2 Stage Number of FEED position 3 Feed Flow rate 50.000000

Feed Thermal Specification:	
(1) S.L (2) S.V (3) Superhe	ated Vapor (4) Subcooled Liquid 2
The Saturated Vapor Pressu	re(Kpa): 101.300000
component	flow rate(mole/time) or composition()
acetone:	0.167000
chloroform:	0.333000
water:	0.500000
Stage Number of FEED pos	ition 4
Feed Flow rate 100.0	00000
Feed Thermal Specification:	
(1) S.L (2) S.V (3) Superhe	ated Vapor (4) Subcooled Liquid 1
The Saturated Liquid Pressu	re(Kpa): 101.300000
component	flow rate(mole/time) or composition()
acetone:	0.600000
chloroform:	0.200000
water:	0.300000
Maximum Number of Phases	s in the Tower 3
The second liquid phase rich	component (water) index: 3
Number of Heat Input 0	
0 NON-Condenser(def	ault) 1 Total Condenser 2. Partial
Condenser	
Condenser_INDEX: 2	
The liquid distillate rate:	40.000000
The vapor distillate rate:	0.001000
Reflex ratio: 2.500000	
The sidewithdraw ratio for v	vater non-rich (1st)liquid phase 0.285000
The sidewithdraw ratio for v	vater rich (2nd)liquid phase 0.285000
0 NON-REBOLIER(d	efault) 1 REBOILER
REBOILER_INDEX: 1	
The Specified Bottom flow 1	rate for Reboiler: 110.000000
The Number of Stage which	has side-withdrawal 0
Choices of Initial Temperatu	re Procedure
1. Automatic Initialization	
2. Terminal Input Initialization	on (in C)
Choice of Initial Temperatur	e Procedure 1

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How many number of component
                                3
2-propanol
water
benzene
******
    1. Wilson Model 2. UNIFAC
                                3.NRTL
                                                          *
*
    11. Virial 12. Trebble-Bishnoi
                                                          ÷
                          14. Soave-RK 15.Ideal Gas
    13. PengRobinson
*****
                             *****
Choice of thermodynamic model for vapor phase.... 15
Choice of thermodynamic model for liquid phase.... 3
                            benzene
   2-propanol
                   water
                         -398.18
  0.000000e+00
                 154.39
                   1297.9
  826.71
             0.0
  978.52
             1110.3 0.0
********* The INTER-BINARY NRTL ALPHA VALUE ******
  0.000000e+00 4.9141000e-01 2.00000e-01
  4.914100e-01 0.000000e+00 2.00000e-01
  2.00000e-01 2.00000e-01 0.000000e+00
Choice of Standard State Fugacity Calculation
1.Empirical Equation by J.Prausnitz
2. Pure Liquid Fugactity and Poynting Correction(condensable)
3.Henry's Constants (noncondensable)
2-propanol
             1
                                                      1.7315e+02
                                                                    1.8922e-04
               -9.1960e+02
                             1.5250e+04
                                         -4.6193e-01
36 2-propanol
2.6900e-01
water 1
                            -7.0048e+03
                                          3.5888e-03
                                                      -6.6689e+00
                                                                   -8.5054e-07
86 water
                5.7042e+01
2.3800e-01
benzene
             1
60 benzene
                9.7209e+01
                            -6.9761e+03
                                          1.9082e-02 -1.4212e+01
                                                                   -6.7182e-06
2.6960e-01
Choice of thermodynamic model for liquid phase.... 3
Number of Stage:
                   10
Minimum Temperature at Distillation Tower ...(K)
                                             330.000000
Maximum Temperature at Distillation
                                   .....(K)
                                             370,000000
Pressure at Distillation Tower Top......(Kpa)
                                             101.300000
Pressure at Distillation Bottom ......(Kpa)
                                             101.300000
Number of Feed Stream
                                2
Stage Number of FEED position
                                5
```

Feed Flow rate 100.00	0000
Feed Thermal Specification:	
(1) S.L (2) S.V (3) Superhea	tted Vapor (4) Subcooled Liquid 1
The Saturated Liquid Pressur	e(Kpa): 101.300000
component	flow rate(mole/time) or composition()
2-propanol:	0.750000
water:	0.250000
benzene:	0.010000
Stage Number of FEED posit	tion 1
Feed Flow rate 35.0	
Feed Thermal Specification:	
