

## Review Of Binary Distillation - McCabe-Thiele By Computer

Charles R. Koppany, Retired Chemical Engineer

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For many years the McCabe-Thiele graphical method (1) has been the accepted procedure for determining the number of theoretical trays in a binary distillation when constant molal overflow prevails throughout the column. For close boiling separations such as in an ethane-ethylene or propane-propylene splitter, constant molal overflow is very closely attained. However, in the rectifying sections of these columns, relative volatilities are close to one. As a result, the equilibrium curve and upper operating line are very close together, especially in the region of the overhead product composition  $x_D$ . This situation makes it very difficult to graphically step-off theoretical stages, which can be great in number in this region.

The difficulties described above can be circumvented if one is able to solve the McCabe-Thiele method analytically or by numerical methods on the computer or on a PC. Here a BASIC computer program is presented for doing just that. This program should be especially useful, for example, to a process engineer, working on an ethylene plant proposal, who needs to make a quick size (height) estimate for a  $C_2$  or  $C_3$  splitter column. Use of the program is illustrated for a specific example involving a  $C_3$  splitter.

Finally, a brief discussion is presented for estimating the effect of errors in relative volatility on the calculation of the number of theoretical stages.

**Smoker and Underwood equations.** The Smoker (2) and Underwood (3-6) equations are both analytical techniques for determining the number of theoretical stages in binary distillations operating at conditions of nearly constant relative volatility and constant molal overflow. However, these procedures do not provide detailed tray-by-tray liquid and vapor composition profiles that are normally generated by the McCabe-Thiele (MT).

Figure 1 gives the configuration and nomenclature used for a typical distillation column with a total condenser and reboiler.

**Working relationships.** First of all, the working relationships used in developing the program will be briefly described. Attention here will be restricted to single feed, two product binary distillations.

**Equilibrium curve.** The vapor-liquid equilibrium curve is represented by Eqs. 1 and 2.

$$\alpha = Ax^2 + Bx + C \quad (1)$$

$$y = \alpha x / \{1 + (\alpha - 1)x\} \quad (2)$$

Here  $x$  and  $y$  are the mole fractions of the light or lower-boiling component in the liquid and vapor respectively.  $\alpha$  is the relative volatility of the light component with respect to the heavier component ( $K_{lt}/K_{hvy}$ ). The constants  $A$ ,  $B$  and  $C$  are fit to a set of experimental isobaric VLE data, which hopefully ideally cover the full concentration range for the binary system to be distilled. If VLE data are not available, then  $\alpha$  values for the fit will have to be generated by some other means such as from a generalized correlation which is believed to give reasonably accurate predictions.

**Minimum reflux ratio.** The minimum reflux ratio  $(L/D)_{\min}$  is determined by first finding the point where the  $q$ -line intersects the equilibrium curve. This is Point  $a$  shown on Fig. 2. The  $q$ -line is expressed as:

$$y = \{q/(q - 1)\}x + x_F/(1 - q) \quad (3)$$

$q$  is defined as the moles of liquid introduced to the stripping section resulting from the introduction of each mole of feed. It basically characterizes the phase condition (mole fraction liquid) of the feed as it enters the column. Below are summarized the numerical limits for  $q$  depending upon various phase conditions of the entering feed:

<u>Phase Condition</u>	<u><math>q</math></u>
Cold feed	$> 1$
Bubble pt. Fee	$= 1$
Two phase feed	$0 < q < 1$

Dew pt. Feed = 0

Superheated vapor < 0

Eqs. 1-3 are combined to eliminate  $y$  and the resulting expression solved by trial-and-error substitution to give  $x'$ , the liquid mole fraction at the point of intersection of the  $q$ -line and the equilibrium curve.  $y'$  is then calculated from either Eq. 2 or 3. The minimum reflux ratio is then given by

$$R_M = (L/D)_{\min} = (x_D - y')/(y' - x') \quad (4)$$

**Upper operating line.** The equation of the upper operating line for constant molal overflow is

$$y_{n+1} = \{R/(R + 1)\}x_n + x_D/(R + 1) \quad (5)$$

It is shown as the line segment b-c on Fig. 2. Here  $R$  is the actual operating reflux ratio given by some specified percentage over the minimum,  $R_M$ . In order to determine the intersection of the upper operating line and the  $q$ -line (Point b), it is necessary to equate Eqs. 3 and 5. The resulting expression is solved directly for  $x''$ , the liquid composition at this point of intersection.  $y''$  is then easily determined by either Eq. 3 or 5.

