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## ***WORKBOOK FOR PROCESS MODELLING***

### ***DISTILLATION***

### ***BATCH, STEADY STATE & CONTINUOUS***

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## References

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## 1.0 Introduction

This workbook reviews the simulation of distillation processes using CHEMCAD software. It discusses thermodynamic model selection considerations and the basic chemical engineering relationships for vapour liquid equilibrium, mass and energy balances.

Methods are discussed for identifying azeotropes and to determine the feasibility of distillation for a given application. Simulations are developed for simple distillation and the more complex heterogeneous azeotrope distillation .

Distillation is used extensively throughout the process industries to achieve a variety of processing objectives:

- Removal of impurities / unwanted components from reaction mixes.
- Water removal and drying.
- Solvent change between reaction stages on multistage syntheses.
- Concentration prior to crystallisation.
- Heat removal control for reactions at reflux.
- Solvent recovery.

Distillation is probably the most difficult process to simulate and control because:

- Separation is a multi-variable process
- Distillation units are frequently subject to process upsets from upstream units.
- Feed conditions, temperature and vapour fraction, have a dramatic effect on performance
- Column pressure variations, likewise, affect performance
- Control loops are interactive rendering stable control impossible if incorrect selection

CHEMCAD has five basic distillation models:

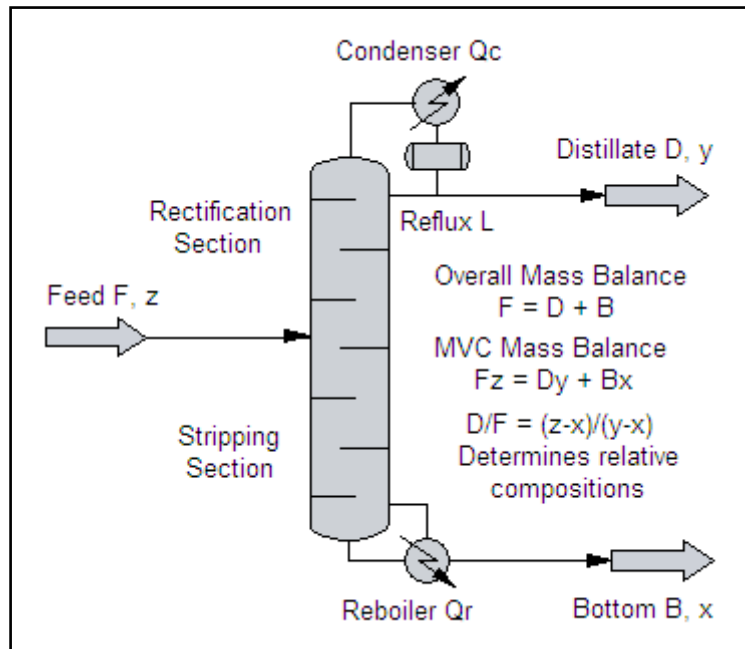
BATCH	Batch distillation based on rigorous Vapor Liquid Equilibrium (VLE) or Mass Transfer models. Simultaneous correction used by SCDS or Inside-Out algorithm used by Tower are available.
SHOR	Short Cut method due to Fenske-Underwood–Gilliland for constant molar bottoms flow.
SCDS	Simultaneous correction distillation with rigorous VLE calculations, particularly suited to activity coefficient models. Applicable for steady state or dynamic models and reactive distillation.
TOWER	Rigorous VLE calculations, particularly suited to equation of state models. Uses the Inside-Out algorithm Applicable for steady state or dynamic models.
TOWER+	Rigorous VLE calculations Allows specification of pump-arounds, side strippers, and side exchangers Useful for modeling fractionating columns Uses the TOWER algorithm as basis

In addition, special modules are available which are used to maintain mass balances, satisfy reaction stoichiometry and control feed, recycle and make-up streams.

1. Component Separator enables component fractions to be split from a stream.
2. Controllers can force a Stream to copy / scale another Stream flow and composition.
3. Stream Reference can fix a recycle flow at a constant value.
4. RAMP controller can change stream parameters and switch streams on or off on a time basis.

**2.0 Fundamentals**  
**2.1 Mass Balance<sup>(1)</sup>**

At steady state the overall material balance must be satisfied for each component. Only one product stream can be set independently making the other product stream a dependent variable. In general, distillate flow is manipulated, directly or through varying reflux ratio, requiring the bottom outlet flow to be adjusted to maintain the material balance which is achieved by holding the reboiler liquid level constant.



The material balance based on the more volatile component (MVC) yields:

$$\frac{D}{F} = \frac{z - x}{y - x}$$

This shows that the flow ratio **D/F** determines the relative composition of each product such that if feed composition **z** changes then **D/F** must be manipulated to maintain constant **x** and **y**.

**2.2 Separation Criteria**

The separation factor **S** for a binary mixture based on the MVC is defined as:

$$S = \left( \frac{y}{1-y} \right) \left( \frac{1-x}{x} \right) \quad y = \frac{S x}{1 + x (S-1)} \quad x = \frac{y}{y + S (1-y)}$$

The relative volatility  $\alpha$  of a binary system consisting of components 1(MVC) and 2 for an ideal system is the ratio of the pure component partial pressures at the same temperature.

$$\alpha = \frac{p_1^0}{p_2^0}$$

$\alpha$  can be obtained by using the Antoine equation or the simplified Cox equation.

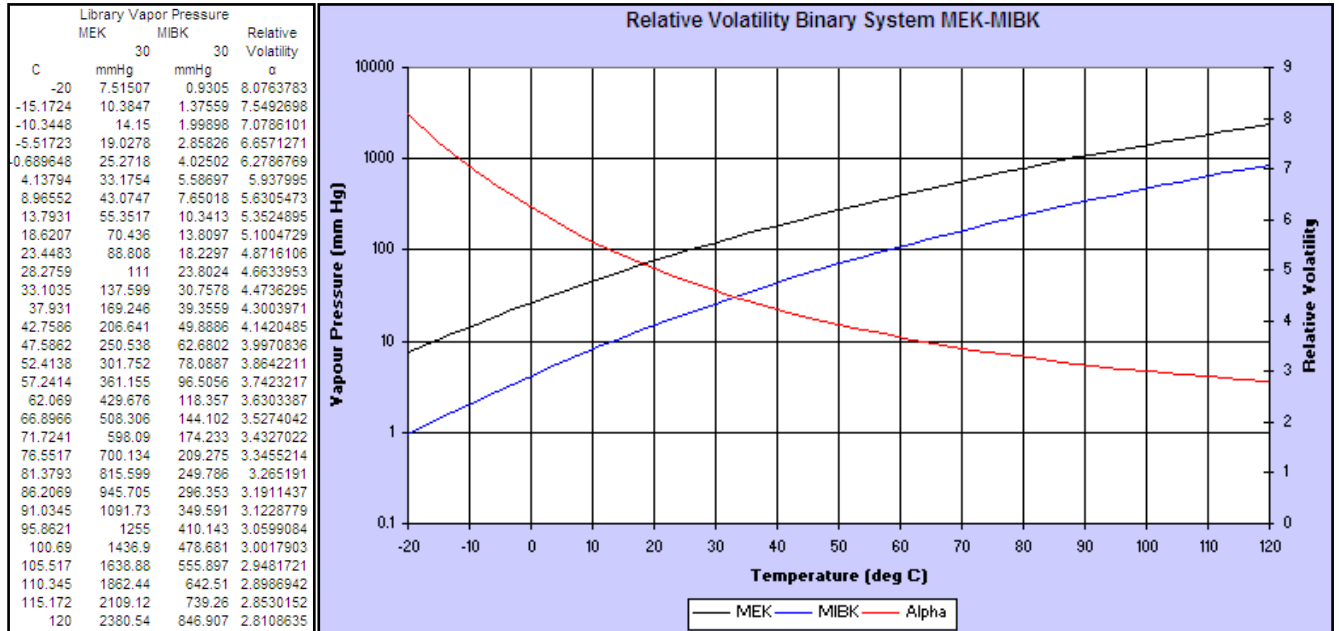
Antoine Equation (mm Hg, °K, ln) 
$$\ln p = A - \frac{B}{C + T}$$

Cox Equation (mmHg, °K, log<sub>10</sub>) 
$$\log_{10}(p) = A_c - \frac{B_c}{T + 230}$$

Antoine Coefficients can be found in CHEMCAD: Thermodynamics > Other Data > Parametric Data. To convert from ln→log<sub>10</sub> for the Cox equation  $A_c=(A/2.303)$ ,  $B_c=(B/2.303)$ ,  $C_c=(273+C/2.303)$ .

## 2.2 Separation Criteria

To obtain  $\alpha$  values with CHEMCAD plot the Antoine or library vapour pressures of the components over the operating temperature range then export Chart > Data to Excel CSV file. The  $\alpha$  values are obtained by dividing component 1(MVC) partial pressures by component 2 partial pressures. Excel Chart Wizard has been used to generate the plots shown.



Consider a tower separating an equi-molar mixture of MEK and MIBK into fractions of 1 mol % MIBK in MEK and vice versa. Feed  $z = 0.5$ , distillate  $y = 0.99$  and bottoms  $x = 0.01$ ; calculating for  $S$  gives:

$$S = \frac{(0.99)(0.99)}{(0.01)(0.01)} = 9801 \quad \quad \quad \frac{D}{F} = \frac{0.5 - 0.01}{0.99 - 0.01} = 0.5$$

We can conclude the following:

1. The composition of both product streams is dependent on  $D/F$
2. Changes in feed composition can be compensated for by manipulating  $D/F$
3. For a constant separation, control of the composition of either product results in control of the composition of the other product due to the relationship between  $x$  and  $y$  being fixed.

## 2.3 Theoretical Stages

The Fenske equation can be used to estimate the minimum number of stages  $N_m$  at total reflux:

$$S = \alpha_i^{N_m} \quad \text{substitution and manipulation gives} \quad \left( \frac{y}{1-y} \right) = \left( \frac{x}{1-x} \right) \alpha_i^{N_m}$$

$$N_m \ln \alpha_i = \ln \left( \frac{y}{1-y} \right) - \ln \left( \frac{x}{1-x} \right) = \ln S$$

For the separation of MEK and MIBK assuming a relative volatility  $\alpha = 3.0$

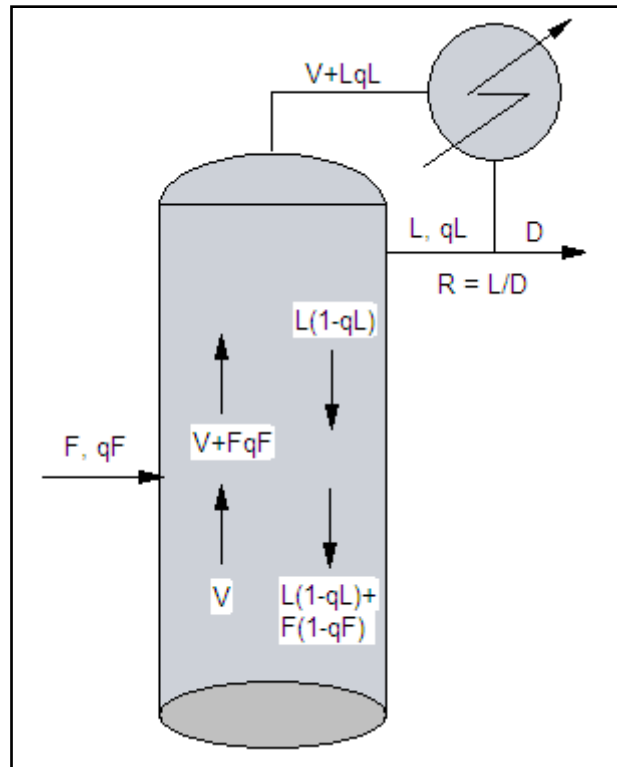
$$N_m = \frac{\ln 9801}{\ln 3.0} = 8.36$$

For a batch distillation we can expect an  $S$  initial value of 99 requiring  $N_m$  of 4.18.

