

**PILOT PLANT TESTING RESULTS IN
SUCCESSFUL LIQUID-LIQUID EXTRACTION
SCALE-UP**

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INTRODUCTION

Pilot plant testing is a powerful tool that process engineers use to generate the data required for accurate design of liquid-liquid extraction (LLE) columns¹. A well-designed and conducted test program followed by empirical scale-up to the production column is the most accurate method used for the design of LLE columns². This paper will cover three (3) case studied where pilot plant testing was used for successful design and implementation of LLE columns. Each of these cases involved new processes for which the author knew of no previous operation for the same application. However, actual feed material from operating plants was available. It is always desirable to use actual feed material and not a synthetic mixture when performing pilot plant tests for scale-up. This will insure that any potential problems such as emulsion formation or mass-transfer inhibition due to trace contamination will be exposed.

Glass shell columns were used for testing each of the applications presented in this paper. For liquid-liquid extraction, the use of a glass column during testing is highly advantageous during process development. Visual observation of the phase behavior (droplet formation, dispersed phase hold-up, coalescence, interface behavior, etc.) allows the engineer or scientist conducting the test to quickly assess the column performance and systematically “tweak” the process conditions to obtain optimal performance.

APPLICATION #1

Extraction of Organic Impurities from an Effluent Sodium Hydroxide Stream

In a refinery operation, an effluent caustic solution was generated that was contaminated with some unreacted monomers and polymer precursors. The presence of these organics in the caustic solution made it environmentally hazardous as a waste stream and also not useful for plant neutralization or pH adjustments. In addition, the organic contaminants polymerized upon heating causing fouling of equipment handling this stream. Thus, removal of the organic contaminants prior to heat treatment such as steam stripping was essential in order to generate useful caustic solution for reuse.

The existing operating plant that generated the waste caustic solution also included a purification train for toluene. It was determined that if toluene could be used as the extraction solvent for this application, then the toluene effluent (extract phase) from the LLE step could be brought back into the toluene train for purification, without affecting the final toluene quality.

Laboratory shake tests³ were performed with the waste caustic stream and the plant toluene. The distribution coefficient for the most difficult organic impurity was determined to be approximately 1.5 in the low concentration range tested. The Kremser equation³ was then used to calculate that greater than 99% removal of all the impurities can be achieved with 5-6 theoretical stages at a S/F ratio of 1.0.

With this as the basis, the next step in process development was the selection of an extraction column and pilot plant testing to generate the data for scale-up. During the shake tests it was observed that this system had a high tendency to emulsify. Thus, the KARR[®] Column was selected as the optimal column type for this application⁴. The set-up for the pilot plant test program is shown in Figure 1. The set-up included a 1” diameter KARR[®] Column with up to 10’ plate stack height. The plates and spacers were 316SS.

Data generated in the pilot KARR[®] Column indicated the following:

- The column gave acceptable results for both aqueous and organic phase continuous. However, the tendency for emulsion was observed to be less for the aqueous phase continuous.
- Acceptable extraction efficiency was achieved at a solvent to feed ratio of 1.5 (as is weight basis) with 8’ plate stack height.
- Capacities of 700 and 870 GPH/ft² were tested successfully. However, it was determined that 700 GPH/ft² would be used for scale-up.

Using the data generated in the 1” diameter, pilot KARR[®] Column; the standard scale-up procedure² was employed to design the production column for a waste caustic feed rate of 4740 kg/hr. The resulting KARR[®] Column was 32” diameter x 32’ plate stack height as shown in Figure 2. This column was fabricated and installed in 1999 and has been operating successfully since start-up. This has allowed the end user to sell the effluent caustic solution to a local plant to be used for neutralization purposes.

APPLICATION #2

Aromatic Purification by Fractional Liquid-Liquid Extraction

In fractional extraction, a feed stream consisting of two or more solutes is introduced into the middle of the extraction column and two immiscible solvents are introduced near either end. The heavy solvent will preferentially extract one of the solute(s) and the light solvent will preferentially extract the other solute(s)⁵. High recovery and purity can be achieved for both solute streams by selecting the proper solvent system, solvent ratios, and number of stages above/below the feed location. A typical fractional extraction column is shown in Figure 3

The application here involved a light “tar” feed stream from a refinery operation that included aromatic compounds as well as many organic impurities. The goal was to recover a minimum of 90% of the aromatic compounds with less than 1% impurities. Preliminary laboratory work indicated that a mixed, polar solvent was very effective for removing the aromatic compounds from the feed mixture. However, a significant amount of impurities would also co-extract with the aromatics. Since most of these impurities were non-polar, it was assumed that a straight-chain hydrocarbon that was non-miscible with the polar solvent would be effective for extracting these impurities.

