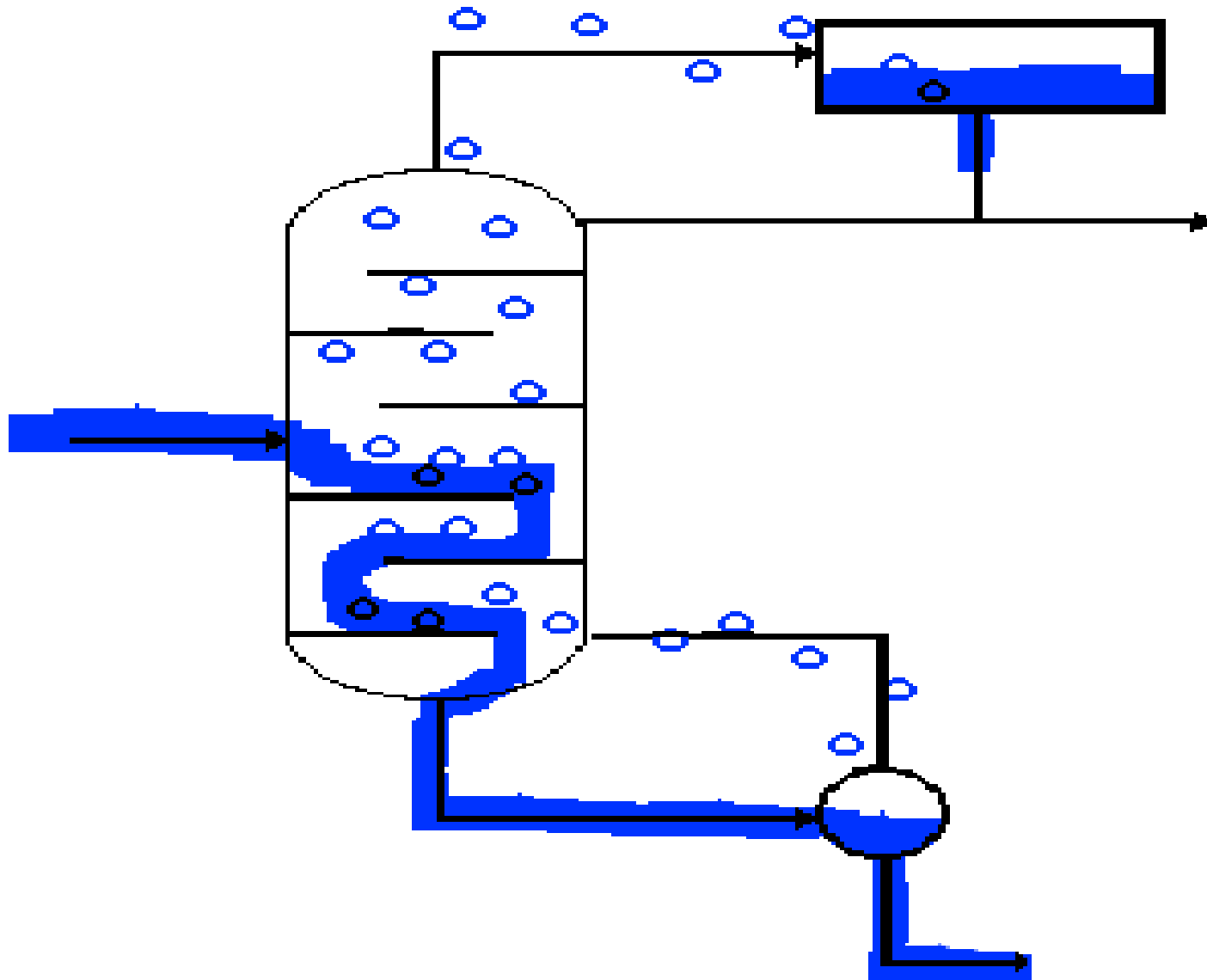


# Separator Analysis

# Distillation Separation



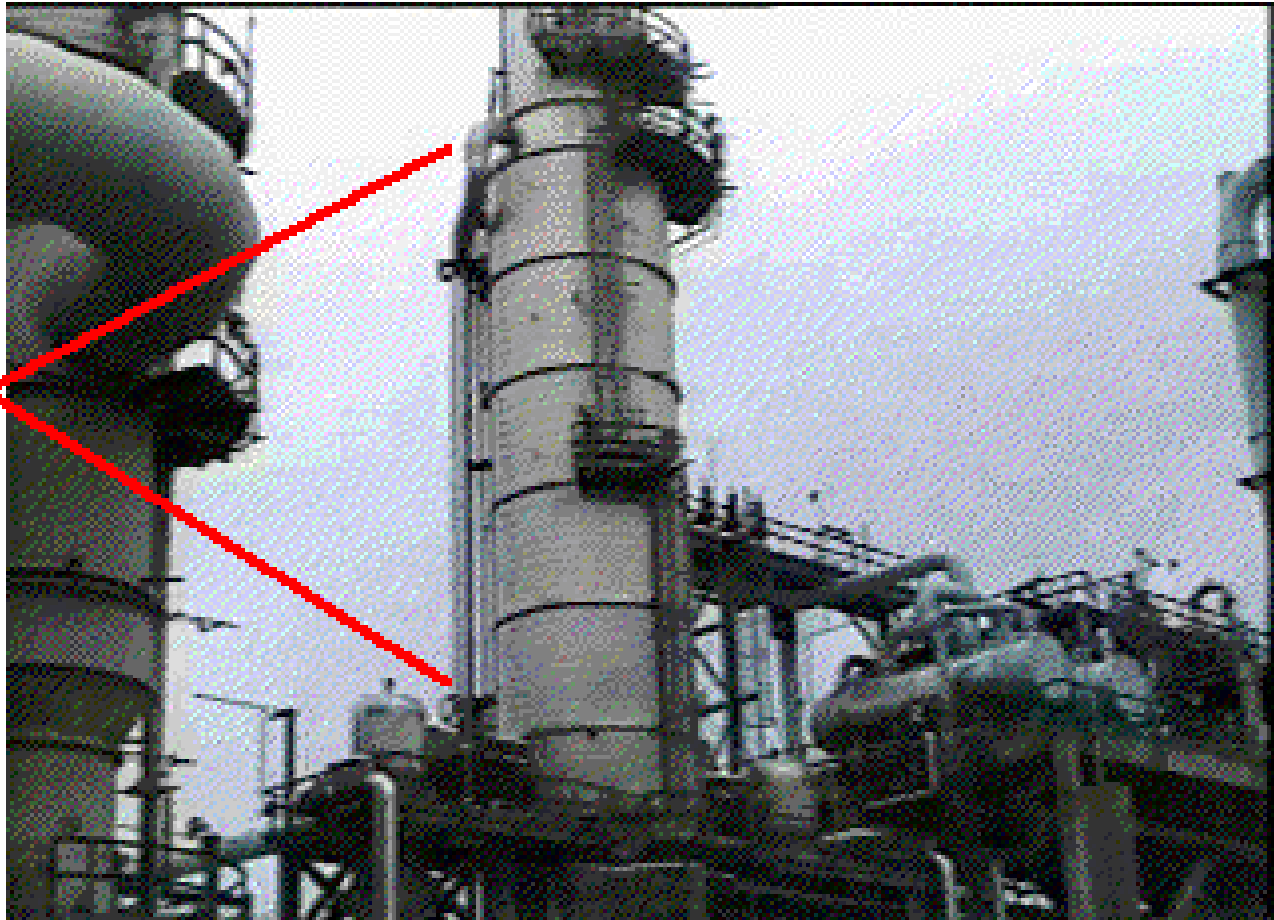
# Commercial Distillation Columns (1)



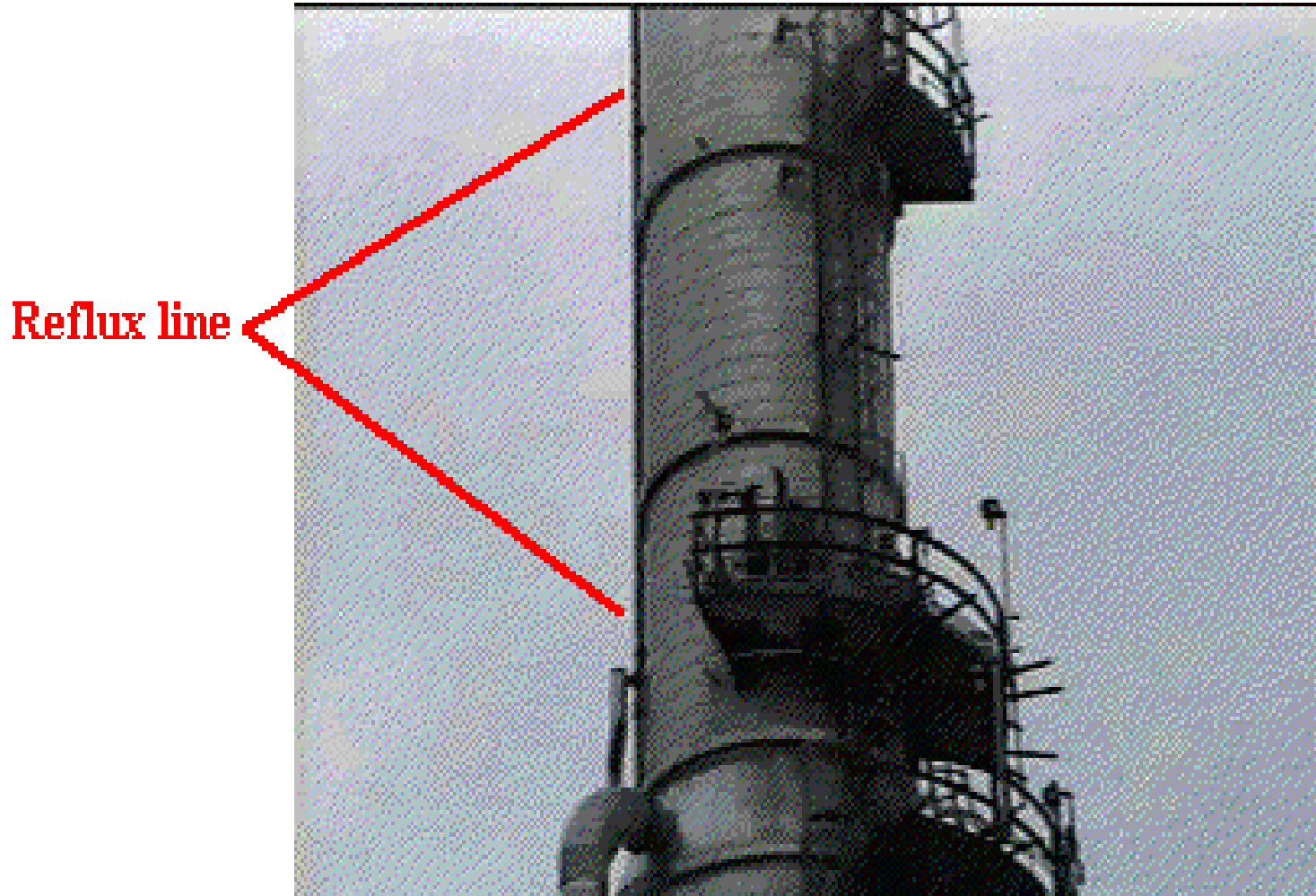
# Commercial Distillation Columns (2)



