

Pilot Plant Testing for Liquid-Liquid Extraction

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When designing a liquid-liquid extraction column, pilot plant testing generates the data necessary for accurate scaleup to the production rate. This article describes how to optimize pilot plant testing.

Pilot plant testing is an integral part of designing a liquid-liquid extraction (LLE) column. Performing pilot plant testing with actual feed liquid, and then relying on known scale-up correlations to size the column, is one of the best and most reliable methods of determining the specific extraction column best suited for an application (1). In general, the design process consists of the following steps (2):

1. Select the solvent and generate liquid-liquid equilibrium data.
2. Use this information and the project requirements to select the column type.
3. Perform a pilot plant test to generate the data for accurate scaleup to the production column.
4. Design and fabricate the column.

This article focuses on optimizing the pilot plant testing methodology. During process development work, pilot plant testing is often hindered by several factors, which include:

- *Availability of the feed materials.* Often, very little, if any, actual feed material is available.
- *Known purity of the solvent.* Because the solvent is usually a recycle stream, the solvent will generally not be pure during actual commercial operation.
- *Time restraints.* Often, testing must be done quickly to meet deadlines.
- *Disposal of waste materials.* It is generally desirable to minimize the amount of waste material generated during pilot plant testing.

For those reasons, it is important to implement an optimized pilot plant testing method that can be completed in a short timeframe using minimal amounts of feed and solvent. For basic research and development (R&D) work, experimental design is a well-proven and accurate method for process optimization. However, for pilot plant testing, experimental design requires significant amounts of feed and solvent and can take a long time.

This article presents a step-by-step method for pilot plant testing that saves both time and material. This method does require some experience, but when it is applied correctly, it can ensure that an extraction column is optimally designed and performs as required.

Laboratory work prior to pilot testing

Before pilot plant testing, the first step in developing an extraction process is selecting the solvent and generating equilibrium data (*e.g.*, distribution coefficient vs. solute concentration). You can do this in several ways, one of which is outlined in Ref. 3.

In addition to obtaining raw equilibrium data, it is just as important to observe the phase behavior of the system, especially for selecting the right type of column for scaleup and developing a test plan for that column. When lab-testing the extraction process, gather the following pieces of data:

- mixing intensity required to generate good phase dispersion
- mass-transfer rate and the time required to reach equilibrium (generally, we have learned that equilibrium can be reached in 2 min with high-speed mixing, except if one or

* This article is based on a presentation at the AIChE Spring Meeting, San Antonio, TX (March 2017).

| Shake Test Datasheet | | | | | | | | | | | | |
|----------------------|-------------|---------|-----------|---------|-----------|---------|-----------------|-------------|-----------------|---------|-----------|---------|
| Project: | | | Feed: | | | | Application: | | | | | |
| Description: | | | Solvent: | | | | | | | | | |
| No. | Description | | Weight, g | | | | Separation Time | Observation | Solute Analysis | | | |
| | Feed | Solvent | Feed | Solvent | Raffinate | Extract | | | Feed | Solvent | Raffinate | Extract |
| | | | | | | | | | | | | |
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▲ **Figure 1.** When performing lab tests for an extraction process, use a datasheet such as this to record liquid-liquid equilibrium data for each test.

both phases are viscous [>100 cP])

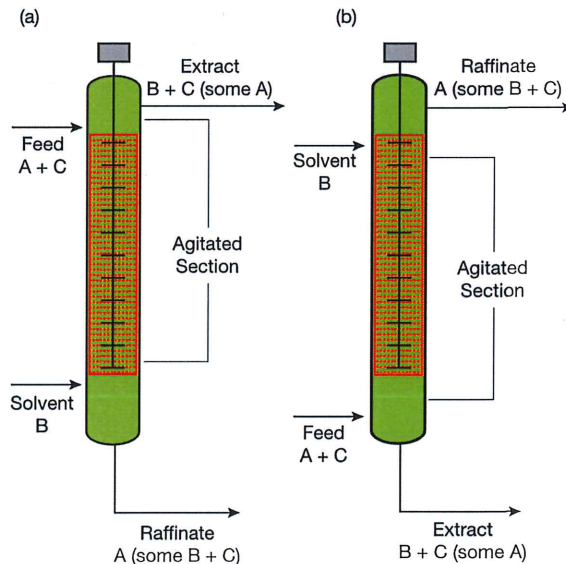
- after mixing, the time for the phases to separate and achieve a clear interface
- the interface behavior — is there a rag layer (of solids) or an emulsion band that forms at the interface?
- entrainment (*i.e.*, discrete, undissolved droplets of one phase flowing out of the column with the other phase) — is some entrainment observed in one or both phases?