Preliminary tests in a 3” diameter, pilot RDC column indicated that many extraction stages were required as well as a high ratios of the non-polar solvent to the polar solvent and to the organic feed. Also, it was determined that the feed location must be near the top of the column, with most of the stages below the feed location (used for extracting the impurities). Due to the large number of theoretical stages required for this application, the RDC column was not a good choice. Instead, the SCHEIBEL® Column was selected as the best design because this column design has a very high stage efficiency⁴.

The set-up for the pilot plant test program is shown in Figure 4. The set-up included a 3” diameter SCHEIBEL® Column with up to 99 agitated stages. Whereas standard LLE testing can generally be completed in 2 – 3 days, testing for fractional LLE can take significantly longer, which was the case for this application. During a 2-week test program, the following variables were evaluated in the pilot plant equipment:

- The total number of stages was varied between 65 – 99 stages. The stages above the organic feed location were varied between 12 – 34 stages, and the stages below the feed location were varied between 42 – 65 stages.
- The overall column capacity (specific throughput) was varied between 515 – 625 GPH/ft².
- Many variations of the ratios for polar solvent to feed and non-polar solvent to feed were tested. The range for the polar solvent to feed was between 0.5:1 and 1.4:1 and the range for the non-polar solvent to feed was 1.1:1 and 3:1.
- The agitation speed range was varied between 400 – 850 RPM.

At the completion of the test program, it was determined that the optimal operating conditions were as follows:

Capacity	600-625 GPH/ft ²
Total Number of Stages	65 agitated stages
Organic Feed Location	Stage 13 from the top of column
Polar Solvent : Feed Ratio	0.7 : 1.0
Non-polar Solvent : Feed Ratio	1.8 : 1.0

For these conditions the aromatic recovery was 92% with <1.0% impurities.

Using the data generated in the 3” diameter, pilot SCHEIBEL® Column, the standard scale-up procedure was employed to design the production column for a light tar feed rate of 13,439 kg/hr. The resulting SCHEIBEL® Column was 70” diameter x 65 agitated stages as shown in Figure 5. This column was fabricated and installed in 2004 and has been successfully started up and is now operating with good performance.

APPLICATION #3

Neutralization / Washing Process

In a specialty chemical plant, a reaction process produced a nitrated organic product contaminated with un-reacted nitric acid. Purification required removal of the nitric acid and salts to very low levels (<10 ppm). Based upon experience with similar systems, it was understood that a single column could be used to neutralize the nitric acid with ammonia solution and also wash out residual salts generated by this reaction with fresh water in a single column. Based upon solubility data, the extract stream (water + salts) would contain a significant amount of the nitrated organic product making it a hazardous waste stream. Thus, a second extraction column was proposed using toluene to extract the nitrated organic from the aqueous stream. After steam stripping the resulting aqueous stream to remove the toluene, the water could be safely disposed through the plants effluent treatment system. The proposed flow scheme for the two-column extraction process is shown in Figure 6.

Due to the hazardous nature of the nitrated organic feed, this material could not be easily shipped to a pilot plant facility for testing. Thus, for this application, the pilot plant equipment was shipped to and set-up in the operating plant. The set-up is shown on the attached Figure 7. Due to the fact that there was a high expectation for emulsion formation in the neutralization/wash column, a 1" diameter x 10' plate stack height KARR[®] Column was used for the test program. Since the organic phase was the continuous phase, the plate stack consisted of PTFE plates and spacers to insure the proper wetting characteristics². The same column was used for testing the toluene extraction column, however 316SS plates and spacers were used because the aqueous phase was the continuous phase for this step.

For the Neutralization/Wash Column, data generated by the test work indicated:

- The optimal design capacity was a specific throughput of 900 GPH/ft².
- The volume ratio for the phases was:
Organic Feed : Ammonia Water : Fresh Water = 1.0 : 0.087 : 0.26
- The full 10' plate stack height was required to give acceptable results. Also, it was determined that the best location for the organic feed was in the middle, with 5' plate stack height above and below.

Using the data generated in the 1" diameter, pilot KARR[®] Column; the standard scale-up procedure was employed to design the production column for a nitrated organic feed rate of 3200 GPH. The resulting KARR[®] Column was 30" diameter x 40' plate stack height.

For the Toluene Extraction Column, data generated by the test work indicated:

- The optimal design capacity was a specific throughput of 1100 GPH/ft².
- The volume phase ratio was:
Toluene : Aqueous Feed = 0.27 : 1.0

- A plate stack height of only 5' was required to achieve the desired removal of the nitrated organic product.

Using the data generated in the 1" diameter, pilot KARR® Column, the standard scale-up procedure was employed to design the production column for a waste water feed rate of 1250 GPH. The resulting KARR® Column was 16" diameter x 15' plate stack height.