**Feed line**



# Commercial Distillation Columns (3)



# Commercial Distillation Columns (4)

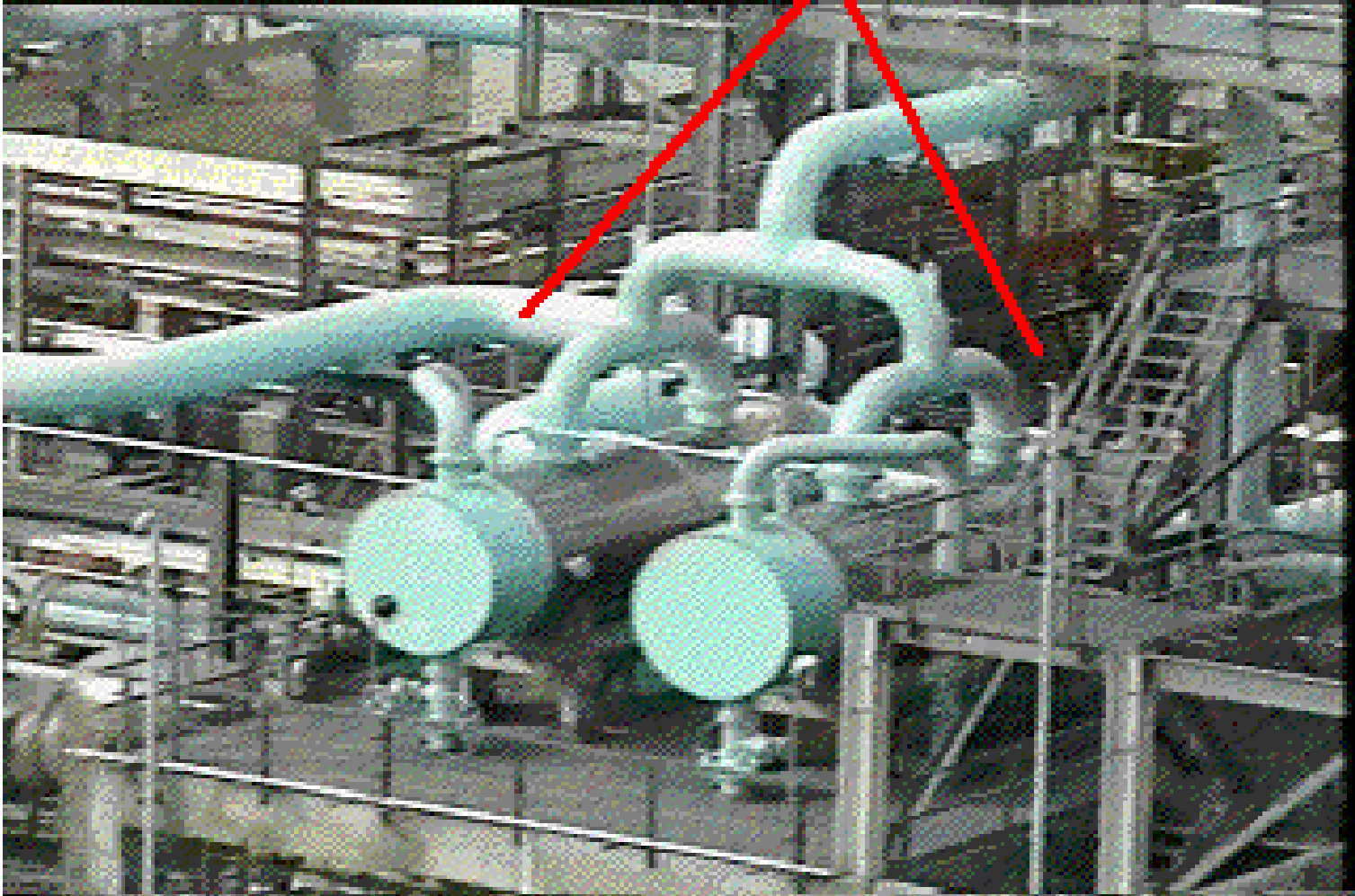


**Vapor outlet**

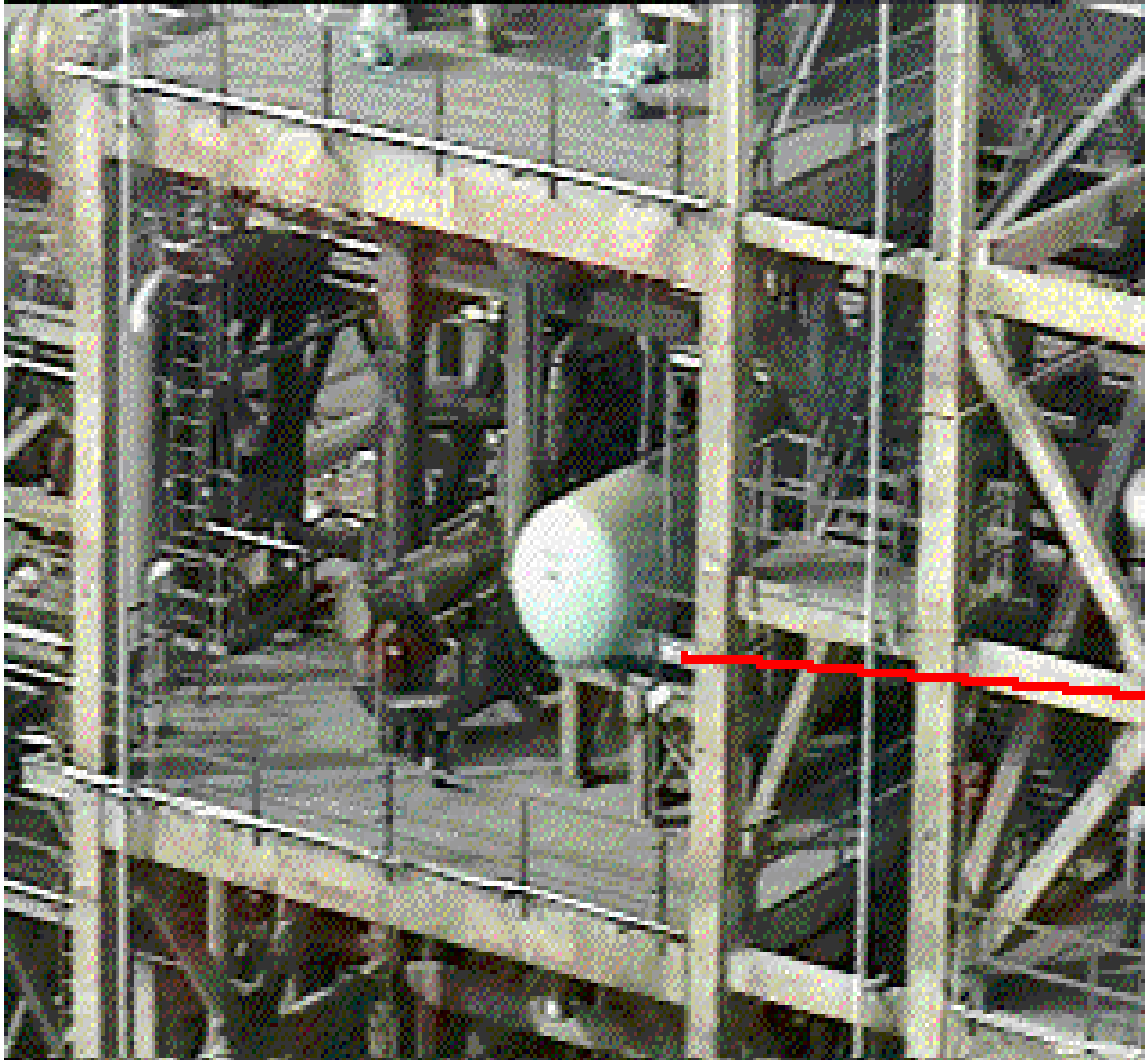


# Commercial Distillation Columns (5)

**Condensers**



# Commercial Distillation Columns (6)

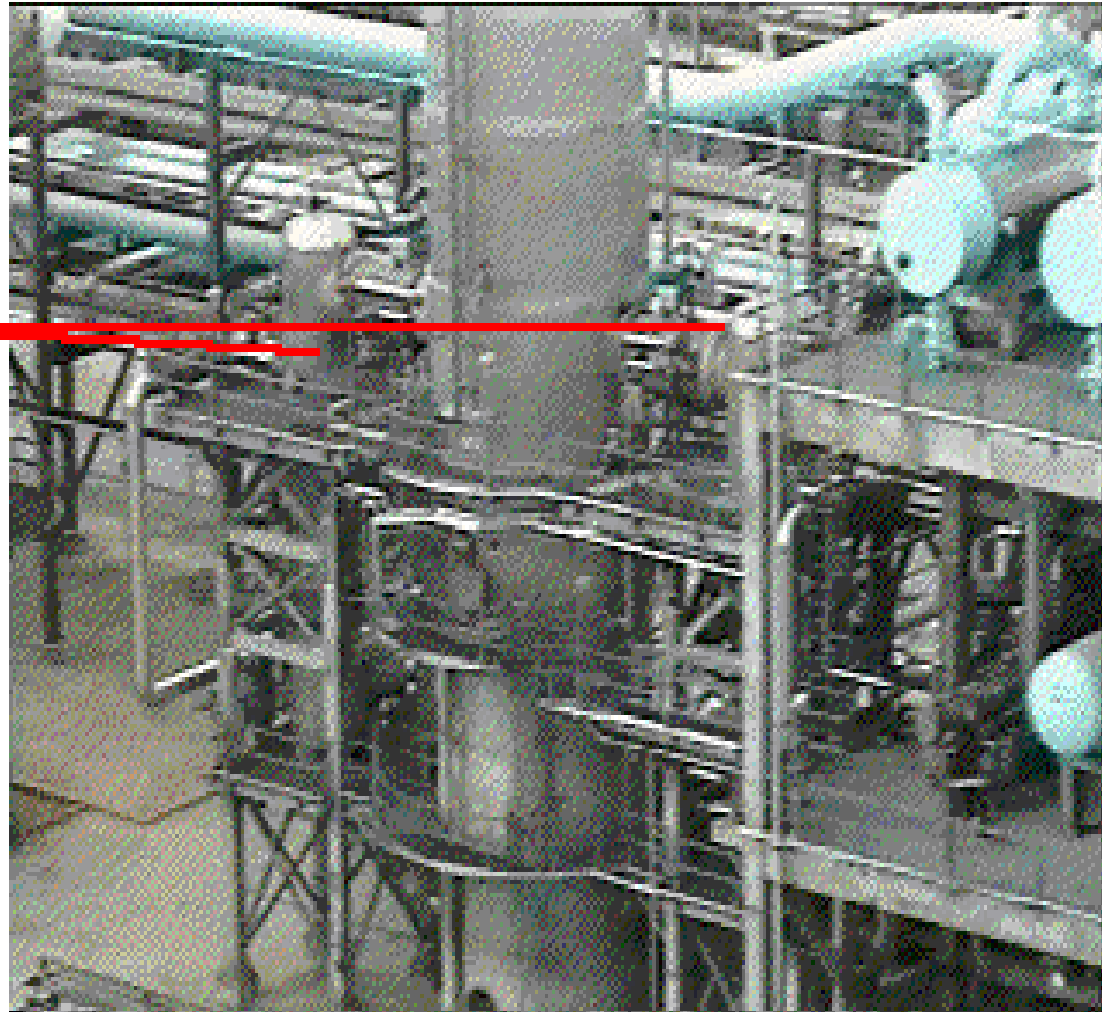


**Reflux Accumulator**

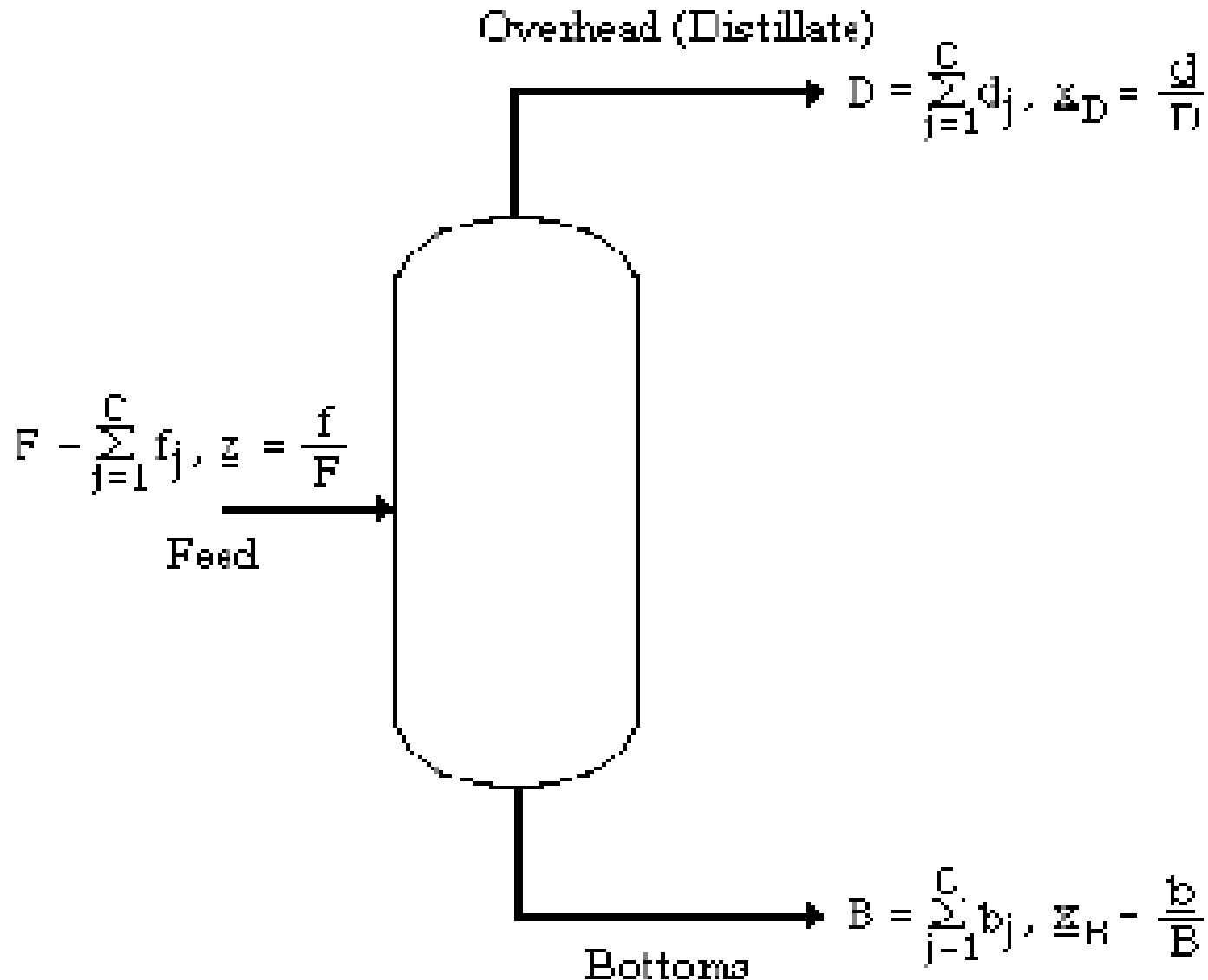


# Commercial Distillation Columns (7)

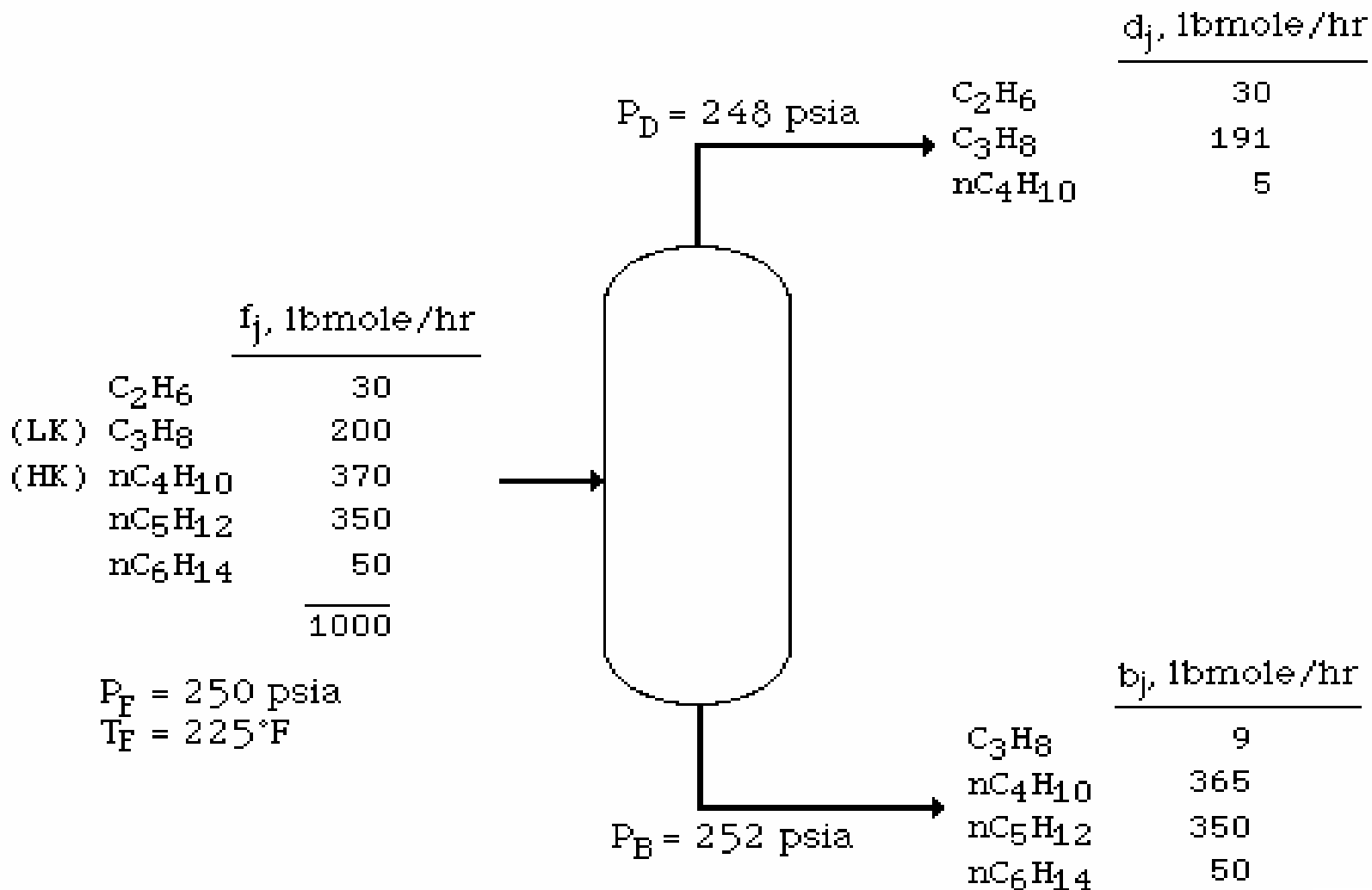
Reboilers



# Simple Column



# A Typical Separation



# Multicomponent Distillation Column Design

- Approximate (Short-cut ) method : Fenske-Underwood-Gilliland
- Rigorous method: Stage by stage calculations

# Short-cut method

Binary system (McCabe-Thiele) indicates:

$$N_{\text{ideal}} = \text{Fcn}(R_{\text{min}}, N_{\text{min}}, R_{\text{act}})$$

# Approximate shortcut methods

Although rigorous calculation techniques are available, it is common practice to use the so called **approximate methods** in order to get preliminary design and/or to optimize the design conditions for a multicomponent distillation problem.

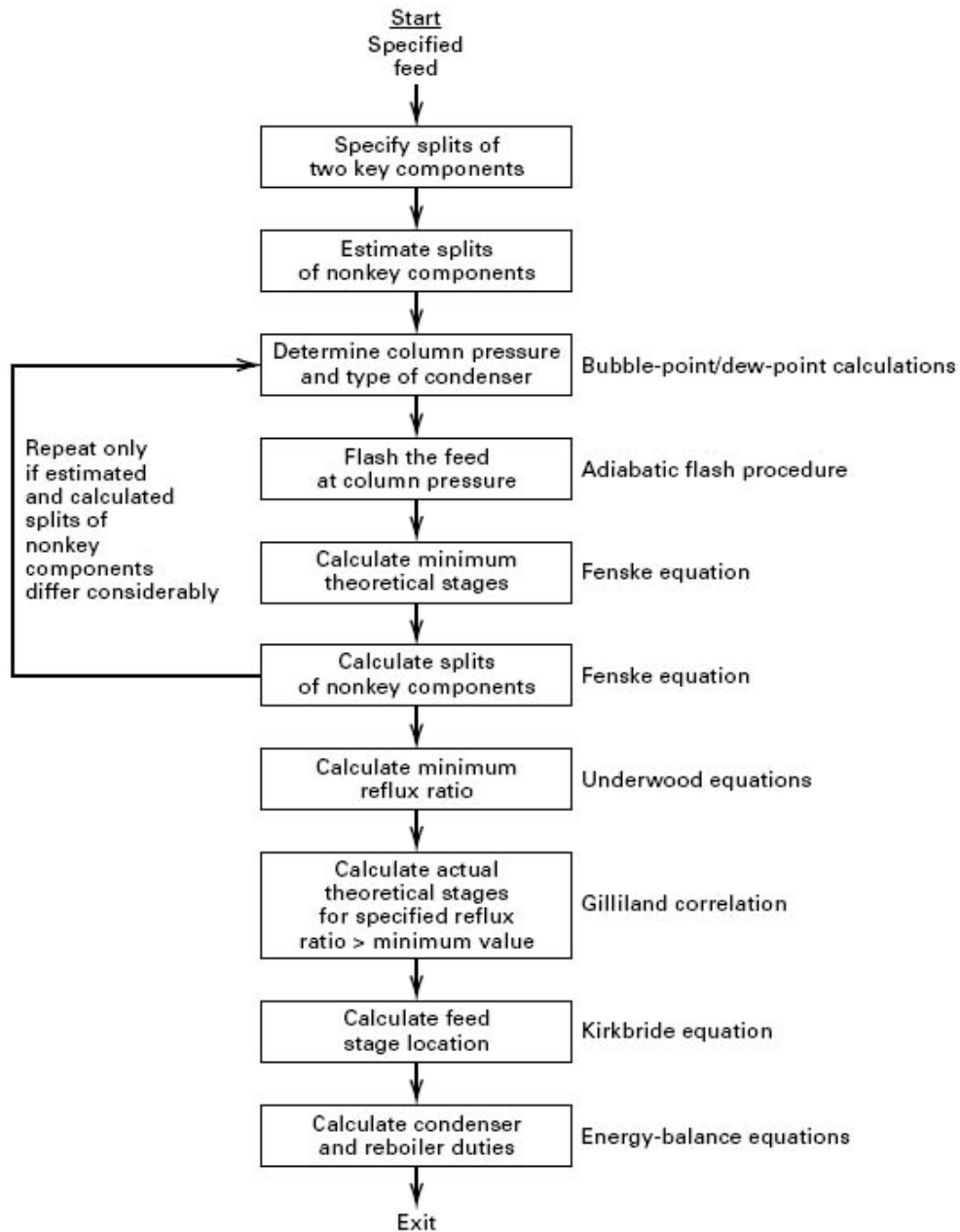
The method, we are going to illustrate in this section, is known under the name of "**Fenske-Underwood-Gilliland**" (FUG), from the three guys which developed the three different parts of the method in order to get the **ideal number of stages** of a multicomponent distillation column.

The method follows the here below sequence of steps:

---

	Equation:	Condition:	To calculate:
1	Fenske	<b>Total reflux</b> ( $R \rightarrow \infty$ )	$N_{\min}$
2	Underwood	<b>Minimum reflux</b> ( $R=R_{\min}$ )	$N \rightarrow \infty$
3	Reflux	$R=f(R_{\min})$	$R=(1.2-1.5)R_{\min}$
4	Gilliland	<b>finite reflux</b>	<b>ideal number of stage N</b>

---



**Figure 9.1** Algorithm for multicomponent distillation by FUG method.

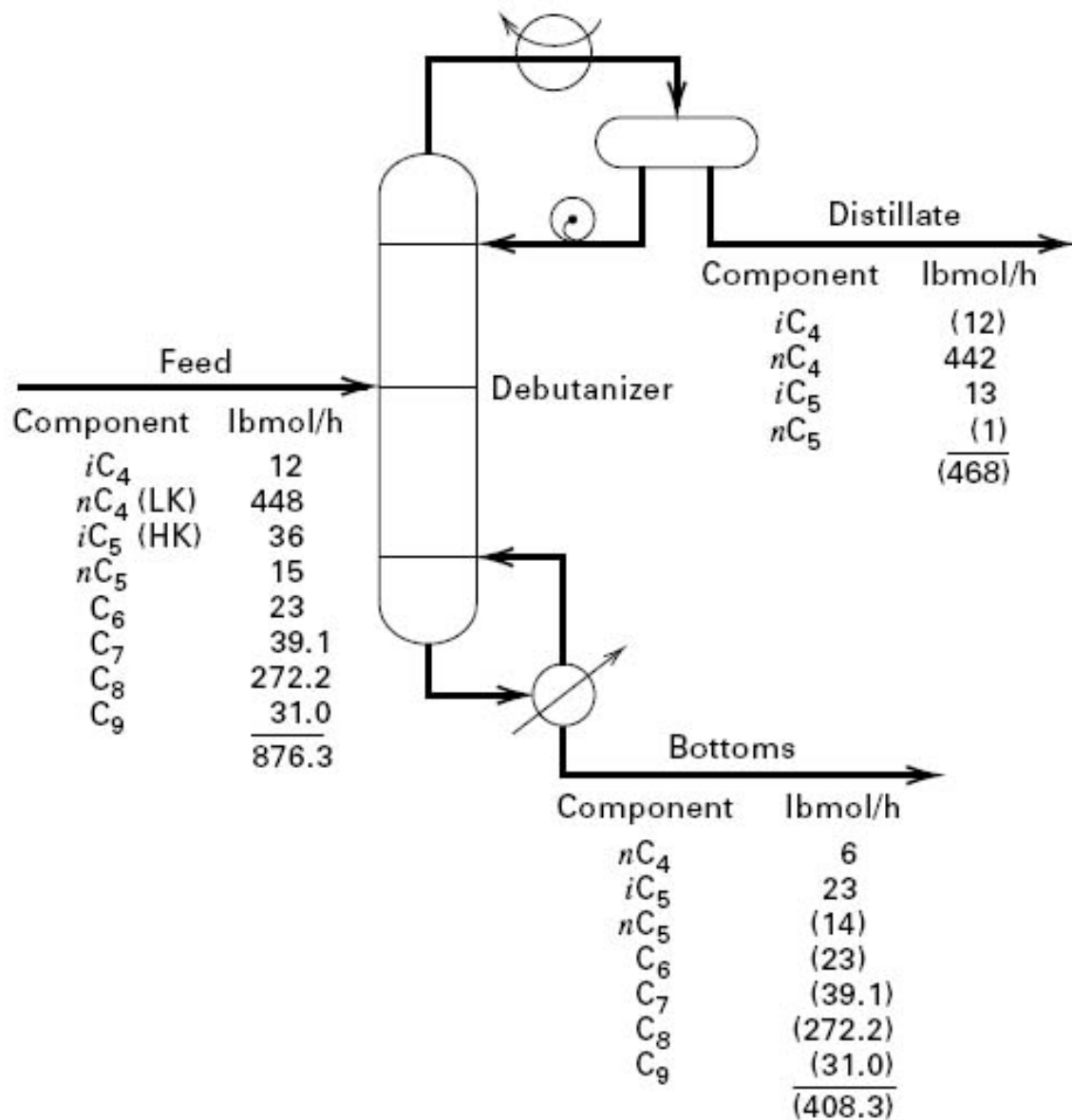


Figure 9.3 Specifications for debutanizer.



# Fenske equation

The Fenske equation allows for the calculation of the minimum number of stage.

The final equation is here below shown in the **two forms (eqs.1 and 2)**, to be used respectively whether **composition or fractional** recovery specifications of the key components in the Distillate and in the Bottoms products are given.

$$1) \quad N_{\min} = \frac{(x_{LK}/x_{HK})_D / (x_{LK}/x_{HK})_B}{\alpha_{LK,HK}}$$

where the constant of relative volatility  $\alpha_{LK,HK}$  is calculated with respect to the heavy key component, taken as a reference:

$$\alpha_{LK,HK} = k_{LK} / k_{HK}$$

$\alpha_{LK,HK}$  depends on the temperature, therefore it is different at every stage of the column.

However, most often, for the seek of simplicity it is possible to use a constant value valid for all the column stages.

When this is not possible an average value of  $\alpha_{LK,HK}$  among all the ( $N=N_{\min}$ ) values must be then calculated, e.g. average between the value at the first stage and at the reboiler:

$$\alpha_{\text{aver.}} = (\alpha_1 \alpha_R)^{1/2}$$

# Fenske equation

## Derivation of the Fenske equation

The concept behind the Fenske equation is really simple.

The column schematized here beside with the hypothesis of total reflux (no feed no products) is taken into consideration. Then the equilibrium and the mass balance equation are written for the two key components starting from the reboiler stage (see envelope in the figure).