**Lower operating line.** The lower operating line is now very easily established. It is simply the segment b-d with slope given by

$$\text{Slope} = (y'' - x_B)/(x'' - x_B) \quad (6)$$

and intercept by

$$\text{Intercept} = x_B(1 - \text{Slope}) \quad (7)$$

**The program.** The computer program, employing all of the above relationships for performing the McCabe-Thiele graphical construction numerically, is listed in Table 1. The program is written in QBASIC and has been adapted to run on a PC computer (MS-DOS).

Lines 30-50 request inputs for the coefficients  $A$ ,  $B$  and  $C$  of Eq. 1, which along with Eq. 2 establishes the equilibrium curve. Lines 100-150 require inputs for the product and feed compositions expressed as mole fraction of the light or lower-boiling component. Lines 160-200 require specification of  $q$ , the feed phase condition, and the ratio of operating to minimum reflux ratio desired. In Line 180 the value of  $q$

is set equal to 0.999999 if it was originally inputted as 1.0 (saturated liquid feed). This step avoids the occurrence of a singularity in Eq. 3.

The necessary parameters generated by Eqs. 1-7 are handled via Lines 210-420. The remainder of the program is devoted to the stage-by-stage computations based on the previously established equilibrium curve and the operating lines. Starting with  $x_B$ , the bottoms liquid composition exiting the reboiler, the vapor composition  $y_B$ , exiting the reboiler in equilibrium with  $x_B$ , is calculated. Obviously, this point ( $x_B$ ,  $y_B$ ) lies on the equilibrium curve as shown on Fig. 3. From the value of  $y_B$  the liquid composition from the bottom theoretical tray is calculated by the equation of the lower operating line. Graphically these calculated points form the bottom triangle on Fig. 3. This is the first theoretical stage in the calculation sequence and represents the reboiler. In this way, the program works its way up the column following the lower operating line and equilibrium curve until the equilibrium vapor composition first exceeds  $y''$  (Point b). At this point the program is ready to switch over to the upper operating line. The number of theoretical stages (triangles) recorded to this point correspond to the exact number required for the stripping section, including the feed tray and reboiler. As a result, the feed tray is easily located. It is basically represented by the triangle with one corner on the lower operating line and the other on the upper operating line.

Finally, the program proceeds to do stage-by-stage computations up the rectifying section by following the upper operating line. When the liquid composition becomes greater than or equal to  $x_D$ , the overhead liquid composition, then the program stops and notes the last stage computed as the top rectifying tray. If the distillate is a dewpoint vapor, this top tray represents a partial condenser.

The program runs very fast. The speed at which the results are printed out is really the controlling time constraint.

**C<sub>3</sub> Splitter example.** Let us consider a feed to a C<sub>3</sub> splitter containing 0.6954 mole fraction propylene with the balance being propane. It enters the column as a subcooled liquid with  $q = 1.2191$ .

It is to be distilled into an overhead liquid product (total condenser) and a bottoms liquid product whose compositions are 0.9874 and 0.01159 mole fraction propylene respectively. We are asked to determine the total number of theoretical trays and tray-by-tray composition profiles if the column is to be operated at a mean pressure of 260 psia and at a reflux ratio (L/D) that is 23.32 % over the minimum.

In 1980 Howat and Swift (7) developed a correlation of propylene-propane VLE data based on the Wilson liquid phase activity coefficient model for the purpose of determining optimum fractionator operating pressures in the manufacture of polymer-grade propylene.

The correlation was developed using a rather broad base of all known published VLE data (8-15) for the propane-propylene system. Employing a database of 216 data points, the authors reported an RMS error of 0.45 % on total pressure. Figure 4 represents a plot of their smoothed  $\alpha$  values versus pressure from 70 to 130 degrees F over the full range of liquid compositions.

For the C<sub>3</sub> splitter application here, values of  $\alpha$  were read from Fig. 4 along the 260 psia isobar, and then the coefficients to Eq. 1 were fitted by least squares with a standard deviation,  $\sigma$ , of 0.01 %.

