# Enriching Liquid-Liquid Extraction

## A step-by-step guide to evaluating and improving column efficiency

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Many of today's liquid-liquid-extraction columns have longer plant tenures than the engineers who are responsible for pushing their buttons. Over time, process engineers come and go, while the original procedures and understanding of the column design become diluted. The upside to this state of affairs is the implication that most columns could be running better. The temptation that must be avoided, however, is jumping right into optimization without first understanding what is going on inside the column.

For an effective step-by-step performance improvement strategy, see Six Steps to Better Liquid-Liquid Extraction (box, right). As demonstrated by these steps, it is important to revisit the design basis when looking for means of improvement.

### SIX STEPS TO BETTER LIQUID-LIQUID EXTRACTION

The best way to improve liquid-liquid extraction performance is to first evaluate the column and process materials. Then optimization can begin.

**Evaluation steps:**

1. Find in the literature or generate the LLE data for the current process streams
2. Obtain a complete material balance around the column, including flowrates and solute concentrations for the feed, solvent, extract and raffinate
3. Use either graphical solution, computer simulation, or the Kremser equation (see main text) to calculate the current number of theoretical stages

**Optimization steps:**

4. Evaluate how changes in the process variables will affect column performance to determine options for optimization
5. Depending on the results obtained in Step 4, perform pilot testing as necessary
6. Based upon the results from Steps 4 and 5, modify equipment and/or process

**TABLE 1. LIQUID-LIQUID EQUILIBRIUM DATA — MIBK, "A" AND WATER**

| Shake # | %A in feed | %A in raffinate | %A in extract | Dist. coeff. (m) |
|---|---|---|---|---|
| 1 | 0.43 | 0.14 | 0.14 | 1.00 |
| 2 | 3.36 | 3.33 | 3.62 | 1.09 |
| 3 | 6.73 | 6.98 | 6.95 | 1.00 |
| 4 | 10.08 | 9.73 | 11.32 | 1.16 |
| 5 | 13.44 | 13.07 | 13.76 | 1.05 |
| **Average** | | | | **1.06** |

## THE FUNDAMENTALS OF EXTRACTION

Liquid-liquid extraction is a mass transfer operation whereby a feed solution is contacted with a liquid solvent that is immiscible with one or more, but not all, of the components of the solution. During this contact, the material to be removed from the feed (the solute) is transferred from the feed phase to the solvent phase. The phases are then separated, generating an extract phase (solvent that has "picked up" the solute) and raffinate phase (original feed solution minus the solute).

The concept of a column-type contactor is to allow the phases to flow countercurrently due to the density difference between the liquids (Figure 1). A well-designed extraction column works by generating a number of theoretical stages within the column to more efficiently transfer the solute from one liquid phase to the other.

Essential to understanding the performance of an extraction column is the liquid-liquid equilibrium (LLE) data set. These data can be shown in tabular format, such as distribution coefficient versus solute concentration (see Table 1 for an example), or in graphical format, using an LLE curve, such as that shown in Figure 2. Note that in extraction, all concentrations are defined on a solute-free basis, which simplifies calculation and achieves straighter equilibrium and operating lines.

An LLE curve basically indicates the steady-state partitioning behavior of the solute between the two phases. The y-axis is the concentration of solute in the extract (solvent) phase, and the x-axis is the concentration of the solute in the raffinate (feed) phase. Every point on the curve also defines the local distribution coefficient $m$:

$$m = y_a / x_a \qquad (1)$$

where a is the solute, $y_a$ is the concentration of component a in the extract liquid and $x_a$ is the concentration of component a in the raffinate liquid.

When the LLE data set is available, and a complete column material balance is known, one can determine the number of theoretical stages that are necessary to achieve a specified separation. One method is via graphical solution, whereby the LLE curve and operating line are plotted on the same graph, and the number of stages stepped off using the standard McCabe-Thiele method that is commonly associated with distillation [*1*].