A typical datasheet for generating liquid-liquid equilibrium data is shown in Figure 1. For each mix-decant cycle, the datasheet will provide the material balance, the solute concentration in both phases, and the observation of the phase behavior. These data will help you select the best extraction column for the process and serve as the starting point for pilot plant testing.

Pilot plant test method

This section presents the optimized method for pilot plant testing an agitated extraction column (Figure 2). Following this section, two case studies exemplify how to use the method.

This method requires fairly quick analysis of the samples generated in the pilot column. The solute concentration in the raffinate is typically the key indicator of the column's performance. It is also highly desirable to perform the test in a glass-shell extraction column so that the operators can observe the phase behavior and tweak the column operating conditions accordingly. The procedure is as follows:



▲ **Figure 2.** Agitated, counter-current extraction units can be set up in one of two ways. (a) When the solvent is lighter than the carrier liquid, the solvent is introduced at the bottom of the column and the solute is carried up toward the top of the extractor. (b) When the solvent is heavier than the carrier, the solvent is introduced at the top of the column and the solute is carried downward by the solvent toward the bottom of the column. The red dots represent the region in which the solute is transferred to the solvent.

1. Select the continuous and dispersed phase for the process. In an extraction process, mass transfer occurs between the droplets (dispersed phase) and the surrounding liquid (continuous phase). Several factors can affect which phase is

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continuous and which phase is dispersed (a topic that is not covered in this article).

2. Select the column for scaleup and then set up the pilot column with multiple inlets. If possible, it is best to set up a column that you expect to be taller than required. A manifold system can be included to vary the inlet location for the dispersed phase. The continuous phase must have a fixed entrance point.

3. Select the initial operating conditions for the test. The height of the column, capacity, solvent-to-feed ratio, temperature, and initial agitation speed should all be established. This may be difficult to do unless you have some previous experience with similar extraction processes.

4. Start up the column in the usual manner (4) and set a low agitation speed, which should be significantly below the flooding point of the process. Observing the phase behavior in the glass-shell column will help you determine this speed. Calculate the turnover time for the process (*i.e.*, the volume of the column divided by the sum of the feed and the solvent flowrates). During the first two column turnovers, the agitation speed can be increased slightly if warranted by observation of the phase behavior. However, after two turnovers, the agitation speed should remain fixed for the duration of the run, which is a total of five turnovers from the initial startup. After five turnovers, take raffinate and extraction samples and analyze their solute concentration.

5. Increase the agitation speed slightly and fix the speed for an additional three turnovers, then take raffinate and extraction samples and analyze them. Repeat this procedure, progressively increasing the agitation speed and sampling after three turnovers each time until you observe flooding in the column. Flooding occurs when the dispersed-phase droplets stop flowing counter-currently against the continuous phase and is often indicated by the formation of a second interface within the agitated region of the column.

For most extraction processes, five column turnovers upon startup followed by three turnovers after making slight system modifications are typically sufficient to reach steady state. However, it is possible that more turnovers may be required for some systems.

6. Determine the next direction for the pilot plant testing based on the results from this first series of tests. Typically, the next direction is optimization of the solvent-to-feed (S/F) ratio vs. the number of stages (height of the column). If the results from the first series of testing are good (the required solute extraction is achieved), then the next test runs should be at progressively lower S/F ratios and/or lower column heights. However, if the initial tests do not achieve the desired solute extraction, then the next test runs should be at progressively higher S/F ratios and/or with more agitated stages. Whether more stages should be added or the S/F ratio

should be increased is generally dictated by the expected economics for the process. Usually, it is more economical to use more stages and thereby minimize solvent usage.