Experience has shown that about  $2.5N_m$  theoretical stages are required for economic operation. In a tray column, efficiencies of 60 to 70% are not uncommon requiring  $3.8N_m$  bearing in mind that the reboiler represents one theoretical stage.<sup>(2)</sup>

## 2.4 Reflux Ratio<sup>(1)</sup>

When it has been established that a given column can achieve the required separation at total reflux, it remains to determine the minimum reflux ratio  $R_m$ . In the diagram the feed and reflux enthalpies  $q_F$  and  $q_L$  are treated as the fraction that is vapourised. At the bubble point  $q = 0$  and for saturated vapour  $q = 1$ ; sub-cooled liquid  $q$  is -ve and superheated vapour  $q > 1$ .



For  $q_L = 0$ , that is no sub cooling of the overheads a mass balance at the top gives:

$$V = L + D$$

Reflux ratio  $R$  is defined as

$$R = \frac{L}{D}$$

Substituting gives

$$\frac{L}{V} = \frac{R}{R+1} = m \quad \text{where } m \text{ is slope of operating line}$$

Underwood's equation for a binary system is given by:-

$$R_m = \left( \frac{1}{\alpha_i - 1} \right) \left[ \frac{y}{z} - \alpha_i \left( \frac{1-z}{1-y} \right) \right]$$

When  $y$  has a high degree of purity  $> 0.995$  mole fraction the above can be simplified to:-

$$R_m = \frac{1}{(\alpha_i - 1) z}$$

For a high separation factor  $S$  a minimum relative volatility of 1.5 is considered reasonable setting a top limit of  $R_m$  at  $2/z$ . For the separation of MEK and MIBK where  $\alpha$  equals 3 we have:

$$R_m = \frac{1}{(3-1) 0.5} = 1:1$$

Batch distillations are started with  $R_m$  equal to that required for a continuous split and it should be noted that  $R_m$  increases as the MVC in the still reduces. Note that at the end of the batch distillation for MEK and MIBK we have  $S=9801$  which results in  $R_m=50:1$ .

## 2.5 Heat Duty<sup>(1)</sup>

The reboiler heat input  $Q_R$  generates a proportional flow of vapour  $V$  :

$$V = \frac{Q_R}{H_V} \text{ where } H_V \text{ is latent heat of vapourisation}$$

Column feed  $F$  is normally below the bubble point (-ve  $q_F$ ) resulting in the vapour flow being reduced by  $Fq_F$ . Reflux is normally sub-cooled (-ve  $q_L$ ) resulting in the vapour flow being reduced by  $Lq_L$  and the internal reflux  $L$  being increased by  $Lq_L$ .

Thus the rectification section vapour flow is  $V+Fq_F$  and  $D = V+Fq_F+Lq_L$

The reboiler heat input must be sufficient to provide the sensible and vapourisation heat duties for the liquid feed, sustain the internal reflux and compensate for heat losses. In addition the  $L/V$  throughout the tower must maintain adequate loading for efficient mass transfer.

Reboiler duty  $Q_R = H_F F(1-q_F) + H_D L(1-q_L) - H_B B + \text{Losses}$

Condenser duty  $Q_C = (H_D + C_P \Delta t_{sub})(V + Fq_F + Lq_L) = (H_D + C_P \Delta t_{sub})(L + D)$

## 2.6 Pressure<sup>(2)</sup>

Vacuum distillation is frequently used to achieve an improved relative volatility or to limit the temperature for sensitive materials. The reduced temperature has a further benefit in increasing the  $\Delta T$  at the reboiler and increasing the thermal efficiency of the factory.

Operating under reduced pressure reduces the vapour density which leads to an earlier onset of flooding requiring an increase in the tower diameter. Reduced pressure operation requires special consideration for pump selection particularly for reboiler forced circulation. Inert gas is also required to break vacuum.

The vacuum achievable with liquid ring vacuum pumps depends on the physical properties and temperature of the sealing fluid. Water can achieve 25 mmHg at 15°C ( $p_{15} = 12.8$  mmHg). Vapour fractions above 50% will result in damage.

Lower pressures can be achieved using steam ejectors in combination with the liquid ring vacuum pump. Multiple stage steam ejectors can achieve 2–15 mmHg.

The composition of an azeotrope varies with absolute pressure. This effect is used to advantage for water-solvent mixtures such as MEK and THF where the water content increases with increasing pressure. Thus two columns, at different pressures, can be run in series to obtain a dry solvent without using an entrainer.

### 3.0 Thermodynamics<sup>(2, 7)</sup>

#### 3.1 Activity Coefficients

The effect of the activity coefficient  $\gamma$  on the relative volatility  $\alpha$  is shown by considering the following:

$$p_1 = \gamma_1 x_1 p_1^0 \quad \text{and} \quad p_2 = \gamma_2 x_2 p_2^0$$

$$\alpha = \frac{\gamma_1 p_1^0}{\gamma_2 p_2^0} = \alpha^0 \frac{\gamma_1}{\gamma_2} \quad \text{where } \alpha^0 \text{ is the ideal mixture value}$$

At the column top where the MVC(1) is nearly pure  $\gamma_1 = 1$  the equation reduces to  $\alpha = \frac{\alpha^0}{\gamma_2}$

Since  $\gamma > 1$  is the usual situation the actual relative volatility is often very much less than the ideal relative volatility particularly at the column top. In the normal range of industrial solvents  $\gamma$  is usually little affected by temperature and pressure.

Values of  $\gamma$  can be calculated throughout the concentration range using van Laar's equation and by reference to the extensive DECHEMA data bank to obtain values of parameter  $A_{xy}$ .

$$\ln \gamma_1 = A_{12} \left( \frac{1}{1 + \frac{A_{12}x_1}{A_{21}x_2}} \right)^2$$

Where  $A_{12} = \ln \gamma_1^\infty$  with  $\infty$  representing infinite dilution

Values of  $\gamma$  can also be calculated at an azeotrope which is very useful due to the extensive azeotropic data available in the literature.

At an azeotrope we have:

$$x_1 = y_1 \quad \text{giving} \quad y_1 P = x_1 \gamma_1 p_1^0 \quad \text{resulting in} \quad \gamma_1 = \frac{P}{p_1^0}$$

Members of homologous series (e.g. benzene, toluene, xylene) tend to form ideal mixtures in which the activity coefficient  $\gamma$  is close to 1 throughout the concentration range. In solvent recovery it is rare to come across a mixture of homologues.

For a multi-component organic-water system, with regressed vapor pressure data, the first choice would be NRTL. An equation of state is unsuitable unless the accentric factor is tuned.

Polar non-electrolyte solutions must be modelled using activity coefficient methods, which require bips for improved accuracy. The vapor phase is taken to be a regular solution giving:

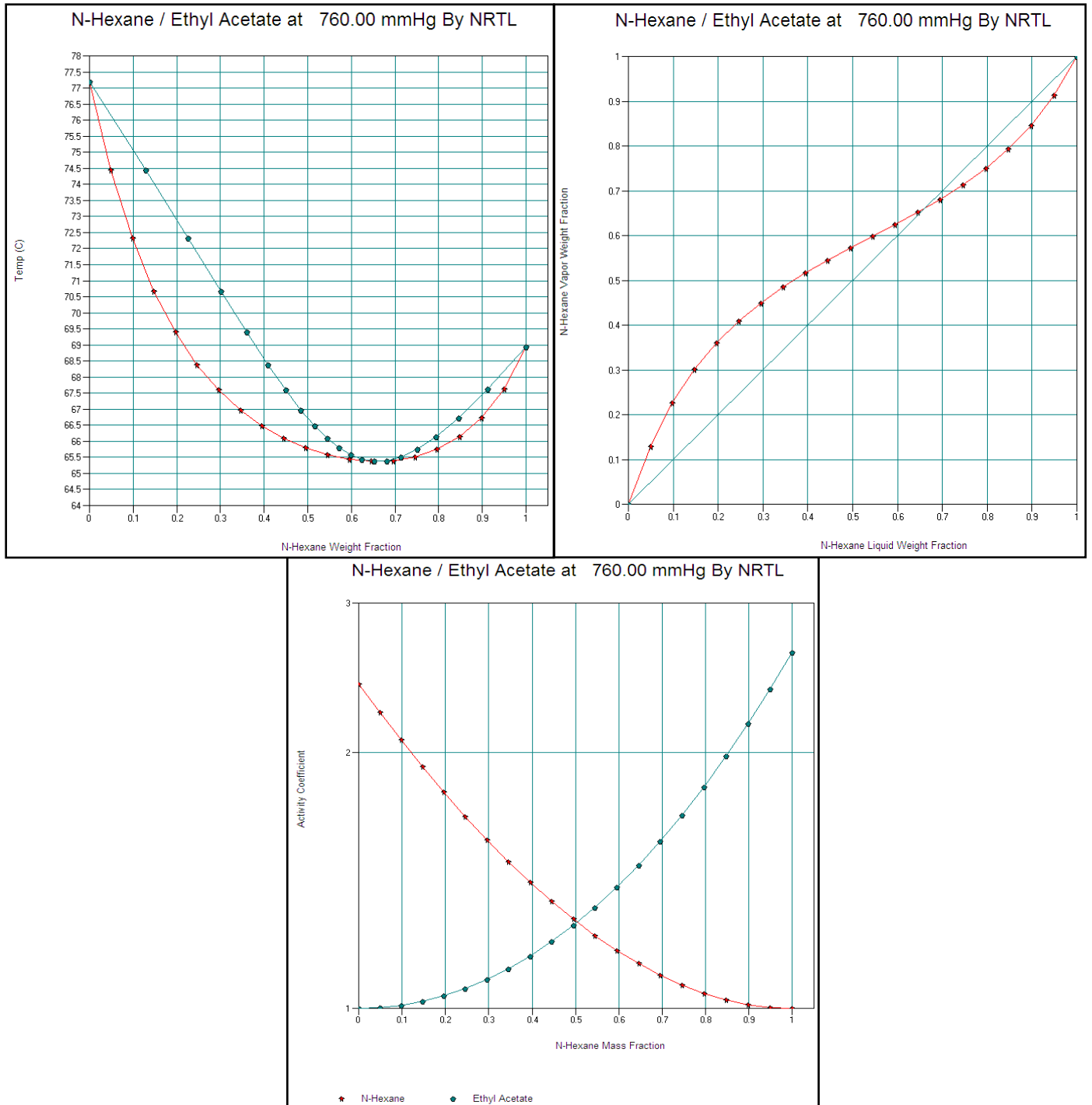
$$K_i = \frac{y_i}{x_i} = \frac{\phi_{li}}{\phi_{vi}} = \frac{\gamma_i f_{li}^0}{\phi_{vi} P}$$

Where

- $f_{li}^0$  standard fugacity comp i
- $\phi_{vi}$  fugacity coefficient vapour comp i
- $\gamma_i$  activity coefficient liquid comp i

3.1 Activity Coefficients

The VLE diagrams for the n-Hexane / Ethyl Acetate system are shown where it can be seen that the model is reasonably accurate against known data. CHEMCAD TPxy plot facilities also provides a plot of the activity coefficients and their influence can be seen at the column bottom and top.