(1) S.L (2) S.V (3) Superhea	ated Vapor (4) Subcooled Liquid 1
The Saturated Liquid Pressur	re(Kpa): 101.300000
component	flow rate(mole/time) or composition()
2-propanol:	0.24
water:	0.26
benzene:	0.50
Maximum Number of Phases	in the Tower 3
	$\sim 10^{-1}$
The second liquid phase fich	component (water) index: 2
Number of Heat Input 0	component (water) index. 2
Number of Heat Input 0 0 NON-Condenser(defa	ault) 1 Total Condenser 2. Partial
Number of Heat Input 0 0 NON-Condenser(defa Condenser	ault) 1 Total Condenser 2. Partial
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2	ault) 1 Total Condenser 2. Partial
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate:	ault) 1 Total Condenser 2. Partial
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate:	component (water) index. 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000	ault) 1 Total Condenser 2. Partial 60.000000 0.000100
The second liquid phase fich Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000 The sidewithdraw ratio for w	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000 The sidewithdraw ratio for w The sidewithdraw ratio for w	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1 vater rich (2nd)liquid phase 0.9
Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000 The sidewithdraw ratio for w 0 NON-REBOLIER(defa)	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1 vater rich (2nd)liquid phase 0.9 efault) 1 REBOILER
The second liquid phase fichNumber of Heat Input 00NON-Condenser(defaCondenserCondenserCondenser_INDEX: 2The liquid distillate rate:The vapor distillate rate:Reflex ratio: 12.000000The sidewithdraw ratio for w0NON-REBOLIER(defaREBOILER_INDEX: 1	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1 vater rich (2nd)liquid phase 0.9 efault) 1 REBOILER
The second liquid phase fich Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000 The sidewithdraw ratio for w 0 NON-REBOLIER(de REBOILER_INDEX: 1 The Specified Bottom flow rates	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1 vater rich (2nd)liquid phase 0.9 efault) 1 REBOILER ate for Reboiler: 40.000000
The second liquid phase fich Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000 The sidewithdraw ratio for w 0 NON-REBOLIER(de REBOILER_INDEX: 1 The Specified Bottom flow ratio The Number of Stage which	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1 vater rich (2nd)liquid phase 0.9 efault) 1 REBOILER ate for Reboiler: 40.000000 has side-withdrawal 0
The second liquid phase fich Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000 The sidewithdraw ratio for w 0 NON-REBOLIER(de REBOILER_INDEX: 1 The Specified Bottom flow ratio The Number of Stage which Choices of Initial Temperature	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1 vater rich (2nd)liquid phase 0.9 efault) 1 REBOILER ate for Reboiler: 40.000000 has side-withdrawal 0 re Procedure
The second liquid phase fich Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000 The sidewithdraw ratio for w 0 NON-REBOLIER(def REBOILER_INDEX: 1 The Specified Bottom flow ratio The Number of Stage which Choices of Initial Temperature 1. Automatic Initialization	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1 vater rich (2nd)liquid phase 0.9 efault) 1 REBOILER ate for Reboiler: 40.000000 has side-withdrawal 0 re Procedure
The second liquid phase fich Number of Heat Input 0 0 NON-Condenser(defa Condenser Condenser_INDEX: 2 The liquid distillate rate: The vapor distillate rate: Reflex ratio: 12.000000 The sidewithdraw ratio for w 0 NON-REBOLIER(de REBOILER_INDEX: 1 The Specified Bottom flow rate The Number of Stage which Choices of Initial Temperatur 1. Automatic Initialization 2. Terminal Input Initialization	component (water) index: 2 ault) 1 Total Condenser 2. Partial 60.000000 0.000100 vater non-rich (1st)liquid phase 0.1 vater rich (2nd)liquid phase 0.9 efäult) 1 REBOILER ate for Reboiler: 40.000000 has side-withdrawal 0 re Procedure