The McCabe-Thiele method is

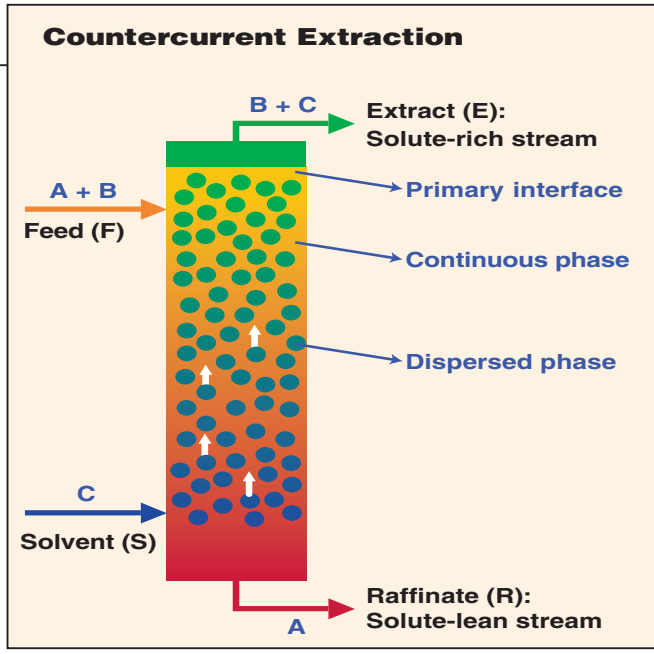


**FIGURE 1.** In an extraction column, phases flow countercurrently due to the density difference between the liquids. The column is sized, whether stacked or agitated, to generate a certain number of theoretical stages required for efficient transfer of the solute from one liquid phase to the other

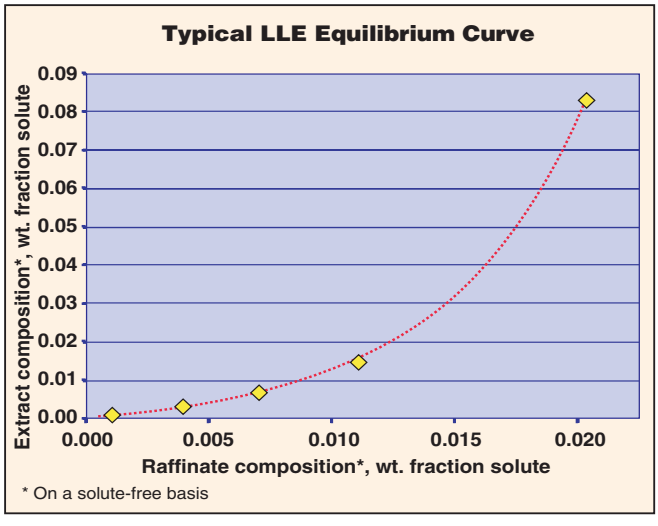


**FIGURE 2.** An LLE curve basically provides the steady-state partitioning of the solute between the two phases. The y-axis is the concentration of solute in the extract (solvent) phase and the x-axis is the concentration of the solute in the raffinate (feed) phase

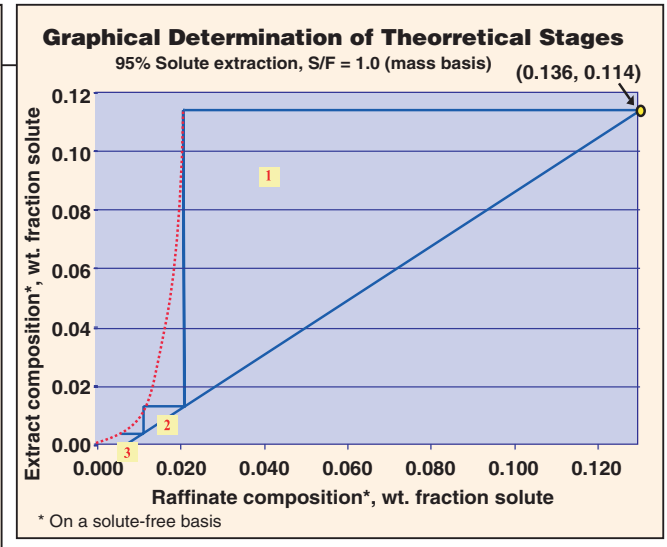


**FIGURE 3.** The number of theoretical stages (column efficiency) can be determined graphically — via the standard McCabe-Thiele method — by stepping them off on the area between the operating line and the LLE curve