### 3.2 Thermodynamic Model Selection <sup>(D.Hill)</sup>

There are two activity coefficient methods:

- 1) Based on subgroups
- 2) Based on binary interaction parameters (bips)

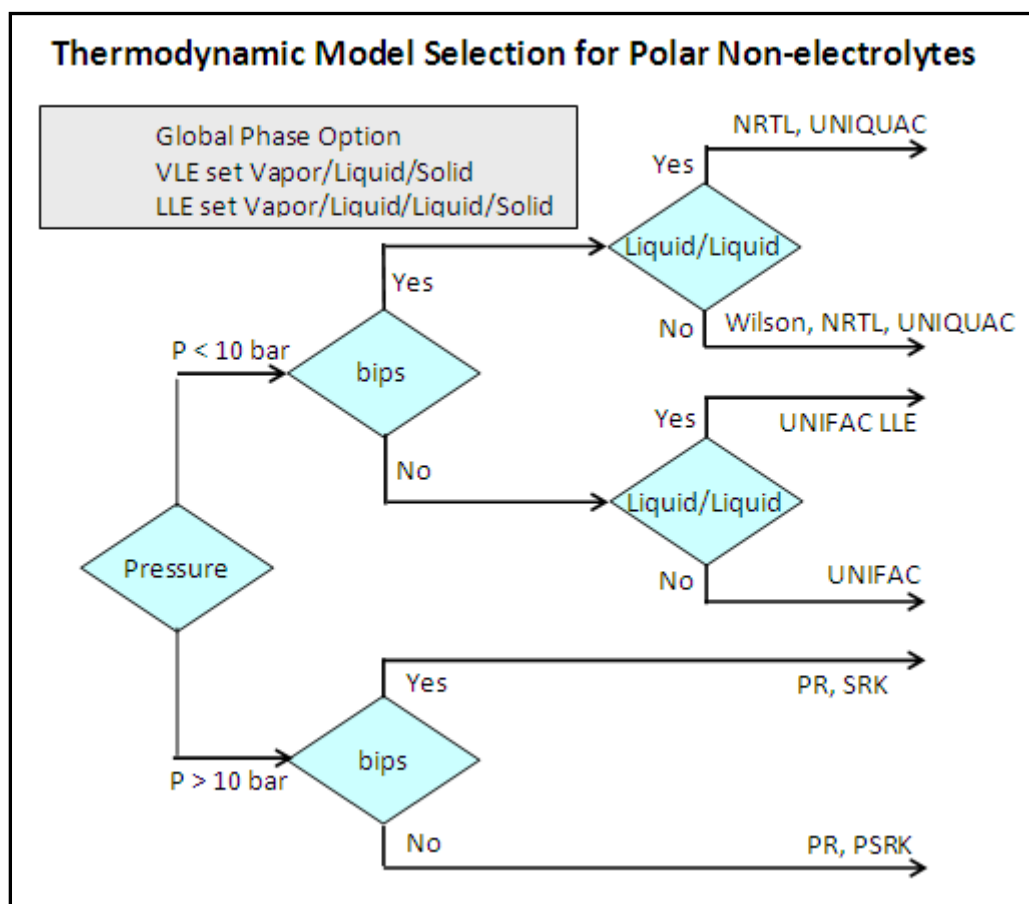
Subgroup methods, such as UNIFAC, build the interaction parameters between subgroups of molecular structures. Using UNIFAC, ethanol and water display an azeotrope because the OH<sup>-</sup> group and water have an interaction parameter that leads to a subgroup. If the subgroups are available Modified UNIFAC is better than UNIFAC. PSRK is better than UNIFAC if light gases are present as some light gases have PSRK specific subgroups.

In the bip method non ideal interaction behaviour is only indicated if there is a bip identified. NRTL is considered the most advanced of the bip methods. If bips are available for the various methods (NRTL, Wilson, van Laar) NRTL is preferred. In practice, users and references may use Wilson bips that have fitted the system successfully and should be considered for further use.

Activity coefficient methods in CHEMCAD include NRTL (Non Random Two Liquid, 3 parameter), UNIFAC (Universal Functional Activity Coefficient), PSRK (Predictive Soave Redlich Kwong), UNIQUAC (Universal Quasi Chemical Parameters), Wilson (1 parameter), T.K.Wilson, van Laar (2 parameter), Margules (3 parameter) and GMAC (Generalised Multicomponent Activity Coefficient). It is worth noting that PSRK is an adaptation of UNIFAC being a combined EoS and activity coefficient method in which SRK is used for the vapour and UNIFAC for the liquid and has special subgroups for the light gases. The older Margules and van Laar methods are less frequently used now, with preference being for the newer methods.

Use Wilson, NRTL or UNIQUAC when sufficient data is available (>50%) and UNIFAC when data is incomplete (<50%) with Wilson only being applicable for completely miscible liquids. If completing an NRTL bip matrix using UNIFAC use UNIFAC LLE if heterogeneous azeotropes are present.

The decision tree <sup>(1)</sup> shows a general basis for the selection of the thermodynamic model:

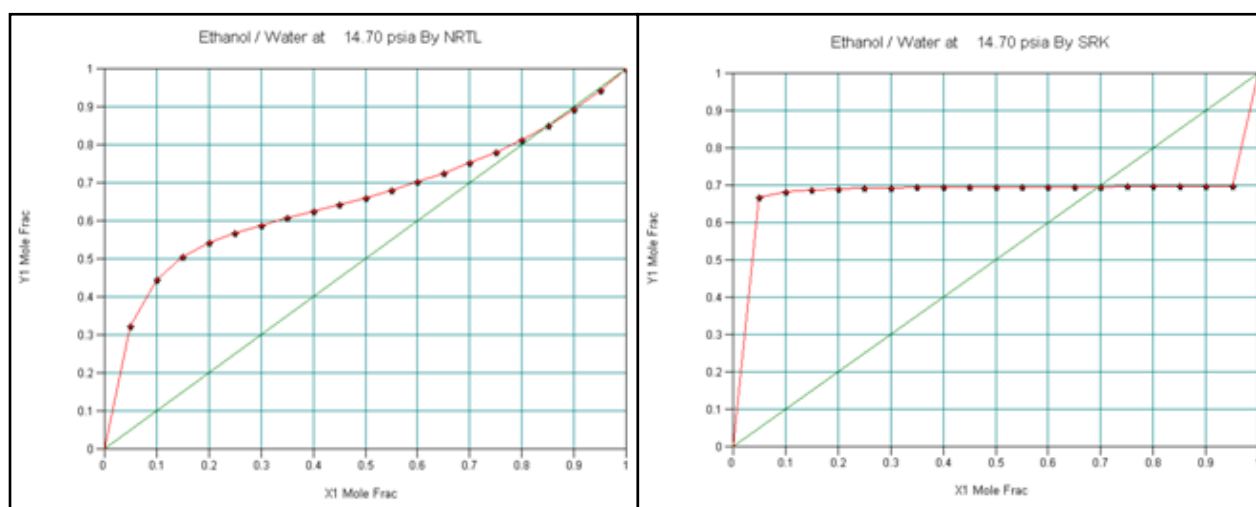


### 3.2 Thermodynamic Model Selection

It is worth noting that when using the pseudo binary method to predict the behaviour of a mixture based on the behaviour of pairs of components to each other, the situation may occur where this may not be valid (phase partitioning, ternary azeotropes) because the system behaves significantly differently than the pseudo binary predicts. When importing bips from UNIFAC this can be a danger. **When uncertain of bips it is not wise to make column specifications based on composition.**

Separation units are highly dependent on the selection of the K value model which are used to calculate the composition of the liquid and vapor phases of a mixture at a given temperature and pressure.

xy plots of the system water – ethanol using NRTL and SRK, respectively are shown below. There is a significant difference between the separations obtained in a simulation using these two models. For this system, NRTL would be a reasonable choice while SRK would be unrealistic. A column model will frequently not run with an unrealistic thermodynamic selection.



### 3.3 Column Convergence

Difficulties experienced in achieving simulation convergence are frequently due to an inappropriate thermodynamic model selection, inappropriate column specification or too rigid convergence constraints. In particular, obtaining column convergence when trying to reach product specifications in pinch zones as in the EtOH / Water system xy diagram for target EtOH mole fractions > 0.8.

There are several courses of action available:

1. Increase the number of default iterations on the Convergence section.
2. Applying a damping factor of 0.6 can sometimes help.
3. Consider using the mass transfer model which is now also available in CC-BATCH.
4. Apply realistic stage efficiencies (or mass transfer model) as actual stages will not be ideal.
5. Slacken target product specifications

Trace facilities are provided in Convergence to identify problems such as if a stage is drying up, too much or too little heat or too high or low a vapour flow in the column.

#### 4.0 Vapour Liquid Equilibrium

##### 4.1 Bubble Point and Dew Point<sup>(4)</sup>

When setting up a Flash UnitOp applying the phase rule<sup>(7)</sup> will ensure that the relevant flash conditions are being set. The stream flash calculation can be used to determine the boiling point and dew point of mixtures with and without inerts present by applying the following:

The bubble point of a liquid at a set pressure is calculated by flashing at a vapour fraction of 0. The dew point of a vapour at a set pressure is calculated by flashing at a vapour fraction of 1. Pure component bubble and dew points are identical so flashing at vapour fractions 0 or 1 yields the same result.

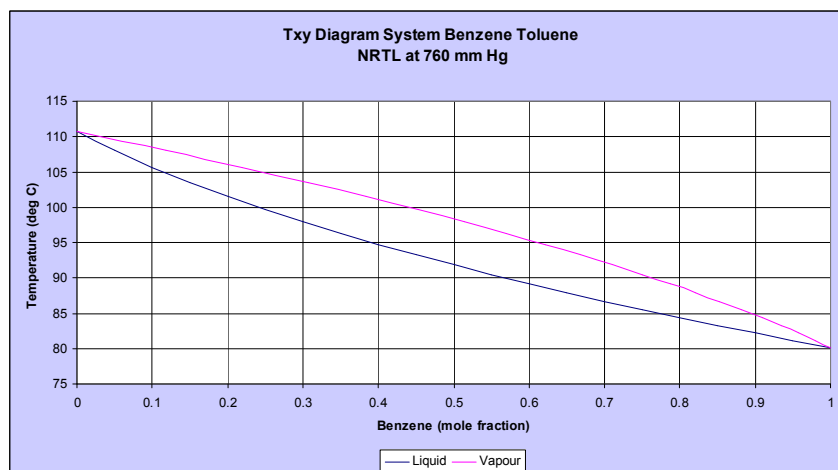
The bubble point of a mixture is determined by trial and error from value of  $T_{bp}$  that satisfies:

$$P = \sum x_i P_i^*(T_{bp})$$

The dew point of a mixture is determined by trial and error from value of  $T_{dp}$  that satisfies:

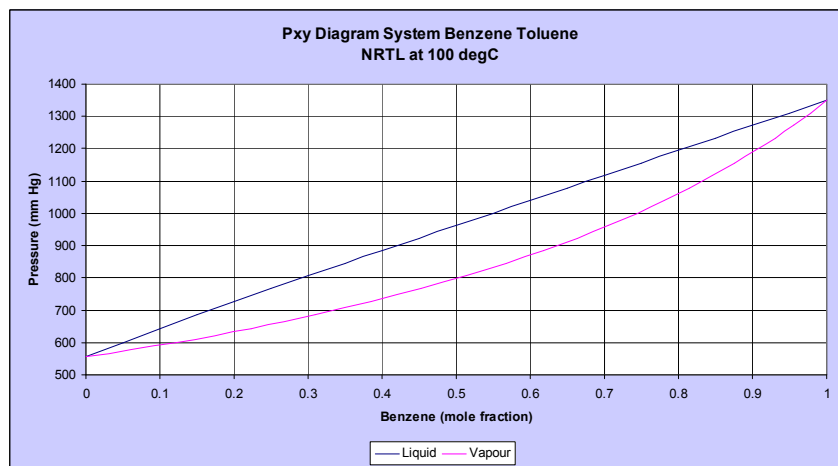
$$\sum \left( \frac{y_i P}{P_i^*(T_{dp})} \right) = 1$$

Consider a Benzene / Toluene system, a near ideal mixture. The Txy diagram at constant pressure enables the bubble point for a given composition to be read from the liquid curve and the dew point to be read from the vapour curve.



