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PRELIMINARY EVALUATION OF ALTERNATIVES TO DISTILLATION FOR ACETIC ACID RECOVERY FROM TEREPHTHALIC ACID FLOWSHEETS

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ABSTRACT

Acetic acid is presently recovered from terephthalic acid flowsheets by distillation. This paper documents a preliminary evaluation of extraction for its recovery and recycle. Experimental data show that the solvent has a selectivity for acetic acid-water of 5 for a 50 wt. percent acid solution and 60 for 5 wt. percent acid solution. Above 10 wt. percent extractant in the solvent, addition of extractant to the solvent has the combined effect of decreasing the solvent loss to the aqueous phase and decreasing the loading of water in the solvent. The high selectivities of the solvent for acid vs. water combined with the high relative volatility of the acid vs. the solvent imply that lower energy costs with an extraction flowsheet over distillation is likely.

INTRODUCTION

Terephthalic acid is a purified intermediate product used in the manufacture of polyester fiber and dimethylterephthalate polymer used to make plastic bottles. Approximately 6.93 billion pounds were produced annually in the United States in 1987. Growth rate of production was 18 percent in 1988. The process of choice (utilized for at least 80 percent of the production) for producing terephthalic acid is the reaction of p-xylene and oxygen in an acetic acid solution. The process requires the purification of an aqueous acetic acid stream for solvent recovery. An initial distillation of water from the acid recovers most of the acid and recovers most of the energy of the oxidation. However, the waste stream from this column contains appreciable acid. Traditionally, recovery from this stream, has been done using azeotropic distillation.

Alternative processing considered in this paper is extraction followed by distillation and stripping rather than the azeotropic distillation now employed. It is anticipated that significantly higher acetic acid recovery at lower cost than present processing will be obtained with the extraction process, thus reducing the burden on wastewater facilities.

PREVIOUS RESEARCH

The recovery of acetic acid from aqueous streams using extraction has received considerable attention. Most academic research has relied on pure acetic acid/water systems to provide equilibrium data (1,2). The pure binary has been used to determine data for processing dilute wastewater streams from several processes (but not those from terephthalic acid plants). Little work has been done to analyze processing using the binary and actual process streams from operating plants. A noted exception is the research of King et al. who analyzed several wastewater process streams. In addition to pure acetic acid/water binary solutions, the distribution in actual process streams was experimentally determined (3,4). Diluents utilized for acetic acid recovery from dilute aqueous streams, described by King and coworkers, and a monofunctional organophosphorous extractant (5) are considered as a possible solvent in this study.

Two review articles, in 1983 and 1988, by C. J. King (6,7) summarize the previous extraction alternatives for aqueous acetic acid streams. The requirements for a successful process rely on the technology transfer from hydrometallurgical processing to the acetic acid flowsheets combined with new chemistry specifically designed for acetic acid. All of the technology recommended has utilized extractant chemistry already used in commercial hydrometallurgical facilities. King concludes that an extractant that is a strong Lewis base, that is high boiling, and not soluble in the aqueous phase is desirable. The best diluents appear to also be capable of extracting acetic acid. In an authoritative and comprehensive review article on recovery of carboxylic acids from fermentation broths, A.S. Kertes and C.J. King (8) state a clear pathway that has not, to date, been explored by industrial researchers:

"...the critical evaluation of the literature data indicate that the conventional extraction systems using water-immiscible alcohols, ketones, or ethers are relatively inefficient for the acid recovery from the dilute aqueous acid solutions found in most fermentation streams. Thus, a good starting point for developing new extractive recovery processes for the weak fermentation product carboxylic acids should be the identification of novel, more powerful extractants. Such are the organophosphorous and aliphatic amine extractants developed initially for the needs of inorganic extractive separation technologies, more specifically in the field of nuclear fuel reprocessing. ..."

