Rigorous Solution of Multicomponent, Multistage Extraction Problems

BUFORD D. SMITH and W. K. BRINKLEY

Humble Oil and Refining Company, Baytown, Texas

A new rigorous calculation and convergence method for multicomponent equilibrium stage processes is presented, and the application to multicomponent, multistage extraction problems is described. The application to the vapor-liquid equilibrium stage processes is discussed briefly.

The rigorous graphical solution of multicomponent extraction problems (*2, 3, 5*) is limited to four component systems. No well-known method exists at the present time for the rigorous solution of multicomponent extraction problems with more than four components in a manner analogous to the complete solution of distillation problems by the widely used Lewis-Matheson (*1*) and Thiele-Geddes (*4*) methods.

The calculation of any equilibrium stage process involves the same basic equilibrium relationships and mass and enthalpy balances. These basic relationships however can be applied in a seemingly endless variety of ways, and a method which works well for one process may not be the most convenient method for another. For example a calculation and convergence method which functions well in distillation where the temperature profile is an iteration variable and a function of composition may not work at all for extraction problems where the temperature profile is specified and the stage temperatures cannot be adjusted to make Σy's or Σx's $= 1.0$.

This paper presents a general calculation and convergence procedure for all equilibrium stage processes. The new method is applied specifically in this paper to multicomponent, multistage extraction problems. The application of the method to distillation, absorption, and stripping calculations is under investigation.

DERIVATION OF ERROR (OR CONVERGENCE) EQUATION

The stage-to-stage calculation method described in this paper for extraction begins with the assumption of an L_1 composition and the phase-rate profiles through the column. A stage-by-stage calculation up the column provides a calculated composition of the fresh solvent based on the L_1 composition and rate profiles assumed. The differences (or errors) between the component concentrations in the calculated solvent composition and those specified in the problem statement are then used to correct the assumed L_1 composition and rate profiles for the next trial. An equation which relates the error in a calculated solvent concentration to the error for the same component in the assumed L_1 composition can be derived in the following manner.

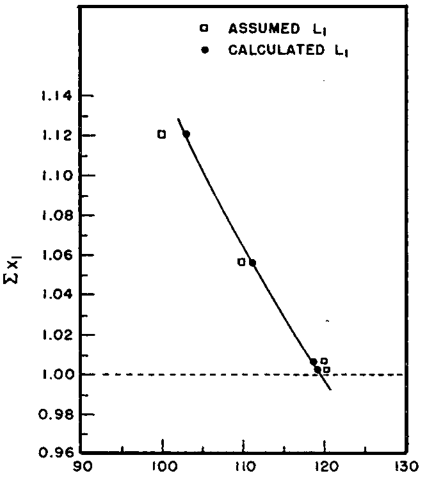

Fig. 1. Results of the four iterations. Convergence is obtained when $\Sigma\ x_1 = 1.0$ or when the calculated L_1 equals the assumed L_1.

Define y_n and x_n as the correct concentrations for the given component in the raffinate and extract phases leaving stage n. The calculated concentrations in all but the last trial will differ from these correct values. Denoting the differences between the calculated and correct values by e_{yn} and e_{xn} one can write the following equalities for each component:

Calculated raffinate concentration

$$= y_n + e_{yn}$$

Calculated extract concentration

$$= x_n + e_{xn}$$

For any given component in stage 1

$$y_1 = K_1 x_1$$

$$y_1 + e_{y1} = K_1(x_1 + e_{x1})$$

$$e_{y1} = (y_1 + e_{y1}) - y_1 = K_1 e_{x1}$$

The use of a material balance around stage 1 gives

$$e_{x2} = \left(S_1 + k \frac{L_1}{L_2} \right) e_{x1}$$

where $k = (1 + gR')/(1 + R')$.