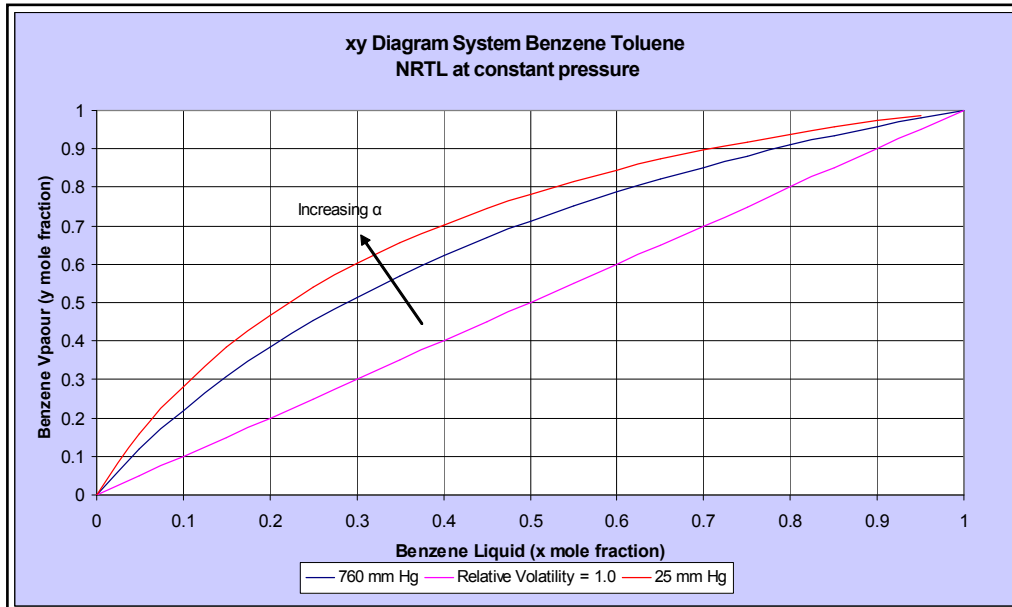
Consider the heating of a 40 mol%(x) benzene and 60 mol% toluene liquid mixture. The starting bubble point is 95°C and the vapour composition will be 62%(y) benzene. If continued until remaining liquid contains 25 mol%(x) benzene the final temperature will be 101°C.

The Pxy (boiling point) diagram at constant temperature provides the equilibrium pressure.



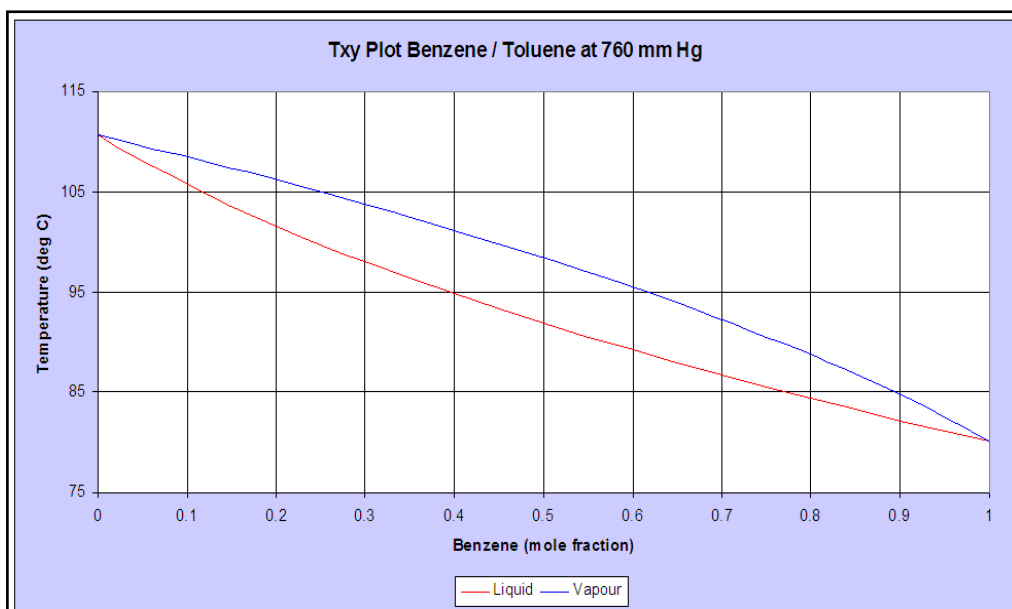
## 4.2 TPxy Plots

TPxy diagrams provide a very useful source of information in relation to the suitability of the K-value selected and the problems presented for the proposed separation. In addition to the plots shown above the vapour liquid equilibrium xy diagram for the more volatile component is also used to analyse the distillation process.



It can be seen that as the pressure is reduced the relative volatility increases which enhances the separation in consequence less theoretical stages are required.

TPxy diagrams are plotted using the K-value method selected and the vapour liquid equilibrium tested against known data for the pure components and the presence of azeotropes.



### 4.3 Residue Curve Mapping<sup>(9, 10)</sup>

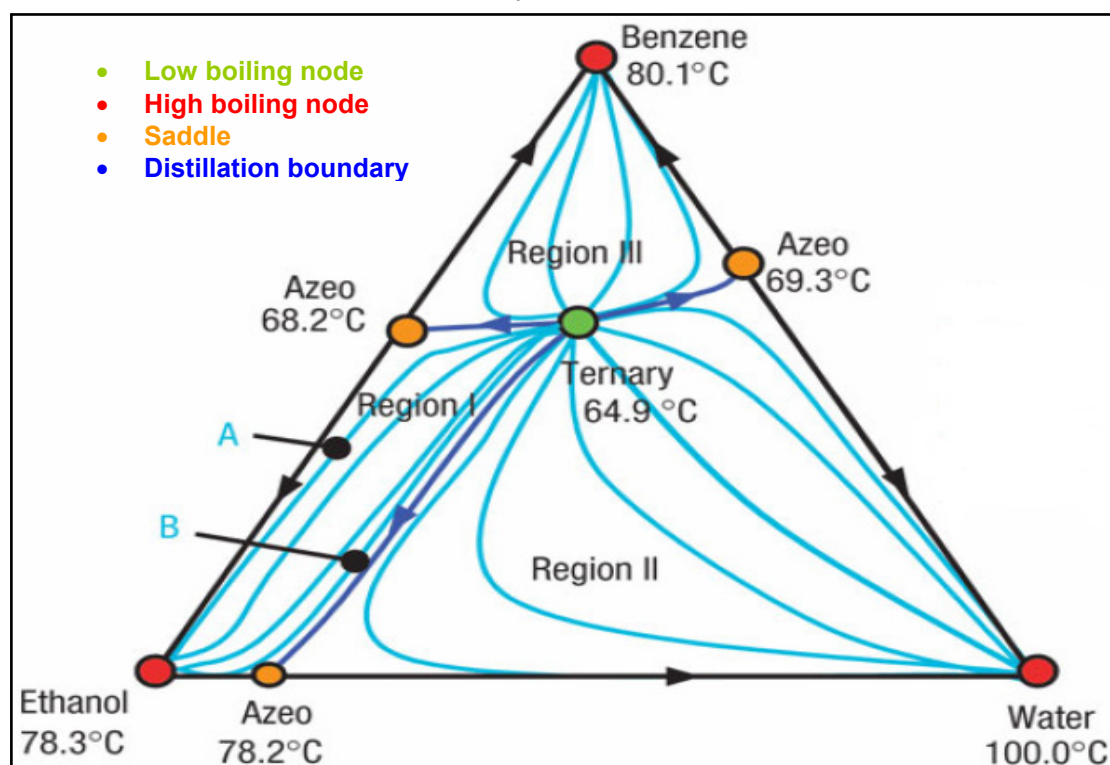
For ternary mixtures a plot of liquid compositions in a simple distillation on a ternary set of axes is known as a residue curve. The residue curve is defined as being the locus of the liquid composition remaining behind in the still bottoms during a simple equilibrium distillation process. Different residue curves are obtained by starting with different liquid compositions. This family of curves is known as a Residue Curve Map (RCM)

All residue curves originate at low-boiling pure components or azeotropic compositions (low-boiling nodes) and end at high boiling compositions (high-boiling nodes). An RCM with more than one origin for residue curves has more than one distillation region. The ethanol/water/benzene system shown has three distillation regions.

Intermediate boiling pure components or azeotropes that are not nodes are called saddles. In a distillation region (three sided) with one saddle, all residue curves track back toward the solitary saddle. However in a region with two non-adjacent saddles (four sided) some residue curves track toward one saddle whilst others track towards the other saddle (curves A and B).

The RCM, together with the mass balance, identifies feasible product regions as the distillate and bottoms will lie on the same residue curve which must be in the same distillation region. For heterogeneous azeotropes, overlaying the RCM with the liquid / liquid phase equilibrium (binodal) diagram indicates valid operational conditions.

In operation, it is better not to try to closely approach the composition of a node but to allow the distillate composition to float more freely with feed and reflux. For the system shown it has been found that feed variations are dampened by allowing the reflux of both phases from the decanter (see Section 7.0). In simulation specifying excessive staging or reflux will cause convergence problems as this constrains the distillate composition.