The tray-by-tray calculations generated from the BASIC program are presented in Table 2. The first portion of the output summarizes all of the input data. The coefficients to Eq. 1 are printed first followed then by the minimum and actual reflux ratios and intersection of the operating lines and the q-line. The remaining output lists stage-by-stage liquid and vapor mole fractions of propylene and the relative volatilities of propylene with respect to propane. For the sake of brevity, results are printed for only a few trays around the reboiler, feed tray, and top tray. There are 60 theoretical stripping trays. Tray 1 is the reboiler and tray 60 is the feed tray. Note here that the vapor from Tray 60,  $y_{60} = 0.7205$  mole fraction propylene, just exceeds  $y^* = 0.7177$ , thus confirming the location of the feed tray. There are  $159 - 60 + 1 = 99$  rectifying trays.

Tray 159 is the top tray because a total condenser is being considered here. The overhead product purity spec of 0.9874 mole fraction propylene is met because the vapor composition from Tray 159 is 0.9879 mole fraction propylene.

It is interesting to note here that, in the region near the top of the rectifier, the change in composition of either vapor or liquid is quite gradual- approximately 0.0011 mole fraction/ tray.

This behavior is indicative of how difficult it would be to perform the graphical version of the McCabe-Thiele method in this section of the column.

Both the Smoker and Underwood correlations were applied to this C<sub>3</sub> splitter example. Average relative volatilities for the rectifying and stripping sections were based on the Howat and Swift VLE data and were subsequently substituted into the Smoker and Underwood equations to determine the number of theoretical trays in each of these sections. These values were then compared against the results from the MT program. The results are quite good and briefly summarized below:

<u>Method</u>	N <sub>R</sub>	N <sub>S</sub>	<u>Total</u>
MT Program	99	60	159
Smoker	104	57	161
Underwood	99	56	155

**Effect of VLE uncertainties.** Following an analysis similar to that conducted by Kister (16) for the effect of VLE uncertainty on tray efficiency, a brief discussion is presented here for estimating the effect of errors in relative volatility on the calculation of theoretical trays.

This analysis is generally performed using Fenske's equation for total reflux (minimum theoretical trays).

$$N_M = \frac{\ln S}{\ln \alpha} \quad (8)$$

where S, the separation factor, is given by

$$S = \frac{\{x_D(1 - x_B)\}}{\{x_B(1 - x_D)\}} \quad (9)$$

Attention will be given here to a fixed separation ( S = a constant). As a result, differentiation of Eq. 8 gives

$$d( N_M \ln \alpha ) = d \ln S = 0$$

or 
$$(dN_M) \text{Ln } \infty + N_M d \text{Ln } \infty = 0 \quad (10)$$

Upon rearrangement, Eq. 10 becomes

$$d N_M / N_M = - d(\text{Ln } \infty) / \text{Ln } \infty \quad (11)$$

If the changes or perturbations are small, then to a good approximation

$$\Delta N_M / N_M = - (\Delta \text{Ln } \infty) / \text{Ln } \infty$$

or 
$$\Delta N_M / N_M = -(\text{Ln } \infty_{\text{pred}} - \text{Ln } \infty_{\text{actual}}) / \text{Ln } \infty_{\text{actual}} \quad (12)$$

If it is further assumed that the effect of errors in  $\infty$  on  $N_M$  are the same as on the number of theoretical trays  $N$  at operating reflux, then

$$\Delta N / N = \Delta N_M / N_M \quad (13)$$

Suppose the true or actual value of  $\infty$  is 1.1, but that a given VLE correlation predicts  $\infty$  high by 5 % such that  $\infty_{\text{pred}} = (1.05) (1.1) = 1.155$

Then by Eq. 12 or 13

$$\Delta N / N = -(\text{Ln } 1.155 - \text{Ln } 1.1) / \text{Ln } 1.1 = -\text{Ln}(1.155/1.1) / \text{Ln } (1.1) = -0.512$$

This means that the number of theoretical trays would be underpredicted by more than 50 %.

Suppose now that the correlation underpredicts  $\infty$  by 5 % or that  $\infty_{\text{pred}} = (0.95)(1.1) = 1.045$ ,

then Eq. 12 predicts that  $N_{\text{theo}}$  will be overpredicted by 53.8 %. At lower values of  $\infty_{\text{actual}}$ , the effect is even more pronounced.