(3) Equilibrium:

$$y_{B,LK} = k_{LK} x_{B,LK}$$

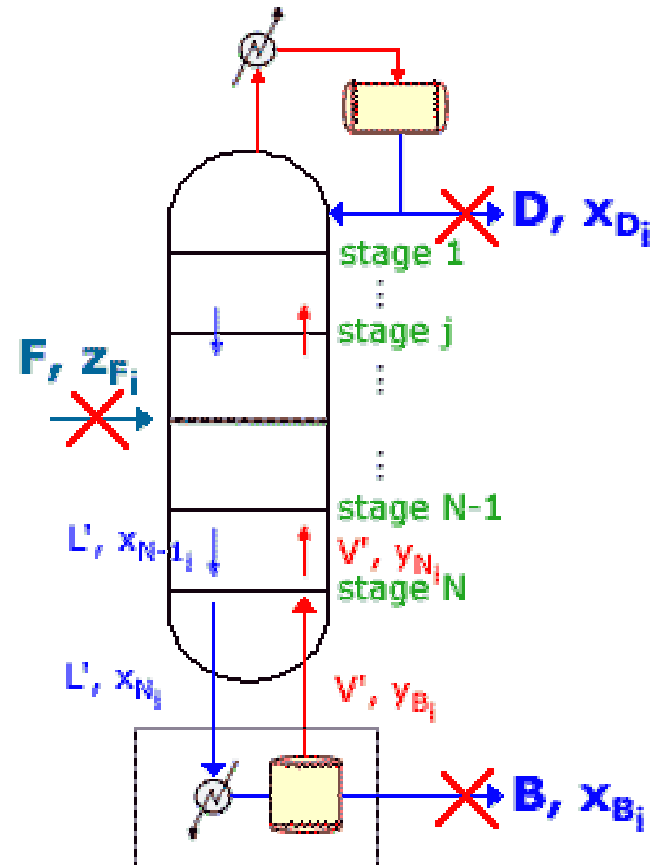
$$y_{B,HK} = k_{HK} x_{B,HK}$$

(4) Mass balance :

$$V' y_{B,LK} = L' x_{N,LK}$$

$$V' = L'$$

Please for the derivation of the Fenske's equation, see the attached [pdf file](#).



# Underwood equations

The Underwood equations allow for the calculation of the minimum reflux  $R_{\min}$ .

where  $\theta$  is a particular constant of relative volatility and it is:

$$1) \quad 1 - q = D \sum_{i=1}^C \frac{\alpha_{i,HK} Z_i}{\alpha_{i,HK} - \theta} \quad \text{Underwood I}$$

$$2) \quad V_{\min} = D \sum_{i=1}^C \frac{\alpha_{i,HK} X_{D,i}}{\alpha_{i,HK} - \theta} \quad \text{Underwood II}$$

$$\alpha_{LK} > \theta > \alpha_{HK}$$

For the seek of simplicity we will not explain why the value of  $\theta$  in the here above way fixed.

It is only important to underline that this value can be so chosen only when two key components are adjacent in the volatility scale:

$$\alpha_{LNK} > \alpha_{LK} > \alpha_{HK} > \alpha_{HNK}$$

# Underwood equations

## Procedure for the calculation of the minimum reflux

**Step 1.** Apply the first Underwood equation for the calculation of  $\phi$ .

**Step 2.** Apply the second Underwood equation for the calculation of  $R_{\min}$ :

$$R_{\min} = \frac{L_{\min}}{D} = \frac{V_{\min}}{D} - 1$$

Please for the derivation of the Underwood's equations, see the attached [pdf file](#).

## Calculation of the finite reflux

The further step is the calculation of the finite reflux. This is done, as for the [binary case](#), using a multiplying factor, as follows:

$$R = (1.05 - 2) R_{\min}$$

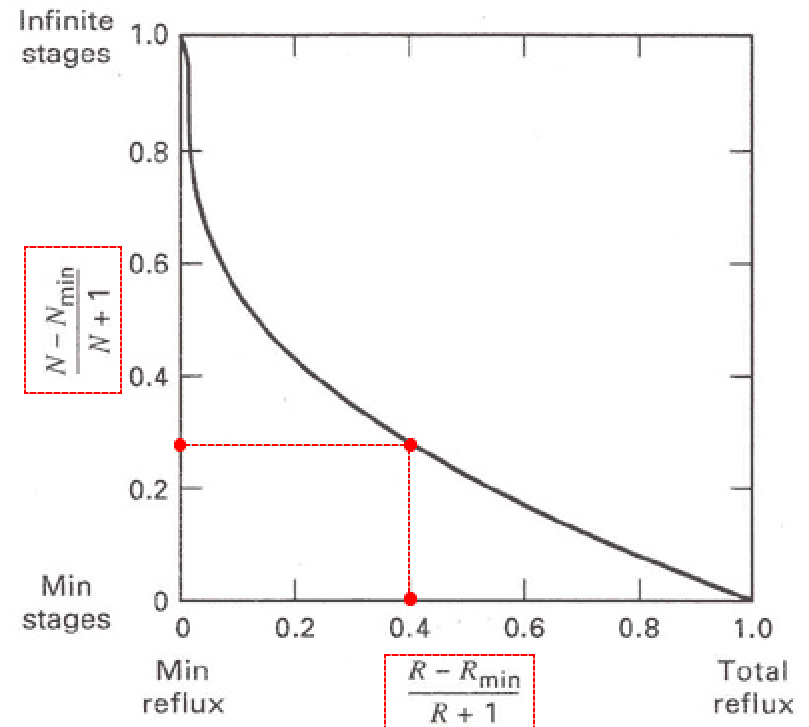
# Gilliland Correlation

Gilliland used an empirical correlation to calculate the **final number of stage N** from the values calculated through the Fenske and Underwood equations ( $N_{\min}$ ,  $R$ ,  $R_{\min}$ ).

The procedure is really simple and use a diagram as the one shown here below.

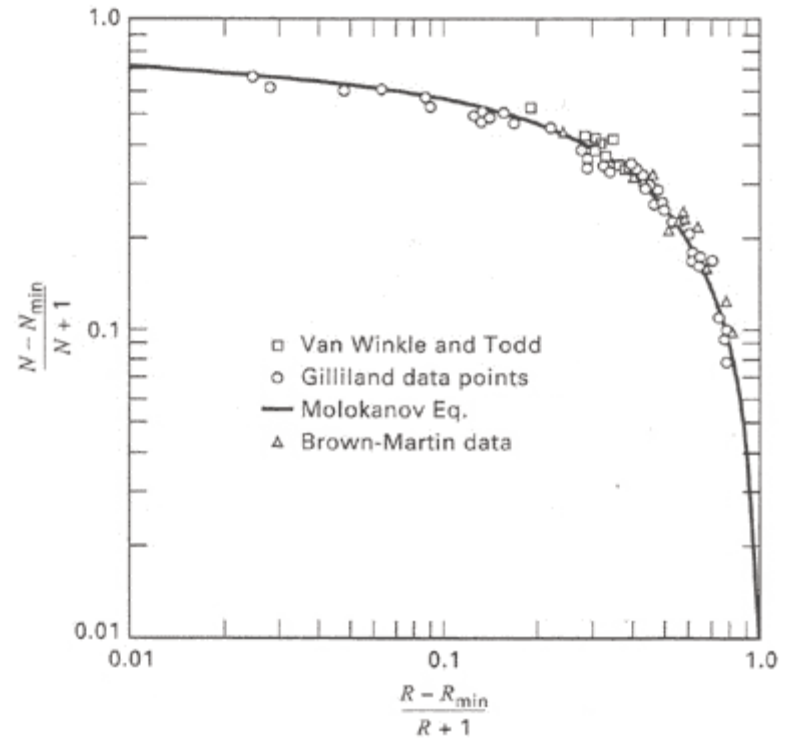
One enters the diagram with the **abscissa** value, which is known, and read the **ordinate** of the corresponding point on the Gilliland curve.

The **only unknown** of the ordinate is the number of stage N.



# Gillilan Correlation

Other authors, besides Gilliland, have developed [similar empirical](#) correlations or have tried to find a [mathematical expression](#) for the Gilliland correlation. Here below some of the most significant result:



# Rigorous Method

MESH is employed to each and every stage  
of the column designed

so-called

Stage by stage computation

# Rigorous Column Design (1)

## Distillation - Rigorous Simulation Using the Unabridged MESH Equations

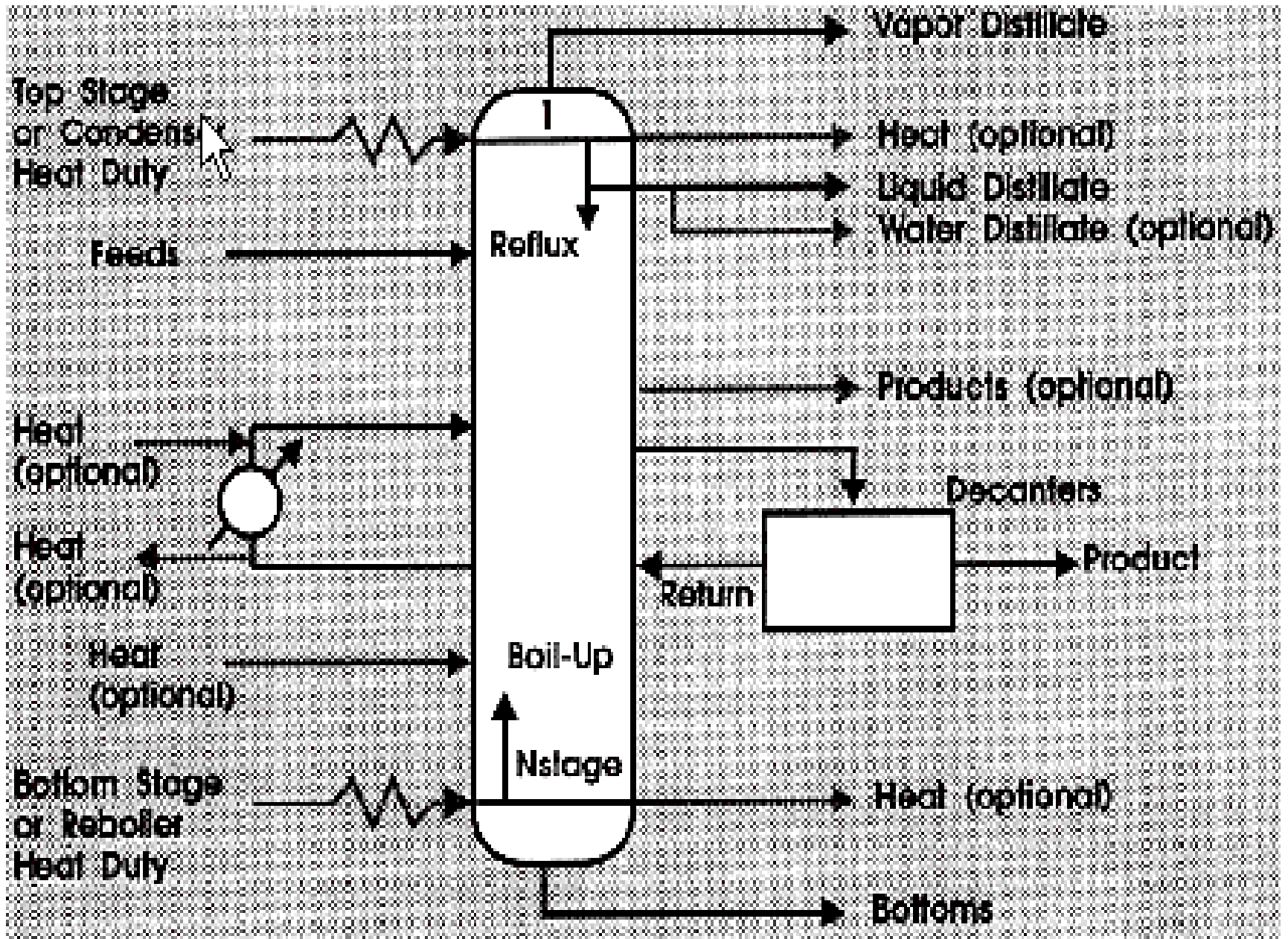
The models involving the unabridged MESH equations are the most accurate and flexible, when phase equilibria are assumed on the stages, but care must be exercised in their use. To obtain convergence, these nonlinear models require feasible specifications which, for highly non-ideal mixtures, can be difficult to determine. For these mixtures, the approximate methods may not give sufficiently good estimates for the number of theoretical stages and the reflux ratio needed to achieve a desired split of two key components. When this is the case, more rigorous methods may be necessary.



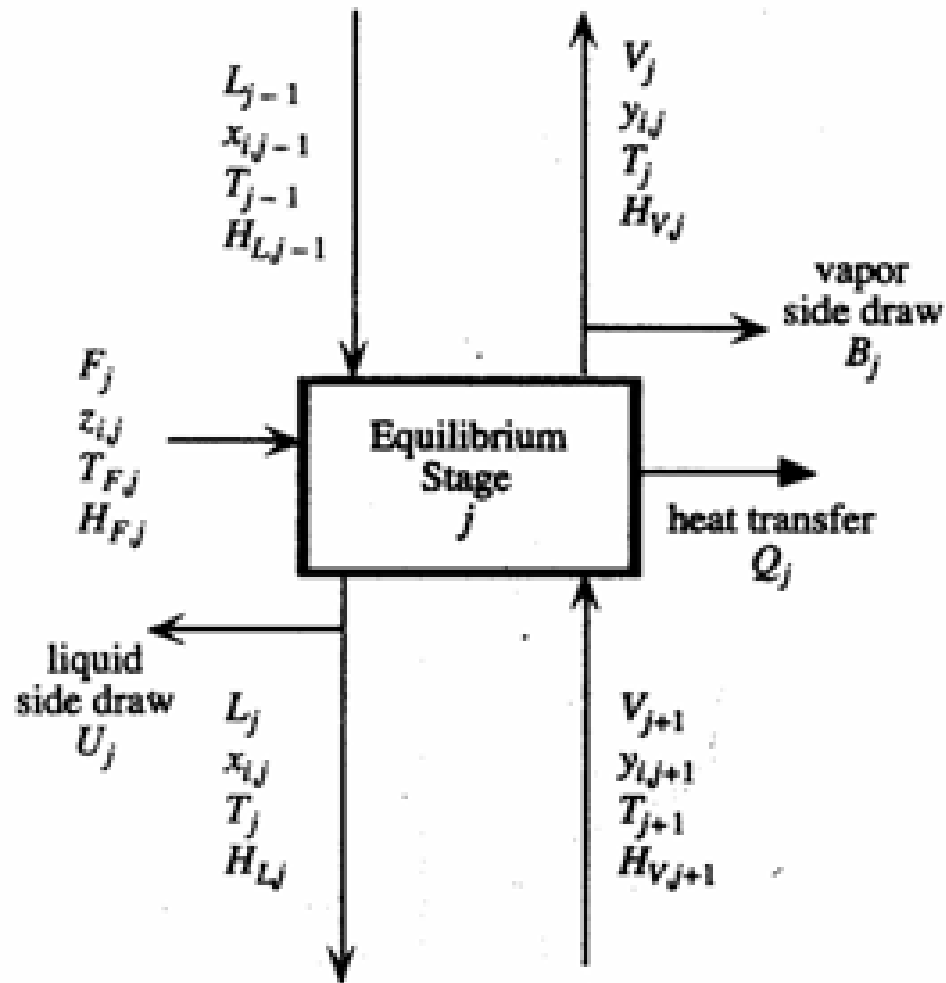
## Rigorous Column Design (2)

Since the late 1970s, many sophisticated, rigorous models have been developed. These permit multiple feed streams and sidedraws, interlinked column sections, heterogeneous operation (that is, two liquid phases on some of the trays), and chemical reaction (in reactive distillation towers).

# Rigorous Column Topology



# Equilibrium Stage Model



# Math Model

1.  $M$  equations—material balance for each component ( $C$  equations for each stage):

$$M_{i,j} = L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_jz_{i,j} - (L_j + U_j)x_{i,j} - (V_j + B_j)y_{i,j} = 0 \quad (6-86)$$

2.  $E$  equations—phase equilibrium relation for each component, here modified to include the Murphree efficiency defined by equation 4-55 ( $C$  equations for each stage):

$$E_{i,j} = E_{MG,j}m_{i,j}x_{i,j} - y_{i,j} - (1 - E_{MG,j})y_{i,j+1} = 0 \quad (6-87)$$

3.  $S$  equations—mole fractions summation (2 for each stage):

$$(S_y)_j = \sum_{i=1}^C y_{i,j} - 1 = 0 \quad (S_x)_j = \sum_{i=1}^C x_{i,j} - 1 = 0 \quad (6-88)$$

4.  $H$  equation—enthalpy balance (one for each stage):

$$H_j = L_{j-1}H_{L,j-1} + V_{j+1}H_{V,j+1} + F_jH_{F,j} - (L_j + U_j)H_{L,j} - (V_j + B_j)H_{V,j} - Q_j = 0 \quad (6-89)$$

## **Equilibrium Distillation Simulation (1)**

The following feed, at 80 °C and 1,035 kPa, is to be fractionated at the rate of 1.0 kmoles/s at the given pressure so that the vapor contains 98% of the propane, but only 1% of the n-butane:

Component	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	n-C <sub>4</sub> H <sub>10</sub>	n-C <sub>5</sub> H <sub>12</sub>	n-C <sub>6</sub> H <sub>14</sub>
$z_F$ , mole fraction	0.03	0.07	0.15	0.33	0.30	0.12

A number of simulations were carried out using the equilibrium model of ChemSep for different column configurations (number of equilibrium stages and feed stage location) and for differing operation specifications (reflux ratio and bottom product rate). Only the specifications and results of our final simulation are reported here.

# Unit Specification (1)

## Operation:

- Simple distillation
- Partial (vapor product) condenser
- Partial (liquid product) reboiler
- 14 equilibrium stages
- Feed to stage 6

## Properties:

- EOS *m*-model
- Soave-RK Cubic EOS
- Excess enthalpy from EOS

## Specifications:

- Column pressure 10.21 atm (constant)
- Feed

  - Pressure 10.21 atm

  - Temperature 80 °C

- Condenser

  - Reflux ratio = 1.2

- Reboiler

  - Bottom product flow rate = 620 moles/s

## **Equilibrium Distillation Simulation (2)**

A sieve-tray distillation column with a partial reboiler and a total condenser is to be designed to separate a mixture of benzene, toluene, and cumene (a common name for isopropyl benzene). The feed flows at the rate of 40 moles/s benzene, 30 moles/s toluene, and 30 moles/s cumene. It enters the column at a pressure of 1.05 atm and 50 mole% vaporized. We desire at least 98.5% recovery of the toluene in the distillate, and at least 98.5% recovery of the cumene in the bottoms. Design the column for a reflux ratio of 2.0.

# Unit Specification (1)

## Operation:

- Simple distillation
- Total (liquid product) condenser
- Partial (liquid product) reboiler
- 10 sieve trays
- Feed to stage 6 (stage 1 is the condenser; stage 12 is the reboiler)

## Properties:

- DECHEMA *m*-model
- UNIFAC activity coefficients
- Equation of state—ideal gas law
- Vapor pressure—Antoine
- Excess enthalpy from UNIFAC model

## Specifications:

- Condenser pressure—1 atm
- Column top pressure—1 atm
- Feed
  - Pressure 1.05 atm, 50 mole% vapor
  - Flowrates (moles/s)

Benzene	40
Toluene	30
Cumene	30
- Condenser
  - Reflux ratio = 2.0
- Reboiler
  - Bottom product flow rate = 30 moles/s

## Design:

	Section 1	Section 2
Stages	2–5	6–11
Mass-transfer coefficient	Chan Fair	Chan Fair
Vapor flow model	Plug	Plug
Liquid flow model	Mixed	Mixed
Fraction of flooding	0.61	0.70
System factor	0.90	0.90



# **ChemCAD**

*Distillation*

# Distillation Calculations

## Distillation Principles

- Techniques
- Short-Cut,
  - SCDS Algorithm (Rigorous)
  - Inside-out Algorithm (Rigorous)

- Specifications
- Degrees-of-freedom,
  - Numerical stability,
  - Guidelines

## Workshop 1- 4

# Distillation Models - SHOR

## ShortCut (SHOR)

- ◎ **Fenske** eqn for  $N_{min}$ .
- ◎ **Underwood** for  $R_{min}$ .
- ◎ **Gilliland** correlation for ideal stages.
- ◎ **Kirkbride/Fenske** for feed location.
- ◎ Rating :
- ◎ Design:
- ◎ One feed 、 two product.