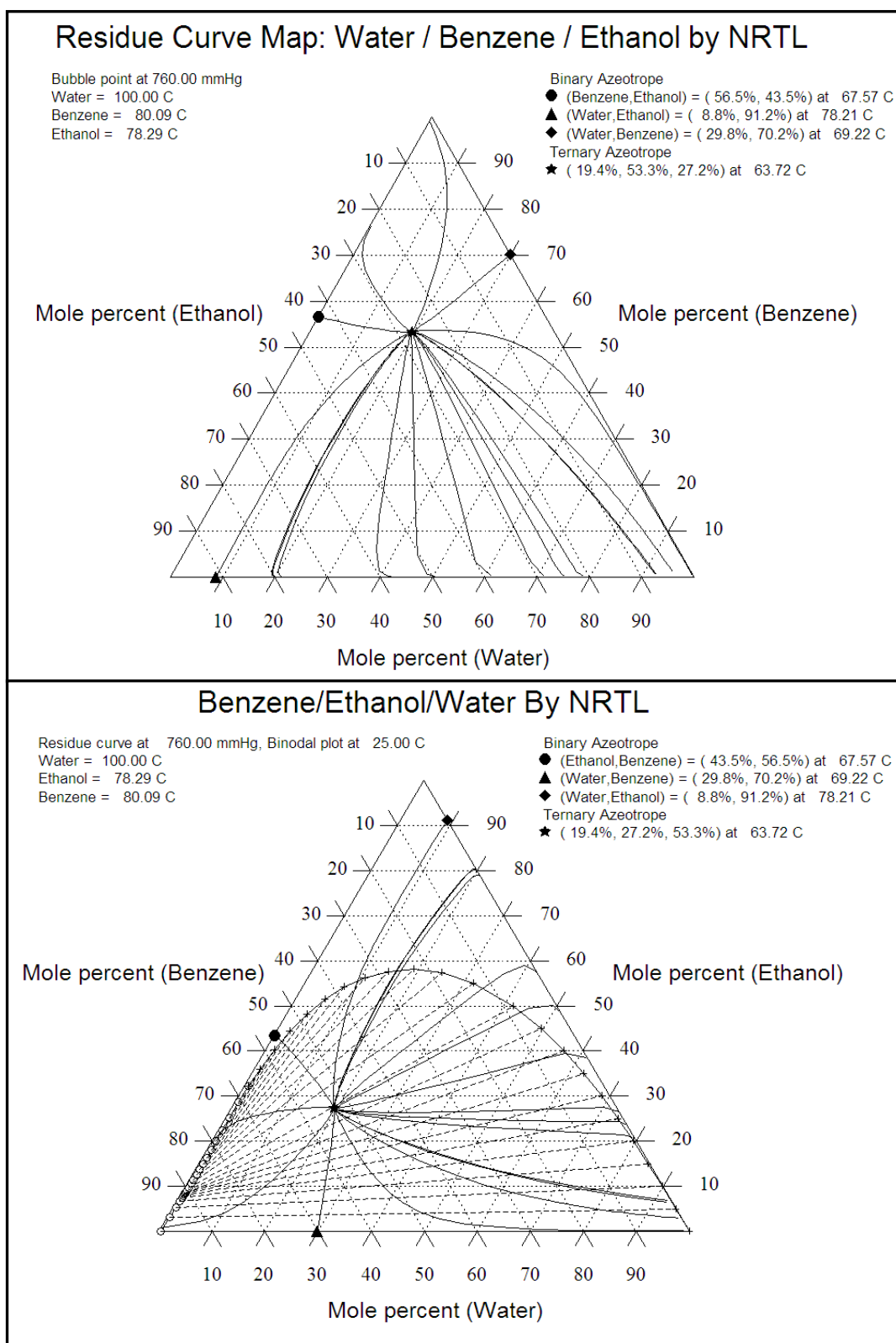


In the RCM shown, we have three binary and one ternary minimum boiling azeotropes. Only one of the binary azeotropes and the ternary azeotrope are heterogeneous. Each pure component is a high-boiling node in one of the three distillation regions, with the ternary being the low-boiling node in all three regions.

Pure ethanol is only obtainable within region 1. Exploitation of the liquid/liquid equilibrium allows us to cross over the distillation boundaries between regions 1, II and III to obtain a benzene rich stream.

4.3 Residue Curve Mapping

A convenient distillate composition in the two phase LLE region is the ternary azeotrope, being the low boiling node in all three regions. The organic layer from the ternary azeotrope is in region III and the aqueous layer is in region II, note that the organic layer can be mixed with the feed to produce a composition in region 1. The RCM and RCM with Binodal plots shown below are obtained from the CHEMCAD Plot facilities.



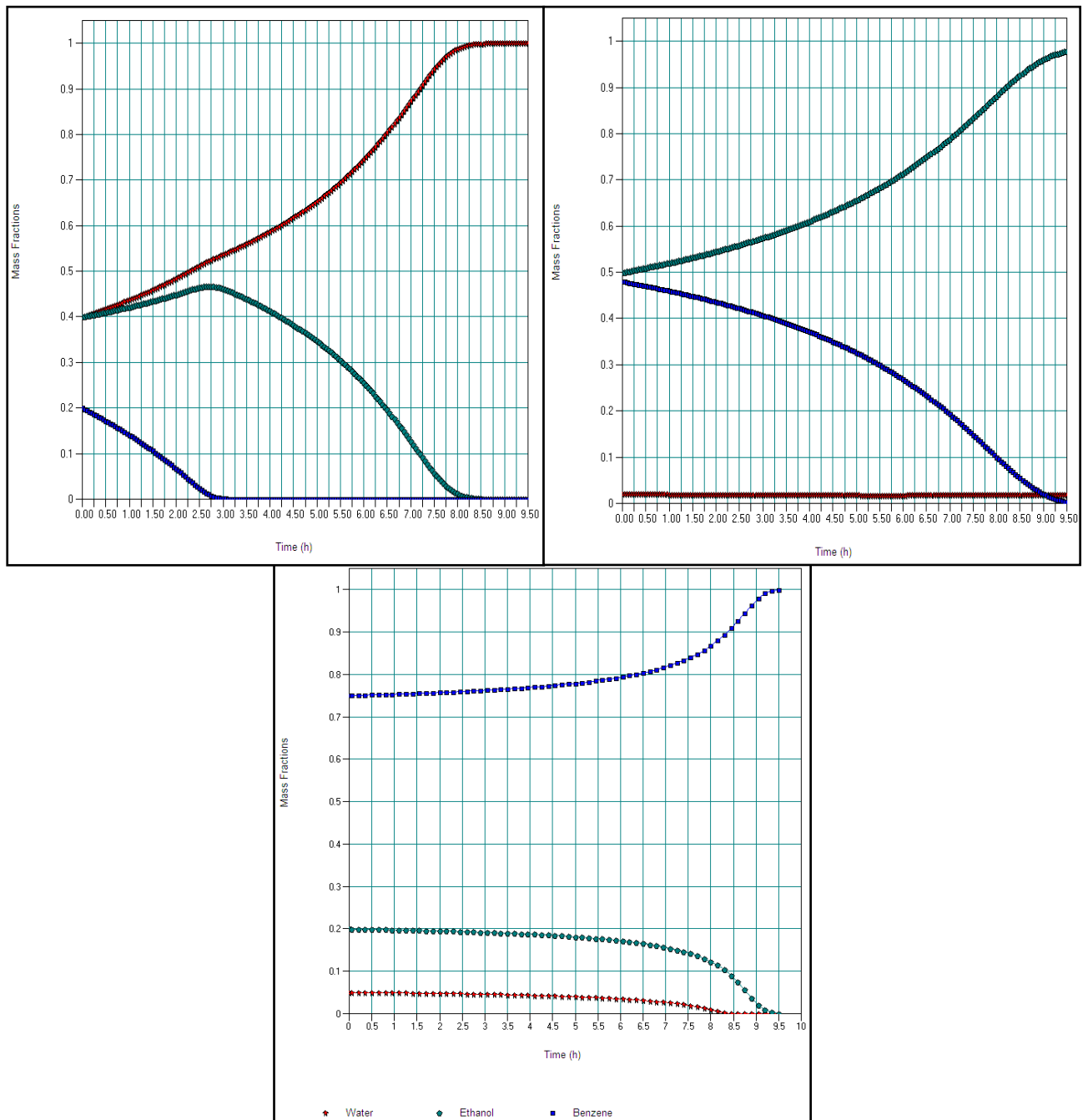
4.3 Residue Curve Mapping<sup>(9, 10)</sup>

CHEMCAD CC-BATCH can be used to obtain the residue curve starting from a known initial composition for the ethanol/water/benzene system.

The Thermodynamics K-model was set for NRTL with Global Phase Option V/L/L/S and the binary interaction parameter matrix filled with UNIFAC LLE.

The distillation used 2 stages to represent the reboiler and condenser, the distillate mass rate was set low at 10 kg/h with reflux was set at 0.001 to give little reflux.

Set the initial still composition in the distillation region of interest and start at total reflux with vapour fraction at 0. The residue curves are shown for distillations starting from each of the three distillation regions.



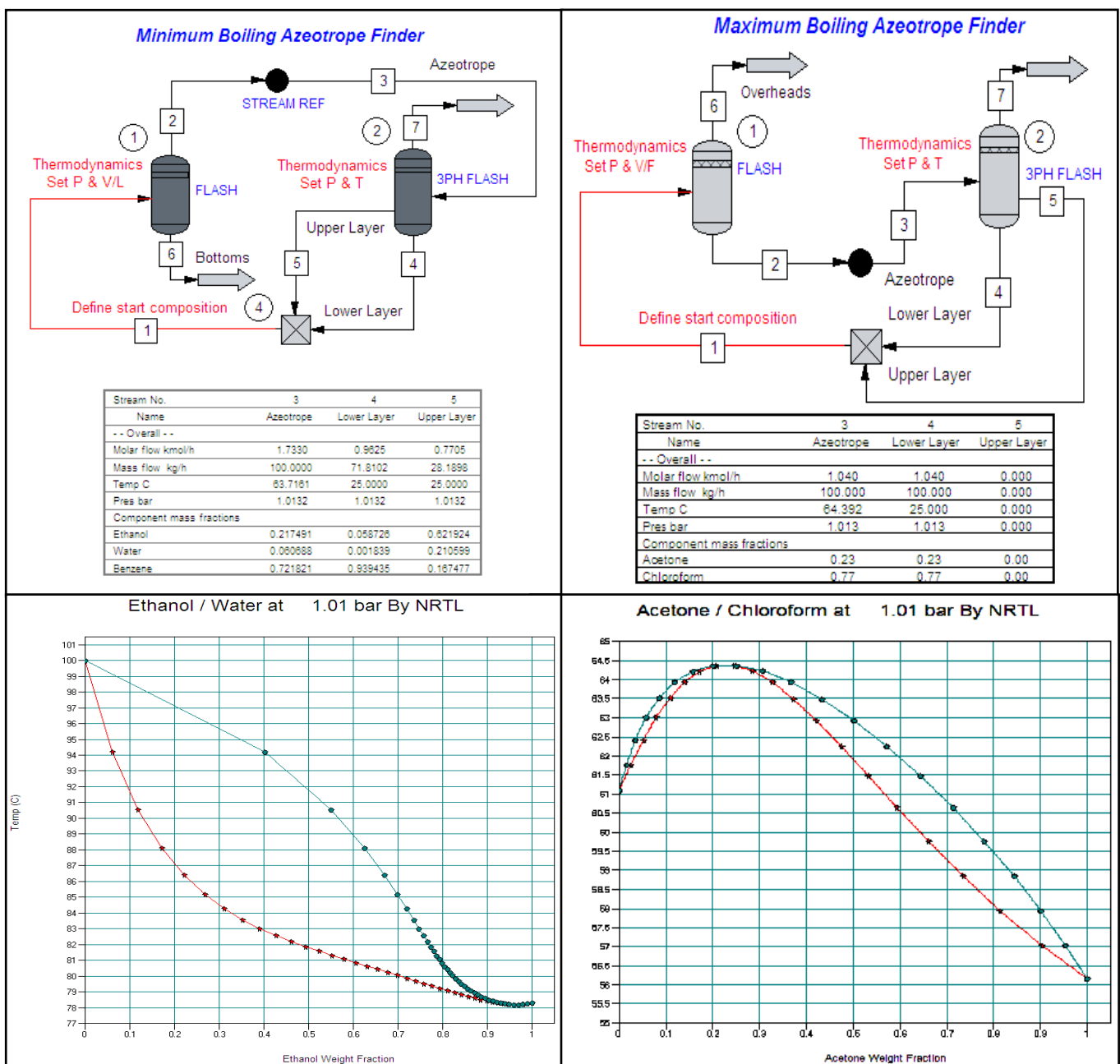
#### 4.4 Azeotrope Finders

Acknowledgements to Hellmouth Haendler formerly of Haltermann Dow for these methods.