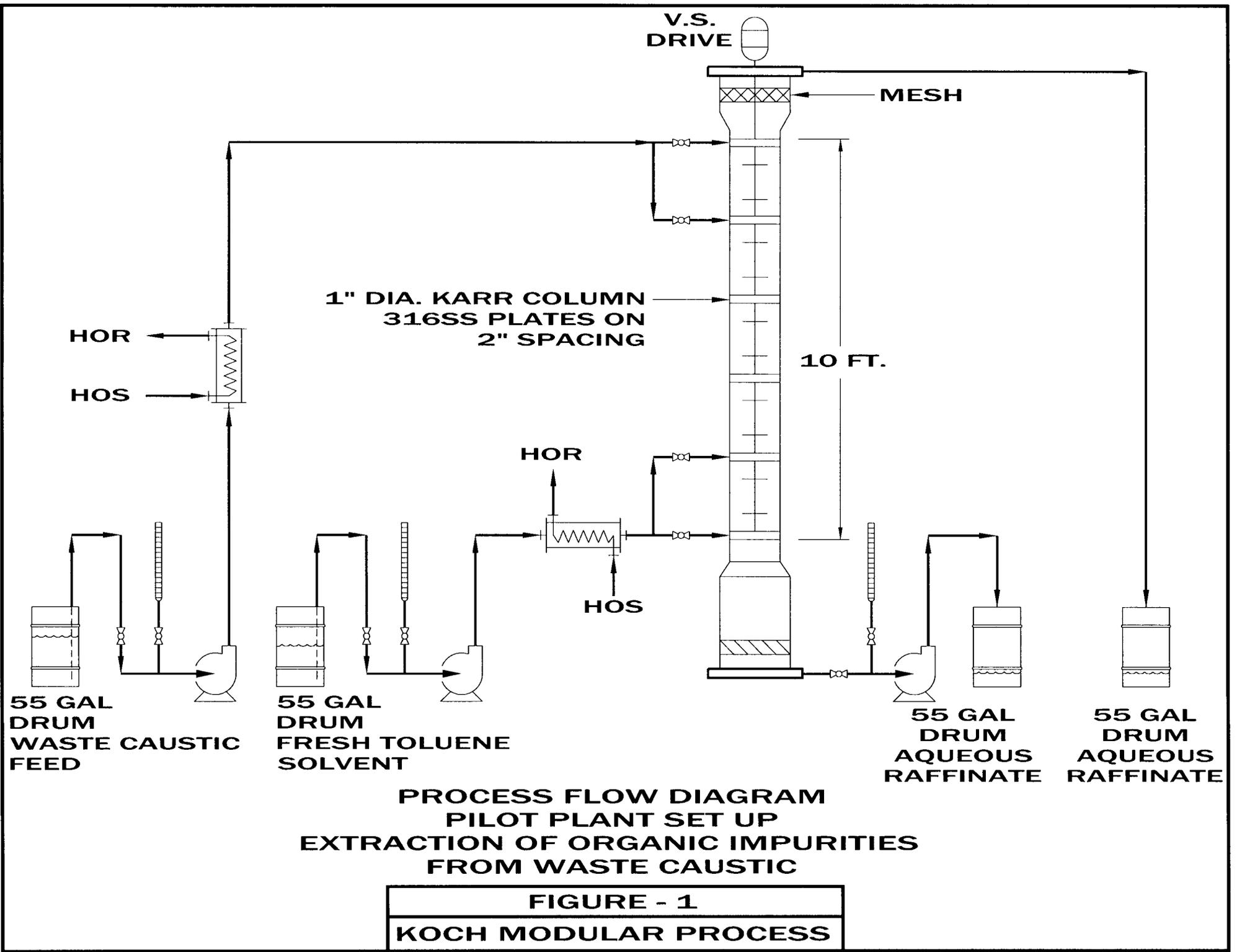
Both KARR® Columns were fabricated and installed in 1999. They have been operating successfully since start up one year later.