7. After optimizing the S/F vs. column height, the next variable to test is capacity. The capacity of an extraction column is typically defined as the combined feed and solvent rates divided by the cross-sectional area of the column. It is important to evaluate higher capacities because diameter has a significant impact on the cost of a production scale extraction column and higher capacity allows for a smaller diameter. Thus, the acceptable design capacity can be evaluated by proportionally increasing both the feed and solvent flowrates. As long as the performance remains acceptable, higher capacities can be tested. However, this progression must be terminated once the performance decreases. Sometimes it is also desirable to test at lower capacity, especially if the production column is scheduled to begin operating at a capacity that will be significantly lower than the design capacity.

8. Finally, if necessary, you can test additional variables, such as temperature, pH, and variable mixing intensity throughout the column (due to variable hydraulic behavior between the two phases from one end of the column to the other).

If applied correctly, this test procedure can usually be completed in three operating days. On the first day, you will determine the optimal agitation speed, day two is for optimizing S/F ratio vs. column height, and on day three, you can evaluate different capacities. A fourth day may be required if any other variables mentioned in Step 8 are tested or if multiple feeds are required.

Example 1. Carboxylic acid extraction

An application required the extraction of acetic acid from a whole fermentation broth using ethyl acetate as the solvent (Figure 3). The goal was to achieve >95% extraction of the acetic acid at the minimum S/F ratio. As expected for fermentation broths, this extraction system was extremely prone to emulsification. As such, the efficiency of the extraction column was expected to be low and only gentle agitation could be applied. The distribution coefficient for this process is approximately 0.9. Using the Kremser equation (5), the number of theoretical stages was calculated for different values of S/F:

- S/F = 2.0, number of theoretical stages = 3.9
- S/F = 1.7, number of theoretical stages = 4.9
- S/F = 1.5, number of theoretical stages = 6.1

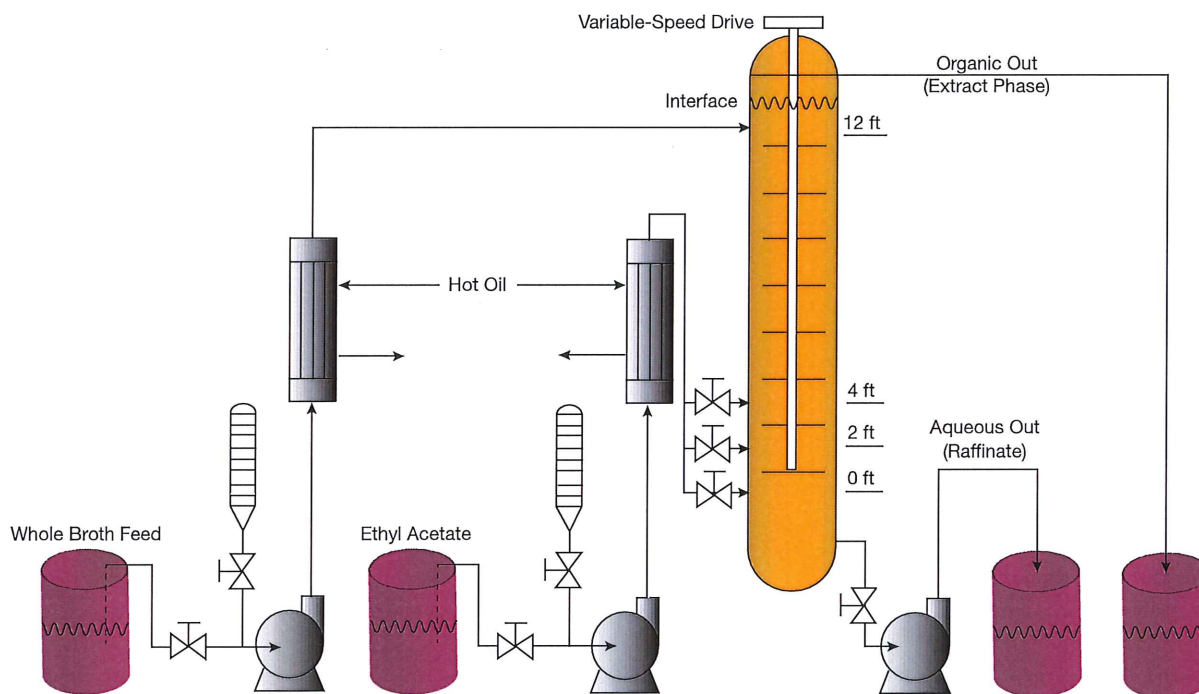
Based on these calculations, plus observation of the slow phase separation and high tendency toward emulsification, a glass-shell KARR column (6) with a 1-in. diameter and 12-ft plate stack height was selected for the testing. The aqueous phase was selected as the continuous phase. Table 1 presents