Continuing up the column by the alternate use of equilibrium and material

---

Buford D. Smith is at Purdue University, Lafayette, Indiana.

balance relationships results in the following general expressions which relate the error in any stream entering or leaving a stage to e_{x1}:

$$e_{y_n} = K_n\left(S_1S_2 \ldots S_{n-1} + k\frac{L_1}{L_2} S_2S_3 \ldots S_{n-1} + \ldots k\frac{L_1}{L_{n-1}} S_{n-1} + k\frac{L_1}{L_n}\right) e_{x1} \quad (1)$$

$$e_{x_{n+1}} = \left(S_1S_2 \ldots S_n + k\frac{L_1}{L_2} S_2S_3 \ldots S_n + \ldots k\frac{L_1}{L_{n-1}} S_{n-1}\, S_n + k\frac{L_1}{L_n} S_n + k\frac{L_1}{L_{n+1}}\right) e_{x1} \quad (2)$$

If R' is zero (no extract reflux), k becomes 1.0. In the absence of raffinate reflux $e_{x_{n+1}} = e_{x_s}$, $L_{n+1} = S$, and Equation (2) relates e_{x_s} to e_{x_1}. If raffinate reflux is used either alone or with extract reflux, Equation (2) does not apply to the solvent stream and the following equation must be used in conjunction with Equation (1) to relate e_{x_s} and e_{x_1}:

$$S\, e_{x_s} = D\, e_{y_N} + L_1\, e_{x_1} \quad (3)$$

The number of feeds and their location have no effect on the error equation. The terms representing feed streams cancel in the derivation owing to the fact that the feed concentrations are specified and contain no errors.

Equations (1) and (2) can be applied directly to any process which involves a series of equilibrium stages. For a simple absorber $k = 1$, and Equation (2) relates an error in the calculated lean oil composition to the error for that component in the originally assumed rich oil composition. In distillation $k = 1$, and Equation (1) relates an error in the vapor leaving the top equilibrium stage (which may be a partial condenser) to the corresponding error in the assumed composition of the liquid leaving the lowest equilibrium stage (which may be a partial reboiler).

EQUILIBRIUM DATA

The representation of the equilibrium data is discussed in the previous article.

The reason for correlating the equilibrium data as a function of those components with the lowest K values is illustrated by Equations (1) and (2). A small K means a small stripping factor, and $e_{x_{n+1}}$ and e_{y_n} will not vary widely from e_{x_1}. On the other hand a large K means a large stripping factor, and as the calculations proceed up the column, the errors may become very large. For example in one system studied the e_{x9} for a component with a K value in the neighborhood of 100 varied between 10^{+8} and 10^{-8} for several trials, even though e_{x_1} never exceeded ± 0.0015. If the equilibrium values are to be read as a function of the calculated phase compositions as the calculations proceed up the column, the K's must be plotted vs. the concentrations of stable components (low K values) since their stage concentrations will be reasonable even in the first trial. However if K profiles based on the corrected stage compositions from the previous trial are to be used, the K's may be correlated as a function of the concentrations of any two of the components. No matter how fantastic the calculated concentrations may be from any trial, application of the error equation provides a good, corrected set of stage compositions which can be used to select K values for the next trial.

CALCULATION PROCEDURE

The calculations begin with the assumption of phase-rate profiles and of the rate and compositon of L_1. Depending upon the number of feeds and refluxes used the following material-balance equations may be useful to calculate the end rates and compositions which correspond to the assumptions:

$$B = \frac{L_1}{1 + R'} (1 - \Sigma g\, x_1) \quad (4)$$

$$V_o y_o = F' y_{F'} + \frac{R'(1-g)}{1+R'} L_1x_1 \quad (5)$$

Equation (5) must be written for each component, and the summation term in Equation (4) includes the gx_1 product for each component.

When one starts with the assumed x_1's and uses the assumed phase-rate profiles, stage-to-stage calculations are made up the column. These calculations are made in the usual manner (alternate use of the equilibrium and material-balance relationships) but with the exception that the calculated y's and x's are never normalized. Normalization of the phase compositions makes the error equation inapplicable. Also the almost correct concentrations of the stable components would be adversely affected by the large errors in the unstable component concentrations. The absence of normalization, in effect, means that each component is calculated through the column separately. The y's and x's in the various phases will sum to 1.0 in the last trial if true convergence is obtained and if the equilibrium data are correct.

The stage-to-stage calculation furnishes calculated compositions of streams V_N and L_{N+1}. If raffinate reflux is not used, $L_{N+1} = S$. If raffinate reflux is used, the calculated solvent concentration of each component is obtained from the following material balance:

$$x_s = \frac{L_{N+1}}{S} x_{N+1} - \frac{R}{R+1}\, \frac{V_N}{S}\, y_N \quad (6)$$

The e_{x_s} for each component is then

$$e_{x_s} = \text{calculated } x_s - \text{specified } x_s \quad (7)$$

Equations (1) and (2), plus Equation (3) if raffinate reflux is used, are now used to calculate the e_{x_1} for each component. The e_{x_1}'s can then be used with Equations (1) and (2) to correct all the phase concentrations throughout the column.