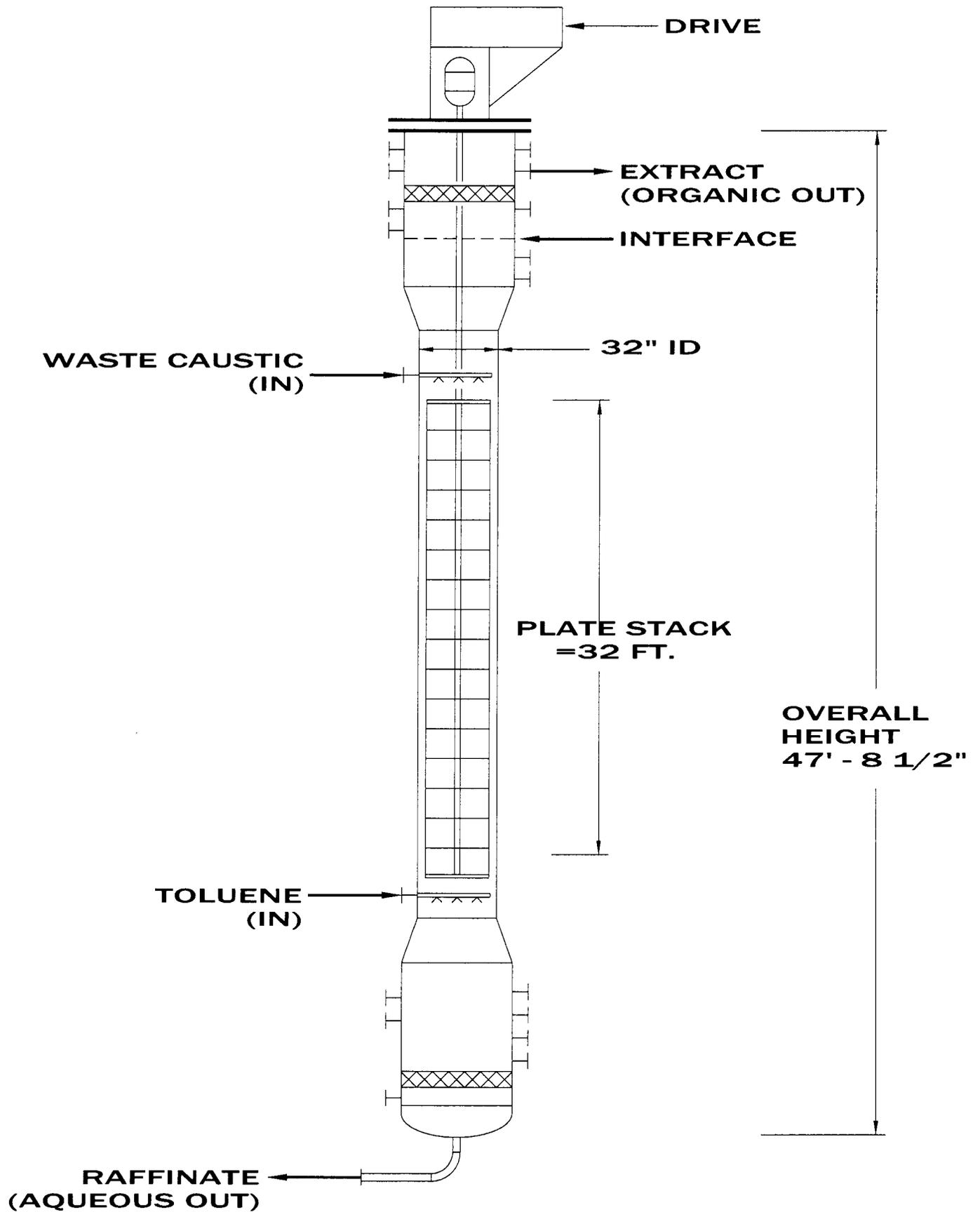
CONCLUSION

Pilot plant testing followed by empirical scale-up is the most reliable and effective method for the design of liquid-liquid extraction columns. This report presented three case studies where data was generated in a glass-shell, pilot extraction column and this data was used to design the required production size columns. In each case, smooth start-up and operation was achieved in the plant after installation of these columns.

