TROUBLESHOOTING LIQUID-LIQUID EXTRACTION COLUMNS
Evaluating Column Efficiency

Process engineers can be faced with the task of understanding and optimizing the performance of an existing liquid-liquid extraction (extraction) column. Often times, an extraction column has been operating many years, and the performance is not well understood by the personnel responsible for its operation. Since this technology is not treated comprehensively during most under-graduate Chemical Engineering programs, the engineer given the responsibility to evaluate the column usually lacks the tools for making an accurate evaluation. This article will show how with just a little understanding of basis extraction principles, a relatively simple engineering study can provide accurate understanding of the column performance. Taking these principles a step furthers will provide reliable options for improving the performance.

Understanding Liquid-Liquid Extraction

Liquid-liquid extraction is a mass transfer operation whereby a feed solution is contacted with an immiscible liquid (solvent). During this contact, the material to be removed from the feed, identified as the solute, is transferred from the feed phase to the solvent phase. The phases are then separated generating an extraction phase (solvent that has "pick-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 counter-currently due to the density difference between the liquids (Figure 1). By affecting a number of theoretical stages within the column, more efficient transfer of the solute from one liquid phase to the other can be obtained.

A key to understanding the performance of an extraction column, is the liquid-liquid equilibrium (LLE) data. This information is either presented as an LLE curve or as the distribution coefficient vs solute concentration. A typical LLE curve is shown in Figure 2. Basically this curve 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. Every point on the curve also defines the distribution coefficient m:

$$m = y_a / x_a$$

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

Once the LLE data is available, and the concentration of the solute is known for the feed and solvent inlets, and the extract and raffinate outlets, the number of theoretical stages (column efficiency) can be determined. 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 commonly associated with distillation. This method is demonstrated in Figure 3. The LLE curve shown was

generated experimentally (method discussed later) and the operating line drawn in by analytically measuring the concentration of solute for all inlet and outlet streams from the operating extraction column. The point at the upper right hand corner of the operating line is the concentration of solute for the inlet feed (X_F) and outlet extract (Y_E) phases and the point at the lower left corner is the concentration of solute in the inlet solvent (Y_S) and outlet raffinate (X_R) phases. As shown in this example the number of theoretical stages required to achieve 95% extraction of the solute, at a S/F = 1.0 is approximately 3 stages.

When the distribution coefficient is constant for all concentrations of solute between the feed and final raffinate (i.e. straight line LLE curve), then the Kremser equation can be used to calculate the number of theoretical stages. The Kremser equation is defined as follows:

$$n_S = \frac{Log\left[\left(\dfrac{x_f - \dfrac{y_S}{m}}{x_n - \dfrac{y_S}{m}}\right)\left(1 - \dfrac{1}{E}\right) + \dfrac{1}{E}\right]}{Log\ E}$$

Where:
N = number of theoretical stages
X_F = concentration of solute in the feed
X_N = concentration of solute in the raffinate
Y_S = concentration of solute in the solvent
E = the extraction factor = (m) x (S/F)

In addition to calculation methods for theoretical stages, it is also important to have some understanding about the hydraulic behavior and how this can affect efficiency. For example, efficiency curves for several agitated extraction columns are shown in Figure 4. The curves show how the column efficiency (height per theoretical stage) changes with capacity (feed + solvent rate divided by cross-sectional area of column). 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 begins to fall off steadily after this point. Thus, if you are not operating near the optimal capacity point, the number of theoretical stages that will be produced will be significantly reduced. The curve for the Karr Column however, is significantly flatter over a broad range of capacities. Thus, this type column can operate with peak efficiency over a much broader capacity range than the RDC. This issue of capacity vs efficiency will be addressed later in the example presented about improving column performance.

Evaluation of an Extraction Column

Applying the principles of extraction towards understanding the operation of an existing column is best illustrated via an example. The authors recently were presented with a request to evaluate the performance of a Karr Column that had been operating for over 20

years. The column was used to extract a product we will designate as "A" from an aqueous feed stream using methyl isobutyl ketone (MIBK) as the solvent.