The brief table below summarizes the effect of a 5 % perturbation in  $\infty$  on  $N_{\text{theo}}$  for a range of  $\infty_{\text{actual}}$  values typically found in a  $C_3$  splitter.

<u><math>\infty_{\text{actual}}</math></u>	Effect on $N_{\text{theo}}$ if $\infty$ perturbed by	
	<u>+ 5 % error in <math>\infty</math></u>	<u>- 5 % error in <math>\infty</math></u>
1.1	-51.2	+ 53.8

1.2	- 26.8	+ 28.1
1.5	- 12.0	+ 12.7

-8-

## NOMENCLATURE

A, B and C	Coefficients to Eq. 1
D	Overhead distillate product rate, moles/hr
L	Liquid reflux rate from the condenser, moles/hr
$N_{\text{theo}}$ or N	Total number of theoretical trays at the operating reflux ratio, R
$N_M$	Minimum number of theoretical trays at total reflux
$N_R$	Number of theoretical trays in the rectifying section
$N_S$	Number of theoretical trays in the stripping section
q	Moles liquid introduced to stripping section resulting from introduction of each mole of feed
R	Operating reflux ratio at some percentage over the minimum, L/D
$R_M$	Minimum reflux ratio (infinite stages) or $(L/D)_{\text{min}}$
S	The separation factor, defined by Eq. 9
x	Mole fraction of lower boiling or light component in the liquid
$x'$	Liquid mole fraction of lower boiling or light component at the intersection of the q-line and equilibrium curve
$x''$	Liquid mole fraction of lower boiling or light component at the point of intersection of the operating lines and the q-line
$x_B$	Mole fraction of lower boiling or light component in the bottoms product
$x_D$	Mole fraction of lower boiling or light component in the distillate product
$x_F$	Mole fraction of lower boiling or light component in the feed
y	Mole fraction of lower boiling or light component in the vapor
$y_B$	Mole fraction of lower boiling or light component in vapor exiting the reboiler, entering the bottom theoretical tray



NOMENCLATURE Continued-

$y'$	Vapor mole fraction of lower boiling or light component at the intersection of the q-line and the equilibrium curve
$y''$	Vapor mole fraction of the lower boiling or light component at the point of intersection of the operating lines and the q-line
$\alpha$	Relative volatility of lower boiling component with respect to the higher boiling component or equilibrium ratio of lower boiler/equilibrium ratio of higher boiler, $K_{lt}/K_{hvy}$
$\sigma$	Standard deviation, percent

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## Listing of the McCabe-Thiele Tray-By-Tray Program (QBASIC)

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10 LPRINT "BINARY DISTILLATION COLUMN DESIGN-SINGLE FEED"
20 LPRINT
30 INPUT "A="; A
40 INPUT "B="; B
50 INPUT "C="; C
60 LPRINT "A", "B", "C"
70 LPRINT A, B, C
80 LPRINT
97 LPRINT
100 INPUT "DISTILLATE COMPOSITION, XD="; XD
110 LPRINT "DISTILLATE COMPOSITION, XD="; XD
120 INPUT "BOTTOMS COMPOSITION, XB="; XB
130 LPRINT "BOTTOMS COMPOSITION, XB="; XB
140 INPUT "FEED COMPOSITION, XF="; XF
150 LPRINT "FEED COMPOSITION, XF="; XF
160 INPUT "FEED THERMAL CONDITION, Q="; Q
170 LPRINT "FEED THERMAL CONDITION, Q="; Q
180 IF Q = 1 THEN Q = .999999
190 INPUT "R/RMIN="; R0
200 LPRINT "R/RMIN="; R0
210 X0 = .5
220 A0 = A * X0 * X0 + B * X0 + C
230 Y0 = (A0 * X0) / (1 + (A0 - 1) * X0)
240 X1 = (Y0 - XF / (1 - Q)) * (Q - 1) / Q
250 E = ABS(X1 - X0)
260 IF E < .0001 THEN 290
270 X0 = X1
280 GOTO 220
290 RM = (XD - Y0) / (Y0 - X0)
300 LPRINT
310 LPRINT "RMIN="; RM
320 R = R0 * RM
330 LPRINT
340 LPRINT "RACTUAL="; R
350 M1 = R / (R + 1)
360 I1 = XD / (R + 1)
370 X2 = (XF / (1 - Q) - I1) / (M1 - Q / (Q - 1))
380 Y2 = M1 * X2 + I1
390 LPRINT
400 LPRINT "INTERSECTION OF O.L.'S AND Q-LINE, X,Y="; X2, Y2
410 M2 = (Y2 - XB) / (X2 - XB)
420 I2 = XB * (1 - M2)
430 N = 1
440 AL = A * XB * XB + B * XB + C
450 YB = (AL * XB) / (1 + (AL - 1) * XB)
460 LPRINT
470 LPRINT "STAGE", "X,LIQUID", "Y,VAPOR", "ALPHA", "TEMP,F"
480 LPRINT N, XB, YB, AL
490 Y = YB
500 X = (Y - I2) / M2