LITERATURE CITED

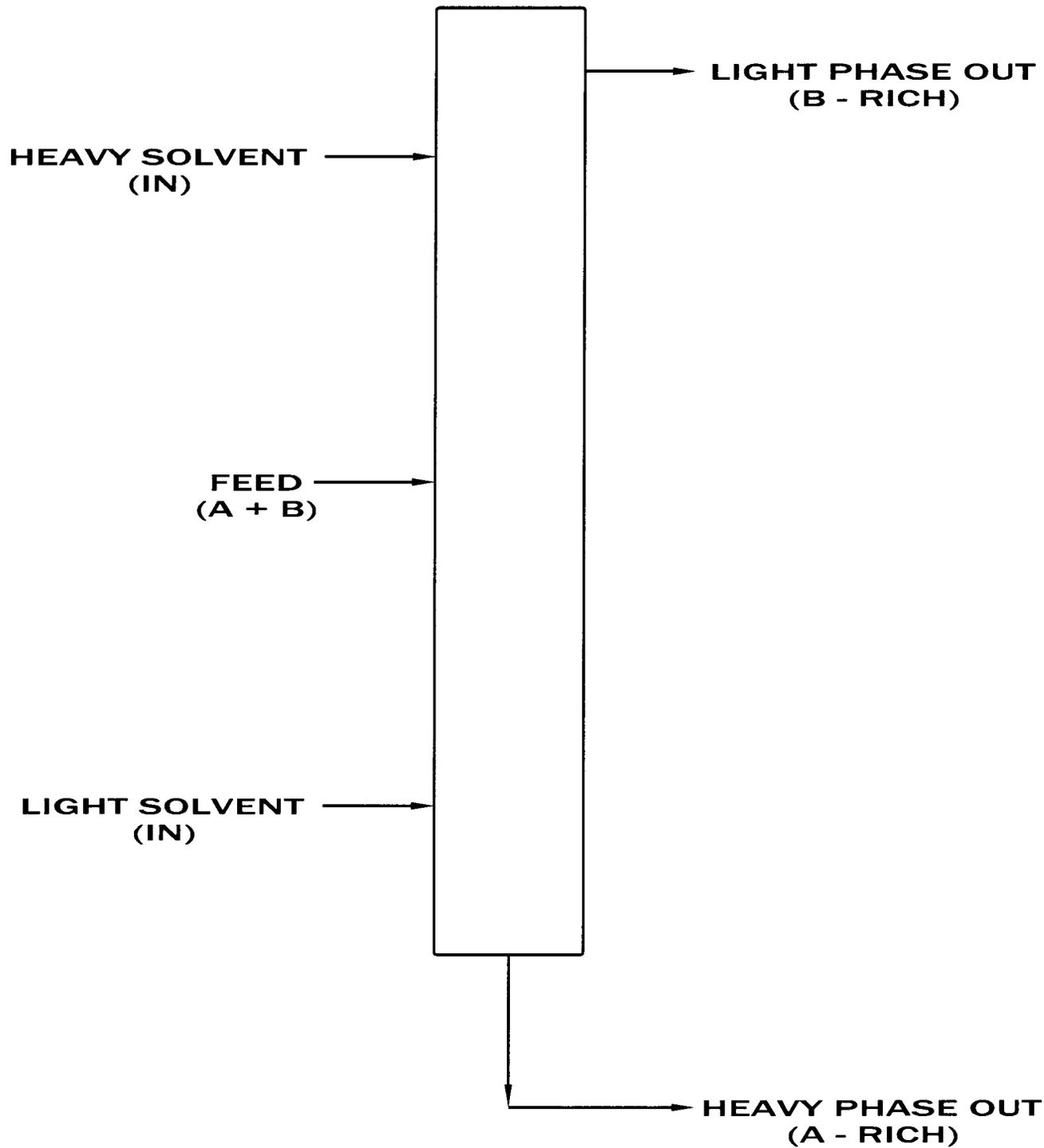
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