How many number of component 3 n-butanol water ethanol ****** 1. Wilson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi 13. PengRobinson 14. Soave-RK 15. Ideal Gas Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 3 water ethanol n-butanol 0.000000e+00 -3.183500e+02 -1.658000e+01 4.267900e+02 0.000000e+00 1.528700e+03 0,000000e+00 1.412000e+01 1.916000e+01 ******** The INTER-BINARY NRTL ALPHA VALUE ***** 3.038000e-01 0.000000e+00 2.000000e-01 0.000000e+00 2.945000e-01 2.000000e-01 0.000000e+00 2.945000e-01 3.038000e-01 Choice of Standard State Fugacity Calculation 1. Empirical Equation by J. Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable) 1 n-butanol 8.9569e-06 1.4677e+00 2.1605e+01 -8.0399e+03 -2.8619e-02 45 n-butanol 2.5900e-01 water 1 3.5888e-03 -6.6689e+00 -8.5054e-07 5.7042e+01 -7.0048e+03 86 water 2.3800e-01 ethanol 1 -9.0910e+01 -3.4659e+03 -6.2301e-02 2.0486e+012.0664e-05 25 ethanol 2.5200e-01 Choice of thermodynamic model for liquid phase.... 3 Number of Stage: 11 300.000000 Minimum Temperature at Distillation Tower ...(K) 450.000000 Maximum Temperature at Distillation(K) Pressure at Distillation Tower Top......(Kpa) 101.300000 Pressure at Distillation Bottom(Kpa) 101.300000 Number of Feed Stream 1 7 Stage Number of FEED position

0.500000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 4 The Saturated Liquid Pressure(K): 325.0000 The Saturated Liquid Pressure(Kpa): 101.300000 flow rate(mole/time) or composition() component 0.030000 n-butanol: water: 0.750000 ethanol: 0.220000 Maximum Number of Phases in the Tower 3 The second liquid phase rich component (water) index: 2 Number of Heat Input 0 Partial Total Condenser 2. 0 NON-Condenser(default) 1 Condenser Condenser INDEX: 2 The liquid distillate rate: 0.140000 The vapor distillate rate: 0.000001 Reflex ratio: 3.000000 The sidewithdraw ratio for water non-rich (1st)liquid phase 0.250000 The sidewithdraw ratio for water rich (2nd)liquid phase 0.250000 REBOILER NON-REBOLIER(default) 0 1 **REBOILER_INDEX: 1** The Specified Bottom flow rate for Reboiler: 0.360000 The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1

How many number of component 4 propylene benzene n-hexane water ***** 1. Wilson Model 2. UNIFAC 3.NRTL * 11. Virial 12. Trebble-Bishnoi 14. Soave-RK 15.Ideal Gas 13. PengRobinson Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 2 Total Sub_group 5 For component propylene-(1): Total sub group: 2 sub.No Group No. Rk. Ok main.No sub main 1.1760 5 1 1.3454 2 CH2=CH C=C 0.9011 0.8480 1 CH3 1 CH2 1 For component benzene-(2): Total sub group: 1 Qk sub.No Group No. Rk main.No sub main 0.4000 0.5313 3 ACH 9 6 ACH For component n-hexane-(3): Total sub group: 2 sub.No Group No. Rk Ok main main.No sub 0.9011 0.8480 2 CH3 1 CH₂ 1 0.6744 0.5400 CH₂ 2 4 CH₂ 1 For component water-(4): Total sub group: 1 sub.No Group No. Rk Ok main.No sub main 0.9200 1.4000 H20 20 1 H₂O 7 ******UNIFAC INTERACTION PARAMETER******* 0.000000e+00 2.520000e+03 3.407000e+02 5.996000e+02 2 C=C -2.000000e+02 0.000000e+00 6.113000e+01 1.318000e+03 CH2 1 -9.478000e+01 -1.112000e+01 0.000000e+00 9.038000e+02 ACH 3 5.117000e+02 5.806000e+02 3.623000e+02 0.000000e+00 H2O 7 Choice of Standard State Fugacity Calculation 1.Empirical Equation by J.Prausnitz 2. Pure Liquid Fugactity and Poynting Correction(condensable) 3.Henry's Constants (noncondensable)

propylene 1 1.0078e+02 -4.3740e+03 3.9936e-02 -1.6503e+01 -1.9271e-05 28 propylene 0.0000e+00 benzene 1 1.9082e-02 -1.4212e+01 -6.7182e-06 9.7209e+01 -6.9761e+03 60 benzene 2.6960e-01 n-hexane 1 8.8924e-05 3.3183e+03 -2.0259e-01 6.8498e+01 70 n-hexane -3.5052e+02 2.6350e-01 water 1 -7.0048e+03 -6.6689e+00 -8.5054e-07 86 water 5.7042e+01 3.5888e-03 2.3800e-01 Choice of thermodynamic model for liquid phase.... 2 Number of Stage: 5 Minimum Temperature at Distillation Tower ...(K) 100.000000 Maximum Temperature at Distillation 500.000000(K) Pressure at Distillation Tower Top......(Kpa) 101.300000 Pressure at Distillation Bottom(Kpa) 101.300000 Number of Feed Stream 1 Stage Number of FEED position 3 Feed Flow rate 200.000000 Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 101.300000 flow rate(mole/time) or composition() component 0.450000 propylene: benzene: 0.300000 n-hexane: 0.200000 0.050000 water: Maximum Number of Phases in the Tower 3 The second liquid phase rich component (water) index: 4 Number of Heat Input 0 Partial NON-Condenser(default) **Total Condenser** 2. 1 0 Condenser Condenser INDEX: 2 The liquid distillate rate: 70.000000 The vapor distillate rate: 0.000010 Reflex ratio: 2.500000 The sidewithdraw ratio for water non-rich (1st)liquid phase 0.285714 The sidewithdraw ratio for water rich (2nd)liquid phase 0.285714 REBOILER NON-REBOLIER(default) 1 0 **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 130.000000 The Number of Stage which has side-withdrawal 0

Choices of Initial Temperature Procedure...