Once a corrected set of y_D's and x_1's are obtained, a new L_1 rate can be calculated by a simple component balance around the column. The solvent component with the lowest K value should be used in this balance since use of a less stable component may slow convergence. When extract reflux is used, the balance becomes somewhat com-

TABLE 2. CONCENTRATION PROFILES AND K VALUES FROM A TYPICAL TRIAL

System: acetone (A)—chloroform (C)—water (W)—acetic acid (H) at 25°C.

		x_A			x_C	
Stage	K_A	Calculated	Corrected	K_C	Calculated	Corrected
1	2.05	0.226	0.254	11.8	0.007	0.006
2	2.22	0.118	0.133	13.5	0.020	0.016
3	2.36	0.070	0.079	15.4	0.053	0.041
4	3.41	0.023	0.050	25.6	0.246	0.024
5	3.85	—0.073	0.036	30.8	7.41	0.021
S	—	—0.519	0.0	—	292.3	0.0

		x_W			x_H	
Stage	K_W	Calculated	Corrected	K_H	Calculated	Corrected
1	0.089	0.556	0.539	0.279	0.211	0.210
2	0.077	0.574	0.556	0.275	0.225	0.224
3	0.067	0.592	0.573	0.269	0.232	0.231
4	0.035	0.644	0.624	0.273	0.295	0.293
5	0.028	0.650	0.629	0.292	0.325	0.322
S	—	0.671	0.650	—	0.352	0.350

plicated, but the new L_1 can be calculated directly from

$$L_1 = \frac{F(y_F - y_D) + S(x_s - y_D) + F'(y_{F'} - y_D)}{x_1 \dfrac{(1 + gR')}{(1 + R')} + jy_D} \qquad (8)$$

where $j = (R'/1 + R')\ (1 - \Sigma g x_1) - 1.0$. If no extract reflux is used, $R' = 0$ and the denominator reduces to $x_1 - y_D$.

Since V_0 is specified as a feed or can be calculated from the new $L_1 x_1$'s by Equation (5), it is now possible to calculate new rate profiles by means of solvent balances around the bottom end of the column (cutting V_0 and L_1). The next trial can then be made with the new rate profiles and the new rate and composition of L_1. The K values can be based on the corrected stage compositions from the previous trial or on the stage compositions obtained as the calculations move up the column.

The iteration described in the previous paragraphs converges rapidly (2 to 5 trials) to a constant set of rate profiles and to a constant L_1 rate and composition. The solution obtained however is determined by the L_1 and x_1's originally assumed. In other words repetition of the calculations with a different set of originally assumed L_1 and x_1's will produce a different solution. The correct solution is that one where the calculated x_1's and all the other stage concentrations sum to 1.0. To pinpoint the correct solution it is necessary to make three iterations with different assumed L_1 rates. The original x_1's assumed can be the same for all three iterations or they can be varied. After two of the three iterations are completed, a plot of the calculated Σx_1 vs. the calculated L_1 will indicate the L_1 at which $\Sigma x_1 = 1.0$. The third iteration with this L_1 will be close to the correct solution. It is not necessary to obtain convergence in the two preliminary iterations. One trial in each is usually sufficient to provide a Σx_1 which can be plotted to indicate the L_1 for the third trial.

The over-all convergence in distillation calculations is simpler than in extraction, absorption, or stripping. In distillation the L_1 or bottoms rate can be specified conveniently, and only one iteration is necessary. The convergence within this iteration may be slowed somewhat since in distillation there is no stream with fixed composition at the top comparable to the solvent in extraction or the lean oil in absorption. The change in the assumed overhead composition from trial to trial causes the error equation to be somewhat less effective as a convergence device and may increase the required number of trials slightly.

The time required per trial is roughly that required for any stage-to-stage distillation calculations with heat balances. For the four component, five stage extraction example presented below, the time per trial was about 5 hr. For three iterations with one trial for each of the first two iterations and two trials in the final iteration, the total calculation time for an experienced person would be about 20 hr. The number of trials required in any one iteration is independent of the number of stages and components.