the results from three days of pilot plant testing. Tests were conducted over a series of three days.

Runs 1–6 were performed on Day 1 at a broth feed rate of 83 cm³/min, S/F = 1.7 weight basis, and room temperature (23°C). The agitation speed starting point for Run 1 was 30 strokes per minute (spm). This was increased to 40 spm for Run 2 and 50 spm for Run 3, at which point the column flooded. The desired acid extraction was achieved in Run 2.

Runs 4 and 5 with an 8-ft plate stack height failed to achieve the desired acid extraction, whereas a 10-ft plate stack height in Run 6 did achieve the desired extraction. It was decided to conservatively use a plate stack height of 12 ft for all additional runs.

Runs 7–9 were performed on Day 2 at a lower S/F ratio of 1.5. Initially, the feed rate and solvent rates were adjusted to maintain the same combined flowrate as the



▲ Figure 3. The pilot plant column in Example 1 was able to extract acetic acid from fermentation broth using ethyl acetate as the solvent.

Table 1. Example 1 Pilot Plant Test Results. Acetic Acid Extraction from Broth using Ethyl Acetate

| | Run No. | Agitated Height, ft | Feed Rate, cm ³ /min | Temperature, C | S/F Ratio | Agitation, spm | Acid Recovery, % |
|-------|---------|---------------------|---------------------------------|----------------|-----------|----------------|------------------|
| Day 1 | 1 | 12 | 83 | 23 | 1.7 | 30 | 95.0 |
| | 2 | 12 | 83 | 23 | 1.7 | 40 | 97.5 |
| | 3 | 12 | 83 | 23 | 1.7 | 50 | Flooded |
| | 4 | 8 | 83 | 23 | 1.7 | 30 | 93.3 |
| | 5 | 8 | 83 | 23 | 1.7 | 40 | Flooded |
| | 6 | 10 | 83 | 23 | 1.7 | 30 | 96.3 |
| Day 2 | 7 | 12 | 90 | 23 | 1.5 | 30 | 94.3 |
| | 8 | 12 | 83 | 23 | 1.5 | 30 | 96.5 |
| | 9 | 12 | 65 | 23 | 1.5 | 40 | 97.6 |
| Day 3 | 10 | 12 | 83 | 45 | 1.5 | 30 | 98.3 |
| | 11 | 12 | 83 | 45 | 1.5 | 50 | 98.7 |
| | 12 | 12 | 83 | 45 | 1.5 | 60 | Flooded |

Data generated in 25-mm-dia. KARR column; Total amount of fermentation broth used = approximately 70 gal

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previous runs, *i.e.*, the new feed rate was 90 cm³/min. The desired acid recovery was not achieved in Run 7. In Runs 8 and 9, the feed rate was adjusted down to 83 cm³/min and 65 cm³/min respectively, while maintaining the S/F ratio of 1.5, and the desired recovery was achieved for both runs. The engineering team decided to lock in the capacity at 83 cm³/min and S/F of 1.5.

On Day 3, the temperature in the column was increased to 45°C. This proved to be an excellent operating temperature for the process. The operators reported that the phase behavior was more stable at this temperature. Run 11 demonstrated successful operation at 50 spm that achieved almost 99% acid extraction. This was determined to be the scale-up run for the process.

Based on these results, a 22-in.-dia. KARR Column was designed and built, and it has operated successfully for this process. In total, the testing used only 70 gal of fermentation feed broth.