Automatic Initialization
 Terminal Input Initialization (in C)
 Choice of Initial Temperature Procedure.... 1

Appendix C

Reactive Separation Examples

How many number of component 6 sec-butylbenzene m-xylene hexamethylbenzene tert-butylbenzene benzene p-xylene 4.UNIOAC 5. Ideal Solution * 1.Wlson Model 2. UNIFAC 3.NRTL 11. Virial 12. Trebble-Bishnoi 13 PengRobinso 14. Soave-RK 15. Ideal Gas ***** Choice of thermodynamic model for vapor phase.... 15 Choice of thermodynamic model for liquid phase.... 5 Choice of Standard State Fugacity Calculation 1.Empirical Equation by J.Prausnitz 2.Sat.Vapor Pressure Correction(condensable): 1.Antonie; 2.Reid's 3.Henry's Constants (noncondensable) sec-butylbenzene 2 vapor pressure choice: 1 -7.6150e+01 0.0000e+00 100 sec-butylbenzene 1.4949e+01 4.4400e+03 0.0000e+00 0.0000e+00 m-xylene 2 vapor_pressure choice: - 1 101 m-xylene 3.4810e+03 -5.3500e+01 0.0000e+000.0000e+00 1.4329e+01 0.0000e+00 hexamethylbenzene 2 vapor pressure choice: 1 0.0000e+00 101 hexamethylbenzene 1.5988e+01 5.0310e+03 -3.0150e+01 0.0000e+00 0.0000e+00 tert-butylbenzene 2 vapor pressure choice: 1 0.0000e+00 102 tert-butylbenzene 1.5345e+01 4.3680e+03 -3.4150e+01 0.0000e+00 0.0000e+00 2 benzene vapor pressure choice: 1 2.3090e+03 -8.0150e+01 105 benzene 1.3114e+01 0.0000e+00 0.0000e+00 0.0000e+00

p-xylene 2 vapor pressure choice: 1 106 p-xylene 3.5410e+03 -4.9150e+01 0.0000e+00 0.0000e+00 1.4409e+01 0.0000e+00 Choice of thermodynamic model for liquid phase.... 5 Number of Stage: 12 Minimum Temperature at Distillation Tower ...(K) 200.000000 Maximum Temperature at Distillation(K) 500,000000 Pressure at Distillation Tower Top......(Kpa) 5.860000 Pressure at Distillation Bottom(Kpa) 7.2119 Number of Feed Stream 2 2 Stage Number of FEED position 0.790000 Feed Flow rate Feed Thermal Specification: (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid 1 The Saturated Liquid Pressure(Kpa): 5.890000 flow rate(mole/time) or composition() component sec-butylbenzene: 0.665200 m-xylene: 0.00001 hexamethylbenzene: 0.00001 tert-butylbenzene: 0.124800 benzene: 0.00001 0.00001 p-xylene: Stage Number of FEED position 12 1.220000 Feed Flow rate Feed Thermal Specification: 1 (1) S.L (2) S.V (3) Superheated Vapor (4) Subcooled Liquid The Saturated Liquid Pressure(Kpa): 7.2119 flow rate(mole/time) or composition() component sec-butylbenzene: 0.00001 m-xylene: 0.573400 hexamethylbenzene: 0.00001 tert-butylbenzene: 0.00001 benzene: 0.00001 p-xylene: 0.646600 Maximum Number of Phases in the Tower 2 Number of Heat Input 0 Partial NON-Condenser(default) **Total Condenser** 2. 0 1 Condenser Condenser_INDEX: 1 Reflex ratio: 2.00000 NON-REBOLIER(default) REBOILER 0 1 **REBOILER INDEX: 1** The Specified Bottom flow rate for Reboiler: 1.560000

The Number of Stage which has side-withdrawal 0 Choices of Initial Temperature Procedure... 1. Automatic Initialization. 2. Terminal Input Initialization (in C) Choice of Initial Temperature Procedure.... 1 Number of Reactions within the Column: 2 . For Reaction (1)'s stoichometric equation (C1OH14)+ -1 (C8H10)+1 (C12H18)+1 (C1OH14)+ 0 (C6H6)+ 0 -1 (C8H10)+ The Phase Index for the Reaction (1): 2 For Reaction (2)'s stoichometric equation (C1OH14)+ -1 (C1OH14)+1 (C6H6)+ 0 (C8H10)+1 (C12H18)+ -1 0 (C8H10)+ The Phase Index for the Reaction (2): 2 The Stage Number where the Reaction is absent: 10

Appendix D

Derivatives of Model Equations

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Derivatives of equations for reactive distillations

The Jacobian matrix in the proposed simultaneous correction method consists of the derivatives of the model residual functions with respect to the iterative or independent variables. The iterative variables include inverse temperature (1/T), phase fractions (α), phase stability factor (θ) and the overall component flow rate (m).