# Distillation Models - SCDS

## Simultaneous Corrections Distillation Method (Rigorous)

- ◎ Plate efficiency included.
- ◎ Conversion :  $\text{Run Time} = B \times (\text{Ncomp})^2 \times (\text{Nstage})$
- ◎ Good conversion for non-ideal system.
- ◎ w/o Side stripper 、 Pump around
- ◎ Appropriate for reactive, electrolyte system, and ternary phase distillation.
- ◎ Applicability : Absorbers 、 Reboiled Absorbers 、  
Strippers 、 Fractionators

# Distillation Models - TOWER

## Rigorous Inside-out (TOWER)

- ◎ No plate efficiency selection.
- ◎ Conversion:  $\text{Run Time} = A \times (\text{Ncomp}) \times (\text{Nstage})^2$
- ◎ Not proper for non-ideal system.
- ◎ w/o Side stripper 、 Pump around
- ◎ Applicability : Absorbers 、 Reboiled Absorbers 、  
Strippers 、 Fractionators .

# Distillation Models (TOWR PLUS)

## Rigorous Inside-out (TOWR PLUS)

- ◎ No plate efficiency option.
- ◎ Conversion:  $\text{Run Time} = A \times (\text{Ncomp}) \times (\text{Nstage})^2$
- ◎ Not a good choice for non-ideal system.
- ◎ With Side stripper 、 Pump around
- ◎ Good for crude distillation.

# Degrees of Freedom

<b>Equipment Item</b>	<b>D.O.F.</b>
Simple Absorber	0
Reboiler	1
Condenser	1
Side Exchanger	1
Pumparound	2
Side stripper	1

# Distillation Specification Option

- ⊙ Condenser
- ⊙ Reboiler
- ⊙ Heater/coolers
- ⊙ Side Streams
- ⊙ Pumparounds
- ⊙ Tray Conditions



## Usual Specifications (Typical Column)

### ◎ Relatively “Safe”

One Material Bal Spec. (Dist. or Bot)

One Heat Bal Spec. (R/D, V/B)

### ◎ Poor Choices

Top and Bottom Flows

Pure Stream Temperature

### ◎ Good Choices

Pure Stream Composition

Mixed Stream Temperature

Known Heat Load or Split

Best Choice

# Column Estimates Guidelines

- ◎ No estimate Better than Poor Estimate
- ◎ Avoid Pure Component Temperature
- ◎ Avoid Azeotrope Temperature
- ◎ Tray 2, N-1 Temps. for Unusual Problems
- ◎ Use Phase Envelopes for Guidance
- ◎ Use Material Balance for Overhead Flow
- ◎ Use Profile Options for Difficult Problems

## **Workshop: Distillation 1.**

### **Short-Cut & Rigorous Distillation (SCDS)**

Please design a distillation column with a partial reboiler and a total condenser to separate a mixture of benzene, toluene, and 1,2,3-trimethylbenzene. The feed, 40mol% benzene, 30% toluene, and 30% trimethylbenzene, enters the column as a sat'd vapor. A 95% recovery of benzene in the distillate and 95% Trimethyl-Benzene in the bottoms. The reflux returns as a sat'd liquid and the operating pressure is 1 atm.

Step 1: Use Short-Cut for a preliminary design.

Step 2: Choose Rigorous model for further simulation.

Step 3: Try Equip. Sizing for internal details.

## Workshop: Distillation 2.

### Rigorous Distillation (SCDS)

- Feed : 10 moles/hr MeOH, 90 moles/hr water, sat. at 20 psia
- Thermo :
- SCDS Col : 20 stages(including condenser and reboiler)  
feed on stage 10, 15 psia top pressure, 2psi pressure drop
- Spec set 1 : Set the bottoms flow to 90 moles/hr,  $R/D = 20$
- Spec set 2 : Set the bottoms flow to 90 moles/hr,  $R/D = 0.5$
- Observe : Mole Fraction of MeOH at  $R/D=0.5$  (Column is Pinched, see Profile)
- Spec set 3 : Overhead spec set the mole fraction of MeOH at  $R/D=0.5$
- Observe : Column will not likely converge even though we solved this case.

## **Workshop: Distillation 3. Rigorous Distillation (SCDS)**

Feed : 100 lbmoles Nitrogen and 11 lbmoles Hydrogen Chloride

SCDS Col : 10 stages, HCl/N<sub>2</sub> feed on stage 10, water feed on stage 1  
15 psia top pressure, 2psia pressure drop

Spec set 1 : No reboiler and No condenser

Thermo :

**Case 1: Heat of solution for enthalpy correction**

**Case 2: No Heat of solution for enthalpy correction**

*Compare Temperature Profiles for both cases.*

# Workshop Distillation 4. Atmospheric Crude Unit

## COMPONENTS

<u>ID</u>	<u>Name</u>
62	Water
4	Propane
5	i-Butane
6	n-Butane
5001+	pseudo comps. (From Crude Characterization)

## THERMODYNAMICS

K-VALUES - Grayson-Streed  
WATER - Immiscible

ENTHALPY - Lee Kesler

## STREAM 1 - CRUDE FEED

Temp, F	300
Pres, psia	100

## FLASH

Mode	2 (Isothermal)
Parameter #1	410 (Temperature out)
Parameter #2	55 (Pressure out)

## TOWER CONFIGURATION

No. of side strippers	2
No. of pumparounds	1
No. of side exchangers	1

### MAIN COLUMN

No. of stages	16
Pres. of tower top, psia	23
Col. Pres. drop, psi	2
Bottom steam, lbmol/hr	83.3
Steam temp., F	335
Steam pres., psia	115
First feed stage	14

### CONDENSER

Condenser type	2 (Total w/H <sub>2</sub> O decant)
Condenser pres., psia	20
Est. cond. temp, F	100
Subcooled cond. temp, F	100 (Specification)

### REBOILER

Estimated temp., F	600
Reboiler option	N (No reboiler)

## SIDE STRIPPERS

Stripper no.	1	2
No. of stages	2	2
Draw stage	8	12
Return stage	7	11
Bottom vol., BPSD	3780	3765
Steam lbmol/hr	33.33	36.11
Temp. F	335	335
Pres. psia	115	115

## PUMPAROUNDS

Pumparound no.	1
Draw stage	12
Return stage	10
Vol. flow rate, BPSD	4700
Heat duty, MMBTU/HR	-7.31

## SIDE EXCHANGERS

Side exchanger no.	1
Location	14

## TRAY CONDITIONS

Tray no.	16	7335 BPSD
Tray no.	13	5 % Overflash



## CRUDE CHARACTERIZATION - STREAM 1

### CORRELATION METHODS

Molecular Wt. Equation	1	(Coade)
Critical Properties	1	(Cavett)

### CUT BREAKDOWN

<u>Temp. Range</u>	<u>No. Cuts</u>
50- 150 F	4
150- 550 F	16
550- 750 F	4
750-1250 F	5

### STREAM #1 ASSAY INFORMATION

Assay type	3	(TBP)
Gravity type	1	(API)
Bulk gravity	35	
Flow units	1	(BPSD)
Total flow rate	25000	
Light ends unit	1	(Vol %)

**TBP ASSAY****GRAVITY CURVE**

<b>Volume</b>	<b>Temp</b>	<b>Volume</b>	<b>API</b>
<b>%</b>	<b>F</b>	<b>%</b>	<b>Gravity</b>
3.83	98	12	66.7
5.00	125	19	55.3
10.00	167	40	37.6
20.00	227	62	27.0
30.00	291	82	19.0
40.00	370		
50.00	460		
60.00	552		
70.00	643		
80.00	799		
90.00	1023		
100.00	1440		

**LIGHT-END ANALYSIS**

<b>ID</b>	<b>Name</b>	<b>Volume %</b>
62	Water	.00
4	Propane	.18
5	i-Butane	.30
6	n-Butane	.69

# **ChemCad**

*Absorption and Stripping*

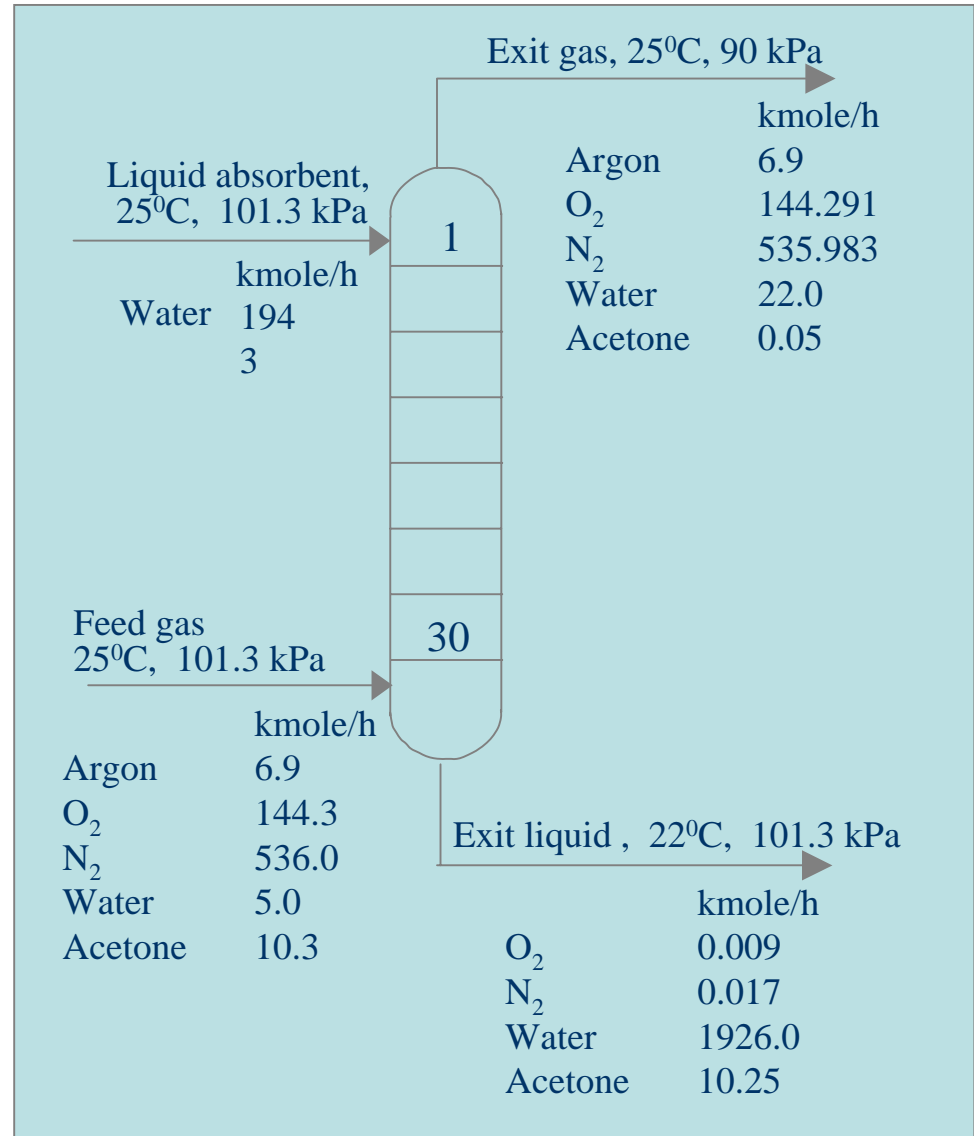
# Contents

- **Typical absorption and stripping process**
- **General design consideration**
- **Thermodynamic consideration**
- **Simulate absorption and stripping by using CHEMCAD**
  - **Physical absorption (stripping)**
  - **Chemical absorption**
- **Absorber and stripper Sizing**

# Typical absorption process

## In this case

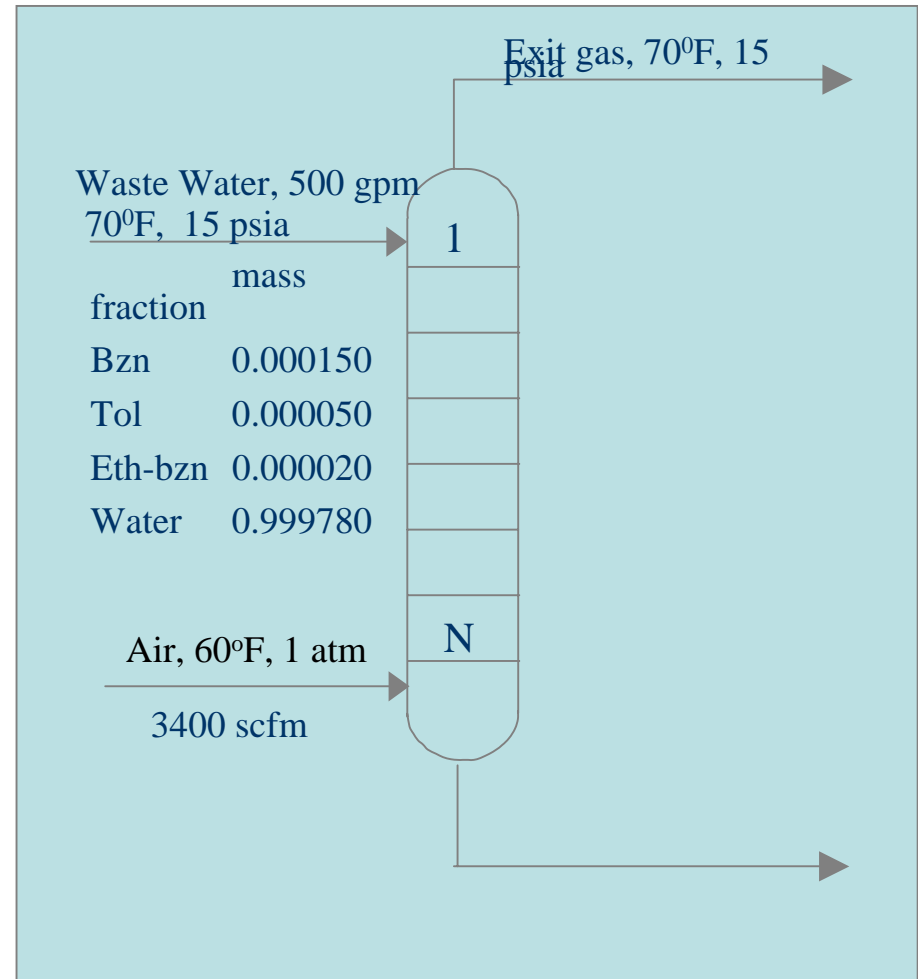
- Feed gas - from dryer
- Remove 99.5% of acetone  
or acetone <100 PPM in  
Exit gas
- Liquid absorbent : pure  
water
- the exit gas is almost  
saturated with water vapor
- the exit liquid is almost  
saturated with air
- 3 deg C decrease because  
of some water vaporization



# Typical stripping process

## In this case

- Waste Water from process
- Remove 99.9% of VOC or  
VOC < 10 PPM in exit  
liquid
- Stripped by air
- the exit gas is almost  
saturated with water vapor
- the exit liquid is almost  
saturated with air
- the temperature of exit liquid  
decrease because of some  
water vaporization



# General design considerations

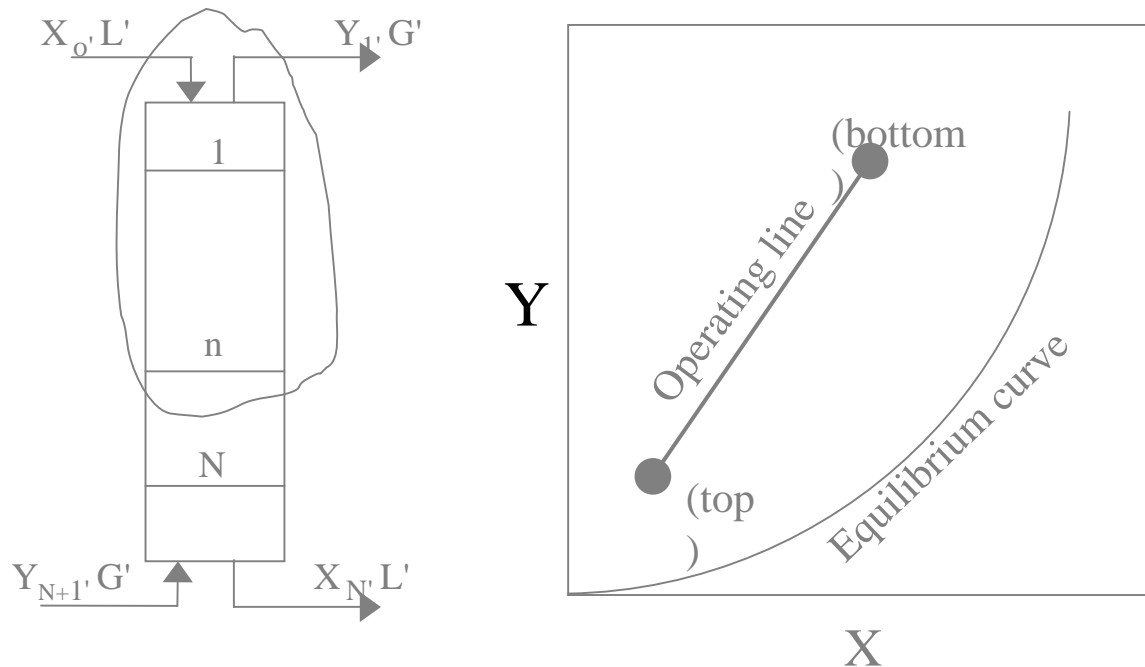
- Entering gas flow rate, composition, temperature and pressure (Feed)
- Desired degree of recovery of one or more solutes (Spec.)
- Choice of absorbent (stripping agent)
- Operating pressure and temperature, and allowable gas pressure drop (constrain)
- Minimum absorbent (stripping agent) flow rate and actual absorbent (stripping agent) flow rate as a multiple of the minimum rate needed to make the separation
- Number of equilibrium stages
- Heat effects and need for cooling (heating)
- Type of absorber (stripping) equipment
- Height of absorber (stripping)
- Diameter of absorber (stripping)

# The ideal absorbent

- Have a high solubility for the solute  
to minimize the need for absorbent
- have a low volatility  
to reduce the lose from vent and to facilitate separation of absorbent and solute
- be stable to maximize absorbent life  
to reduce absorbent makeup requirement
- be non-corrosive  
to permit user of common materials of construction
- have a low viscosity  
to provide low pressure drop and high mass and heat transfer rates
- be non-foaming when contact with the gas  
to make it unnecessary to increase absorber dimensions
- be nontoxic and nonflammable  
to facilitate its safe use
- be available, if possible, within the process  
to make it unnecessary to provide an absorbent from external sources

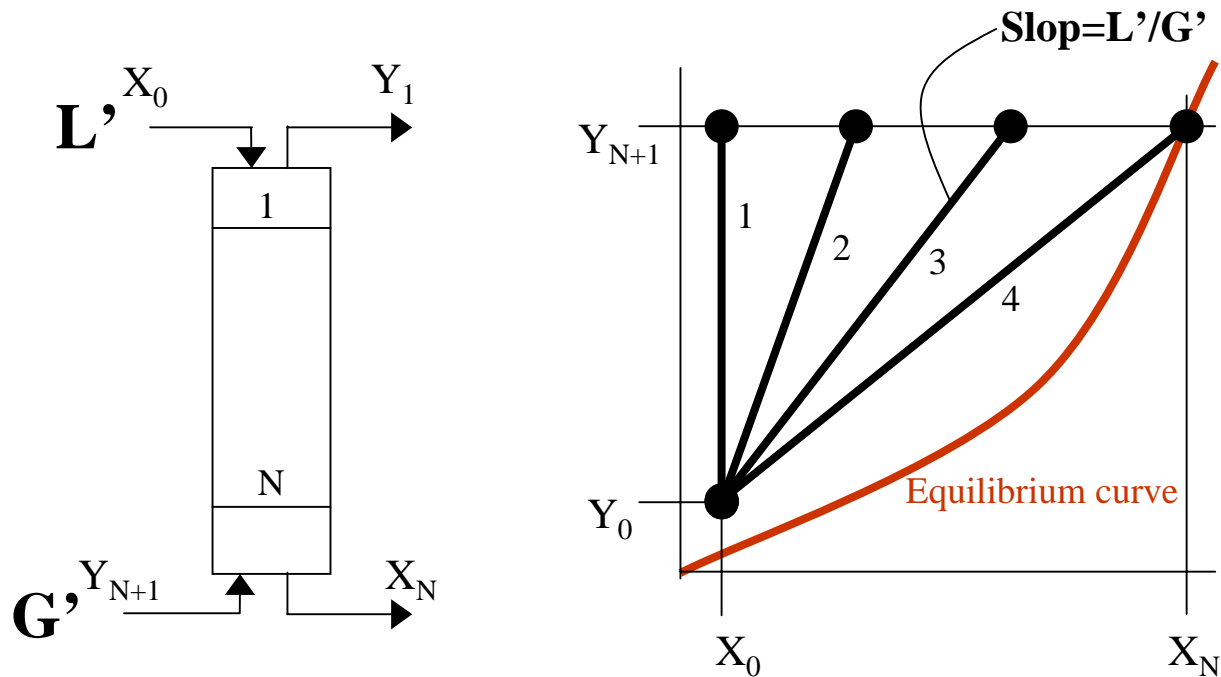


# Absorption column



- fraction of a component absorbed =  $f(\text{no of stages, absorption factor})$
- Absorption factor,  $A = L/(KG)$
- if  $A > 1$ , any degree of absorption can be achieved.
- The larger the value of  $A$ , the fewer the no. of stages required, however the larger absorbent flow rate required