Example 2. Methanol extraction

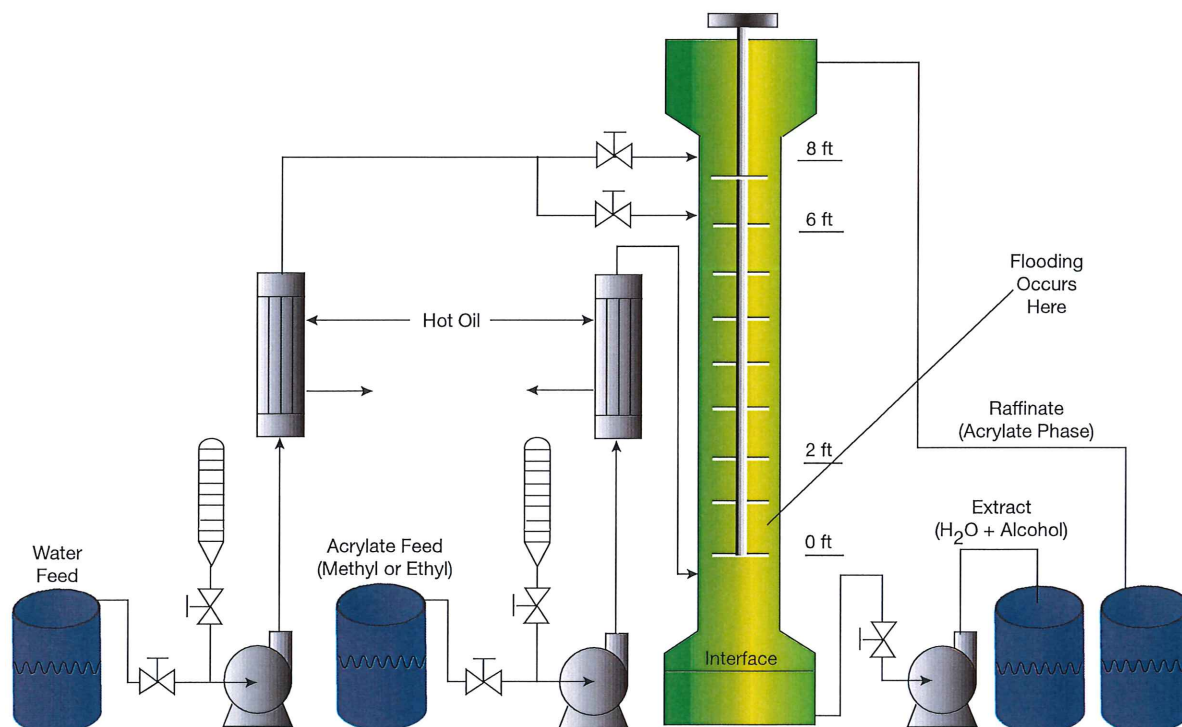
An application required the extraction of methanol from an organic stream using water as the solvent. The objective was to reduce the methanol concentration in the organic phase from 2.5% to less than 0.1% using a specified amount of water (S/F = 0.32, weight basis). The liquid-liquid equilibrium data indicated that five or six theoretical stages were required. A pilot KARR column was set up as shown in

Figure 4. Because the S/F ratio (low water feed rate relative to the organic feed rate) was low, the organic phase (light phase) was selected as the continuous phase and thus the interface was controlled at the bottom. Table 2 presents the results from two days of pilot plant testing.

All test runs were made using a plate stack height of 6 ft (and the upper water inlet was never used). All tests were performed at room temperature (20–25°C). The first three runs were made using standard 2-in. plate spacing throughout the agitated zone, a feed rate of 150 cm³/min, and progressively higher agitation speed. The column flooded at 110 spm, but had not achieved the desired alcohol concentration in the raffinate stream.

Observation of the column during the first three runs revealed that the dispersed-phase water droplets descended through the column fairly rapidly, with little holdup, until they reached a point approximately 2 ft above the organic-phase inlet. This was the point where flooding initiated during Run 3. The column was shut down and drained. The plate stack was removed and the spacing between the perforated plates was modified as follows: from the bottom, 1 ft of 6-in. spacing, followed by 1 ft of 4-in. spacing, and then the standard 2-in. spacing for the remainder of the plate stack. Thus, at any given agitation speed, significantly less power would be imparted into the bottom 2 ft of the agitated zone.