Component Mass Balance Equations:

$$G_{ij}^{m} = -m_{ij} + F_{ij} + (1 - w_{j+1,1}) \beta_{ij+1,1} m_{ij+1} + \sum_{k=2}^{\pi} (1 - w_{j-1k}) \beta_{ij-1k} m_{ij-1}$$

$$= -m_{ij} + F_{ij} + (1 - w_{j+1,1}) \beta_{ij+1,1} m_{ij+1} - (1 - w_{j-1,1}) \beta_{ij-1,1} m_{ij-1} + \sum_{k=1}^{\pi} (1 - w_{j-1k}) \beta_{ij-1k} m_{ij-1}$$

$$= -m_{ij} + F_{ij} + (1 - w_{j+1,1}) \beta_{ij+1,1} m_{ij+1} - (1 - w_{j-1,1}) \beta_{ij-1,1} m_{ij-1} + m_{ij-1} - \sum_{k=1}^{\pi} w_{j-1k} \beta_{ij-1k} m_{ij-1}$$

where $\sum_{k=1}^{\pi} \beta_{ij-1k} = 1$
 $i = 1...NS$ (number of stages)
 $j = 1...NC$ (number of components)
 $k = 1...\pi$ (number of phases)

$$\frac{\partial G_{ij}^{m}}{\partial m_{ij}} = -1$$

$$\frac{\partial G_{ij}^{m}}{\partial m_{ij+1}} = (1 - w_{j+1,1})\beta_{ij+1,1}$$

$$\frac{\partial G_{ij}^{m}}{\partial m_{ij-1}} = 1 - (1 - w_{j-1,1})\beta_{ij-1,1} - \sum_{k=1}^{\pi} w_{j-1k}\beta_{ij-1k}$$

$$\frac{\partial G_{ij}^{m}}{\partial \frac{1}{T_{j}}} = 0$$

$$\frac{\partial G_{ij}^{m}}{\partial \frac{1}{T_{j+1}}} = (1 - w_{j+1,1}) m_{ij+1} \frac{\partial \beta_{ij+1,1}}{\partial \frac{1}{T_{j+1}}}$$

$$\frac{\partial G_{ij}^{m}}{\partial \frac{1}{T_{j-1}}} = -(1 - w_{j-1,1}) m_{ij-1} \frac{\partial \beta_{ij-1,1}}{\partial \frac{1}{T_{j-1}}} - \sum_{k=1}^{\pi} w_{j-1k} m_{ij-1} \frac{\partial \beta_{ij-1k}}{\partial \frac{1}{T_{j-1}}}$$

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$$\frac{\partial G_{ij}^{m}}{\partial \alpha_{jp}} = 0$$

$$\frac{\partial G_{ij}^{m}}{\partial \alpha_{j+1p}} = (1 - w_{j+1,1}) m_{ij+1} \frac{\partial \beta_{ij+1,1}}{\partial \alpha_{j+1p}}$$

$$\frac{\partial G_{ij}^{m}}{\partial \alpha_{j-1p}} = -(1 - w_{j-1,1}) m_{ij-1} \frac{\partial \beta_{ij-1,1}}{\partial \alpha_{j-1p}} - \sum_{k=1}^{\pi} w_{j-1k} m_{ij-1} \frac{\partial \beta_{ij-1k}}{\partial \alpha_{j-1p}}$$

where $p = 1...\pi$

$$\frac{\partial G_{ij}^{m}}{\partial \theta_{jp}} = 0$$

$$\frac{\partial G_{ij}^{m}}{\partial \theta_{j+1p}} = (1 - w_{j+1,1}) m_{ij+1} \frac{\partial \beta_{ij+1,1}}{\partial \theta_{j+1p}}$$

$$\frac{\partial G_{ij}^{m}}{\partial \theta_{j-1p}} = -(1 - w_{j-1,1}) m_{ij-1} \frac{\partial \beta_{ij-1,1}}{\partial \theta_{j-1p}} - \sum_{k=1}^{\pi} w_{j-1k} m_{ij-1} \frac{\partial \beta_{ij-1,k}}{\partial \theta_{j-1p}}$$

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Energy Balance Equations:

$$G_{j}^{E} = -\sum_{k=1}^{\pi} \sum_{i=1}^{N_{c}} \beta_{ijk} h_{ijk} m_{ij} + \sum_{i=1}^{N_{c}} (1 - w_{j+1,1}) \beta_{ij+1,1} h_{ij+1,1} m_{ij+1}$$
$$+ \sum_{k=2}^{\pi} \sum_{i=1}^{N_{c}} (1 - w_{j-1k}) \beta_{ij-1k} h_{ij-1k} m_{ij-1} + Hf_{j} + Qf_{j}$$

$$\frac{\partial G_j^E}{\partial m_{ij}} = -\sum_{k=1}^{\pi} \beta_{ijk} h_{ijk}$$
$$\frac{\partial G_j^E}{\partial m_{ij+1}} = (1 - w_{j+1,1}) \beta_{ij+1,1} h_{ij+1,1}$$
$$\frac{\partial G_j^E}{\partial m_{ij-1}} = \sum_{k=2}^{\pi} (1 - w_{j-1k}) \beta_{ij-1k} h_{ij-1k}$$

$$\frac{\partial G_{j}^{E}}{\partial \frac{1}{T_{j}}} = -\sum_{k=1}^{\pi} \sum_{i=1}^{N_{c}} \frac{\partial (\beta_{ijk} h_{ijk})}{\partial \frac{1}{T_{j}}} m_{ij}$$

$$\frac{\partial G_{j}^{E}}{\partial \frac{1}{T_{j+1}}} = \sum_{i=1}^{N_{c}} (1 - w_{j+1,1}) m_{ij+1} \frac{\partial (\beta_{ij+1,1} h_{ij+1,1})}{\partial \frac{1}{T_{j+1}}}$$

$$\frac{\partial G_{j}^{E}}{\partial \frac{1}{T_{j-1}}} = \sum_{k=2}^{\pi} \sum_{i=1}^{N_{c}} (1 - w_{j-1k}) m_{ij-1} \frac{\partial (\beta_{ij-1k} h_{ij-1k})}{\partial \frac{1}{T_{j-1}}}$$

The derivatives of $\frac{\partial(\beta_{ijk})}{\partial \frac{1}{T_j}}$ and $\frac{\partial(h_{ijk})}{\partial \frac{1}{T_j}}$ are described later.