The production column was operating at a capacity of 1,200 GPH/ft^2 and S/F of 1.24. Typical feed was 14.2% A and the average raffinate concentration was 0.26% A. There were 3 criteria for the evaluation:

1. Understand the performance in the existing production column
2. Evaluate changes in the process variables that will produce a reduction in the raffinate concentration of A from 0.26% to 0.1%
3. Estimate the affect for increasing the capacity by 50%

The first step was the generation of LLE data for the process. This data is generally generated via a procedure know as "Shake Tests". Figure 5 shows one type of equipment often used to perform Shake Tests. This is a 1000 – 2000 ml reactor type flask (glass) that is jacketed (for temperature control) and mixed with a standard laboratory type agitator and half-moon impellor. Feed solutions with varying solute concentration are added to the flask along with the desired amount of solvent (depending on the S/F). The 2-phase mixture is allowed to heat up to the desired temperature and then the phases are mixed vigorously for a length of time determined to reach stead-state (generally about 2 minutes for most applications). The phases are then allowed to separate and both phases are analyzed to determine the solute concentration. A total of 5-6 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 level of solute content. 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 must be used.

For the current example, the equilibrium data is shown in Table 1. For this system, the distribution coefficient is in the range of 0.99 – 1.16. This is certainly close enough to be considered constant and the average value of 1.06 can be used with the Kremser equation to accurately reflect the extraction process.

Summarizing the plant operating conditions:

	Concentration of "A"
X_F = Feed (in)	14.2 %
X_N = Raffinate (out)	0.26 %
Y_S = Solvent (in)	0.07 %
S/F =	1.24

It is observed that the concentration of solute (A) in the solvent is not zero, but 0.07%. This is because following the extraction column, the MIBK extract phase is distilled to generate a purified product A stream and a 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. Often 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 looking to improve the performance of the extraction column.

The column performance data and the distribution coefficient of 1.06 are plugged into the Kremser equation, and the number of theoretical stages is calculated to be 10.6 stages.

Optimizing Column Performance

At this point we can use the known column performance and the Kremser equation to evaluate the affect of the key process variables. For this example, this is best done by setting up a spread sheet utilizing the Kremser equation. By changing individual input variable, we can quickly calculate the affect on the column performance. This has been done as reflected in Table 2 and outlined as follows:

Run 1: This run shows the current performance of the extraction column. With 10.6 theoretical stages and S/F = 1.24, the raffinate concentration is 0.26%.

Run 2: Here we see that for the same operating conditions, 16.9 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 efficiency column design, or (3) increasing the efficiency in the existing column. Obviously, the first 2 options will involve equipment modification 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 testing in the production column, or a pilot plant test in a scaled down version of this column. The benefit for 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 expenditure.

Run 3: This run demonstrates that in the existing column, if pure solvent were used (no solute in the solvent), then an increase to 13.0 theoretical stages would be required. Therefore, even if fresh solvent were used, the existing column cannot generate 0.1% raffinate concentration unless the stage efficiency can be improved or more stages are added to the column.

Run 4: 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 affect of the solute in the recycle solvent has a minor impact on the final raffinate concentration.

Run 5: This run shows that increasing the solvent to feed ratio from 1.24 to 1.52 will produce the required raffinate concentration of 0.1%. This is obviously the easiest solution for improving the recovery of Product A. However, this value of the increased

product recovery must also be evaluated against the increased operating cost required to distill and recycle 23% more MIBK.

Run 6: Early process development reports were found the covered the initial pilot plant testing in a 1" diameter Karr Column (Figure 7). This data indicated that when the capacity of the column was increased by 50% (1,200 to 1,800 GPH/ft^2), that the efficiency was decreased by 25%. For this run we have applied this reduction (12.6 to 8.0 theoretical stages) and calculated the raffinate concentration for S/F = 1.24. As shown, the raffinate concentration is expected to increase to 0.48%. Thus, the engineer has the option to operate this column at higher capacity, however increasing raffinate concentration is expected as the column approaches 1,800 GPH/ft^2. If previous pilot data is not available, then the authors recommend caution when increasing the capacity in a production column. Flooding will occur when the capacity exceeds that for which the column can handle. Thus, it is usually best to perform tests in a pilot size column (Figure 8) before significantly increasing the capacity of an operating column.

To Summarize

Accurate evaluation of an existing extraction column requires the following steps:

1. Generate the LLE data for the current process streams

2. Obtain solute concentrations for the feed, solvent, extract, and raffinate for the current column

3. Use either graphical solution or the Kremser equation to calculate the current operating efficiency (theoretical stages)

4. Evaluate how changes in the process variables will affect column performance to determine options for optimization.