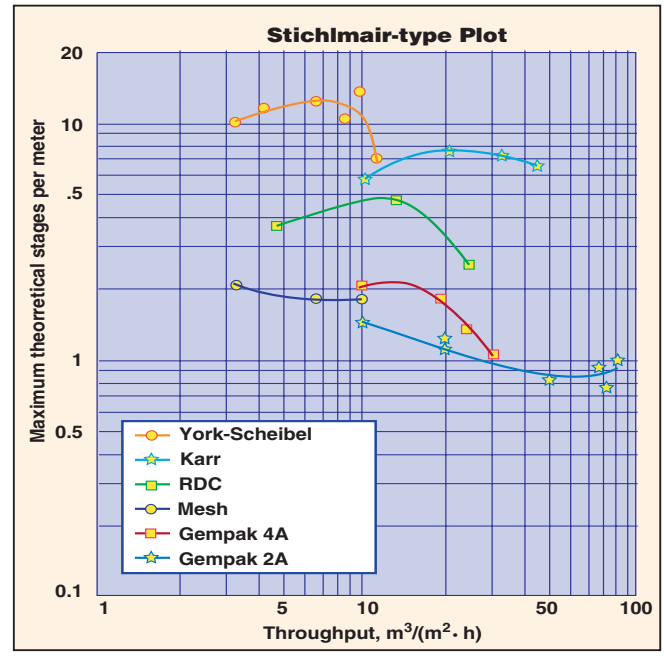


**FIGURE 4.** Given that its optimal capacity range is wider than that of the RDC column, the Karr column can operate over a broader range of capacities without significantly lowering the number of theoretical stages that will be produced within a given column height

demonstrated in Figure 3. The LLE curve data set for this particular example was generated experimentally (method discussed later), while the operating line was drawn by making use of the solvent to feed ratio ($S/F$) and the concentration of solute for all of the column's inlet and outlet streams. The point at the upper right hand corner of the operating line shows the concentration of solute for the inlet feed ($X_F$) and outlet extract ($Y_E$) phases. The point at the lower left corner shows the concentration of solute in the inlet solvent ($Y_S$) and outlet raffinate ($X_N$) phases. As shown in this example the number of theoretical stages required to achieve 95% extraction of the solute, at a $S/F$ of 1.0 is approximately three stages.

When the distribution coefficient is constant for all concentrations of solute between the feed and final raffinate — indicated by a straight-line LLE curve — the Kremser equation can be used to calculate the number of theoretical stages ($n_s$). The Kremser equation is defined as follows:

$$n_s = \frac{\text{Log}\left[\left(\frac{X_F - \frac{Y_S}{m}}{X_N - \frac{Y_S}{m}}\right)\left(1 - \frac{1}{E}\right) + \frac{1}{E}\right]}{\text{Log}\,E} \quad \textbf{(2)}$$

where:

$n_s$ = number of theoretical stages

$X_F$ = Mass concentration of solute in the feed (solute-free basis)

$X_N$ = Mass concentration of solute in the raffinate (solute-free basis)

$Y_S$ = Mass concentration of solute in the solvent (solute-free basis)

$m$ = Distribution coefficient

$S/F$ = Mass ratio of solvent rate to feed rate

$E$ = extraction factor = $m \cdot (S/F)$ (3)

In addition to knowing calculation methods for theoretical stages, it is also important to have some understanding about the hydraulic behavior of extrac-

**Bench-Scale Test Apparatus**

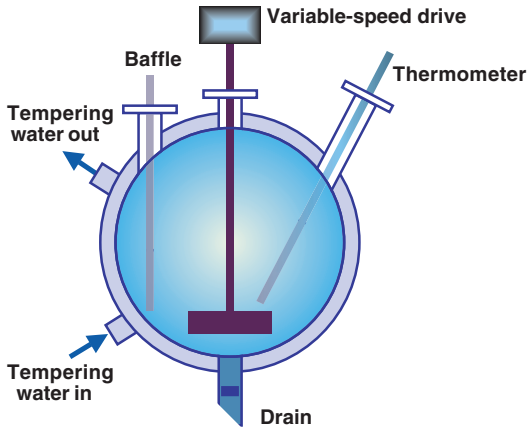


**FIGURE 5.** This 1,000–2,000-ml reactor-type flask (glass) is jacketed for temperature control and fitted with a standard laboratory type agitator and half-moon impeller. A total of five to six feed samples, with a solute content ranging between the feed concentration and the desired raffinate concentration, are tested. The analytical results from each pair of samples are then used to calculate the distribution coefficient for each shake test