The difference in the physical operation of the column



▲ Figure 4. In Example 2, extracting methanol from an organic stream of acrylate was achieved using water as the solvent.

was dramatic. As shown in Table 2, much higher agitation speeds were possible (without flooding) and the dispersed-phase holdup was observed to be significantly higher throughout the column. After Runs 4 and 5, the operators determined that higher capacity could easily be achieved with the modified plate spacing. For Runs 6–9, the feed rate was increased to 180 cm³/min. The desired raffinate concentration was achieved at 200 spm (Run 9). One additional run was made at a feed rate of 210 cm³/min and the desired raffinate concentration was again achieved at 175 spm.

Based on these results, a 45-in.-dia. KARR column was designed and built, and has since operated successfully for this process. The total amount of organic feed used for the testing was approximately 55 gal.

Additional optimization from pilot testing

Pilot plant testing in a glass-shell extraction column also allows you to identify and optimize key design variables. In fact, pilot plant testing may be the only way that some of these variables can be recognized and the correct design modification implemented. Some of the most common are:

- **Materials of construction.** The column's material of construction should be selected based on the wetting characteristics of the system. The dispersed-phase droplets should not coalesce or form a film on internal surfaces.

- **Entrainment.** The amount of entrainment out of each end of the column can usually be measured by immediate centrifuge of samples leaving the column. If the process will not tolerate a certain level of entrainment, then modifications can include expanding the disengaging chamber, installing a coalescing element in the disengaging chamber, or adding an external separator.

- **Interface behavior.** Often, a solids layer (rag layer) or an emulsion band will form at the interface in an extraction process. The amount of solids formation is typically not a concern during pilot testing, but if it is observed to be significant, an external filtration system should be considered for the production column. The thickness of an emulsion band can generally be controlled by the process conditions, *i.e.*, capacity, agitation speed, and temperature. Thus, the formation of the emulsion band may govern the optimization of these variables for a given extraction process.

Article continues on next page

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Table 2. Example 2 Pilot Plant Test Results. Extraction of Methanol from Acrylic Feed Stream Using Water.

| Run No. | Plate Stack | Feed Rate, cm ³ /min | Water Feed Rate, cm ³ /min | Agitation Speed, spm | Raffinate Alcohol Concentration (Target <0.1%) |
|---------|---|---------------------------------|---------------------------------------|----------------------|--|
| 1 | 1 | 150 | 45 | 75 | 0.165 |
| 2 | 1 | 150 | 45 | 100 | 0.124 |
| 3 | 1 | 150 | 45 | 110 | Flooded |
| 4 | 2 | 150 | 45 | 110 | 0.169 |
| 5 | 2 | 150 | 45 | 140 | 0.112 |
| 6 | 2 | 180 | 54 | 100 | 0.203 |
| 7 | 2 | 180 | 54 | 125 | 0.146 |
| 8 | 2 | 180 | 54 | 150 | 0.118 |
| 9 | 2 | 180 | 54 | 200 | 0.078 |
| 10 | 2 | 210 | 63 | 175 | 0.084 |
| Notes: | KARR Column with 1 in. diameter x 6-ft plate stack height Plate Stack #1 has constant 2-in. plate spacing throughout Plate Stack #2 from bottom: 1 ft of 6-in., 1 ft of 4-in., and 4 ft of 2-in. spacing between plates Total amount of organic feed used = 55 gal | | | | |

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- *Co-extraction.* If co-extraction of other components in the feed besides the desired solute occurs, how can it be handled? This may require a backwash section in the column or it may necessitate using a fractional extraction technique (7).
- *Flooding.* When flooding occurs, how is this handled in order to return the column to smooth operation? It is best to learn this during pilot plant testing so that it can be applied in the future at full-scale operation.

Closing thoughts

Liquid-liquid extraction processes usually consist of several different unit operations. Thus, when finalizing the design of the process, a complete systems approach must be used so that the entire process is optimized. Often, downstream recovery and recycle of the solvent has greater impact on the operating cost than the extraction column itself. Thus, the most economical extraction column (from an operating cost standpoint) is the one that minimizes the amount of solvent required and reduces the energy needed for the downstream distillation steps.

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