# Operating line for an Absorber - absorbent flow rate



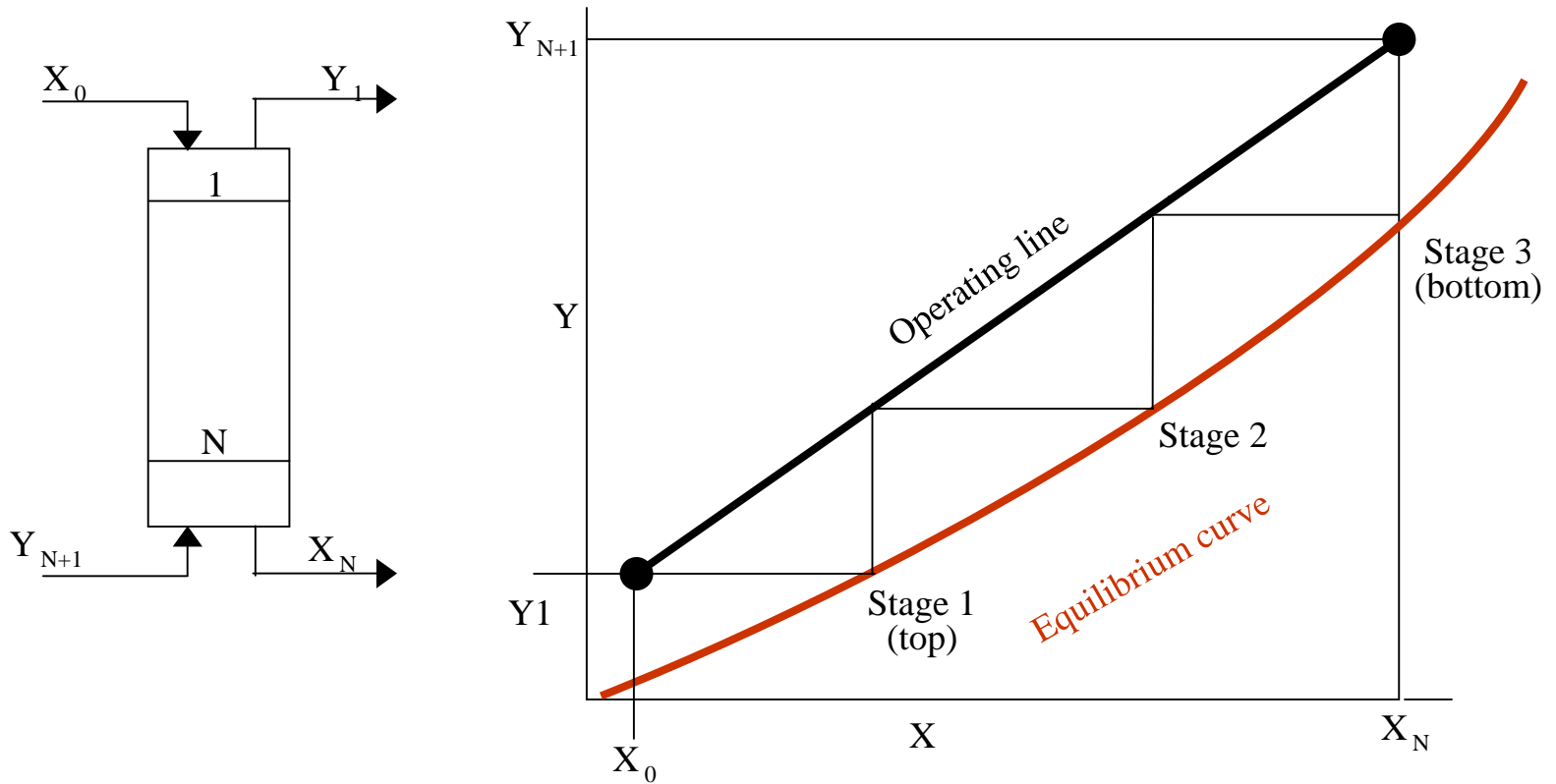
$$Y_{N+1} = X_N(L'/G') + Y_1 - X_0(L'/G')$$

Operating line 1: no. of stages = 0; but infinite absorbent rate

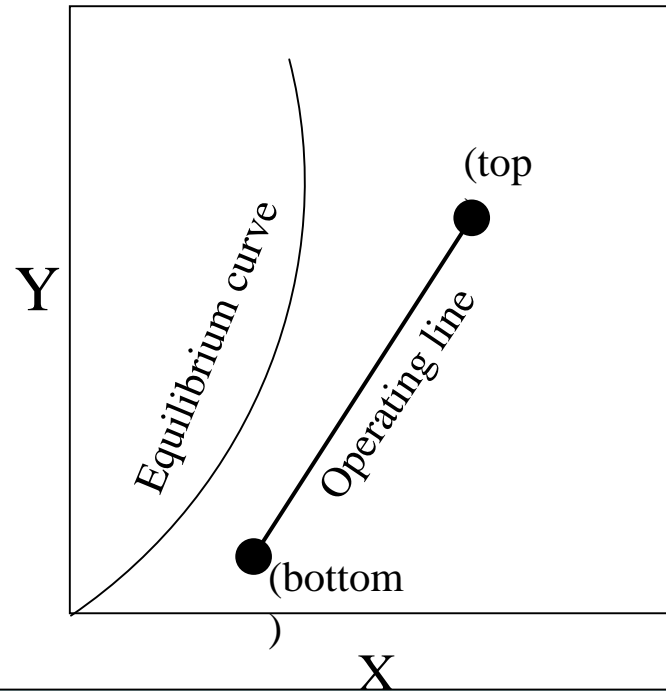
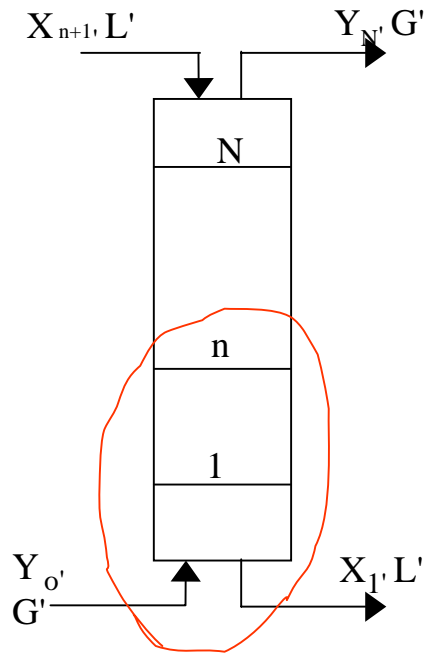
Operating line 4: minimum absorbent rate; but no. of stages = infinite

Actual operating absorbent flow rate = (1.1 ~ 2.0) \* minimum absorbent flow rate

# Graphical determination of the no. of stages for absorber

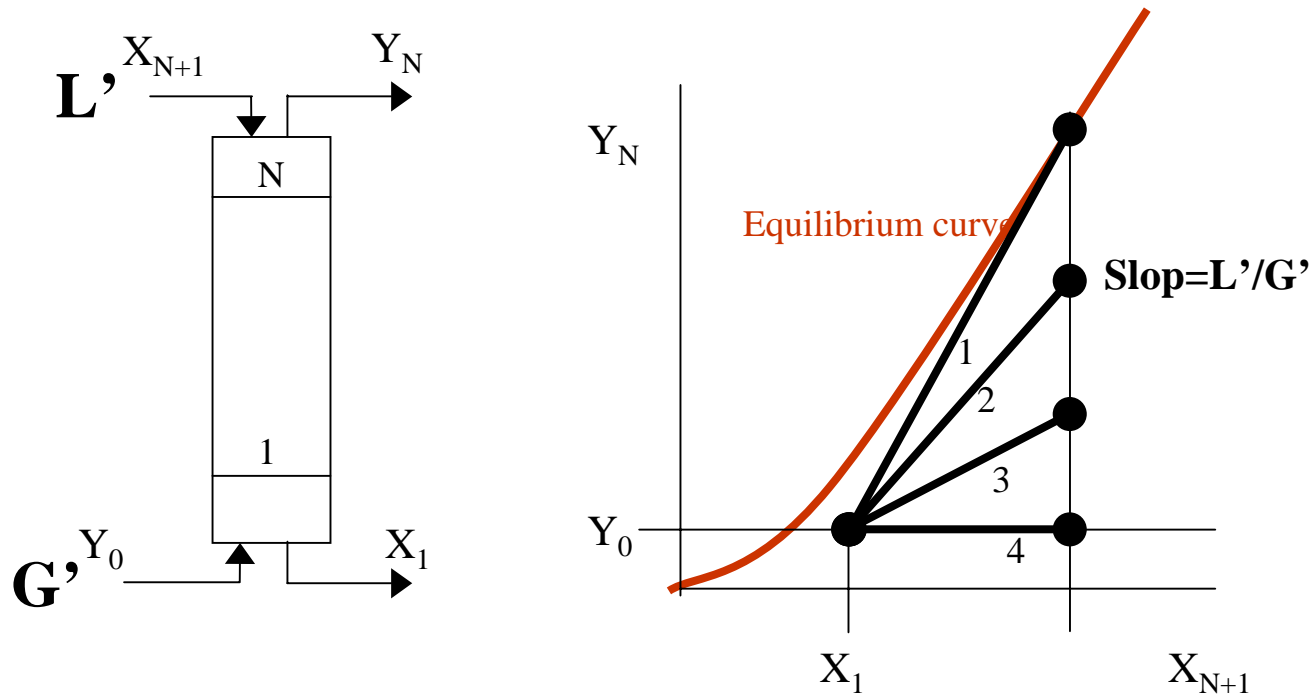


# Stripping column



- the fraction of a component stripped =  $f(\text{no of stages, stripping factor})$
- stripping factor,  $S = (KG)/L$
- if  $S > 1$  then any degree of stripping can be achieved.
- The larger the value of  $S$ , the fewer the no. of stages required, however the larger stripping gas required

# Operating line for a Stripper - stripping agent flow rate



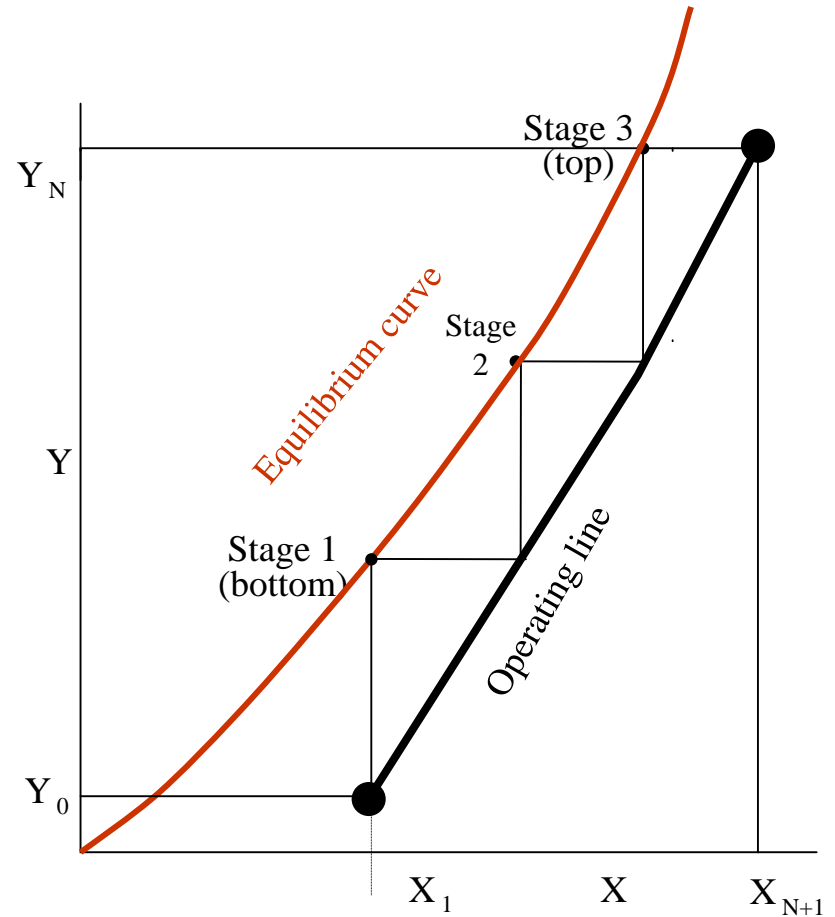
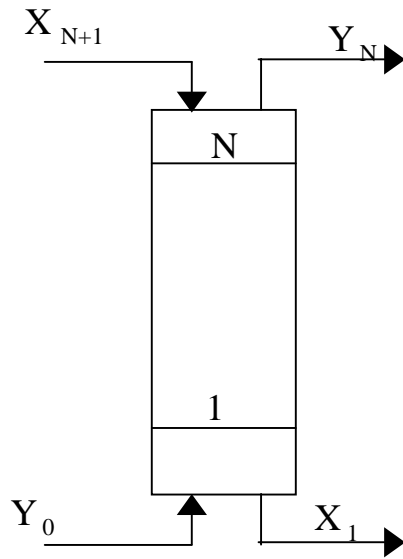
$$Y_N = X_{N+1}(L'/G') + Y_0 - X_1(L'/G')$$

Operating line 1: minimum stripping agent rate; but no. of stages = infinite

Operating line 4: no. of stages = 0; but infinite stripping agent flowrate

Actual operating stripping agent flow rate = (1.1 ~ 2.0) \* minimum stripping agent flow rate

# Graphical determination of the no. of stages for stripper



# Why Computer simulation needed?

We make some assumptions before:

- Carrier gas is insoluble
- Solvent is nonvolatile
- The system is isothermal and isobaric
- The heat of absorption is negligible

The problems:

- **fixes the no. of stages** rather than recover the percent of solute
- **more than one solute**
- when the best operating conditions of temperature and pressure are to be determined so that the location of the **equilibrium curve is unknown**
- **very low or very high concentrations** force the graphical construction to the corners of the diagram so that **multiple y-x diagrams** of varying sizes and dimensions are needed

# Thermodynamic for Absorber and Stripper

Phase equilibrium  $\hat{f}_i^v = \hat{f}_i^L$  where  $\hat{f}_i^v = Py_i \hat{\phi}_i^v = y_i \gamma_{iv} f_i^v$   
 $\hat{f}_i^L = Px_i \hat{\phi}_i^L = x_i \gamma_{iL} f_i^L$

$y_i \hat{\phi}_i^v = x_i \hat{\phi}_i^L \implies K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^v}$   
 $Py_i \hat{\phi}_i^v = x_i \gamma_{iL} f_i^L \implies K_i = \frac{y_i}{x_i} = \frac{\gamma_{iL} f_i^L}{P \hat{\phi}_i^v}$

$f_i^L = P_i^{sat} \phi_i^{sat} \exp\left[\int_{P_i^{sat}}^P \left(\frac{V_i^L}{RT}\right) dP\right]$   
 Poynting Factor

$K_i = \frac{\gamma_{iL} P_i^{sat} \phi_i^{sat}}{P \hat{\phi}_i^v}$  (medium pressure)  
 $K_i = \frac{\gamma_{iL} P_i^{sat}}{P}$  (low pressure) **modified Raoult's law**  
 $K_i = \frac{P_i^{sat}}{P}$  (ideal solution) **Raoult's law**

$K_i = \frac{P_i^{sat}}{x_i^* P}$  **Solubility**  
 $K_i = \frac{H_i}{P}$  **Henry's law**

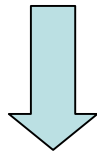
Note: Dissolved non-condensable gases:  
 (1) Henry's Gas Law - light gases dissolved in water  
 (2) TSRK method - light gases dissolved in methanol



# Thermodynamic consideration for absorber

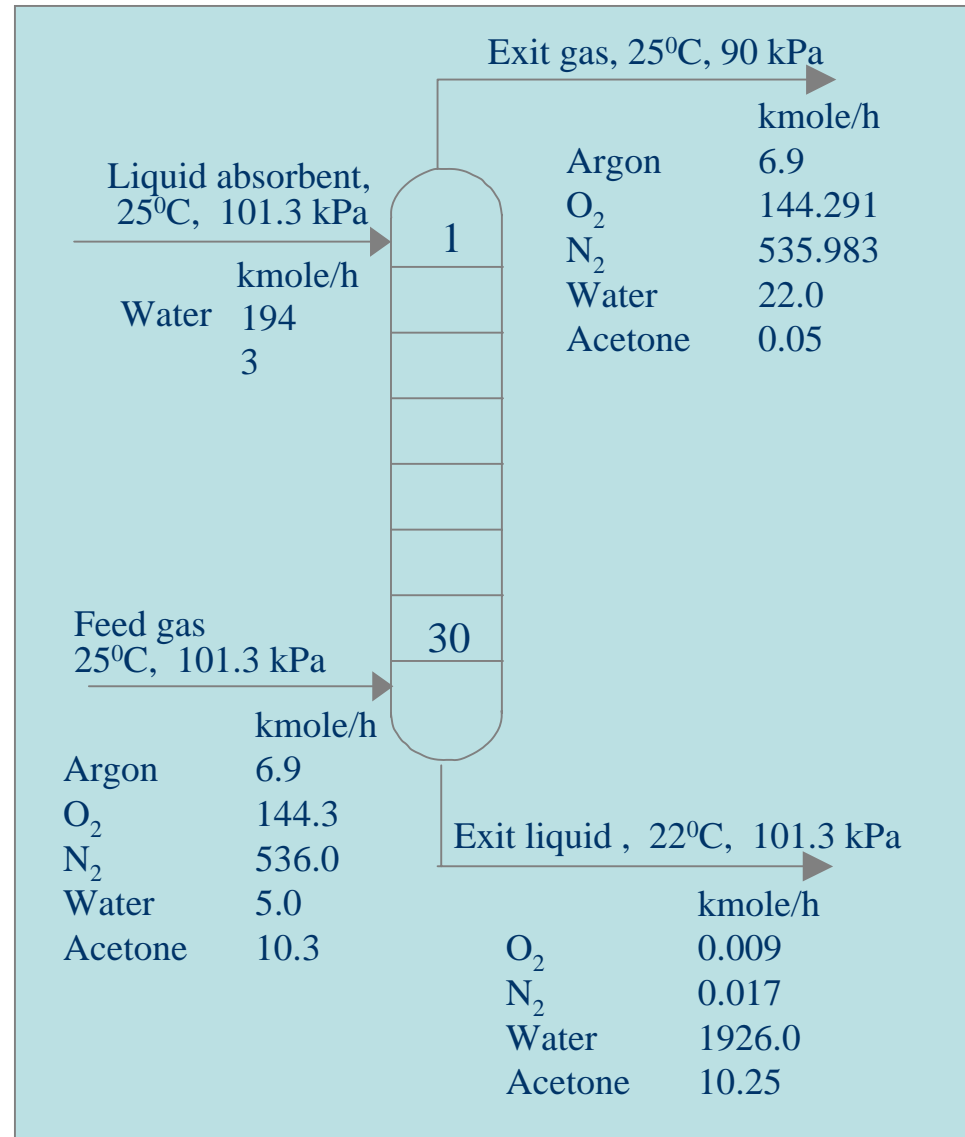
## For Absorption

- Acetone - modified Raoult's law  
- Raoult's law
- N<sub>2</sub>, O<sub>2</sub> - Henry law
- Argon - Henry law