King and coworkers recommend the extractants TOPO (trioctyl phosphine oxide) and a commercial tertiary tri-octyl/decyl amine mixture (Alamine 336) for acid recovery from low concentration aqueous streams. Recommended practical diluents are high boiling ketones that have low aqueous solubility. Extraction with diisobutyl ketone (DIBK) diluent/Alamine 336 extractant and with 2-hepanone diluent/TOPO extractant has been reported.

At low concentrations, the economics of acetic acid recovery from a low concentration feed solution was considered by Ricker et al. (4). They showed that there was little sensitivity of the economic optimum, and that the capital costs could be recovered rapidly.

EXPERIMENTAL

The chemicals in this work were used in the condition in which they were supplied. No further purification was needed. The technical grade diisobutyl ketone (DIBK) was obtained from Aldrich and a mass spectrometry analysis determined it to be 71.2% diisobutyl ketone, 23.7% 2,4-dimethyl-6-heptanone, and 5.1% a $C_6H_{13}OH$ alcohol. ChemService, Inc. supplied the standards grade DIBK and their analysis showed it to be 96% DIBK. The 96% purity is the highest purity that is readily available. The extractant, Cyanex 925 was furnished by American Cyanamid, and it is a mixture of 85% di-2,4,4-trimethylpentyl-n-octyl phosphine oxide and 15% tri-2,4,4-trimethylpentyl phosphine oxide. Fisher supplied the glacial acetic acid, and deionized water was used in the aqueous solutions. The terephthalic acid (PTA) stream solution was supplied from a terephthalic acid flowsheet feed solution from an operating plant. Plant samples taken over a three week period were analyzed by GC-Mass Spectrometry and determined to contain no significant variation in composition.

All concentrations were measured with a Hewlett-Packard Model 5840A gas chromatograph equipped with an integrator and a thermal conductivity detector. The column was a Supelco 80/120 mesh Carbopack B/3% SP-1500 packed column with a recommended use for organic solvents. An injection temperature of 230° C and a detector temperature of 260° C were used for each run. The carrier gas was Helium with a flow rate of 60 ml/min. The oven temperature was programmed to be initially 125° C for 36 seconds and then ramped to 210° C at a rate of 30° C/minute. Peak areas were converted to weight fractions by comparison to the areas determined by external standards for the aqueous phase and for the organic phase. Since the Cyanex concentration could not be measured on the GC and its solubility in water is extremely low, it was assumed that all the Cyanex was in the organic layer. The maximum difference from the actual calibrated mass fraction in a series of runs was usually less than 5%. K_D values for acetic acid and water were calculated from the weight percents as follows:

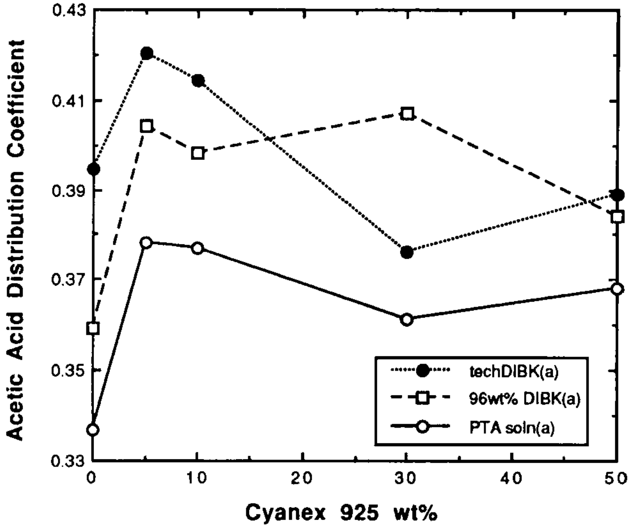
$$K_D = \frac{(X_A)_{org}}{(X_A)_{aq}}$$

For each extraction experiment, a known concentration of an aqueous acetic acid solution was mixed with a known organic phase in a 50 ml stoppered flask. The total volume of both solutions was consistently about 30 ml. The flasks were turned over about 20 times by hand at room temperature. Further experiments with agitation by a magnetic stirrer for 12 hours, revealed the technique was adequate. The phases separated easily and were allowed to settle for 2 hours before analysis.