As an alternative to using Residue Curve Maps to find the presence of azeotropes the following methods can be used.

By combining a simple Flash UnitOp (Set P and V/F=0.5) with a Three Phase Flash UnitOp (Set P and T) and connecting streams as shown results in simulation convergence at the azeotrope, if present, composition. The start composition needs to be in the relevant distillation region. The StreamRef UnitOp is used to fix the flow at 100 kg/h.

Thermodynamics K model preferred is NRTL with the Global Phase Option set for Vapor/Liquid/Liquid/Solid. The NRTL bip Parameters Sets should be complete for all binary combinations; if not use the fill matrix UNIFAC LLE option to complete.



## 5.0 Batch Distillation

A batch distillation simulation is started at steady state under total reflux. Distillate is continuously withdrawn in accordance with the reflux control strategy. Cuts are taken by switching to different receivers, following a time or overhead composition strategy, at which point simulation conditions, pressures, additions and operational parameters, may be changed whilst starting from the current condition.

Batch distillations can be operated as follows <sup>(12)</sup> :

- **Constant reflux ratio, varying overhead composition.**  
Distillation is continued until the desired composition is achieved in the still or the distillate receiver as required.
- **Constant overhead composition, varying reflux ratio.**  
As the distillation proceeds the still is depleted of the lighter component with the reflux ratio continually increasing. The stage is terminated at a maximum economic reflux ratio or achieving the desired still composition. This technique can be extended to a multi-component mixture.
- **Cyclical total reflux.**  
The unit is operated at total reflux until equilibrium is established and then distillate is withdrawn as total draw off for a short period of time before returning to total reflux. This technique is useful when required to separate a light end with a low overhead composition.
- **Minimum time, varying reflux ratio.**  
This provides the most cost effective mode of operation consistent with achieving the desired separation.

The distillation is normally operated at atmospheric pressure. Reduced pressure operation is sometimes required to achieve the desired separation, to reduce operating temperature for economic reasons, or for processing temperature sensitive materials. The boil up rate achievable with stirred jacketed reactors is dependent upon many factors associated with heat transfer <sup>(13)</sup> and is not considered in the Chemstations BATCH module.

The primary objective in batch distillation is to minimise the batch cycle time by optimising the heat input and reflux ratio to achieve the required separation. The process variables are interdependent as determined by the mass and energy balances and the mode of operation.

The heat input **Q** for variable top composition, achieved by setting a fixed reflux ratio **R** is given by:-

$$Q = \lambda_m (B_0 - B_1)(R + 1)$$

Where

<b>B<sub>0</sub></b>	total moles in reboiler at start
<b>B<sub>1</sub></b>	total moles in reboiler at end
<b>A</b>	total moles in receiver
<b>λ<sub>m</sub></b>	mean latent heat of vapourisation

The heat input for a fixed top composition, achieved by varying the reflux ratio to maintain a fixed top temperature at constant pressure is given by:-

$$Q = \lambda_m (B_0 - B_1) \int_{R_0}^{R_1} f(R) dR$$

Both relationships indicate that the reflux ratio must be kept to a minimum, subject to satisfying the requirements for the desired separation specification, to optimise the heat input.

When it has been established that a given column can achieve the required separation at total reflux it remains to determine the minimum reflux ratio **R<sub>min</sub>** as discussed previously. Batch distillations are started with **R<sub>min</sub>** equal to that required for a continuous split and it should be noted that **R<sub>min</sub>** increases as the more volatile component in the still reduces.

5.0 Batch Distillation

The mass balance demonstrates that the top composition is established by the **D/V** ratio which is dependant on the reflux ratio. If the **D/V** ratio is high, separation will be low, and withdrawal of distillate must be stopped at a relatively high value of **X<sub>D</sub>**, i.e. light ends recovery will be poor.

If the **D/V** ratio is reduced to enhance recovery the distillation may consume an uneconomic amount of time and energy. A mass balance on the MVC yields the following relationship, known as the Rayleigh equation:-

$$dB \ X_A = d \ (B X_B) \quad \ln \left( \frac{B_0}{B_1} \right) = \int_{X_{B1}}^{X_{B0}} \left( \frac{dX_B}{X_A - X_B} \right)$$

Where

<b>X<sub>A</sub></b>	mole fraction MVC in receiver
<b>X<sub>B</sub></b>	mole fraction MVC in reboiler
<b>X<sub>B0</sub></b>	mole fraction MVC in reboiler at time 0
<b>X<sub>B1</sub></b>	mole fraction MVC in reboiler at time 1

The overall mass balance for the system, i.e. still and receiver, yields:-

$$B_0 - B_1 = A$$

A mass balance on the MVC yields the following:-

$$B_0 X_{B0} - B_1 X_{B1} = A X_A \quad \text{and transposing gives}$$

$$X_{B1} = \frac{B_0 X_{B0} - A X_A}{B_1} \quad \frac{A}{B_0} = \frac{X_{B0} - X_{B1}}{X_A - X_{B1}} \quad B_1 = B_0 \left( \frac{X_{B0} - X_A}{X_{B1} - X_A} \right)$$

The batch time **θ** at constant reflux ratio is given by:-

$$\theta = \frac{R + 1}{V} (B_0 - B_1) = \frac{\lambda_m}{V} \quad \text{from above for constant reflux}$$

The mass and energy balances demonstrate the interdependence of the process parameters. Setting one process parameter results in all dependent parameters being set. The setting of two independent process parameters defines the batch distillation operational state.

A sound modelling strategy is to define the still condition by specifying the reboiler duty or boil up rate which should be adequate to sustain the overhead condition specified, i.e. fixed or variable composition. As the distillation proceeds, i.e. less MVC in the system, the reboiler duty requirement will increase to sustain the same boil up rate and to satisfy the increasing reflux ratio if operating at constant top composition. The following should be taken into consideration when selecting specification modes.

1. Distillate temperature for constant pressure operation sets the distillate composition.
2. At a constant boil-up rate the reflux ratio sets the distillate withdrawal rate.
3. Reflux ratio and distillate rate cannot be independently set.
4. Reboiler duty and condenser duty cannot be independently set.

## 6.0 Simple Distillation

### Column Specification

The stage numbering convention in CHEMCAD is from top to bottom, 1 to N. A stage is considered the space above a plate. If a condenser is present it is stage 1; if a reboiler is present it is stage N. To model a column which has ten stages plus condenser and reboiler 12 stages (10+condenser+reboiler = 12) must be specified.

If a condenser is present, the feed must not enter stage 1, as that is the reboiler. Top stage feeds should enter stage 2, the top stage (plate), if a condenser is present. Likewise, if a reboiler is present a bottom plate feed is connected to stage (N-1), not stage N.

### Convergence

Typically the user has a product specification, mass fraction of a key component in either the bottoms or tops, for a column design or to achieve with an existing column.

Converging a column model in simulation is similar to converging a column in the real world; it is difficult to go directly to high purity separation. It is best to start with an easy target, such as reflux ratio and bottoms flowrate. Once the column is converged to this simple specification, we 'tighten' the specifications toward the target specification. Use the following procedure:

1. Set up the column: number of stages, condenser, reboiler, operating pressure.
2. Generate TPxy and RCM plots to verify that the target is thermodynamically feasible with your selected VLE K model.
3. On the SPECIFICATIONS page, set 'loose' specifications such as 'Reflux Ratio' and 'Bottoms Flowrate' or Reboiler Heat Input.
4. Run the column and converge. Change the specifications if necessary.
5. Go to the CONVERGENCE page of the column dialog. Set the initial flag to **0 Reload Column Profile**. This setting instructs CHEMCAD to use the current converged profile as its starting point (initial conditions) in iterative calculations.
6. On the SPECIFICATIONS page change to more tight specifications. Run the column.
7. If the column converges, tighten the specifications and run again. If the column fails to converge, do not save the profile of the failed attempt. Relax the specifications and run the column again.
8. Repeat from step 6 until you reach the target.

Often it is difficult to obtain the first convergence on a column. If the column is run with no condenser or reboiler, one does not have the option of 'loose' specifications. If the column has a condenser or reboiler, relaxing specifications does not always help.

1. On the convergence page of the column dialog, specify estimates if you can make reasonable estimates. Note that a bad guess will make the column more difficult to converge than no estimate.
2. Remove non key components from the feed(s) to obtain the first convergence. Now set the initial flag to **0 Reload Column Profile**, return the other components, and run the unit again.
3. Specify a larger number of iterations on the convergence page of the column dialog. The default is 50, but possibly 52 iterations will find the answer.
4. Try an alternate column model. If you are currently using the SCDS try the same separation with a TOWR or vice versa. The two models use different mathematical models; often one will find an answer in 10 iterations while the other is difficult to converge. It is not possible to obtain different answers with the columns; the models are numerical methods to find a stable composition profile.
5. Consider a partial condenser. If you have a condenser present but have a significant amount of light ends, you may have difficulty converging the column. The default condenser type, total, requires that no vapor leaves stage 1. If light ends are present, this may not be possible without cryogenic temperatures. Change condenser mode to partial and the light ends gases will slip past the condenser.