## For Absorption simulation

- Acetone, Water - NRTL, UNIQUAC, ...
- N<sub>2</sub>, O<sub>2</sub>, Argon - Henry law



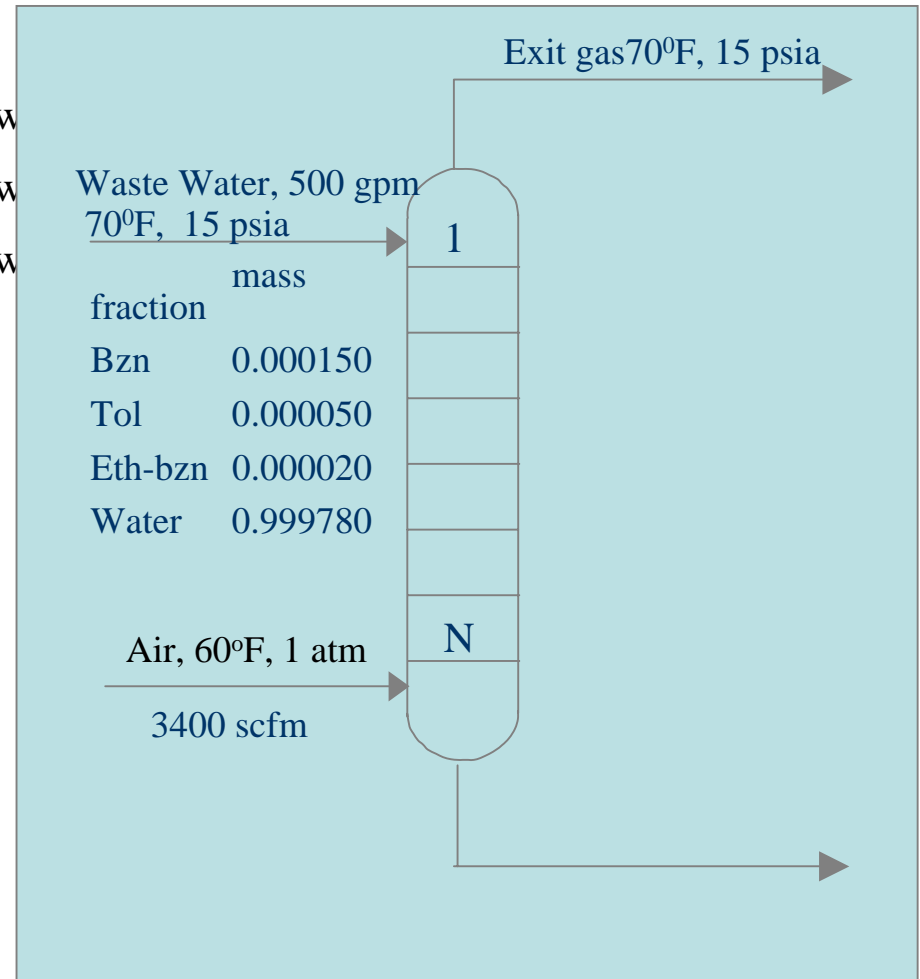
# Thermodynamic consideration for stripper

For stripper

- benzene - modified Raoult's law
- Toluene - modified Raoult's law
- Ethylbenzene - modified Raoult's law
- Water - Raoult's law
- air - Henry law

For stripper simulation

- benzene - NRTL, UNIQUAC, ...
- Toluene - NRTL, UNIQUAC, ...
- Ethylbenzene - NRTL, UNIQUAC, ...
- Water - NRTL, UNIQUAC, ...
- air - Henry law



# Chemical absorption ( reactive absorption)

## Non-electrolyte approach

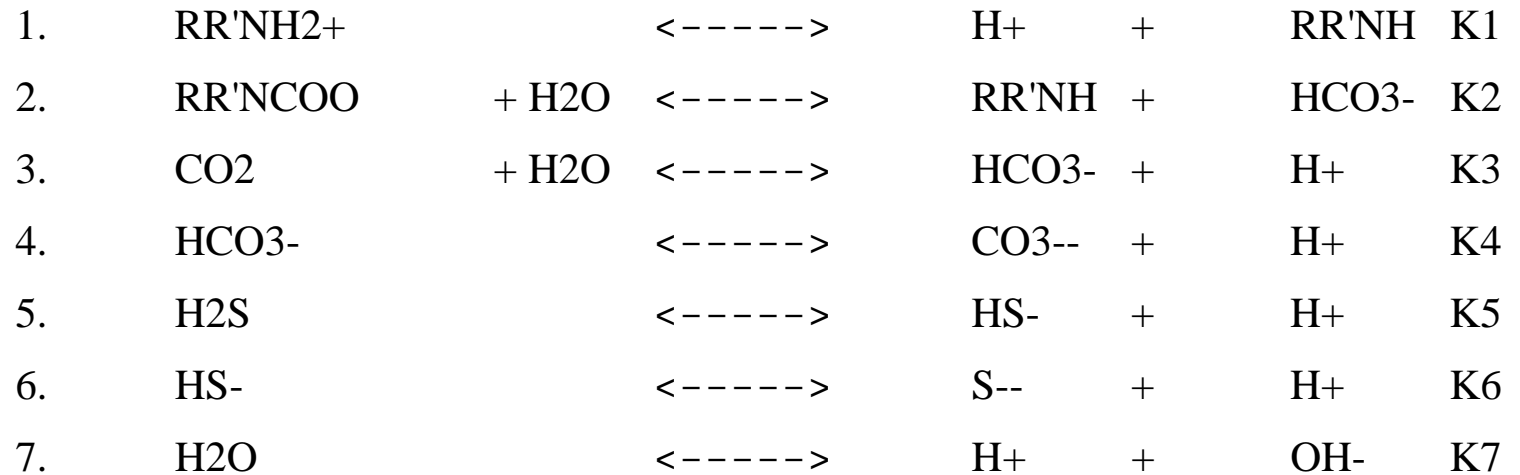
- Amine - for the removal of sour gases (H<sub>2</sub>S, CO<sub>2</sub>) from hydrocarbon streams using MEA, MDEA or DEA.
- Sour - for modeling systems with CO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, and other compounds dissolved in water.
- PPAq - used for the modeling of ionic type compounds, such as HCl or HNO<sub>3</sub>, which dissolve in water and disassociate.

## Electrolyte approach

- Ideal
- Pitzer
- NRTL for electrolyte 1982
- NRTL for electrolyte 1986

# Amine Model

The chemical reactions in an H2S-CO2-Amine system are described by the following reactions:



where R and R' represent alcohol groups. The reaction equations are solved simultaneously to obtain the free concentration of H<sub>2</sub>S and CO<sub>2</sub>. The partial pressure of H<sub>2</sub>S and CO<sub>2</sub> are calculated by the Henry's constants and free concentration in the liquid phase. Reference: Kent, R. L. and Eisenberg, Hydrocarbon Processing, Feb. 1976, p. 8

# SOUR WATER Model

The chemical reactions in H2S-CO2-NH3 systems are represented by the following reactions:

1.  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$   
K1
  2.  $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{--} + \text{H}^+$   
K2
  3.  $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$   
K3
  4.  $\text{NH}_3 + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{NCOO}^- + \text{H}_2\text{O}$   
K4
  5.  $\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$   
K5
  6.  $\text{HS}^- \rightleftharpoons \text{S}^{--} + \text{H}^+$   
K6
  7.  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$   
K7
- Reference: EPA-600/2-80-067 A New Correlation of NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>S Volatility Data from Aqueous Sour Water Systems by Grant M, Wilson EPA Grant No. R804364010.

The addition of NaOH or Carbolic acid is also considered in CHEMCAD.

The dissociation of Phenol and Hydrogen Cyanide is also included in the program.

# Partial Pressures of Aqueous mixtures Model (PPAQ)

1. The K-value of the solute is calculated by the following equation,

$$K = PP/(XP_T) = (PP/P_T)/X$$

PP = the solute partial pressure, calculated by interpolating the user-provided table

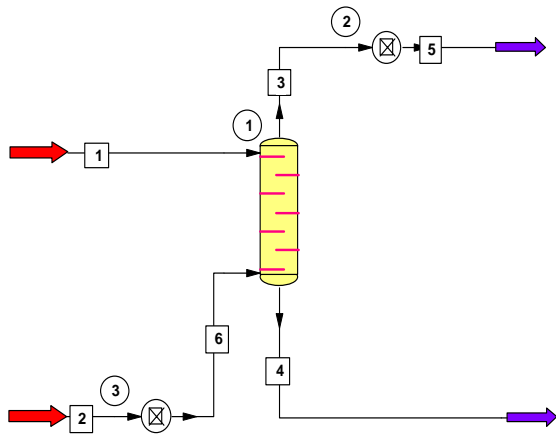
P<sub>T</sub> = the system pressure

X = the liquid molar concentration of the solute

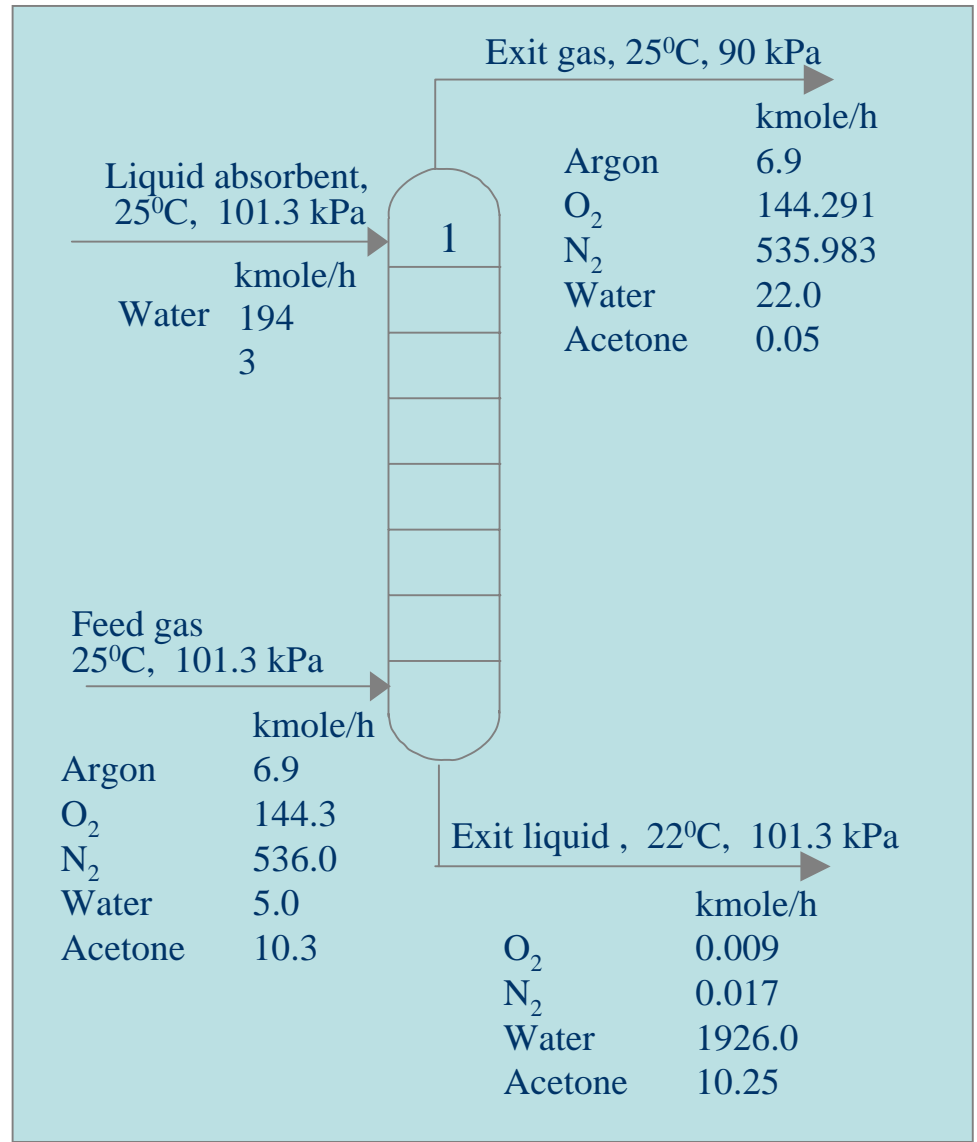
2. The K-value of water is calculated using the partial pressure data given in the .PPA file.
  3. K-values for all other components are calculated using Henry's Gas Law.
  4. If the HGL data is not present for a given compound, the program will fall back to the MSRK method. If the MSRK parameters for a given compound are not present, the program will use the SRK method.
- using partial pressures to calculate the equilibrium of the solute.
  - HCl or HNO3 is already considered in CHEMCAD.

# Simulate absorber using ChemCAD

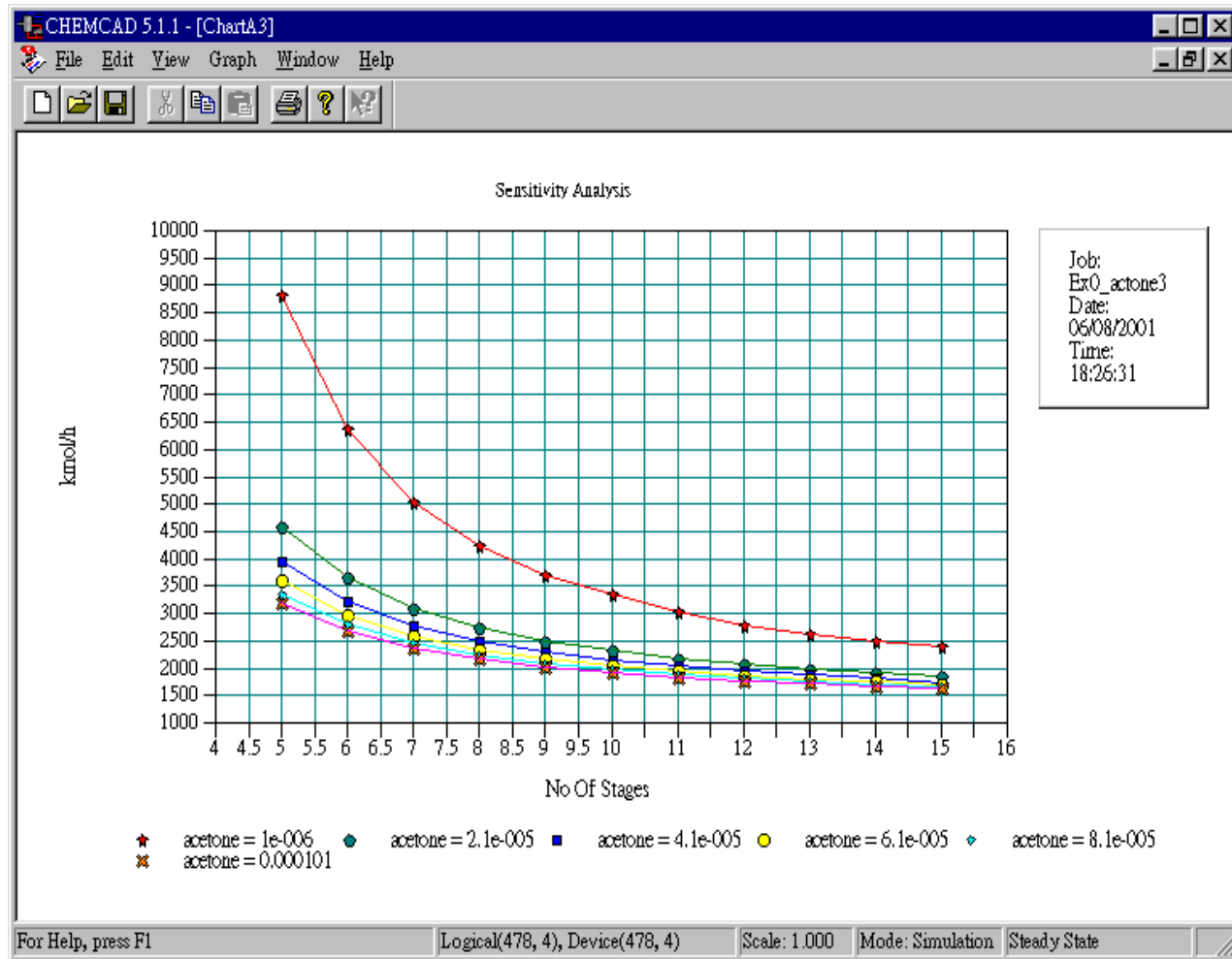
Remove acetone down to 100 ppm



Stream No.	1	6	3	4
-- Overall --				
Molar flow kmol/h	484.2522	702.5000	691.5662	495.1859
Mass flow kg/h	8723.8021	20596.9013	19989.6598	9331.0409
Temp C	25.0000	25.0000	27.5198	38.6127
Pres kPa	101.3000	101.3000	590.0000	601.3000
Vapor mole fraction	0.0000	1.000	1.000	0.0000
Enth kcal/h	-3.3065E+007	-8.2339E+005	-2.9296E+005	-3.3596E+007
Actual vol m <sup>3</sup> /h	8.7526	17182.7439	2927.1054	9.5782
Std liq m <sup>3</sup> /h	8.7252	23.7343	22.9770	9.4825
Std vap 0 C m <sup>3</sup> /h	10853.8570	15745.5861	15500.5215	11098.9225
Component mole fractions				
Argon	0.000000	0.009822	0.009976	0.000001
Oxygen	0.000000	0.205409	0.208641	0.000022
Nitrogen	0.000000	0.762989	0.775023	0.000041
H2O	1.000000	0.007117	0.006260	0.979275
Acetone	0.000000	0.014662	0.000100	0.020661



# Using sensitivity analysis to explore major variables



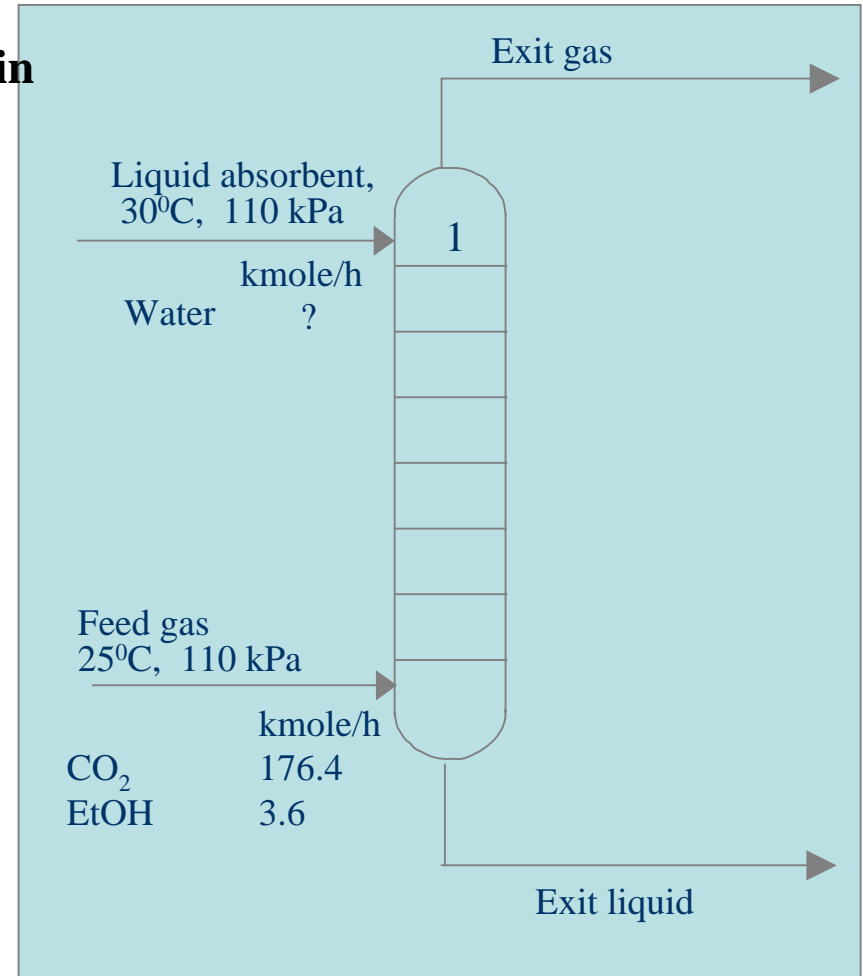
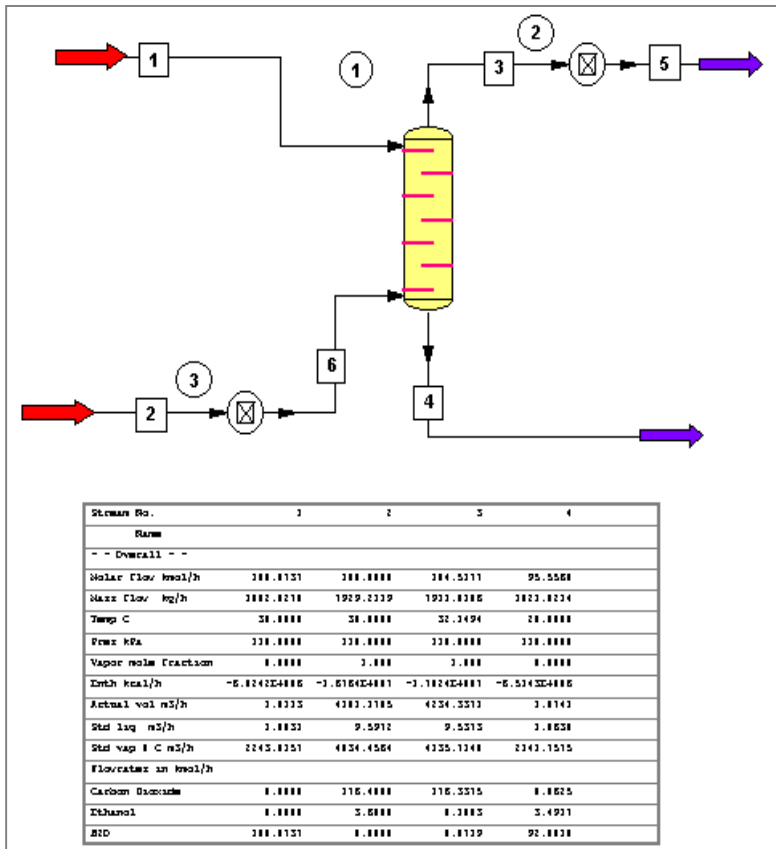