EXAMPLE PROBLEM

The four component extraction example described in the previous paper was solved by the proposed rigorous method. Four iterations were made. The assumed and calculated L_1 rates and the Σx_1 for each iteration are shown in Figure 1. A plot of Σx_1 vs. the calculated L_1 rate for the first two iterations indicated an $L_1 = 120$ as the correct value. Two iterations were made at an assumed L_1 of 120 to check the effect of varying the assumed x_1's. Better values of the x_1's improve the trial results, but the L_1 rate seems to be the important iteration variable. A plot of Σx_1 vs. the calculated L_1 rate is essentially a straight line despite the two sets of assumed x_1's used.

Typical trial values of calculated and corrected stage compositions are shown in Table 1. The calculated values were the results of the stage-to-stage calculations, and the corrected values were obtained by application of the error equation. The values shown are from the first trial of the last iteration in Figure 1. Note the effect of the size of K on the reasonableness of the calculated concentrations. Note also that regardless of how unreasonable the stage concentrations become in the stage-to-stage calculation, application of the error equations furnishes reasonable corrected values. These corrected values would be the correct solution if it were not necessary to correct the rate profiles for the second trial. The second trial provided e_{x_s}'s of 0.119, −108.9, 0.0, and −0.0012 for the four components compared with the values shown in Table 2 of −0.519, 292.3, 0.021, and 0.002. It was not necessary to make a third trial since the rate profiles calculated for use in trial 3 were identical to those used in trial 2. Also the K values were essentially unchanged. The stripping factors would be unchanged for the third trial, and therefore the error equation can predict from the e_{x_s}'s from trial 2 the exact x_1's which will reduce all the e_{x_s}'s to zero in the next trial. In practical calculations the correction to x_1 necessary to make $e_{x_s} = 0$ for a component with a K as large as that of chloroform is beyond the number of decimal places carried in the calculations.

One other point warrants discussion, and that is the role played by the equilibrium data in the achievement of true convergence. The solution obtained where $\Sigma x_1 = 1.0$ will be the correct solution only if the equilibrium data and its graphical representation are exactly correct. If the K values are correct, then not only will $\Sigma x_1 = 1.0$ but also $\Sigma y_1 = 1.0$, $\Sigma x_2 = 1.0$, etc. In the example problem the K values used for chloroform were evidently too large. It was necessary to use an x_1 of approximately 0.007 to reduce the e_{x_s} of chloroform to zero. Solubility data indicate an x_1 for chloroform of approximately 0.03 based on the concentrations of the other three components. This fourfold error in the x_1 concentration of chloroform coupled with the large K value for this component caused the Σy's and Σx's to be less than 1.0 until the feed stage was reached. At that point the large amount of chloroform entering in the feed overshadowed the error in its L_1 concentration. Above the feed the phase concentrations summed to approximately 1.0. The probability of errors in the K values for chloroform is high since the concentration of chloroform in the extract phase in the tie-line determinations was usually below 0.05 wt. fraction.

The final results for the example are shown in Figure 2 of the preceding paper, where they are represented by the open circles. Comparison with the short-cut method results and the manner in which the results were checked by the graphical method of Powers (2) are described in the preceding paper.

NOTATION

B = heavy or extract product rate, moles, weight, or volume per unit time

D = light or raffinate product rate, moles, weight, or volume per unit time

e = calculated stream concentration minus correct stream concentration for the component under consideration

e_{x_n} = error in calculated value of x_n

e_{y_n} = error in calculated value of y_n

F = upper feed rate, moles, weight, or volume per unit time

F' = lower feed rate, moles, weight, or volume per unit time. If only one feed is used $F' = 0$ and $M = 0$

g = $S_E\, x_{SE}/L_1 x_1$ = fraction of a given component in L_1 which is removed with S_E

j = $(R'/1 + R')\ (1 - \Sigma g x_1) - 1.0$
k = $(1 + gR')/(1 + R')$
K = y/x = distribution coefficient
L = heavy or extract phase rate, moles, weight, or volume per unit time
M = number of theoretical stages below the feed stage $M + 1$
n = subscript referring to any stage which may take on any value from 1.0 to N
N = total number of theoretical stages including partial reboiler if any but excluding partial condenser if any
R = external reflux ratio at top or raffinate end of column, amount of reflux/amount of product
R' = external reflux ratio at bottom or extract end of column, amount of reflux/amount of product
S = fresh solvent rate, moles, weight, or volume per unit time
S_E = solvent rich material recovered in the extract solvent recovery equipment, moles, weight, or volume per unit time
S_n = $K_n V_n / L_{n+1}$ = component stripping factor where the subscript n can take on any stage number from 1.0 to N
V = light or raffinate phase rate, moles, weight, or volume per unit time
x = concentration in heavy or extract phase, units consistent with units on rates
y = concentration in light or raffinate phase, units consistent with units on rates