**Typical Extraction System**

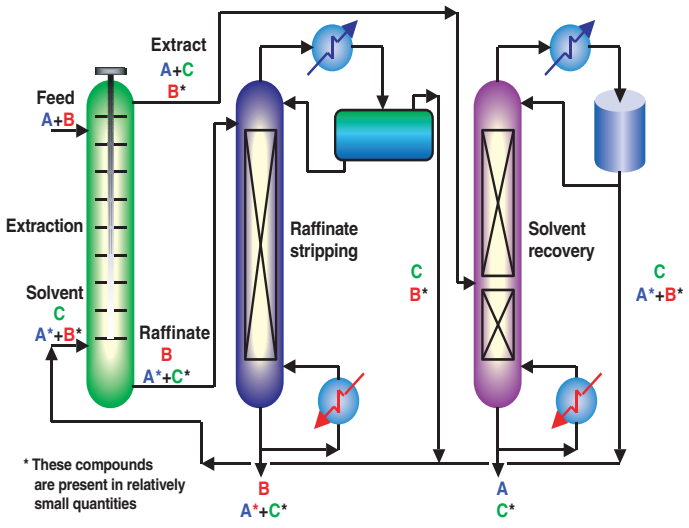


**FIGURE 6.** After leaving the extraction column, the two product streams are distilled to generate a purified Product A stream and an MIBK overhead stream that is recycled back to the extraction column. Thus, in this case the concentration of solute (A) in the solvent is not zero, but 0.07%

tion columns and how it can affect efficiency. For example, efficiency curves for several agitated extraction columns are shown in Figure 4 [2]. The curves show how the column efficiency (on these curves, theoretical stages per unit height) changes with throughput (sum of the flowrates of both phases, divided by column cross-sectional area).

Looking at the curve for the RDC (rotating disc column) reveals that the efficiency initially increases steadily for increasing capacity, then reaches a maximum, and finally begins to fall off steadily after this point. Thus, if the column is not operating near the optimal capacity point, a significantly lower number of theoretical stages will be produced within a given column height. The curve for the Karr Column on the other hand, is much flatter over a broad range of capacities. Thus, it can operate with peak efficiency over a wider range of capacities than the RDC.

## EVALUATION STEPS

The first steps of extraction column optimization are generally evaluation steps. For illustration of them, consider a performance evaluation for a Karr column that had been operating for over 20 years. The column was used to extract a product — designated here as "A" — from an aqueous feed stream using methyl isobutyl ketone (MIBK) as the solvent.

The production column was operating at a throughput of 1,200 (gal/h)/ft$^2$ and a $S/F$ of 1.24. Typical feed contained 14.2% A and the average raffinate concentration was 0.26% A. There were three objectives of the evaluation:

1. Understand the performance in the existing production column
2. Evaluate changes in the process variables that will reduce $X_N$ from 0.26% to 0.1%
3. Determine the effects of increasing the capacity by 50%

### Step 1. Generate LLE data

These data are generated via a procedure known as a "shake test" that establishes a perfect equilibrium stage. Figure 5 shows one type of equipment often used to perform these tests. This 1,000–2,000-ml reactor type flask (glass) is jacketed for temperature control and outfitted with a standard laboratory type agitator having a half-moon impeller. Feed solutions with varying solute concentrations are added to the flask along with the desired amount of solvent (depending on the $S/F$).

The two-phase mixture is allowed to heat up to the desired temperature and then the phases are mixed vigorously for the length of time needed to reach steadystate (generally about 2 minutes for most applications). The phases are then allowed to separate, and both phases are subsequently analyzed to determine the solute concentration. A total of five to six feed samples are tested with solute content ranging between those of the feed concentration and the desired raffinate concentration. The analytical results from each pair of samples are then used to calculate the distribution coefficient for each shake test.