# Simulate absorber using ChemCAD

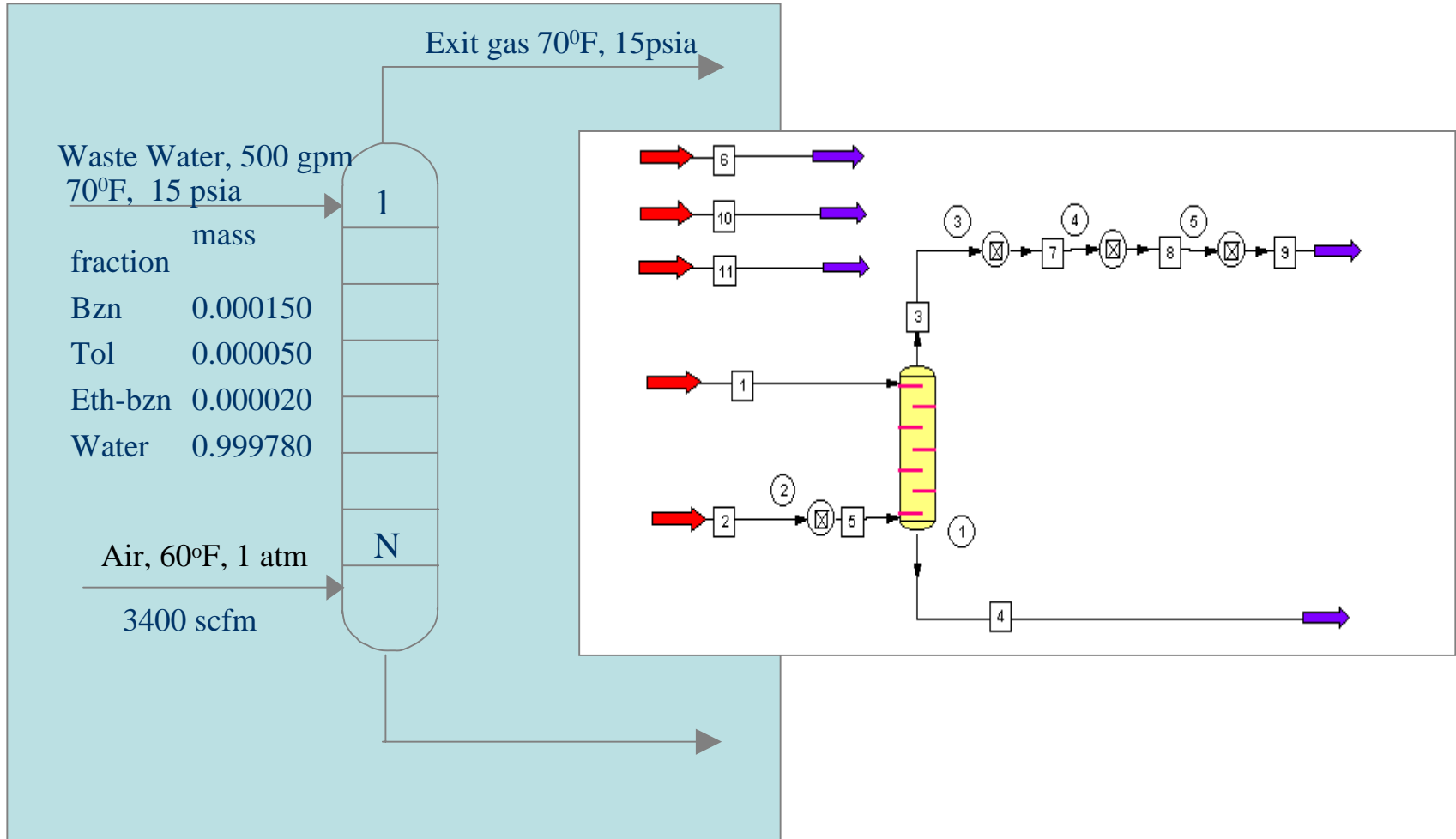
97% EtOH must be removed

find: 1. Lmin

2. no. of stages when 1.5\* Lmin

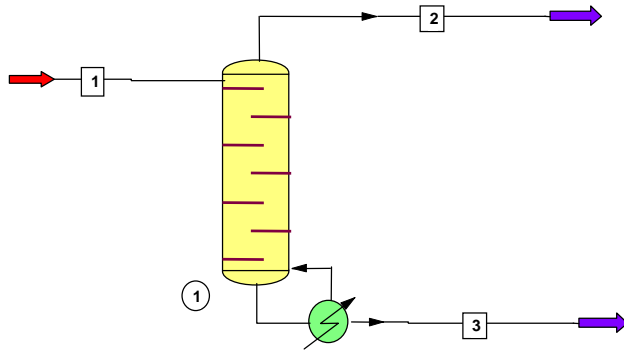


# Simulate stripper using ChemCAD



# Simulate Sour water stripper using ChemCAD (SOUR)

Remove H<sub>2</sub>S and NH<sub>3</sub> from wastewater down to 5 ppm

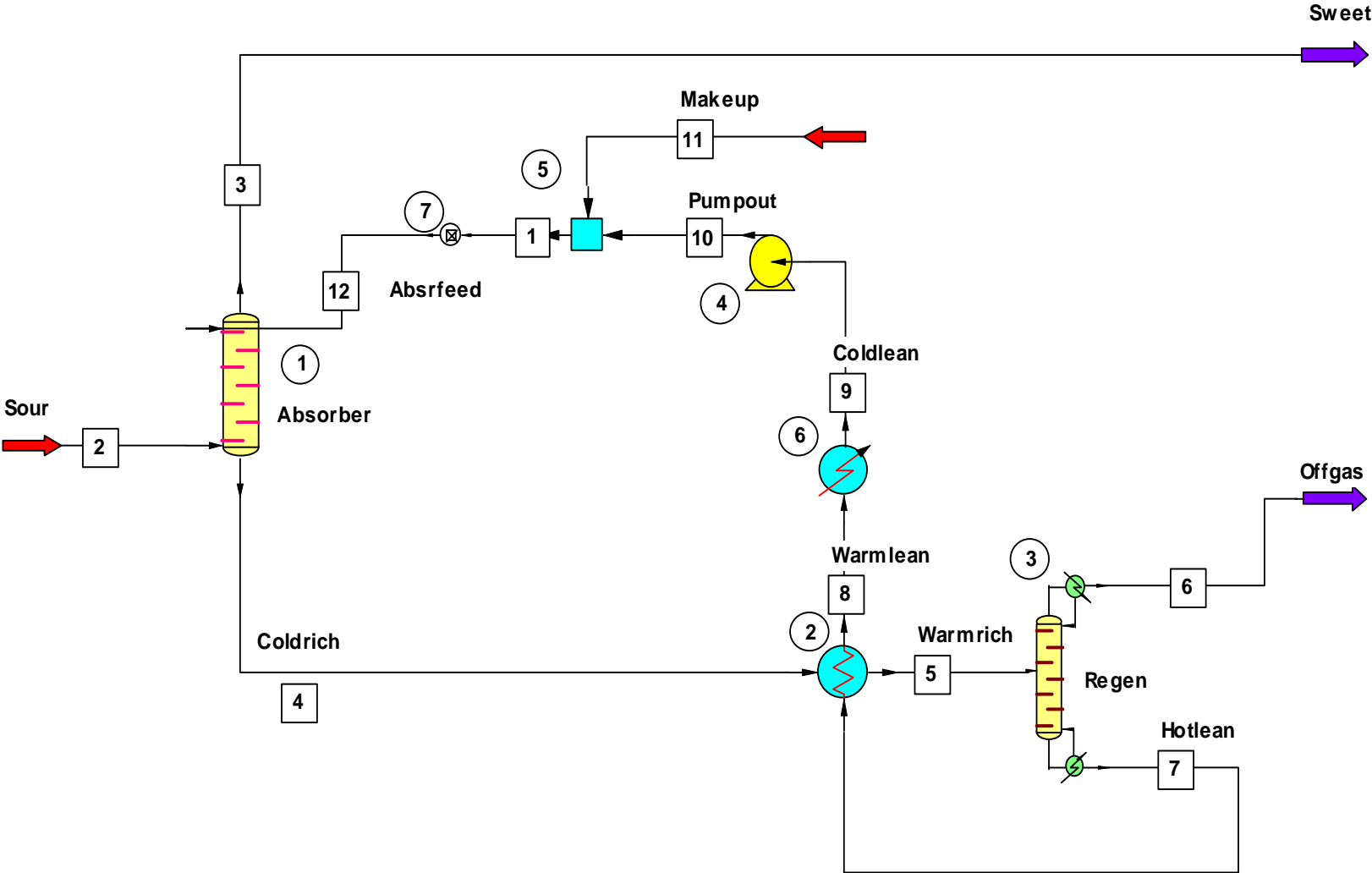


Stream No.	1	2	3
Name			
- - Overall - -			
Molar flow lbmol/h	3854.5125	15.4541	3839.0581
Mass flow lb/h	69503.8516	343.2190	69160.6250
Temp F	140.0000	147.9073	218.7682
Pres psia	56.8972	14.3580	16.7800
Vapor mole fraction	0.0000	1.0000	0.0000
Enth MMBtu/h	-468.44	-0.56860	-462.24
Actual vol ft3/hr	1165.9974	6971.4404	1212.2500
Std liq ft3/hr	1115.3810	7.3525	1108.0283
Std vap 60F scfh	1462705.1250	5864.5171	1456840.5000
Component mass fractions			
Hydrogen Sulfide	0.002194	0.444269	0.000000
H <sub>2</sub> O	0.996045	0.199916	0.999996
Ammonia	0.001761	0.355815	0.000004

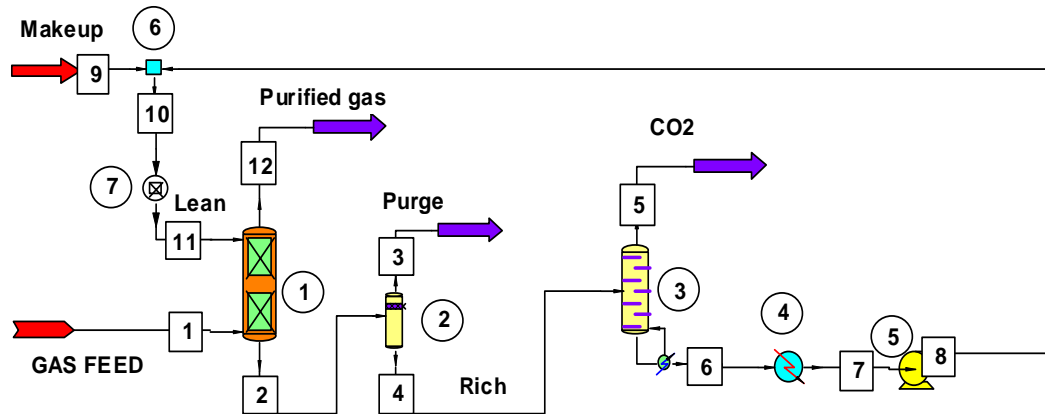
Tower Plus Summary			
Tower Plus # 1			
Configuration:			
No. of strippers	0	No. of pumparounds	1
No. of side exchangers	0	No. of side products	0
Main Column:			
Colm No. of stgs	15		
Press of colm top (psia)	14.3580		
Column press drop psi	2.4220		
1st feed stage #	4		
Condenser:			
Reboiler:			
Have a reboiler? (Y/N)	Y		
Heat duty MMBtu/h	13.3000		
Pumparounds:			
Pumparound no.	1		
From stage no.	3		
To stage no.	1		
Mol. flow rate (lbmol/h)	3796.3999		
Tray Specifications:			
Tray no.	1		
Vap mole flow lbmol/h	15.4540		
Convergence Parameters:			
Initialization flag	1		



# Selective H<sub>2</sub>S Removal with MDEA



# CO2 removal by hot carbonate /Benfield/ Process (K2CO3)

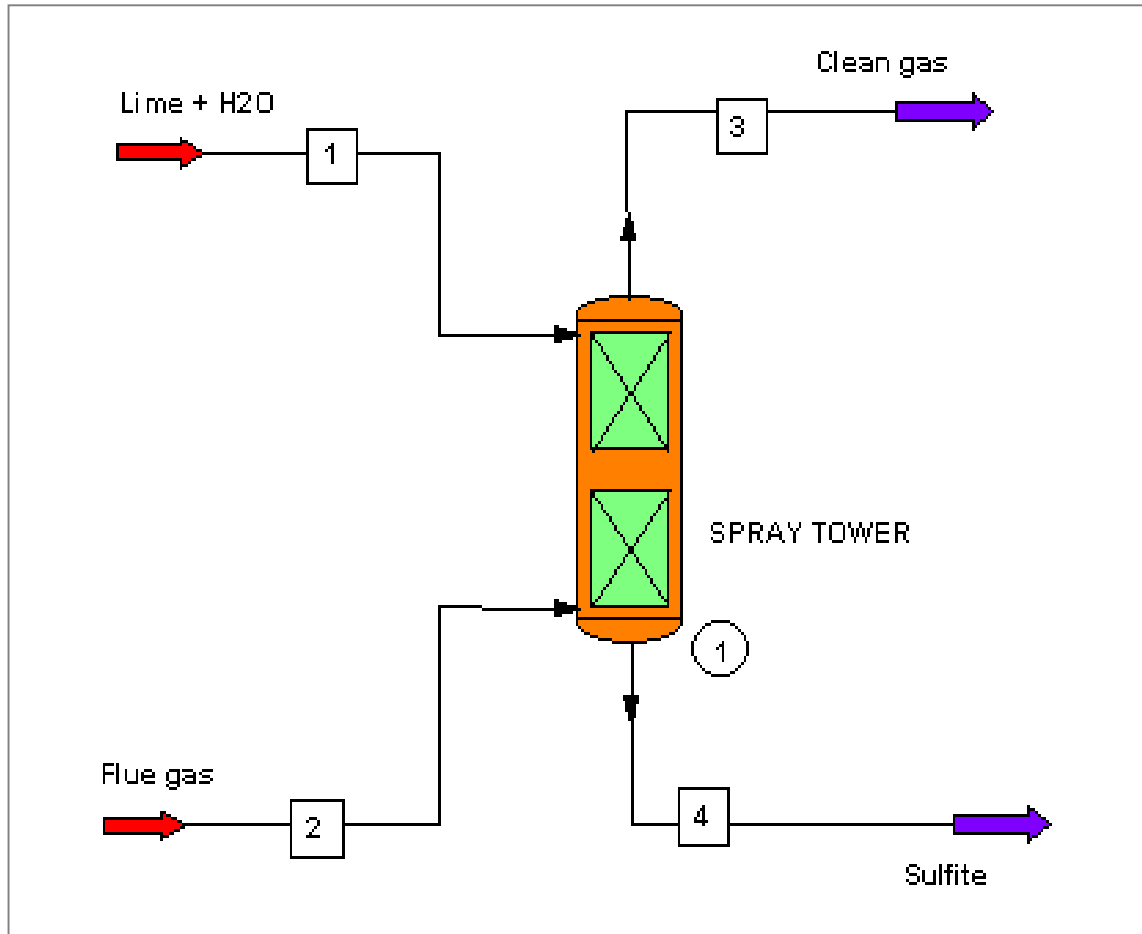


Stream No.	1	12	3	5
Name	GAS FEED	Purified gas	Purge	CO2
- - Overall - -				
Temp C	33.00	83.70	86.35	93.70
Pres bar	22.20	21.50	1.50	1.30
Actual vol m3/h	1888.10	2197.02	129.59	7191.99
Std vap 0 C m3/h	38668.52	36527.86	146.48	6925.29
Component mole fractions				
Ethylene	0.1959	0.2060	0.3009	0.0007
Oxygen	0.0453	0.0479	0.0166	0.0000
Carbon Dioxide	0.0682	0.0000	0.0503	0.3792
Water	0.0006	0.0170	0.2708	0.6198
Nitrogen	0.0248	0.0263	0.0054	0.0000
Argon	0.0609	0.0643	0.0394	0.0000
Methane	0.6008	0.6347	0.3151	0.0002
Ethane	0.0036	0.0038	0.0016	0.0000

Stream No.	11	4
Name	Lean	Rich
- - Overall - -		
Molar flow kmol/hr	6923.38	6895.30
Mass flow kg/hr	163428.61	168079.00
Temp C	83.49	86.35
Pres bar	28.50	1.50
- - Liquid only - -		
PH value	11.19	10.03
Flowrates in kmol/hr		
Ethylene	0.00	0.22
Oxygen	0.00	0.00
Carbon Dioxide	0.01	0.16
Water	5550.93	5407.40
Nitrogen	0.00	0.00
Argon	0.00	0.01
Methane	0.00	0.07
Ethane	0.00	0.00

# Wet Desulfurization of Flue Gas

Reactive ionic absorption of  $\text{SO}_2$  in aqueous  $\text{CaCO}_3$



# Absorber and Stripper Sizing by using ChemCAD

- **Tray tower**
  - **Sieve tray**
  - **Valve tray**
  - **Bubble cap**
  
- **Pack column**
  - **Sherwood-Eckert for Random Packing**
  - **Mackowiak for Structure/Random Packing**
  - **Billet and Schultes Correlation for Structure/Random Packing**



# ChemCAD

*VLE, LLE data regression  
and  
Extractor Simulation*

# ChemCAD Regression

- Properties of Pure Components
- BIP Regression (VLE, LLE)
  - Vapor-Liquid Equilibrium (VLE)
  - Liquid-Liquid Equilibrium (LLE)
  - Regression VLE, LLE data
  - VLE, LLE Phase Diagram
  - Flash Calculation (VLE, VLLE)
  - Extractor Calculation
- Electrolyte Regression
- Rate Equation Regression

# Regression of Pure Components Properties

- ◎ **Antoine Vapor Pressure**
- ◎ **Library Vapor Pressure**
- ◎ **Heat of Vaporization**
- ◎ **Liquid Density**
- ◎ **Liquid Heat Capacity**
- ◎ **Liquid Viscosity**
- ◎ **Liquid Thermal Conductivity**
- ◎ **Liquid Surface Tension**
- ◎ **Ideal Gas Heat Capacity**
- ◎ **Vapor Viscosity**
- ◎ **Vapor Thermal Conductivity**