In this experiment, three different solutions were analyzed. An aqueous solution of 60.0% acetic acid was contacted with an organic phase of extractant and two different diluents, 96% purity DIBK and technical grade DIBK. For these solutions, the initial solvent to feed ratio was 1 to 3. The third solution tested was an acetic acid aqueous solution from an industrial terephthalic acid production process. This solution was contacted with the technical grade DIBK solution only, with a solvent to feed ratio of 1 to 1.

Figure 1 shows the effect of varying the concentration of Cyanex 925 on the extraction of acetic

Figure 1, Variation of Acetic Acid Distribution Coefficient with Extractant Weight Percent



acid for the three solutions. This figure shows that the K_D reaches a maximum at 5 wt. % Cyanex and than declines slightly. Also, the K_D for the technical grade DIBK solution is higher than the 96% grade and the PTA solution, except at 30 wt. % extractant. At this concentration, the 96% grade K_D is higher than the others and is the maximum K_D for this solution. The isomer in the technical grade solution that improves the extraction of acid at lower concentrations no longer improves the K_D after about 18 wt. % extractant, and at 50 wt. % they are about the same. The effect of Cyanex concentration on the water K_D is similar to the effect on the acid K_D. Figure 2 shows K_D is largest with the technical grade DIBK and smallest with the PTA solution. Again at 30 wt. % extractant, the 96% grade K_D is the highest.

The selectivity, β, of an extractant is defined as:

$$\beta = \frac{(K_D)_{acid}}{(K_D)_{water}}$$

The variation of selectivity with extractant concentration is shown in Figure 3. The selectivity increases with increasing extractant concentration with the selectivity of the PTA solution largest at all

Figure 2, Variation of Water Distribution Coefficient with Extractant Weight Percent

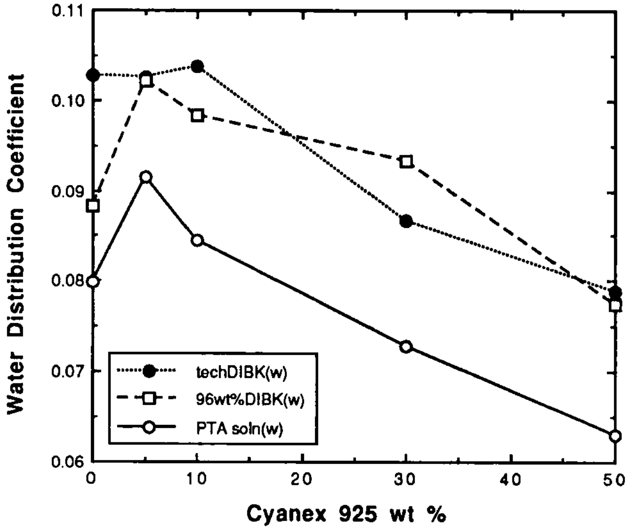
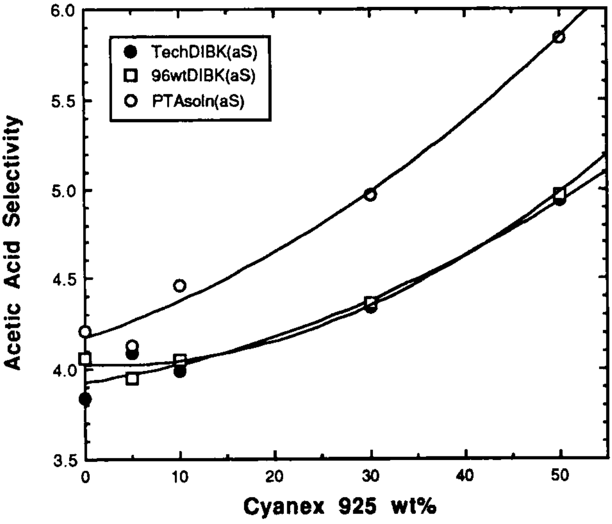


Figure 3, Acetic Acid Selectivity vs. Extractant Weight Percent



concentrations. The selectivities for the technical and 96% grade DIBK solutions are very similar.