$$\frac{\partial G_j^E}{\partial \alpha_{jp}} = -\sum_{k=1}^{\pi} \sum_{i=1}^{N_c} h_{ijk} \ m_{ij} \frac{\partial \beta_{ijk}}{\partial \alpha_{jp}}$$
$$\frac{\partial G_j^E}{\partial \alpha_{j+1p}} = \sum_{i=1}^{N_c} (1 - w_{j+1,1}) \ m_{ij+1} \ h_{ij+1,1} \frac{\partial \beta_{ij+1,1}}{\partial \alpha_{j+1p}}$$
$$\frac{\partial G_j^E}{\partial \alpha_{j-1p}} = \sum_{k=2}^{\pi} \sum_{i=1}^{N_c} (1 - w_{j-1k}) \ m_{ij-1} \ h_{ij-1,1} \frac{\partial \beta_{ij-1k}}{\partial \alpha_{j-1p}}$$

$$\frac{\partial G_{j}^{E}}{\partial \theta_{jp}} = -\sum_{k=1}^{\pi} \sum_{i=1}^{n_{c}} h_{ijk} m_{ij} \frac{\partial \beta_{ijk}}{\partial \theta_{jp}}$$

$$\frac{\partial G_{j}^{E}}{\partial \theta_{j+1p}} = \sum_{i=1}^{n_{c}} (1 - w_{j+1,1}) m_{ij+1} h_{ij+1,1} \frac{\partial \beta_{ij+1,1}}{\partial \theta_{j+1p}}$$

$$\frac{\partial G_{j}^{E}}{\partial \theta_{j-1p}} = \sum_{k=2}^{\pi} \sum_{i=1}^{n_{c}} (1 - w_{j-1k}) m_{ij-1} h_{ij-1,1} \frac{\partial \beta_{ij-1k}}{\partial \theta_{j-1p}}$$

The derivatives of
$$\frac{\partial(\beta_{ijk})}{\partial \alpha_{jp}}$$
 and $\frac{\partial(\beta_{ijk})}{\partial \theta_{jp}}$ are given later.

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Component Summation Equations:

$$G_{jk}^{s} = \sum_{i=1}^{n_{c}} \left(\frac{\beta_{ijk}}{\alpha_{jk}} - \frac{\beta_{ijr}}{\alpha_{jr}} \right) m_{ij}$$

$$\frac{\partial G_{jk}^{s}}{\partial m_{ij}} = \frac{\beta_{ijk}}{\alpha_{jk}} - \frac{\beta_{ijr}}{\alpha_{jr}}$$

$$\frac{\partial G_{jk}^{s}}{\partial \frac{1}{T_{j}}} = \sum_{i=1}^{N_{c}} m_{ij} \left\{ \frac{1}{\alpha_{jk}} \left(\frac{\partial \beta_{ijk}}{\partial \frac{1}{T_{j}}} \right) - \frac{1}{\alpha_{jr}} \left(\frac{\partial \beta_{ijr}}{\partial \frac{1}{T_{j}}} \right) \right\}$$
$$\frac{\partial G_{jk}^{s}}{\partial \alpha_{jp}} = \sum_{i=1}^{N_{c}} m_{ij} \left\{ \frac{\partial \frac{\beta_{ijk}}{\alpha_{jk}}}{\partial \alpha_{jp}} - \frac{\partial \beta_{ijr}}{\partial \alpha_{jp}} \right\}$$

$$\frac{\partial G_{jk}^{s}}{\partial \theta_{jp}} = \sum_{i=1}^{N_{e}} m_{ij} \left\{ \frac{\partial \frac{\beta_{ijk}}{\alpha_{jk}}}{\partial \theta_{jp}} - \frac{\partial \frac{\beta_{ijr}}{\alpha_{jr}}}{\partial \theta_{jp}} \right\}$$

Phase Summation Equations:

$$G_{j}^{ps'} = \sum_{k=1}^{\Pi} \alpha_{jk} - 1$$
$$\frac{\partial G_{j}^{ps}}{\partial \alpha_{jp}} = 1$$

Phase stability Equations:

$$G_{jk}^{ST} \stackrel{\cdot}{=} \frac{\alpha_{jk} \theta_{jk}}{\alpha_{jk} + \theta_{jk}}$$

$$\frac{\partial G_{jk}^{ST}}{\partial \alpha_{jp}} = \delta(p,k) \frac{\theta_{jk}^{2}}{\left(\alpha_{jk} + \theta_{jk}\right)^{2}}$$
$$\frac{\partial G_{jk}^{ST}}{\partial \theta_{jp}} = \delta(p,k) \frac{\alpha_{jk}^{2}}{\left(\alpha_{jk} + \theta_{jk}\right)^{2}}$$

The dependent variable, β , is the component phase fraction. It is defined as a function of the temperature, phase fraction and phase stability factor, that is:

$$\beta_{ijk} = \frac{\alpha_{jk} e^{\theta_{jk}} K_{ijk}}{\sum_{p=1}^{\pi} \alpha_{jp} e^{\theta_{jp}} K_{ijp}}.$$

The derivatives of the variable β with respect to the independent variables are calculated as follow:

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$$\frac{\partial \beta_{ijk}}{\partial \frac{1}{T_j}} = \frac{\partial \left(\frac{\alpha_{jk} e^{\theta_{jk}} K_{ijk}}{\sum\limits_{p=1}^{\pi} \alpha_{jp} e^{\theta_{jp}} K_{ijp}} \right)}{\partial \frac{1}{T_j}}$$
$$= \beta_{ijk} \sum_{p=1}^{\pi} \left\{ \left(\frac{\partial \mathbf{n} K_{ijk}}{\partial \frac{1}{T_j}} - \frac{\partial \mathbf{n} K_{ijp}}{\partial \frac{1}{T_j}} \right) \beta_{ijp} \right\}$$