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```
520 AL = A * X * X + B * X + C
530 Y = (AL * X) / (1 + (AL - 1) * X)
540 N = N + 1
550 LPRINT N, X, Y, AL, T
555 IF Y > Y2 THEN 570
560 GOTO 500
570 LPRINT "TOP OF STRIPPING SECTION"
580 LPRINT
590 LPRINT
600 X = (Y - I1) / M1
610 IF X > XD THEN 670
620 AL = A * X * X + B * X + C
630 Y = (AL * X) / (1 + (AL - 1) * X)
640 N = N + 1
650 LPRINT N, X, Y, AL, T
660 GOTO 600
670 LPRINT "TOP OF RECTIFYING SECTION"
999 END

, "TEMP,F"
480 LPRINT N, XB, YB, AL
490 Y = YB
500 X = (Y - I2) /
```

Table 2. Program output for C<sub>3</sub> splitter example.

BINARY DISTILLATION COLUMN DESIGN- ANALYTICAL MCCABE-THIELE

A = 9.057862E-04      B = -7.776908E-02      C = 1.167902

DISTILLATE COMPOSITION, XD = 0.9874

BOTTOMS COMPOSITION, XB = 0.01159

FEED COMPOSITION, XF = 0.6954

FEED THERMAL CONDITION, Q = 1.2191