The effect of acetic acid concentration on K_D and selectivity was studied. An organic phase of 50 wt. % DIBK and 50 wt. % Cyanex was contacted with aqueous solutions of varying acetic acid concentrations. In Figure 4 the K_D for acetic acid is shown to decrease with increasing aqueous acid concentrations. The decrease is greater below 30 wt. % acid. For water, the K_D gradually increases with increasing acid concentration. Therefore at low acid concentrations, the Cyanex is very selective in extracting acetic acid over water, and this is shown in Figure 5. The selectivity decreases with increasing acid concentration, and the decrease is more rapid at lower acid concentrations. Figure 6 shows the equilibrium diagram for the technical grade DIBK solution has an upward curvature reflecting the decrease in K_D with increasing acid concentration.

An important factor in an extraction process is the amount of solvent lost to the aqueous phase. Figure 7 shows that the amount of solvent lost decreases with increasing extractant concentration. Except for the 10 wt. % concentration, the 96% grade solution has the highest solvent loss while the PTA solution has the lowest solvent loss.

Figure 4, Variation of Distribution Coefficients with Initial Acetic Acid Concentration

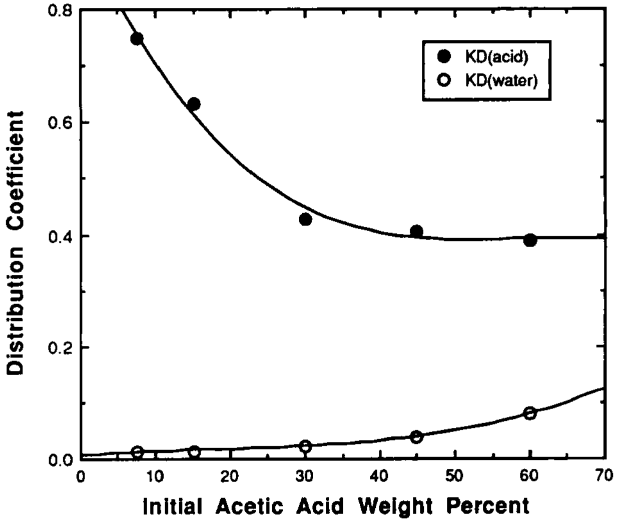


Figure 5, Selectivity vs. Aqueous Acetic Acid Weight Fraction (50% Cyanex 925 solution)

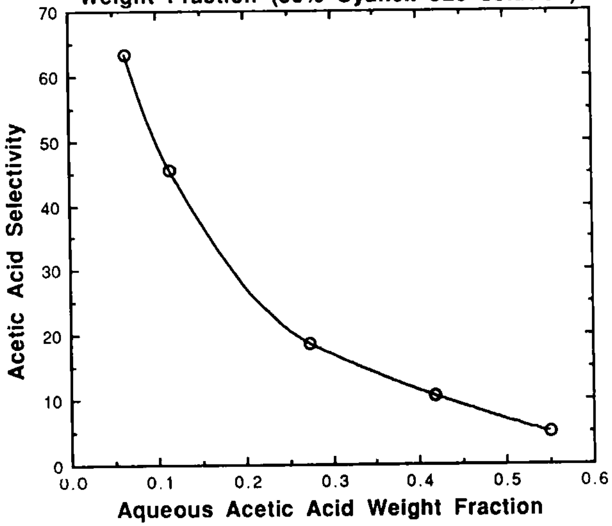


Figure 6, Distribution Diagram for Acetic Acid (50 wt% Cyanex Solvent)