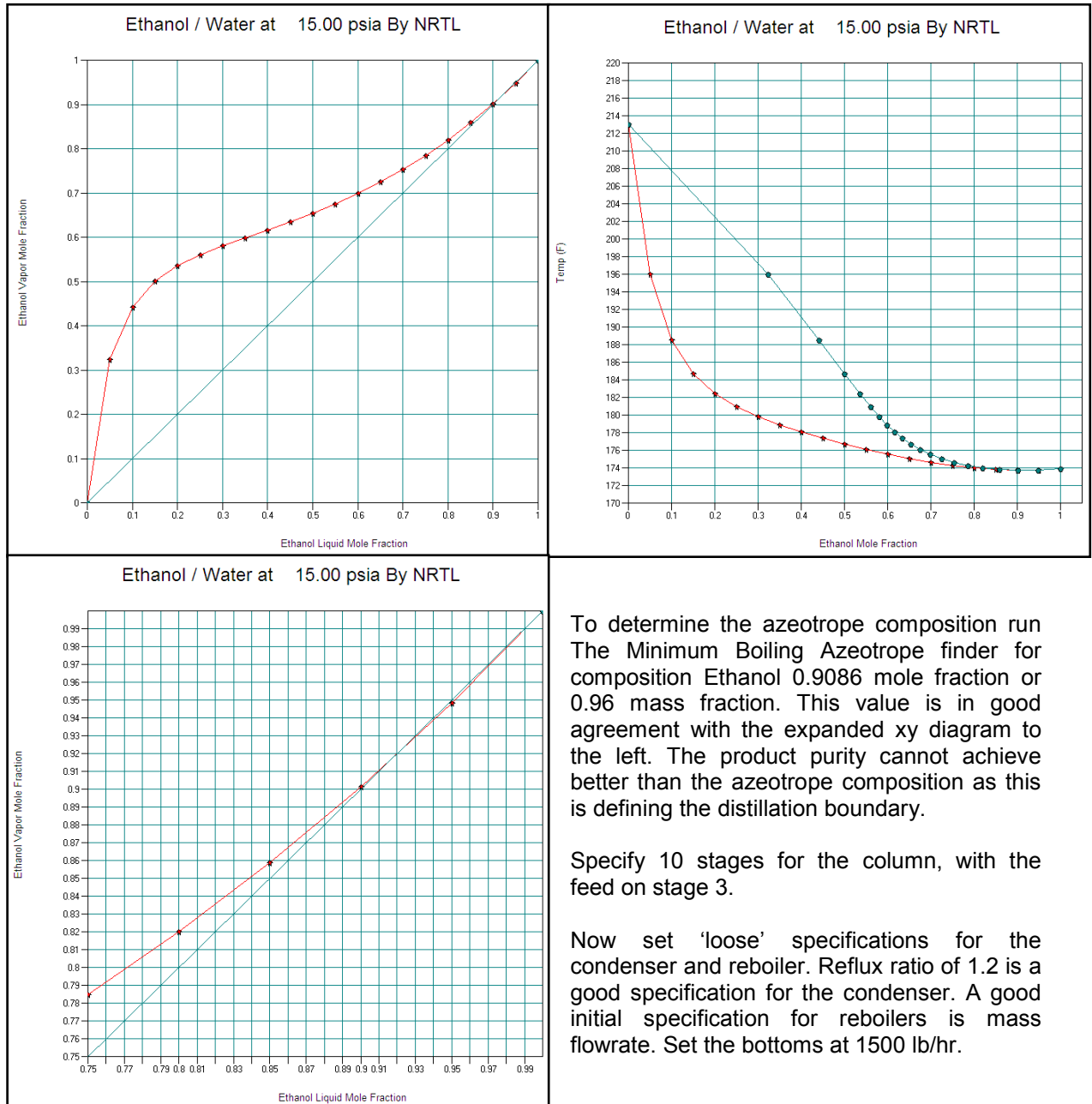
6.0 Simple Distillation

**Example**

Consider the recovery of high purity ethanol without the use of an entrainer. An SCDS column with 8 stages, a condenser, and reboiler is used to separate a mixture of ethanol and water. The specification is to obtain as a high purity ethanol in the distillate as practical.

Consider a total feed of 2000 lb/h with a composition of 0.5 mass fraction ethanol. Temperature is 70°F and pressure is 15 psia.

The K model is set to NRTL for modeling this non-ideal system. Obtain the TPxy plots which indicate the presence of an azeotrope at high levels of alcohol.



To determine the azeotrope composition run The Minimum Boiling Azeotrope finder for composition Ethanol 0.9086 mole fraction or 0.96 mass fraction. This value is in good agreement with the expanded xy diagram to the left. The product purity cannot achieve better than the azeotrope composition as this is defining the distillation boundary.

Specify 10 stages for the column, with the feed on stage 3.

Now set 'loose' specifications for the condenser and reboiler. Reflux ratio of 1.2 is a good specification for the condenser. A good initial specification for reboilers is mass flowrate. Set the bottoms at 1500 lb/hr.

The column converges with overheads mass fraction of ethanol 0.84 and bottoms flow is ~950 lb/hr of water. Tighten the specification toward the target. Set the condenser specification to "Distillate Component Mass Fraction", set Ethanol as the component with mass fraction 0.93. Change the reboiler specification to "Bottom Component Mass Flowrate, set the component to Water, and specify 990 lb/hr.

6.0 Simple Distillation

Set “Initialisation” to Mode 1: Reload Column Profile.

This setting instructs the model to use the current temperature, pressure, and composition profile of the column as the starting values for the next calculation. By starting from the currently converged profile, the numerical methods can find a tighter solution. Note that there are other modes which allow you to specify a profile yourself. These are particularly useful in starting a model of an existing unit when you already have a rough profile across the stages.

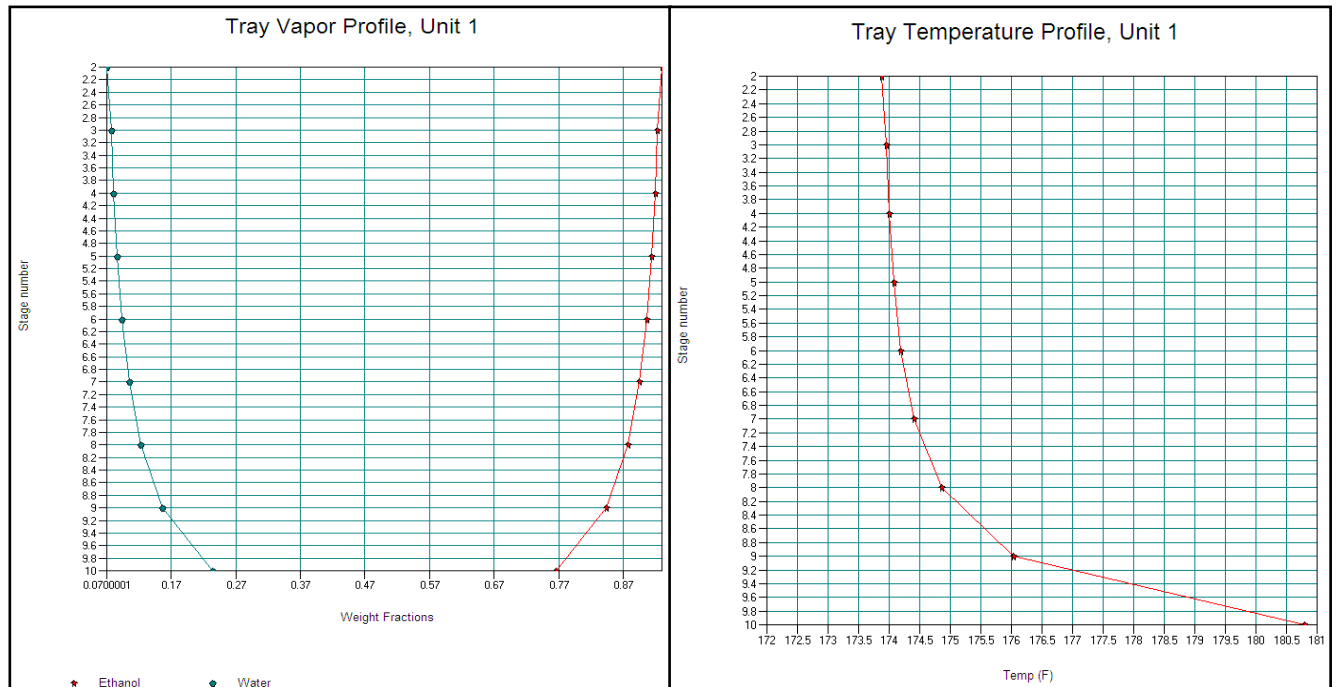
Run the flowsheet. It will converge. Now change the setting on the condenser to 0.95 mass fraction and run the column. The following message will appear.

The column has not converged. CHEMCAD is asking if you want to save the current profile, which is not a converged result. If you save the profile you may run more iterations of the column methods; sometimes this leads to a solution. If more iterations does not converge the column, you will have to start this column over from the beginning. This can be tedious; it is often easier to make small changes rather than jumps.

The jump from 0.91 to 0.95 was too large to be solved in 40 iterations (default number of iterations for SCDS) so try a smaller change. Set the top specification to 0.93 and the bottom specification to 990. Run the column.

We are now quite close to the azeotrope. It will be difficult to obtain higher purity without more stages. The reboiler specification should be changed to a bottoms component mass fraction.

Inspect the column profiles by using the Plot > UnitOps > Tower profile facilities. Top temperature at 173.8°F is now very close to the azeotropic boiling point



## 7.0 Heterogeneous Azeotrope Distillation <sup>(8)</sup>

Heterogeneous azeotropic distillation is a widely used for the dehydration of a wide range of materials. It involves separating close boiling components by adding a third component, called an entrainer, to form a minimum boiling, normally ternary azeotrope which carries the water overhead and leaves dry product in the bottom. The overhead is condensed to two liquid phases; the organic, "entrainer rich" phase being refluxed while the aqueous phase is decanted.

Due to the non-idealities, phase splitting, distillation boundaries, and the possible existence of multiple steady, columns like these can be difficult to simulate and to operate. When simulating such systems, the following should be considered:

1. Generate a residue curve map and binodal plot. The residue curve map should have the liquid phase envelope superimposed. The binodal plot should be at anticipated condenser conditions.
  2. The key feature of feasible heterogeneous azeotropic distillation is that entrainers and top tray vapor compositions are selected to generate liquid-liquid tie lines which straddle at least one of the distillation boundaries dividing the two regions containing the two components to be separated. In this way, each column is provided with a feed composition in the different distillation regions. This is why the condenser must be two-liquid phase with the organic phase being refluxed and the aqueous phase decanted.
  3. Distillation boundaries in homogeneous mixtures cannot be crossed by residue curves, and for all practical purposes they cannot be crossed by the steady-state liquid composition profile in a distillation column either. Therefore, in order to isolate two pure components which lie in two different distillation regions, it is necessary to have two different feed compositions (one from each of the two regions) and two distillation columns.
  4. The distillate and bottoms product must lie on the same residue curve.
  5. The feed, distillate, and bottoms product must satisfy the mass balance.
  6. Reflux, makeup, and process feed should be entered near the top of the column.
  7. The composition of the vapor leaving the top tray must be near the ternary azeotrope.
  8. If possible the column should be operated such that only one liquid phase exists on the stages. Since the condenser must be operated in the heterogeneous region, this means that the vapor coming from the top tray must be in equilibrium with a single liquid phase, but must condense to two liquid phases. This narrows the selection of top tray vapor compositions considerably and in fact can only be achieved by careful manipulation of the condenser operating conditions and/or a mix of the decanter organic and aqueous phases in the reflux.
- For minimum boiling, heterogeneous azeotropic systems, this can be accomplished by either adding water to the decanter in order to shift the overall composition into the two liquid phase region, or by lowering the temperature of the condensate in order to enlarge the two-liquid phase region enough to encompass the distillate composition.
9. It is important to note that the liquid boiling envelope is not a simple liquid-liquid binodal curve at a fixed temperature, but the projection of the heterogeneous liquid boiling surface onto the composition base plane. This is critical because the top tray equilibrium liquid composition must lie outside the liquid boiling envelope. It is not enough to lie outside the condenser binodal plot heterogeneous envelope.
  10. The composition of the two-liquid phases generated in the condenser must be taken from tie lines on a binodal plot calculated at condenser conditions, not top tray conditions.
  11. The relative proportions of the two-liquid phases in the condenser is given by the lever rule

$$\phi = \frac{\text{Reflux}}{\text{Distillate}} = \frac{y_{e,i} - x_{aq,i}}{y_{e,i} - x_{org,i}}$$

7.0 Heterogeneous Azeotrope Distillation

12. The vapor composition in equilibrium with a (liquid) point on a residue curve must lie on the tangent to the residue curve. For homogeneous systems, each residue curve has an associated vapor boil-off curve, and they are related by this tangency condition. However, in the heterogeneous region there is only one vapor boil-off curve, namely, the vapor line. Therefore, the vapor composition in equilibrium with a point on a heterogeneous residue curve lies at the intersection of the tangent to the residue curve and the vapor line.

Note that in the two-liquid phase region, the vapor line lies very close to the heterogeneous distillation boundary. However, these two curves coincide exactly only when the distillation boundary is linear. In all other cases, the vapor line must lie to the convex side of the distillation boundary as required by the tangency condition.

All liquid compositions lying on the liquid boiling envelope will produce equilibrium vapor compositions on the vapor line. As the liquid composition moves away from the liquid boiling envelope, into the homogeneous region, the corresponding equilibrium vapor composition moves off the vapor line. However, the cusp in the vapor surface on either side of the vapor line is normally quite steep.