$$\frac{\partial \beta_{ijk}}{\partial \alpha_{jp}} = \frac{\partial \left(\frac{\alpha_{jk} e^{\theta_{jk}} K_{ijk}}{\sum\limits_{l=1}^{n} \alpha_{jl} e^{\theta_{jl}} K_{ijl}}\right)}{\partial \alpha_{jp}}$$
$$= \frac{\left(\delta(k, p) - \beta_{ijp}\right)\beta_{ijk}}{\alpha_{jp}}$$
$$= \begin{cases} \frac{\left(1 - \beta_{ijp}\right)\beta_{ijp}}{\alpha_{jp}} & k = p \\ \frac{\left(-\beta_{ijp}\right)\beta_{ijk}}{\alpha_{jp}} & k \neq p \end{cases}$$

where

$$\delta(p,k) = \begin{cases} 1 & k = p \\ 0 & k \neq p \end{cases}$$

$$\frac{\partial \beta_{ijk}}{\partial \theta_{jp}} = \frac{\partial \left(\frac{\alpha_{jk} e^{\theta_{jk}} K_{ijk}}{\sum\limits_{l=1}^{\pi} \alpha_{jl} e^{\theta_{jk}} K_{ijl}}\right)}{\partial \theta_{jp}}$$
$$= \left(\delta(k, p) - \beta_{ijp}\right) \beta_{ijk}$$
$$= \alpha_{jp} \frac{\partial \beta_{ijk}}{\partial \theta_{ip}}$$

$$\frac{\partial \mathbf{n} \frac{\beta_{ijk}}{\alpha_{jk}}}{\partial \alpha_{jp}} = \frac{\partial \mathbf{ln} \beta_{ijk}}{\partial \alpha_{jp}} - \frac{\partial \mathbf{ln} \alpha_{jk}}{\partial \alpha_{jp}}$$
$$= \frac{\left(\delta(k, p) - \beta_{ijp}\right)}{\alpha_{jp}} - \frac{\delta(k, p)}{\alpha_{jp}}$$
$$= \frac{-\beta_{ijp}}{\alpha_{jp}}$$

hence

$$\frac{\partial \left(\frac{\beta_{ijk}}{\alpha_{jk}}\right)}{\partial \alpha_{jp}} = \left(\frac{\beta_{ijk}}{\alpha_{jk}}\right) \frac{\partial \ln \frac{\beta_{ijk}}{\alpha_{jk}}}{\partial \alpha_{jp}}$$
$$= \frac{-\beta_{ijp}}{\alpha_{jp}} \frac{\beta_{ijk}}{\alpha_{jk}}$$

$$\frac{\partial \mathbf{n} \frac{\beta_{ijk}}{\alpha_{jk}}}{\partial \theta_{jp}} = \frac{\partial \mathbf{ln} \beta_{ijk}}{\partial \theta_{jp}}$$
$$= \delta(k, p) - \beta_{ijp}$$

hence

$$\frac{\partial \frac{\beta_{ijk}}{\alpha_{jk}}}{\partial \theta_{jp}} = \left(\delta(k,p) - \beta_{ijp}\right) \frac{\beta_{ijk}}{\alpha_{jk}}$$

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In above derivatives, the term $\frac{\beta_{ijk}}{\alpha_{jk}}$ has to be evaluated as one variable so as to

avoid $\frac{0}{0}$ situation when α_{jk} is zero. The term $\frac{\beta_{ijk}}{\alpha_{jk}}$ is calculated as follow:

$$\frac{\beta_{ijk}}{\alpha_{jk}} = \frac{e^{\theta_{jk}} K_{ijk}}{\sum_{l=1}^{\pi} \alpha_{jl} e^{\theta_{jl}} K_{ijl}} \neq \frac{0}{0}$$

The derivatives of K-value with respect to the temperature are calculated from the approximated K-value models, that is

$$\ln K_{ik}(T) = A_{ik} - B_{ik} \frac{1}{T}$$
$$\frac{\partial \ln K_{ik}}{\partial \frac{1}{T}} = -B_{ik}$$

The derivatives of H-value with respect to the temperature are evalued from the simplified H-value model, that is:

$$h_{ik}(T) = h_i^{ig}(T_o) + \int_{T_o}^{T} c p_i^{ig} dT + \Delta h_{ik}(T)$$
$$\Delta h_{ik}(T) = \Delta h_{ik}(T_b) + C_{ik}(T - T_b)$$

and

$$\frac{\partial h_{ik}(T)}{\partial \frac{1}{T}} = -T^2 \frac{\partial h_{ik}(T)}{\partial T}$$
$$\frac{\partial h_{ik}(T)}{\partial T} = c p_i^{ig}(T) + C_{ik}$$

Derivatives of equations for reactive distillations

For the Chemical Reactive Distillation Column, most of derivatives are remained the same since the reaction extents term only appear in the component mass balance equations. The derivatives of the component mass balance with respect to the reaction extents are straightforward:

Component Mass Balance Equations:

$$G_{ij}^{m} = -m_{ij} + F_{ij} + (1 - w_{j+1,1})\beta_{ij+1,1}m_{ij+1} + \sum_{k=2}^{\pi} (1 - w_{j-1k})\beta_{ij-1k}m_{ij-1} + \sum_{r=1}^{NR} \upsilon_{ir}\delta_{jr}$$

$$i = 1...NS \text{ (number of stages)}$$

$$j = 1...NC \text{ (number of components)}$$

$$k = 1...\pi \text{ (number of phases)}$$