LITERATURE CITED

1. Lewis, W. K., and G. L. Matheson, *Ind. Eng. Chem.*, **24**, 494 (1932).
2. Powers, J. E., *Chem. Eng. Progr.*, **50**, 291 (1954).
3. Smith, J. C., *Ind. Eng. Chem.*, **36**, 68 (1944).
4. Thiele, E. W., and R. L. Geddes, *ibid.*, **25**, 289 (1933).
5. Treybal, R. E., "Liquid Extraction," 1 ed., p. 211, McGraw-Hill, New York (1951).

Manuscript received January 2, 1959; revision received December 17, 1959; paper accepted December 28, 1959.

Effect of Uniformity of Fluidization On Catalytic Cracking of Cumene

ALBERT GOMEZPLATA and W. W. SHUSTER
Rensselaer Polytechnic Institute, Troy, New York

The effect of uniformity of fluidization on the catalytic cracking of cumene, with a silica-alumina catalyst, was studied in a 3-in.–diameter reactor operated at 800°F. Superficial gas velocities were varied from 0.06 to 0.24 ft./sec. for bed heights of 1.5, 3, 5, and 8 in. The percentage conversion in a fluidized bed was found to be lower than in a fixed bed and to be dependent on the type of catalyst support used. A porous plate support was up to 30% more efficient than a screen support, which is attributed to its better gas-distribution characteristics and to its ability to introduce the discontinuous phase as smaller gas bubbles. Indications are that the first few inches of bed are very effective in bringing in contact the continuous and discontinuous phase, and therefore most of the conversion due to the interaction of the two phases takes place here. This can be explained in terms of the rapid growth of gas bubbles as they proceed through the bed.

The nature of the fluid and solid flow in a fluidized bed has been investigated in many studies (*2a, 4, 5, 6, 25, 27*) and the fluidization process has been described (*8* to *13* and *18*). The general solid pattern has been established as being up the center of the column and down the sides (*4, 5, 16*) with the downward-flowing solid particles creating some back mixing of the gas along the sides (*4, 5*). The importance that the homogeneity of dispersion of fluid and particles can have on the properties of a fluidized bed has been realized, and ingenious methods have been proposed to measure bed uniformity (*1, 3, 17, 24*), but unfortunately studies have been mainly of a qualitative nature. Gilliland and coworkers (*6*) in kinetic studies of a gas-phase homogeneous reaction concluded that plug flow is a good assumption for kinetic studies and that the lowering of conversion in a fluidized bed was due mainly to gas bypassing through the gas-solid phase of the bed.

Shen and Johnstone (*23*) studied the catalytic decomposition of nitrous oxide, and Mathis and Watson (*15*) studied catalytic cumene dealkylation in both fixed and fluidized beds under isothermal bed conditions. The conversion obtained under fluidized-bed conditions was always less than for the fixed bed and was attributed to ineffective contact caused by bypassing gas. Both Shen and Johnstone (*23*) and Mathis and Watson (*15*) have proposed mathematical models to aid in the understanding of the behavior of the bed. To make mathematics manageable, quite a few assumptions have to be made and a high degree of error can be expected from such models, but as yet these two studies have not yielded enough data to make any conclusions of the general applicability of the models.

The aim of the present study was to investigate the effect of fluidization on the catalytic cracking of cumene. The cumene-cracking reaction was chosen because of its desirable cracking characteristics and because the reaction mechanism has been studied extensively (*2, 20, 21, 26*).

Special emphasis in this investigation was placed on the effect of uniformity on the cracking reaction, since it was expected that this variable would have a significant effect on the level of conversion attained in a fluidized bed.

MATERIALS AND APPARATUS

The cumene used in the kinetic study was of pure-grade quality that was purified by passing through silica gel to remove cumene hydroperoxide and other polar impurities. After purification it analyzed

Cumene	98.68%
Ethylbenzene	1.30%
Cumene hydroperoxide	0.02%

Albert Gomezplata is at present with the University of Maryland, College Park, Maryland.