If the results show a relatively constant distribution coefficient, then the Kremser equation can be used for theoretical stage calculations. If, however, the distribution coefficient changes significantly with concentration, then the graphical solution method or computer simulation must be used. For the current example, the equilibrium data are shown in Table 1.

### Step 2. Material balance

The equations for the material balance (on a solute-free basis) are as follows:

$$X_F = \frac{\text{Solute concentration in the feed}}{1 - \text{Solute concentration in the feed}} \quad (4)$$

$$X_N = \frac{\text{Solute concentration in the raffinate}}{1 - \text{Solute concentration in the raffinate}} \quad (5)$$

| TABLE 2. EXAMPLE OPERATING CONDITIONS | |
|---|---|
| Stream | Concentration of "A" |
| Feed ($X_F$) | 14.2% |
| Raffinate ($X_N$) | 0.26% |
| Solvent ($Y_S$) | 0.07% |
| S/F | 1.24 |

| TABLE 3. "A" EXTRACTION WITH MIBK IN 24-IN.-DIA. KARR COLUMN | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Run | $X_F$ | $X_N$ | $Y_S$ | $S$ | $F$ | $m$ | $E$ | $n_s$ |
| 1 | 0.142 | 0.0026 | 0.0007 | 1.24 | 1.00 | 1.06 | 1.31 | 10.7 |
| 2 | 0.142 | 0.0010 | 0.0007 | 1.24 | 1.00 | 1.06 | 1.31 | 17.0 |
| 3 | 0.142 | 0.0010 | 0.0000 | 1.24 | 1.00 | 1.06 | 1.31 | 13.1 |
| 4 | 0.142 | 0.0021 | 0.0002 | 1.24 | 1.00 | 1.06 | 1.31 | 10.8 |
| 5 | 0.142 | 0.0010 | 0.0007 | 1.51 | 1.00 | 1.06 | 1.61 | 10.7 |
| 6 | 0.142 | 0.0048 | 0.0007 | 1.24 | 1.00 | 1.06 | 1.31 | 8.0 |

$$Y_S = \frac{\textit{Solute concentration in the solvent}}{1 - \textit{Solute concentration in the solvent}} \quad (6)$$

$$S = \textit{Mass solvent rate} \times (\textit{1–solute concentration in the solvent}) \quad (7)$$

$$F = \textit{Mass feed rate} \times (\textit{1–solute concentration in the solvent}) \quad (8)$$

The plant operating conditions for the example system are summarized in Table 2. The distribution coefficient is in the range of 0.99 to 1.16, which is certainly close enough to be considered constant. Therefore, the average value of 1.06 can be used with the Kremser equation to accurately describe the extraction process.

It should be noted that the concentration of solute (A) in the solvent is not zero, but 0.07%. This is because the MIBK-extract phase, after leaving the extraction column, is distilled to generate a purified Product A stream and an MIBK overhead stream that is recycled back to the extraction column (Figure 6). The design and operation of this distillation column will determine the amount of solute in the recycle solvent stream. In many cases, the amount of solute in the recycle solvent will have a significant impact on the performance of the extraction column. Thus, this aspect should not be overlooked when attempting to improve the performance of the extraction column.

### Step 3. Assess the current number of theoretical stages

Once the column performance data and the distribution coefficient of 1.06 are plugged into the Kremser equation, the number of theoretical stages are calculated to be 10.7 stages.

$$n_s = \frac{Log\left[\left(\frac{0.142 - \frac{0.0007}{1.06}}{0.0026 - \frac{0.0007}{1.06}}\right)\left(1 - \frac{1}{1.31}\right) + \frac{1}{1.31}\right]}{Log\,1.31} \quad (2a)$$

$n_s$ = 10.7 stages

## OPTIMIZATION STEPS

### Step 4. Determine the options for optimization

At this point it is time to use the known column performance and the Kremser equation to evaluate the effect of changes to the key process variables. By changing individual input variables, one can quickly calculate the effect on the column performance. (Keep in mind that the current column height is fixed.) This has been done as shown in Table 3 (which assumes any consistent mass units for $S$ and $F$) and outlined below:

***Run 1. Current performance.*** This run shows the current performance of the extraction column. With 10.7 theoretical stages and $S/F$ = 1.24, the raffinate concentration, $X_N$, is 0.26%.