R/RMIN = 1.2332

RMIN = 11.97034

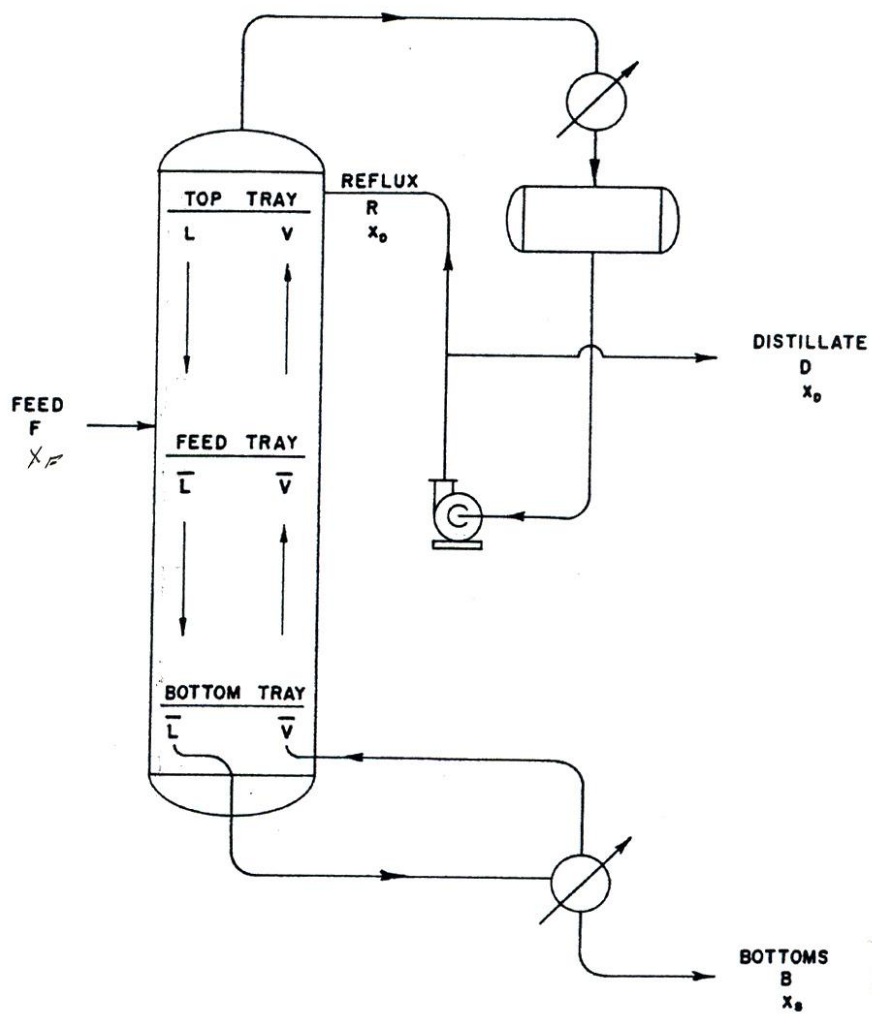
RACTUAL = 14.76182

INTERSECTION OF O. L. 'S AND Q-LINE, X, Y = 0.6994033      0.7176751

STAGE	X-LIQUID	Y-VAPOR	ALPHA	
1	0.01159	0.01350	1.167	REBOILER
2	0.01345	0.01566	1.167	
3	0.01555	0.01810	1.167	
58	0.68939	0.71216	1.115	
59	0.69403	0.71653	1.114	
60	0.69829	0.72054	1.114	FEED TRAY
TOP OF STRIPPING SECTION				
61	0.70246	0.72447	1.114	
62	0.70666	0.72842	1.113	
63	0.71088	0.73239	1.113	
157	0.98451	0.98580	1.092	
158	0.98569	0.98688	1.092	
159	0.98685	0.98794	1.092	TOP TRAY
TOP OF RECTIFYING SECTION				

**Future Paper** In a future article entitled “Review of Binary Distillation – McCabe-Thiele by Computer (Part 2)” the analytical procedure (BASIC program) for performing the McCabe-Thiele method will be extended to handle a two-feed system. In addition, the capability to calculate theoretical tray temperatures will also be incorporated.

FIGURE 1  