# BIP Regression

- ◎ Act. Model from UNIFAC VLE
- ◎ TPXY data VLE
- ◎ TPX data VLE
- ◎ TXX data LLE
- ◎ Regression Gamma data
- ◎ Act. Model from UNIFAC LLE

## Workshop Regression1. Ternary VLE Regression

Comps.: 1. Sec-Butanol (450)  
2. MEK (153)  
3. Water (62)

Literature 2-3 azeotrope at 73.86 °C ( homogeneous)  
2 (MEK) boiling at 79.63 °C  
1-3 azeotrope at 87.00 °C ( heterogeneous)  
1 (2- butanol) boiling at 99.54 °C  
3 (Water) boiling at 100.0 °C

- ◎ Set K-model: Wilson and Regression the BIPs of 1-2, 1-3, 2-3 ( VLE data from literature)
- ◎ Set K-model: NRTL and Regression the BIPs of 1-2, 1-3, 2-3 ( VLE data from literature)
- ◎ Reset k-model: UNIFAC , predict binary VLE and compare it with Know data(azeotrope temp. and compositions)
- ◎ Set K-model: NRTL and Regression the ternary system of 1-2-3 ( VLE data from literature)

## 2-Butanol(1) / Water(2) VLE data

TPXY REGRESSION			
Temp C	Press mmHg	X	Y
92.700	760.00	0.95000E-02	0.11600
91.000	760.00	0.16600E-01	0.21400
89.700	760.00	0.21000E-01	0.30300
89.500	760.00	0.25700E-01	0.34300
88.200	760.00	0.34000E-01	0.38700
88.000	760.00	0.43000E-01	0.38500
87.900	760.00	0.46000E-01	0.38600
88.700	760.00	0.50100	0.45200
88.700	760.00	0.51900	0.46300
89.000	760.00	0.56300	0.47000
89.700	760.00	0.60700	0.49300
89.800	760.00	0.71100	0.52000
92.100	760.00	0.81600	0.62400
94.200	760.00	0.90100	0.73100
95.800	760.00	0.96000	0.80100
97.700	760.00	0.98400	0.89800
98.400	760.00	0.99600	0.95200

## MEK(1) / H<sub>2</sub>O(2) VLE data

TPXY REGRESSION			
Temp C	Press mmHg	X	Y
100.00	760.00	0.00000	0.00000
73.900	760.00	0.48000E-01	0.64400
73.300	760.00	0.66900	0.65800
73.400	760.00	0.73100	0.67600
73.600	760.00	0.80000	0.69700
74.000	760.00	0.84200	0.72400
74.300	760.00	0.86400	0.74800
74.800	760.00	0.88400	0.76900
75.600	760.00	0.91300	0.80800
79.600	760.00	1.00000	1.00000

## MEK(1) / 2-Butanol(2) VLE data

TPXY REGRESSION			
Temp C	Press mmHg	X	Y
99.000	760.00	0.18000E-01	0.4000E-01
97.500	760.00	0.56000E-01	0.11000
94.200	760.00	0.16400	0.29100
92.500	760.00	0.24500	0.40300
91.300	760.00	0.29100	0.45600
88.300	760.00	0.42500	0.59500
86.700	760.00	0.52100	0.67400
84.300	760.00	0.65400	0.76800
83.200	760.00	0.71700	0.81200
82.100	760.00	0.80900	0.87100
80.900	760.00	0.89200	0.96200
79.900	760.00	0.97100	0.98000

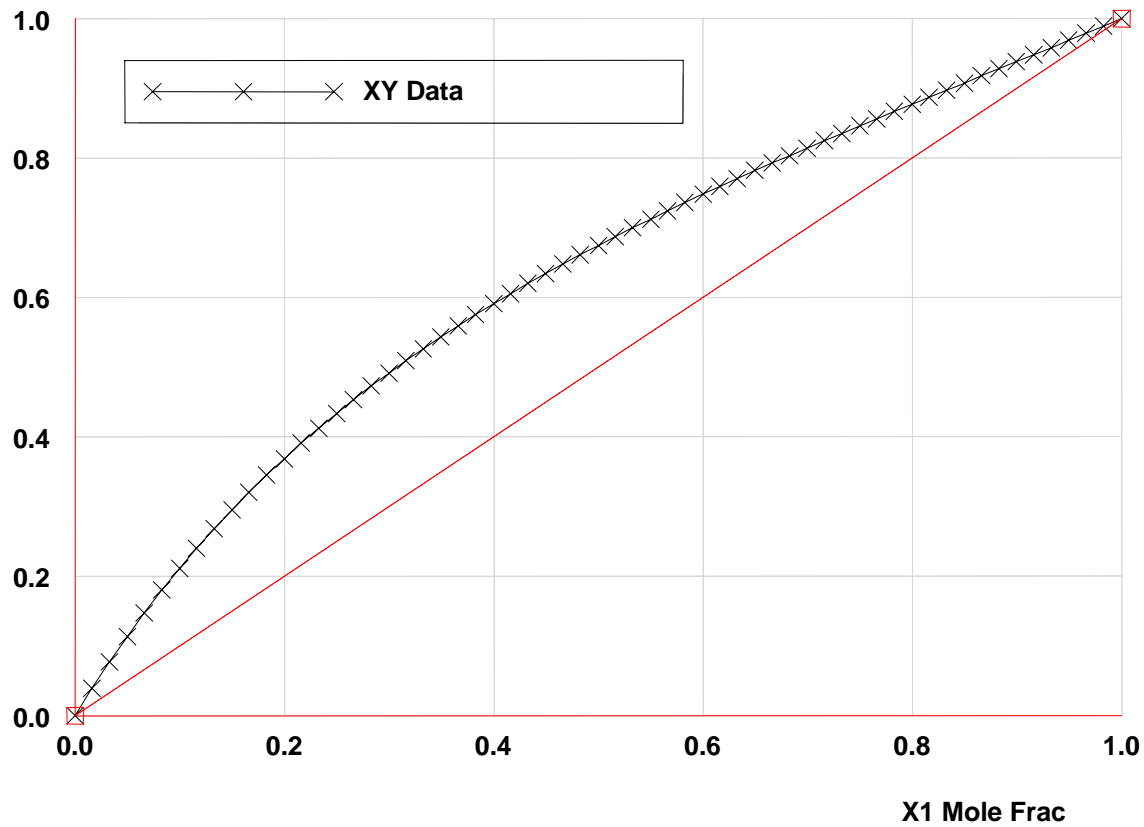


## 2-Butanol(1) / MEK(2) / Water(3) VLE data

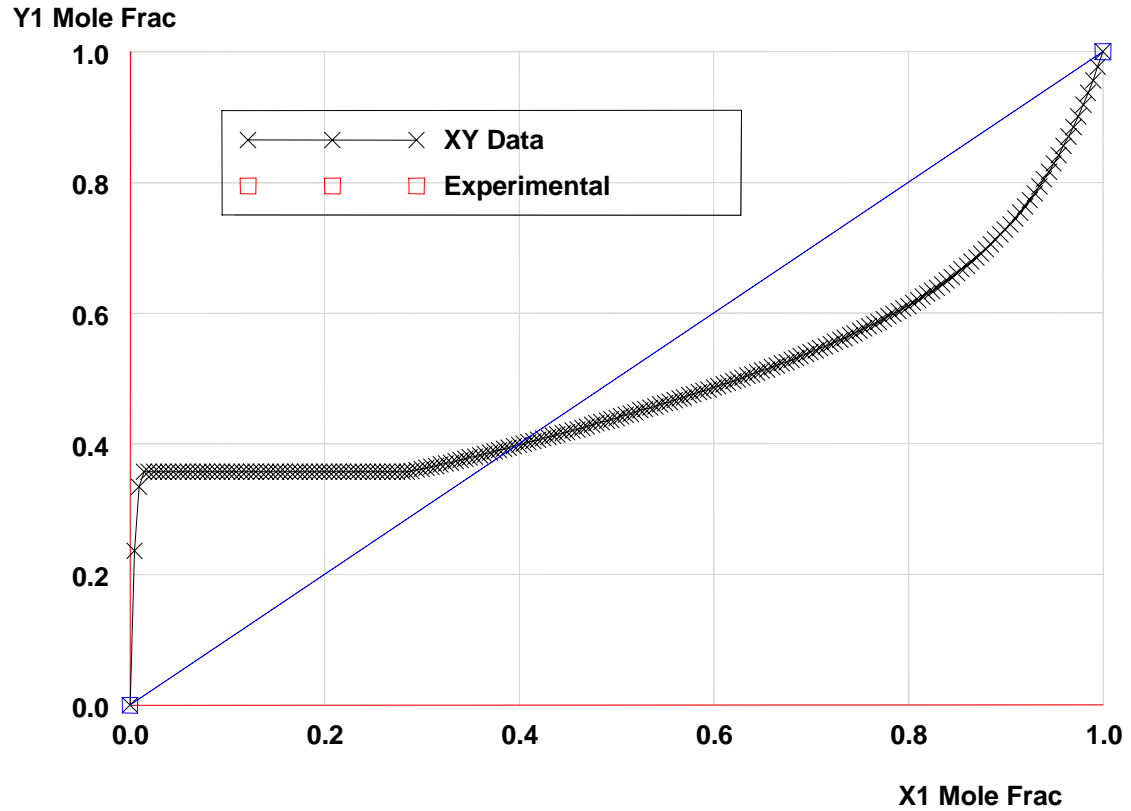
TPXY REGRESSION					
Press mmHg	Temp C	X1	X2	Y1	Y2
760.00	78.411	0.18100	0.72000	0.90000E-01	0.68900
760.00	76.739	0.16000	0.64000	0.95000E-01	0.62100
760.00	76.139	0.14000	0.56000	0.72000E-01	0.58300
760.00	76.050	0.12100	0.47000	0.68000E-01	0.55300
760.00	76.200	0.10100	0.39000	0.63000E-01	0.53600
760.00	79.372	0.50000E-02	0.20000E-01	0.57000E-01	0.50000
760.00	82.700	0.40000E-02	0.16000E-01	0.56000E-01	0.37500
760.00	81.461	0.36200	0.53900	0.19100	0.62000
760.00	79.289	0.32100	0.48000	0.17800	0.53000
760.00	78.472	0.28100	0.42000	0.14600	0.49200
760.00	78.439	0.24000	0.36000	0.13300	0.45700
760.00	78.178	0.20000	0.30000	0.10900	0.45000
760.00	78.572	0.16000	0.24000	0.10700	0.44000
760.00	82.450	0.11000E-01	0.15000E-01	0.95000E-01	0.35000
760.00	85.089	0.90000E-02	0.11000E-01	0.80000E-01	0.35200
760.00	84.661	0.54200E	0.35900	0.30700	0.43800
760.00	82.189	0.48300	0.32000	0.26400	0.42400
760.00	81.878	0.42200	0.28000	0.24000	0.36300
760.00	81.239	0.36000	0.24000	0.21100	0.35000
760.00	81.178	0.30000	0.20000	0.20400	0.35400

MEK(1) / Sec-Butanol(2) at 760.00 mmHg By NRTL

Y1 Mole Frac



### Sec-Butanol(1) / Water(2) at 760.00 mmHg By NRTL



# Extractor Calculations

1. Liquid-Liquid Equilibrium (LLE)
2. Regression LLE data
3. LLE Phase Diagram
4. Three Phase Equilibrium (Three Phase Flash)
5. Extractor Calculation

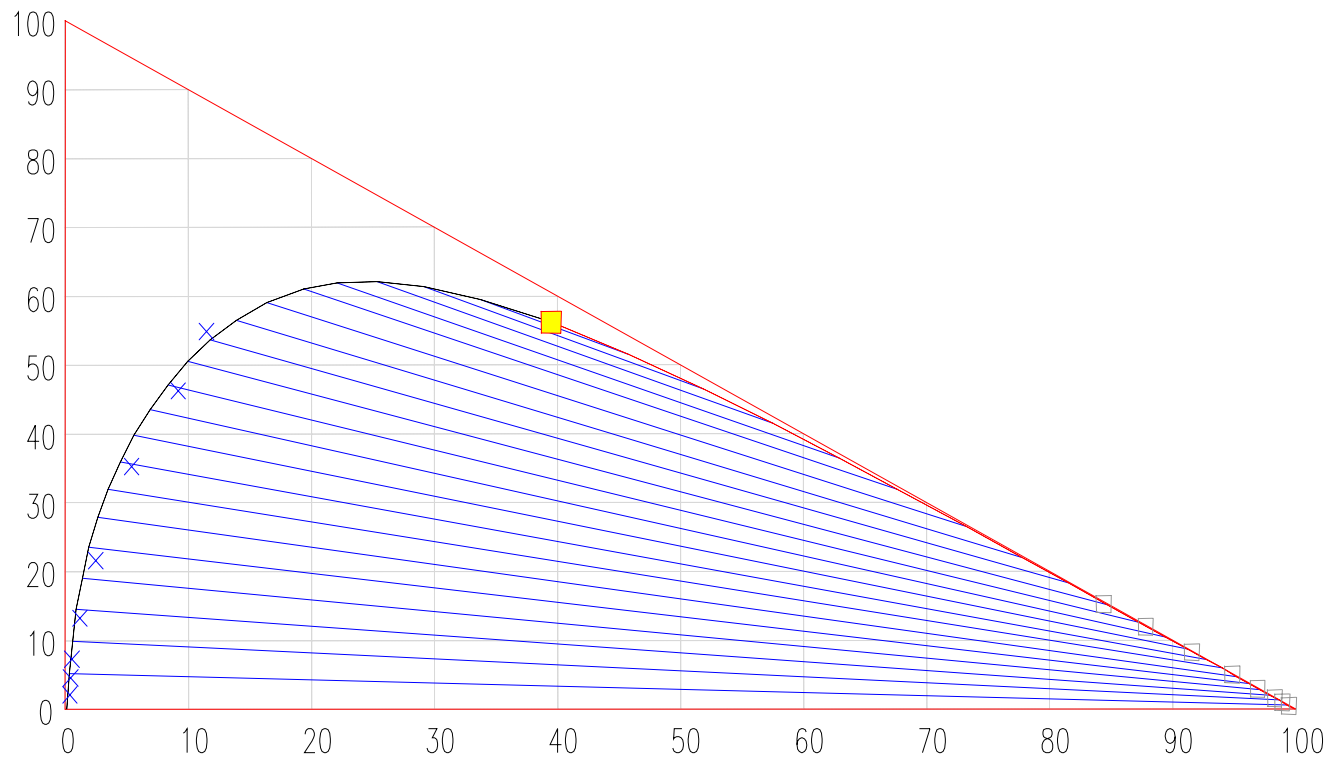
# Regression LLE data

Toluene(1)/Acetone(2)/Water(3) Experimental Data (mole fraction)

<u>T Deg C</u>	<u>X11</u>	<u>X21</u>	<u>X12</u>	<u>X22</u>
30.00	0.9755	0.0204	0.0001	0.0050
30.00	0.9504	0.0450	0.0001	0.0108
30.00	0.9218	0.0722	0.0001	0.0164
30.00	0.8551	0.1329	0.0002	0.0305
30.00	0.7581	0.2169	0.0003	0.0508
30.00	0.5933	0.3526	0.0005	0.0837
30.00	0.4455	0.4625	0.0010	0.1208
30.00	0.3360	0.5487	0.0020	0.1537

# Toluene/Acetone/Water at 30.00 C

Mole Percent of (2)



Mole Percent of (3)

## NRTL Model

The NRTL equation has the following form:

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} X_j}{\sum_k^N G_{ki} X_k} + \sum_j^N \frac{X_j G_{ij}}{\sum_k^N G_{kj} X_k} \left[ \tau_{ij} - \frac{\sum_k^N X_k \tau_{ki} G_{kj}}{\sum_k^N G_{kj} X_k} \right]$$

where

$$\tau_{ji} = A_{ji} + B_{ji} / T$$

$$G_{ji} = \exp(-\alpha_{ji} * \tau_{ji})$$

$$\alpha_{ij} = \alpha_{ji}$$

T = Temperature in degrees Kelvin

# UNIQUAC Model

UNIQUAC equation

$$\ln \gamma_i = \ln \frac{\Phi_i}{X_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i$$

$$- \frac{\Phi_i}{X_i} \sum_j^N X_j l_j - q_i \ln \left[ \sum_j^N \theta_j \tau_{ji} \right] + q_i$$

$$- q_i \sum_j^N \frac{\theta_j \tau_{ij}}{\sum_k^N \theta_k \tau_{kj}}$$

Where

$$\Phi_i = x_i \cdot \chi_i / (\sum x_i \cdot \chi_j)$$

$$\Theta_i = x_i \cdot q_i / (\sum x_i \cdot q_j)$$

$$t_{ij} = \exp [A_{ij} - (U_{ij} - U_{jj}) / RT]$$

$$a_{ij} + b_{ij}/T = A_{ij} + (U_{ij} - U_{jj}) / RT$$

$$- (U_{ij} - U_{jj})/R = b_{ij}$$

$$A_{ij} = a_{ij}$$

T = Temperature in degrees Kelvin

$$l_i = (z/2) \cdot (\chi_i - q_i) - \chi_i + 1$$

z = 10 (coordination number)

q<sub>i</sub> = van der Waals area parameter (A<sub>wi</sub>/ (2.5 \* 10E9) where A<sub>wi</sub> is the van der Waals area)

χ<sub>i</sub> = van der Waals volume parameter (V<sub>wi</sub>/15.17 where V<sub>wi</sub> is the van der Waals volume)



## WILSON Model

WILSON equation

$$\ln \gamma_i = - \ln \left[ \sum_{j=1}^N x_j \Lambda_{ij} \right] + 1 - \sum_k^N \frac{x_k \Lambda_{ki}}{\sum_{j=1}^N x_j \Lambda_{kj}}$$

where

$$\Lambda_{ij} = (V_j/V_i) \exp[ - (\kappa_{ij} - \kappa_{ii}) / RT ]$$

$V_i$  = liquid molar volume of component i

$\kappa_{ij} - \kappa_{ii}$  = an empirically determined energy term in cal/g mol.

$X_i$  = mole fraction of component i

T = temperature in degrees Kelvin

The user may provide either  $\Lambda_{ij}$  and  $\Lambda_{ji}$  or  $(\kappa_{ij} - \kappa_{ii})$  and  $(\kappa_{ji} - \kappa_{jj})$ . If the absolute value of any parameter is greater than 10, the program will assume that you are using  $(\kappa_{ij} - \kappa_{ii})$ 's.

## Rules for Successful Regression

1. Suggestion: Use mole fractions for VLE and LLE data input.
2. Use the VLLS option if two liquid phase are likely to be present.
3. When doing ternary VLE regression, the third NRTL parameter, alpha, will have a default value of 0.3 if there is no value in the BIP list. You can define the alpha with the BIP command.
3. When doing ternary LLE regression, the third NRTL parameter, alpha, will have a default value of 0.2 if there is no value in the BIP list. You can define the alpha with the BIP command.

4. Choose regression data in the range of process requirements.
5. Plot the model fit with the data points. Reasonable curve or not?
6. If the model looks good but a better fit is required, reduce the relative and absolute tolerances.
7. Parameter sets are not unique. Once you have minimized error, you may try a different set of starting estimates.
8. Certain systems are better fit specific models.  
Wilson for strong hyperbolic characteristics (i.e. HCN-H<sub>2</sub>O).  
Data with strong inflections bordering on or including immiscibility may be better fit with 3-parameter (or higher) model such as NRTL.

# Conversion of DECHEMA Parameters to ChemCAD

Model		<b>a<sub>ij</sub></b> , units ( DECHEMA)	<b>a<sub>ij</sub></b> , units ( ChemCAD )	DECHEMA --> ChemCAD
VLE	UNIQUAC	(u <sub>ij</sub> -u <sub>jj</sub> ), cal/mole	(same)	-
	NRTL	(g <sub>ij</sub> -g <sub>jj</sub> ), cal/mole	(g <sub>ij</sub> -g <sub>jj</sub> )/R, deg K	/R
	Wilson	(i <sub>i</sub> -j <sub>j</sub> ), cal/mole	(same)	-
LLE	UNIQUAC	(u <sub>ij</sub> -u <sub>jj</sub> )/R, deg K	(u <sub>ij</sub> -u <sub>jj</sub> ), cal/mole	*R
	NRTL	(g <sub>ij</sub> -g <sub>jj</sub> )/R, deg K	(same)	-