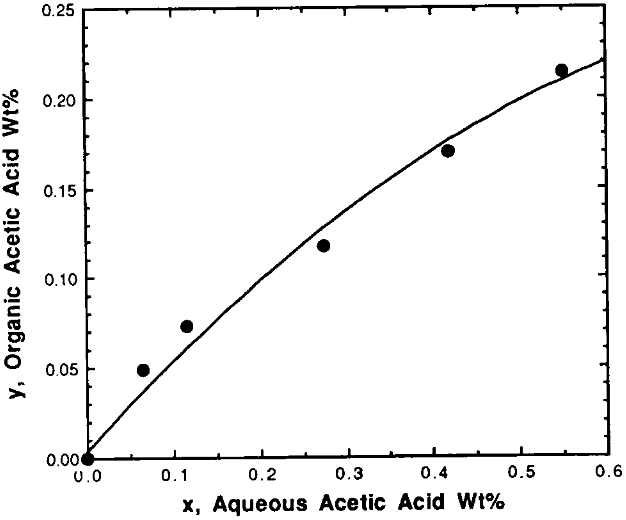
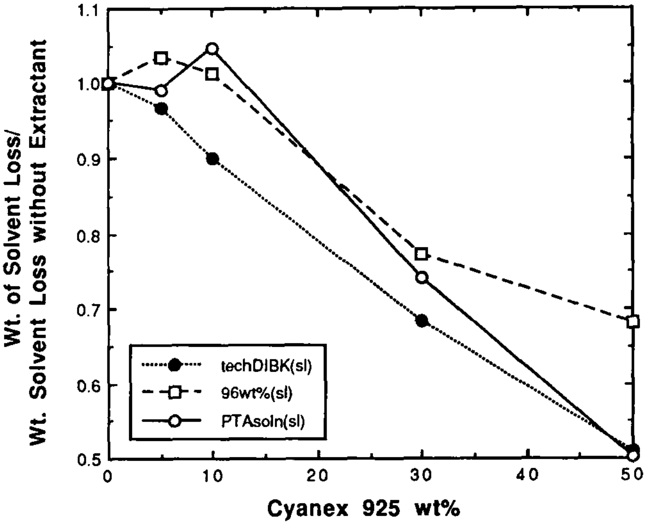


Figure 7, Fractional Solvent Loss vs. Extractant Weight Percent



DISCUSSION

Summarizing the data, below 10 wt. % extractant there is little effect on solvent loss or the K_D values, but above 10 wt. % extractant concentration, increasing extractant concentration decreases the solvent loss, decreases the water K_D, slightly decreases the acetic acid K_D, and increases the acid selectivity. This can be explained by understanding that when the Cyanex complexes with the acid in the aqueous phase, it also complexes with water in the aqueous phase, and at the same time it is complexing with the DIBK in the organic phase.

Below 10 wt. % extractant concentration, adding the Cyanex to the DIBK has little effect on K_D or β because the Cyanex concentration is too low. Above 10 wt. % extractant, the Cyanex readily complexes with the DIBK in the organic phase preventing it from complexing with water in the organic phase. This is advantageous because water is prevented from being extracted into the organic phase and DIBK is prevented from being lost to the aqueous phase. Because acetic acid is a stronger acid than water, it more readily complexes with the Cyanex, the DIBK, and the Cyanex-DIBK complex and is extracted into the organic phase. The selectivities are high because acetic acid is extracted into the organic phase but water is not. As the aqueous acid phase concentration increases, the aqueous phase becomes more similar to the organic phase and therefore the acetic acid K_D decreases, the water K_D increases, and the selectivity decreases.

FLOWSHEET CONCEPTION

Analysis of the experimental liquid-liquid equilibria for high acetic acid concentration aqueous streams shows trends similar to those reported by others (1). In Figure 8 a simplified flowsheet is given. Because the water content for the acetic acid recycle stream is greater than one percent and the aqueous loading can be significantly reduced, the need to dehydrate the product stream can be neglected for recovery of the acid for recycle in terephthalic acid facilities. Contaminants intermediate in boiling point between water and acetic acid are in the feed and are recycled in the existing flowsheet. Obviously, they must be purged at one point in the process.