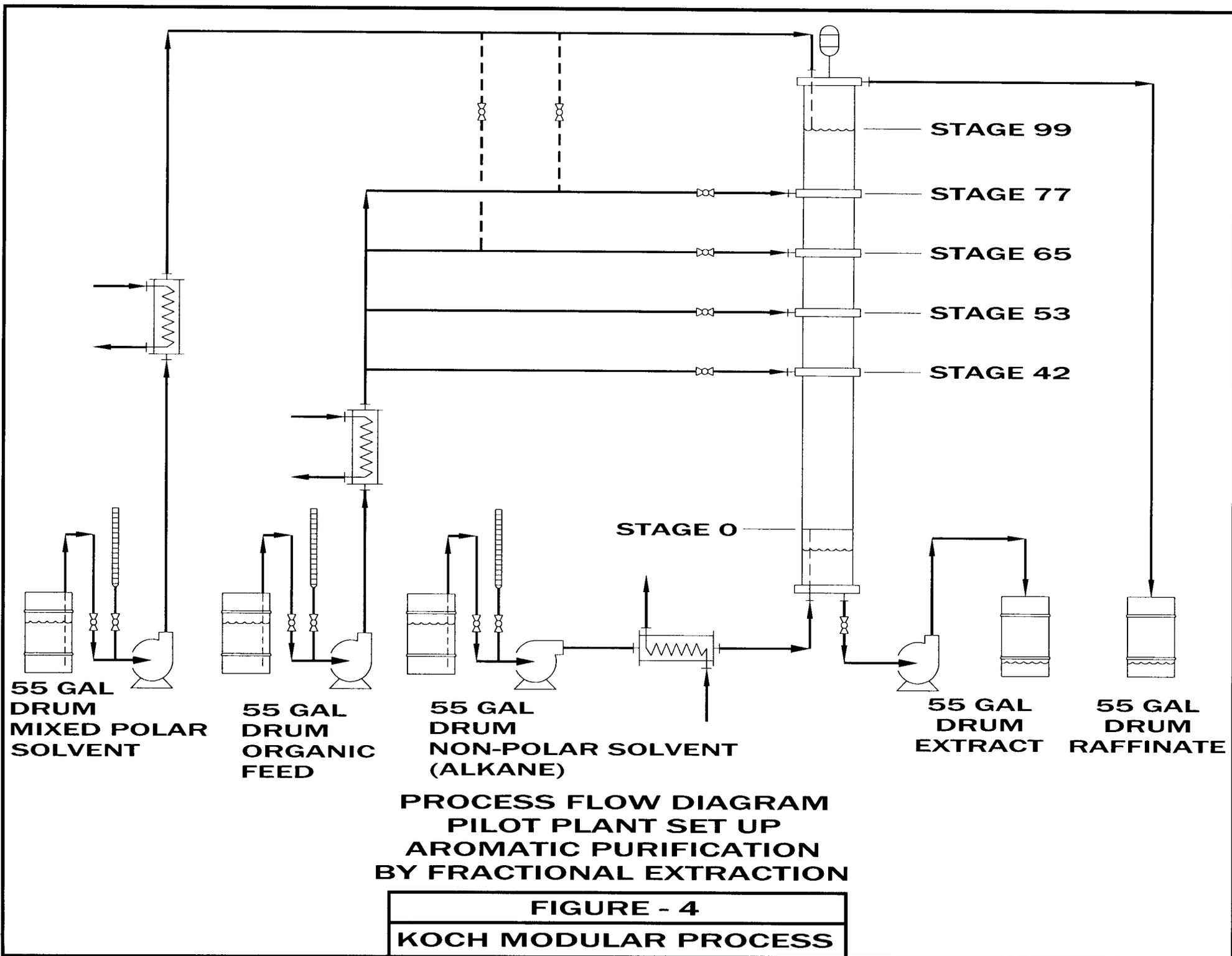
**KARR COLUMN - PRODUCTION UNIT
 WASTE CAUSTIC PURIFICATION**