$$r = 1...NR \text{ (number of reactions)}$$

$$\frac{\partial G_{ij}^m}{\partial \delta_{jr}} = v_{ir}$$

Chemical Equilibrium Relationship:

$$G_{rj}^{R} = KR_{rj} \prod_{\substack{i=1\\v_{b}<0}}^{N_{c}} a_{ijp}^{*\nu_{b}} - \prod_{\substack{i=1\\v_{b}>0}}^{N_{c}} a_{ijp}^{*\nu_{b}}$$
where

$$a_{ijp} = \frac{\hat{f}_{ijp}}{f_{ijp}^{o}} = \frac{\hat{\phi}_{ijp} P_{j}}{f_{ijp}^{o}} y_{ijp} = \frac{\hat{\phi}_{ijp} P_{j}}{f_{ijp}^{o}} \frac{\beta_{ijp}}{\alpha_{ijp}} \frac{m_{ij}}{\sum_{i=1}^{N_{c}} m_{ij}} = \gamma_{ijp} \frac{\beta_{ijp}}{\alpha_{ijp}} \frac{m_{ij}}{\sum_{i=1}^{N_{c}} m_{ij}}$$
$$\ln(\gamma_{ijp}) = \ln(\frac{\hat{\phi}_{ijp} P_{j}}{f_{ijp}^{o}}) = AR_{ijp} + \frac{BR_{ijp}}{T_{j}}$$

p is the phase index where the reaction occurs

AR and BR are inner parameters which will be updated in the outer loop.

$$\frac{\partial G_{rj}^{R}}{\partial m_{ij}} = -\upsilon_{ir} KR_{rj} \frac{\partial \mathbf{n} a_{ijp}}{\partial m_{ij}} |_{vir < 0} \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} - \upsilon_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial m_{ij}} |_{vir > 0} \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}}} \frac{\partial \mathbf{n}_{ij}}{\partial \mathbf{n}_{ij}} |_{vir < 0}^{N_{c}} a_{ijp}^{*v_{tr}} + KR_{rj} \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (-v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \frac{1}{T_{j}}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \frac{1}{T_{j}}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \frac{1}{T_{j}}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \frac{1}{T_{j}}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \frac{1}{T_{j}}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \frac{1}{T_{j}}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \alpha_{jk}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \alpha_{jk}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \alpha_{jk}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \alpha_{jk}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \alpha_{jk}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \alpha_{jk}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \alpha_{jk}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp}}{\partial \alpha_{jk}}) - \prod_{\substack{i=1 \\ vir < 0}}^{N_{c}} a_{ijp}^{*v_{tr}} \sum_{\substack{i=1 \\ vir < 0}}^{N_{c}} (v_{ir} \frac{\partial \mathbf{n} a_{ijp$$

$$\ln a_{ijp} = AR_{ijp} + \frac{BR_{ijp}}{T_j} + \ln(\frac{\beta_{ijp}}{\alpha_{ijp}}) + \ln(\frac{m_{ij}}{\sum_{i=1}^{N_c} m_{ij}})$$

$$\frac{\partial \ln a_{ijp}}{\partial m_{ij}} = \frac{1}{m_{ij}} - \frac{1}{\sum_{i=1}^{N_c} m_{ij}}$$

$$\frac{\partial \ln a_{ijp}}{\partial \frac{1}{T_j}} = BR_{ijp} + \frac{\ln(\frac{\beta_{ijp}}{\alpha_{ijp}})}{\partial \frac{1}{T_j}}$$

$$\frac{\partial \ln a_{ijp}}{\partial \alpha_{jk}} = \frac{\ln(\frac{\beta_{ijp}}{\alpha_{ijp}})}{\partial \alpha_{jk}}$$

$$\frac{\partial \ln a_{ijp}}{\partial \theta_{jk}} = \frac{\ln(\frac{\beta_{ijp}}{\alpha_{ijp}})}{\partial \theta_{jk}}$$

The derivatives
$$\frac{\ln(\frac{\beta_{ijp}}{\alpha_{ijp}})}{\partial a_{jk}}$$
, $\frac{\ln(\frac{\beta_{ijp}}{\alpha_{ijp}})}{\partial \theta_{jk}}$, $\frac{\ln(\frac{\beta_{ijp}}{\alpha_{ijp}})}{\frac{\beta_{ijp}}{T_i}}$ are given the above section. The chemical

equilibrium constant KR is given as:

$$KR_{rj} = RA + \frac{RB}{T} + RC \cdot T + RD \cdot \ln T$$
$$\frac{\partial KR_{rj}}{\partial \frac{1}{T_i}} = RB - RC \cdot T^2 - RD \cdot T$$

where RA, RB, RC and RD are the equilibrium constants and are required input from users.