COLUMN NOMENCLATURE



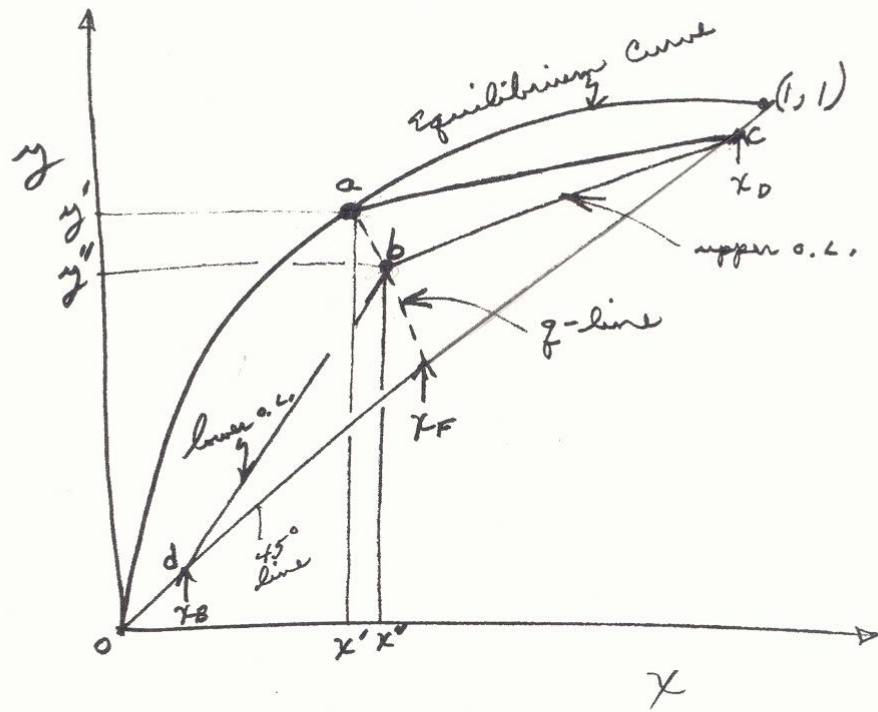


Fig. 2 Determination of Operating Lines





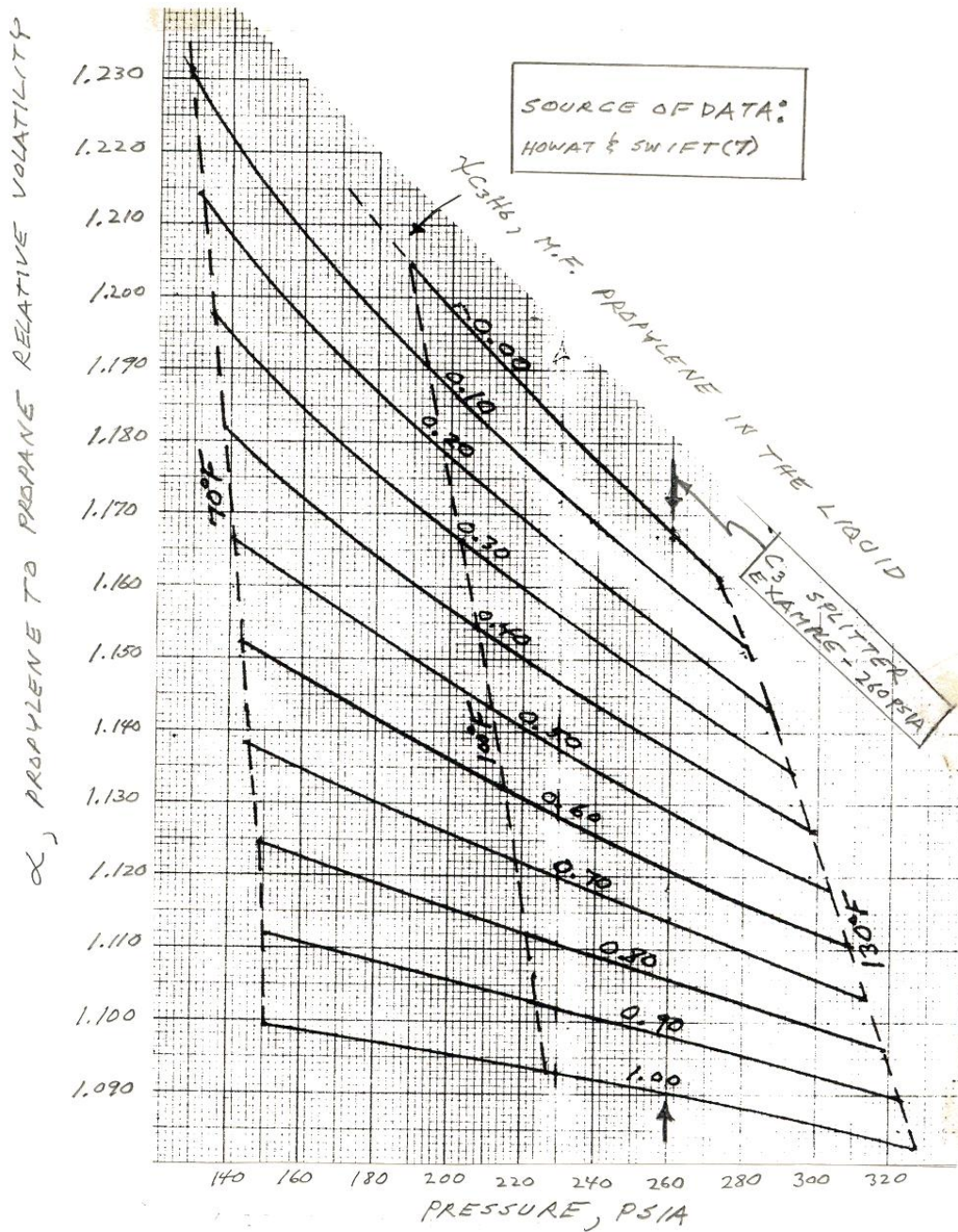


FIG. 4. RELATIVE VOLATILITY OF THE PROPYLENE-PROPANE SYSTEM

## AUTHOR'S BACKGROUND

Dr. Charles R. Koppany is a retired chemical engineer formerly employed by C F Braun & Co/ Brown & Root, Inc. from 1965 to 1994. While at Braun he served in both the Research and Process Engineering departments. Dr. Koppany has also done part-time teaching in the Chemical Engineering Departments at Cal Poly University Pomona and the University of Southern California. He holds B.S., M.S. and PhD degrees in Chemical Engineering from the University of Southern California and is a registered professional engineer (Chemical) in the state of California.

crkoppany@aol.com