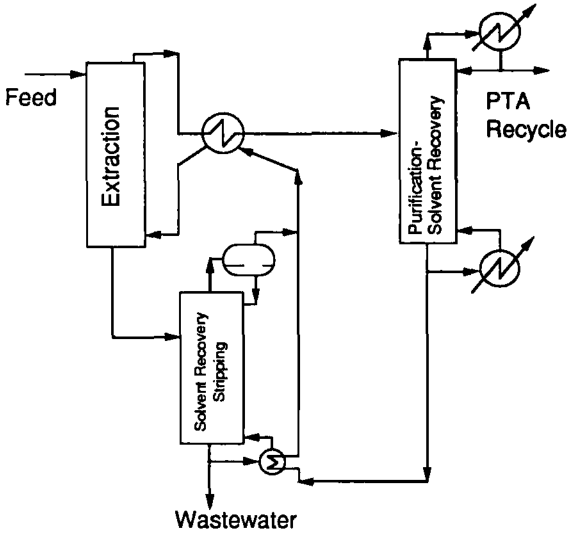


Figure 8, Simplified Acetic Acid Recovery Flowsheet

The simplified flowsheet will apply as long as high purity acid is not required. If higher purity acid is needed, then a more complicated flowsheet is needed. The flowsheet, shown in Figure 9, is a modification of one given by King et al. (3). A dehydration tower is needed to reduce water and intermediate boiling components in the extract. The small modification to this tower permits the flowsheet to have a scrubbing capability to reduce the coextracted intermediates and water. Likewise the addition of some rectification in the solvent recovery stripper permits the intermediate boiling components to have a pathway to the purge.

The energy requirements for the process are associated with the purification-solvent recovery column. The relative volatility of acetic acid-diluent binaries is approximately 4.0. This permits operation at low reflux and low boilup. Solvent degradation considerations may require column operation at low pressures to reduce this effect. If the liquid leaving the reboiler for this column falls below the thermal requirements of the solvent recovery stripper, then its reboiler could be heated by low quality process steam.

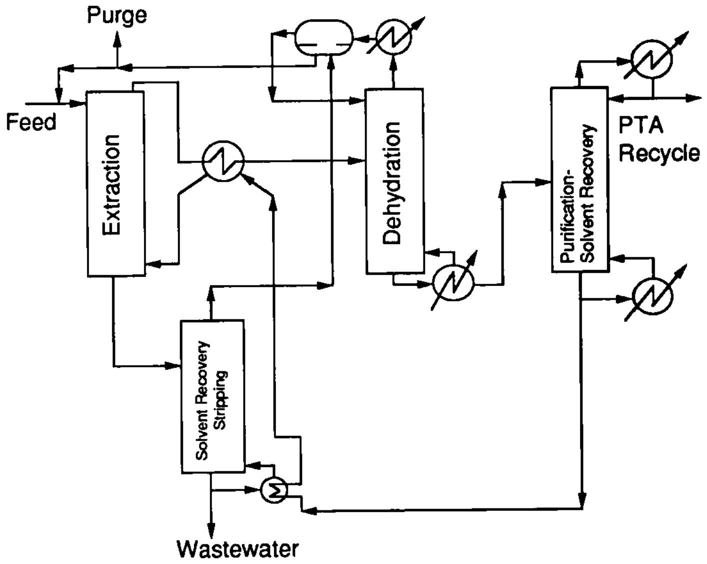


Figure 9, Acetic Acid Recovery Flowsheet (modified from King et al., 1980)

CONCLUSION

Experimental liquid-liquid equilibria for acetic acid-water binary solutions contacted by Cyanex 925/diisobutyl ketone solutions has potential for consideration as a low energy process alternative for acid recovery from terephthalic acid flowsheets.

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