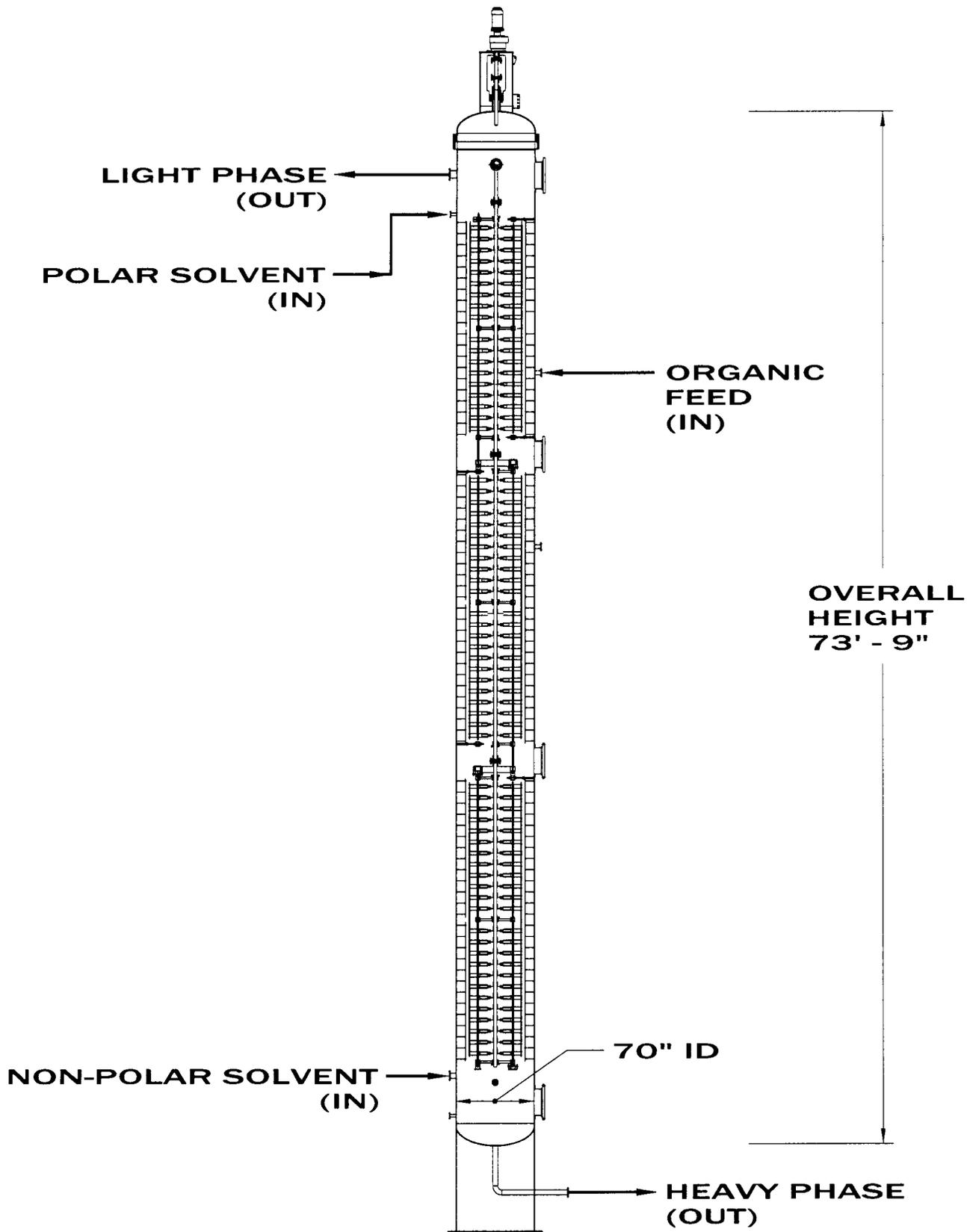
FIGURE - 2
KOCH MODULAR PROCESS



TYPICAL FRACTIONAL
EXTRACTION PROCESS

FIGURE - 3
KOCH MODULAR PROCESS

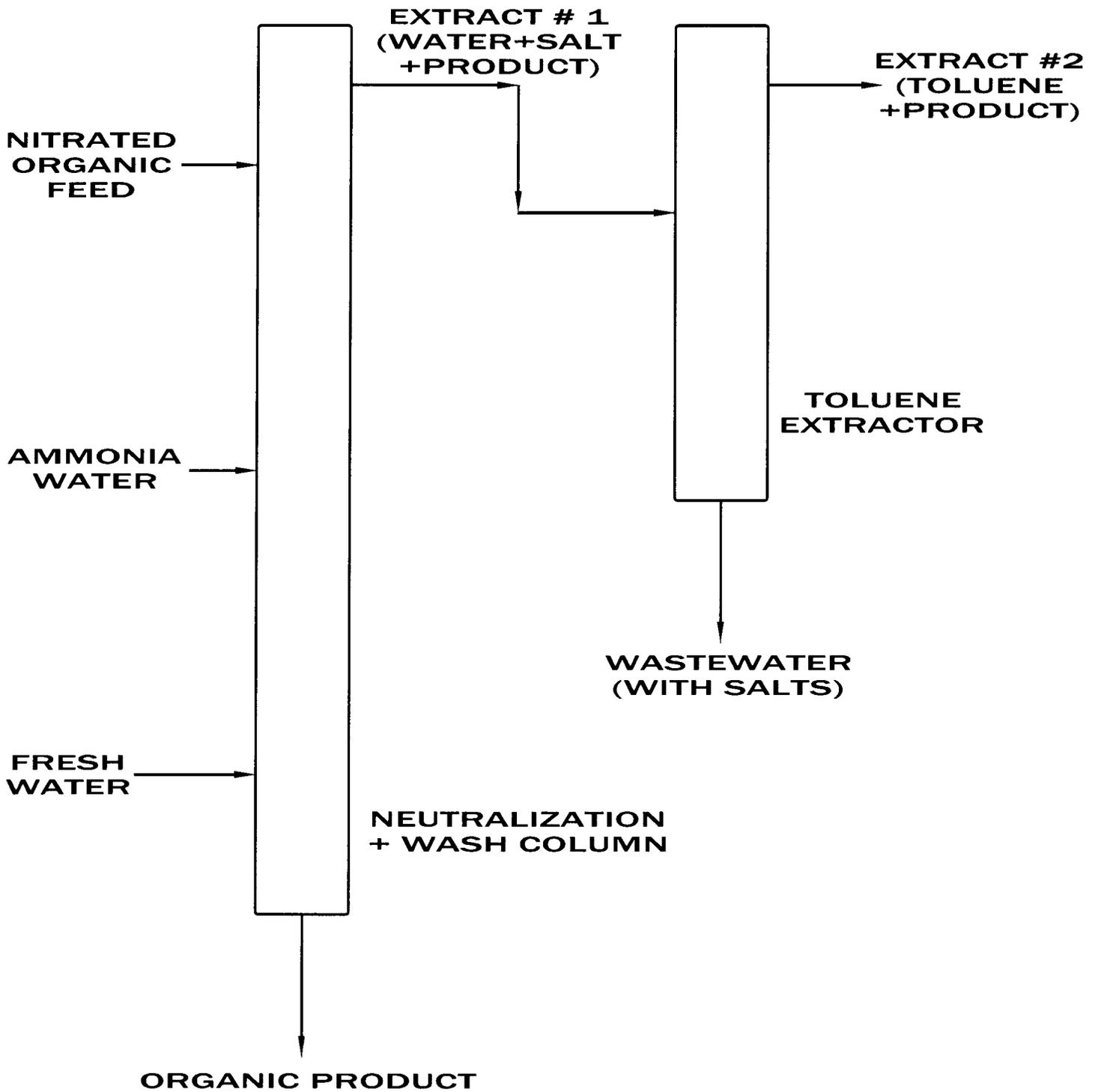




**SCHEIBEL COLUMN - PRODUCTION UNIT
AROMATICS RECOVERY