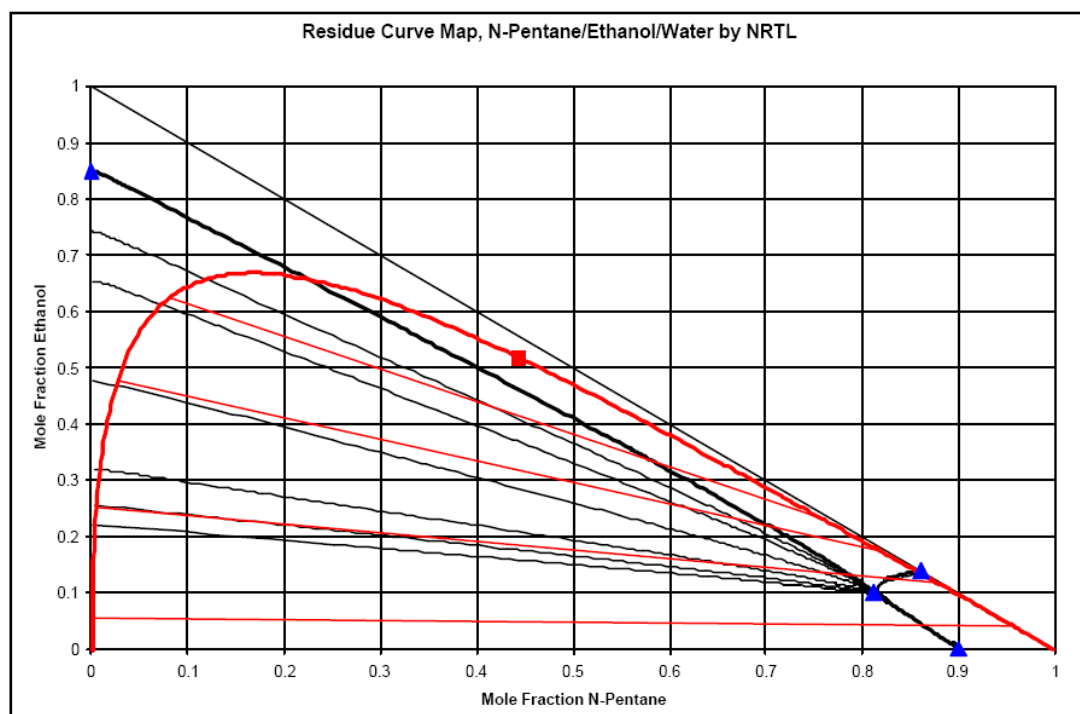
13. Within certain ranges of column specifications, heterogeneous azeotropic distillation systems exhibit multiple steady states. If these steady states are in close proximity, they frequently cause erratic behaviour in the column. This of course makes the column hard to control.

14. Many heterogeneous azeotropic distillation systems show a very high sensitivity to small changes in the operating conditions or requirements.

- Small changes in bottoms products purity specs can significantly impact the column temperature profile and entrainer requirements.
- Small changes in the reflux ratio can dramatically change the temperature profile.
- Small fluctuations in pressure can move the overhead composition outside the heterogeneous region, thus causing column failure.
- Small losses of decanter interface can cause the entire column sequence to shutdown.

### Ethanol/Water/n-Pentane Separation

In this system there are three minimum boiling binary azeotropes and a heterogeneous, minimum boiling ternary azeotrope (low boiler). The residue curve map should have the liquid boiling envelope superimposed. Together the two diagrams look like this:



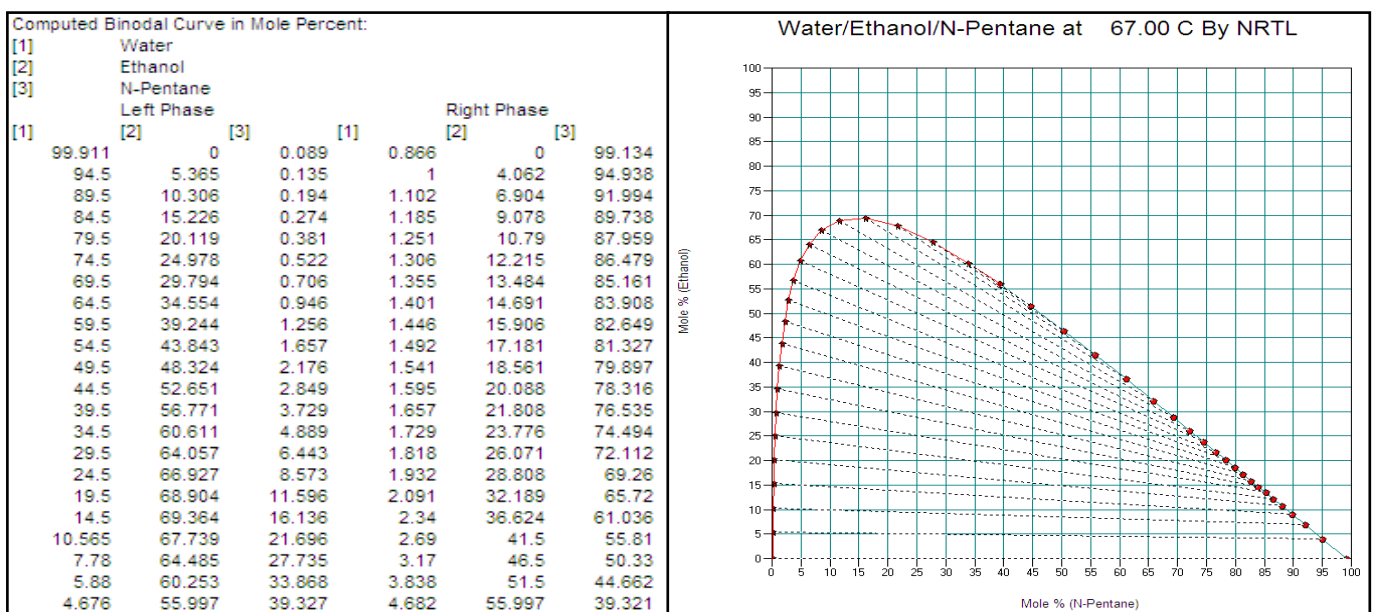
7.0 Heterogeneous Azeotrope Distillation

The map has distillation boundaries which cannot be crossed with conventional distillation. These boundaries partition the system into three regions. If the feed is in region one, a conventional distillation system will drive the ternary azeotrope to the top and pure water to the bottom. If the feed is in region two, the azeotrope will still go to the top but pure n-pentane will come out the bottom. Likewise, a feed in region three will produce the azeotrope at the top and pure ethanol out the bottom. These are the best splits that can be produced. To dehydrate ethanol we need to operate in region three. Ethanol and water will come in at the binary azeotrope (89.5% ETOH, 10.5% H<sub>2</sub>O), but by controlling the amount of benzene used, and by grouping all feeds near the top of the column, we can force the combined feed into region three.

We don't need or even want the vapor leaving the top tray to be right at the azeotrope. Not only would this require unnecessary costs (stages and/or reflux), but it will cause multiple liquid phases to form on the top trays of the column. This can make operations difficult. Therefore, we want to produce a tops vapor which is close enough to the ternary azeotrope to phase split in the condenser but not on the trays. In other words, we want the composition of the vapor leaving the top tray to be such that its equilibrium liquid has a composition outside the two-phase region, but the vapor composition itself is inside the two-phase boundary. This leaves us with a narrow range of choices, all lying near the two-phase boundary on the binodal plot.

Process Data: Column feed = 242 lb moles / hr Ethanol and 40.58 lb moles / hr. water  
Column pressure = 50 psia Condenser Temperature = saturated at 44 psia  
Ethanol purity is to be 99.99%

The residue map and the binodal plot are used for a preliminary material balance of the column.



First find the compositions of the top tray vapor, the condenser aqueous phase, and the condenser organic phase. The objective is for pure ethanol as the bottom product. Select an overhead vapour composition that meets the following criteria:

- (i) The liquid in equilibrium with the selected vapor must be single phase at system conditions.
- (ii) The vapor must condense to two liquid phases at condenser conditions.
- (iii) The composition of the two liquid phases which form in the condenser, must lie in different distillation regions; one aqueous (to be decanted), the other organic (to be refluxed).

The heavy black line represents the two liquid phase boundary. The thin black lines connect acceptable vapor-liquid equilibrium concentrations. A point in the two-phase region represents the possible top tray vapor composition, and a point in the one liquid phase region is the composition in equilibrium with that vapor. To generate this vapor in the column, it will be necessary to reflux some of the decanter aqueous liquid. Criteria (ii) and (iii) can be satisfied by picking a tie line that passes through the region 2. The closer to the azeotrope the harder it will be to satisfy criteria (i) later on and the more stages will be required. The closer to the two phase boundary, the greater the required reflux.

7.0 Heterogeneous Azeotrope Distillation

A composition just inside region three is selected as top tray composition:  
82.665% n-pentane, 12.33% ethanol, and 5.01% water.

The end point compositions (mol %) of an acceptable tie line are:

Aqueous phase = 0.43% P, 23.81% E, 75.76% W  
Organic phase = 87.88% P, 11.6% E, 0.52% W

Component	Top Tray (mol %)	Left Phase (mol %)	Right Phase (mol %)
n-pentane(3)	82.756	0.43	87.88
ethanol (2)	12.326	23.81	11.6
Water (1)	5.018	75.76	0.52

Calculate the flows of the overhead vapor, reflux, and distillate (decant). Since all the water leaves the top of the column, the aqueous phase composition can be used to determine the distillate flow.

Water flow = 40.58 lb mole / h  
Ethanol = (23.81/75.76)\*40.58 = 12.753 lb mole / h  
n-Pentane = (0.43/75.76)\*40.58 = 0.23 lb mole /h to be replaced by make-up  
Distillate flow = 40.58 + 12.753 + 0.23 = 53.563 lb mole / h

The lever rule states 
$$\phi = \frac{\text{Reflux}}{\text{Distillate}} = \frac{\text{Reflux}}{53.56} = \frac{y_{e,i} - x_{aq,i}}{y_{e,i} - x_{org,i}}$$

n-Pentane basis  $\phi = \frac{0.8266 - 0.0043}{0.8266 - 0.8788} = 15.74$  check ethanol basis  $\phi = \frac{0.1233 - 0.2381}{0.1233 - 0.116} = 15.82$

Reflux flow = 53.56 x 15.74 = 843.082 lb moles/h with the following composition:

n-Pentane = 843.08 x 0.8788 = 740.9 lb mole/h  
Ethanol = 843.08 x 0.116 = 97.8 lb mole/h  
Water = 843.08 x 0.0052 = 4.58 lb mole/h

Vapour flow = 843.08 + 53.563 = 896.643 lb moles/h

n-Pentane = 896.64 x 0.8266 = 741.17 lb mole/h (0.23 + 740.9 = 741.13)  
Ethanol = 896.64 x 0.1232 = 105.6 lb mole/h (12.753 + 97.8 = 110.55)  
Water = 896.64 x 0.052 = 45.01 lb mole/h (40.58 + 4.58 = 45.16)

Calculate bottoms Ethanol = 242 - 12.753 = 229.247 lb moles / hr

Check the overall mass balance

Flow in = 242.0+40.58+0.23 = 282.81 lb moles/hr Flow out = 53.56+229.247= 282.81 lb moles /hr