***Run 2. Calculate the number of stages required to achieve 0.1% A in raffinate with 0.07% A in solvent.*** Here we see that for the same operating conditions, 17.0 theoretical stages are required to achieve 0.1% raffinate concentration. There are three ways to provide more theoretical stages; (1) Increasing the existing column height by 60%, (2) changing to a more-efficient column design, or (3) increasing the efficiency in the existing column.

Obviously, the first two options will involve equipment modifications and significant capital spending. Also, it is doubtful that a more efficient column than the Karr column can be utilized for this process. The third option will generally require either EVOP (evolutionary optimization) testing in the production column, or a pilot-plant testing in a scaled-down version of this column. The benefit of increased product recovery (and possible reduced effluent treatment cost) for all options would need to be weighed against the cost of the testing and/or capital expenditures.

***Run 3. Calculate potential effects (on number of stages required to achieve 0.1% A in raffinate) of using pure solvent.*** This run demonstrates that in the existing column, if pure solvent were used (no solute in the solvent), then an increase to 13.1 theoretical stages would be required. Therefore, even if fresh solvent were used, the existing column could not generate 0.1% raffinate concentration unless the stage efficiency was also improved or more stages were added to the column.

***Run 4. Calculate $X_N$ for current theoretical stages and 0.02% A in solvent.*** This run shows that decreasing the solute in the recycle solvent from 0.07% to 0.02% (with no other changes) will result in a decrease in the raffinate concentration from 0.26% to 0.21%. Thus, based upon the calculations for Runs 3 and 4, the effect of the solute in the recycle solvent has only a minor impact on the final raffinate concentration.

***Run 5. Calculate S/F required to achieve 0.1% A in raffinate for current theoretical stages.*** This run shows that increasing the solvent-to-feed ratio from 1.24 to 1.51 will produce the required raffinate concentration of 0.1%. This is obviously the easiest solution for improving the recovery of product A. However, the value of the increased product recovery must also be evaluated against the increased operating cost required to distill and recycle 22% more MIBK. In addition, the downstream distillation equipment and the extractor must have enough excess capacity for this option to be viable.

***Run 6. Calculate A in raffinate for 1,800 (gal/h)/ft², 0.07% A in solvent and S/F = 1.24.*** Early process development reports were found that documented the initial pilot-plant testing in a 1-in. dia. Karr column. This data set indicated that when the throughput of the column was increased by

50% (1,200 to 1,800 (gal/h)/ft$^2$), the column's efficiency decreased by 25%.

Since the height of the current column is effectively fixed, a lower efficiency would translate into a reduction in the number of theoretical stages (from 10.7 to 8.0) that are achieved inside the column. As shown, the resulting raffinate concentration (for $S/F$ = 1.24) is expected to increase to 0.48%. In short, the engineer has the option to operate this column at higher capacity, but with the disadvantage of higher raffinate concentration as the column approaches 1,800 (gal/h)/ft$^2$.

### Step 5. Perform pilot testing as necessary

If previous pilot data are not available, then the authors recommend caution when increasing the capacity in a production column. Flooding (inability to separate the phases) will eventually occur when the required throughput is greater then the maximum that the column can process. Thus, it is usually best to perform tests in a pilot-size column to determine the systems limitations before significantly increasing the capacity of an operating column.

### Step 6. Modify equipment or process

The action taken in this final step will depend on the options discovered in Step 5 and their associated costs. And, even if the methods for improvement are infeasible for the short term, a better understanding of your column is valuable at any time. ■

*Edited by Rebekkah Marshall*

### References


1. Cusack, R., Fremeaux, P., and Glatz, D., A Fresh Look at Liquid-Liquid Extraction, *Chem. Eng.*, February 1991, pp. 66–76.
2. Cusack, R., Holmes, T., Karr, A., The Otto H. York Co., paper delivered at AIChE Summer National Meeting, August 17, 1987.


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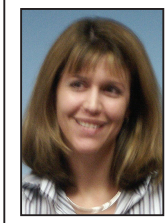


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