AND PURIFICATION**

FIGURE - 5

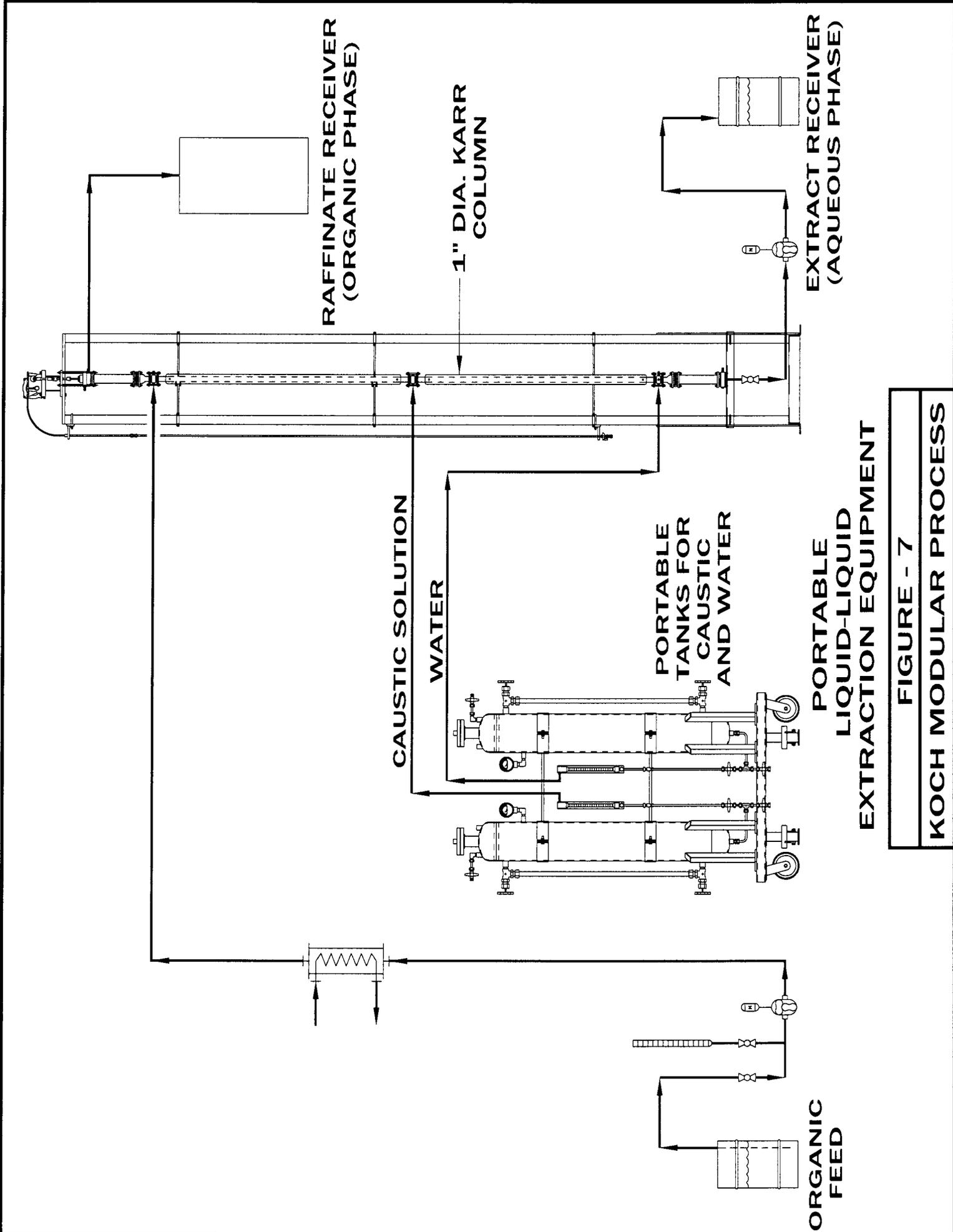
KOCH MODULAR PROCESS



**PURIFICATION PROCESS
FOR NITRATED ORGANIC**

FIGURE - 6

KOCH MODULAR PROCESS



PORTABLE LIQUID-LIQUID EXTRACTION EQUIPMENT

FIGURE - 7
KOCH MODULAR PROCESS