

Recovery of acetic acid from waste streams by extractive distillation

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Abstract Wastes have been considered to be a serious worldwide environmental problem in recent years. Because of increasing pollution, these wastes should be treated. However, industrial wastes can contain a number of valuable organic components. Recovery of these components is important economically. Using conventional distillation techniques, the separation of acetic acid and water is both impractical and uneconomical, because it often requires large number of trays and a high reflux ratio. In practice special techniques are used depending on the concentration of acetic acid. Between 30 and 70% (w/w) acetic acid contents, extractive distillation was suggested. Extractive distillation is a multicomponent-rectification method similar in purpose to azeotropic distillation. In extractive distillation, to a binary mixture which is difficult or impossible to separate by ordinary means, a third component termed an entrainer is added which alters the relative volatility of the original constituents, thus permitting the separation. In our department acetic acid is used as a solvent during the obtaining of cobalt(III) acetate from cobalt(II) acetate by an electrochemical method. After the operation, the remaining waste contains acetic acid. In this work, acetic acid which has been found in this waste was recovered by extractive distillation. Adiponitrile and sulfolane were used as high boiling solvents and the effects of solvent feed rate/ solution feed rate ratio and solvent type were investigated. According to the experimental results, it was seen that the recovery of acetic acid from waste streams is possible by extractive distillation.

Keywords Acetic acid; extractive distillation; recovery

Introduction

Acetic acid is one of the most widely used carboxylic acids. It is used in many reactions, for example, the synthesis of acetic esters, or it can be used as a solvent in the manufacturing of cellulose acetate or pharmaceutical products. Dilute acetic acid wastewater streams are produced in large quantities by some parts of the synthetic organic chemical industry (Kirk-Othmer, 1980).

The recovery of acetic acid from its dilute aqueous solutions is a major problem in both the petrochemical and fine chemical industries. The conventional methods of recovery of acetic acid are azeotropic distillation, extractive distillation, simple distillation and liquid-liquid extraction (Saha *et al.*, 2000). Of course, the particulars of each application must be fully evaluated, to uncover any nonobvious factors that might affect the separation choice. As illustrated in Table 1, the choice of technology depends upon the starting concentration of the acetic acid (Lee and Gentry, 1997).

Table 1 Rules of thumb for choosing a separation method for recovering acetic acid (Lee and Gentry, 1997)

Recommended separation technology	Acetic acid concentration in feed, %
Distillation	>70
Azeotropic distillation	50–80
Extractive distillation	30–70
Liquid-liquid extraction (low boiling solvent)	7–25
Liquid-liquid extraction (high boiling solvent)	2–30
Hybrid acid recovery process	0.5–5

Separation of binary azeotropes or nonazeotropic binary systems (that are not so easy to separate by rectification) is an important process in the chemical industry. The separation is characterized by the fact that it is impossible to perform by means of simple distillation. The most common approach to solve this problem is to add a third component, called an entrainer which enables the separation of the components forming the binary azeotrope. Depending on the thermodynamic properties of the mixture, the separation can be performed either entirely by distillation (the homogeneous case) or by distillation and decantation of two liquid phases (the heterogeneous case) (Andersen *et al.*, 1995).

Extractive distillation involves the addition of a third component to a binary system to facilitate the separation of the system by distillation. The added component modifies liquid activity coefficients and hence the vapor-liquid equilibria of the other two components in a favorable direction (King, 1980). The added solvent is, however, of low volatility and is itself not appreciably vaporized in the fractionator.

Extractive distillation works because the solvent is specially chosen to interact differently with the components of the original mixture. Because these interactions occur predominantly in the liquid phase, the solvent is continuously added near the top of the extractive distillation column so that an appreciable amount is present in the liquid phase on all of the trays below. The mixture to be separated is added through a second feed point further down the column. In the extractive column, the component having the greater volatility, not necessarily the component having the lowest boiling point, is taken overhead as a relatively pure distillate. The other component leaves with the solvent via the column bottom. The solvent is separated from the remaining components in a second distillation column and then recycled back to the first column (Yee, 2000).

Extractive distillation has been practised for more than 50 years. More recently, extractive distillation has been used as a standalone operation or as a supplementary step in many applications, including:

- aromatics,
- alcohols,
- olefin/paraffin mixtures,
- naphthene/paraffin mixtures,
- carboxylic acid from aqueous streams,
- styrene/aromatics mixtures,
- diolefins from olefins and paraffins.

In comparison to the other techniques, the extractive distillation process has a number of advantages:

- It is operated like a conventional distillation process; so it is easily adapted to an existing plant scheme.
- It can make use of two key variables, namely the polarity as well as the boiling point differences of the key components to be separated.
- It does not require additional steps to purify products or recover trace amounts of solvent from product streams.
- Relatively simple modification can convert an existing distillation column into an extractive distillation column (Lee and Gentry, 1997).

In extractive distillation the following operating variables are important:

- reflux ratio,
- solvent ratio,
- solvent temperature,
- state of feed,
- distillation pressure.

One of the most important steps in developing a successful extractive distillation sequence is selecting a good solvent. In general, selection criteria include the following:

- should enhance significantly the natural relative volatility of the key component
- should not require an excessive ratio of solvent to nonsolvent
- should remain soluble in the feed components
- should be easily separable from the bottom product
- should be stable at the temperature of the distillation and solvent separation
- should be nonreactive with the components in the feed mixture
- should not form an azeotrope with the low boiling component (Larian, 1958).

There is often more than one way to design a system for separating chemical components. Because of the natural advantages of extractive distillation for many applications, we anticipate that this technique will be chosen more frequently in the future.

Experimental

The waste stream

In our department, acetic acid is used as a solvent during the obtaining of cobalt(III) acetate from cobalt(II) acetate by an electrochemical method. After the operation, the remaining waste contains acetic acid, so this acetic acid must be recovered. In this study, acetic acid which has been found to be 51 w% in this waste stream was aimed to be recovered by extractive distillation.

Extractive distillation column

Experiments were performed in a 5 cm inner diameter column glass (pyrex) packed with 135 cm of 0.5 cm outer diameter glass Raschig rings packing. The reboiler was heated by an electric heating mantle. The condenser was water cooled. The input flows were made through valves which were placed on the column and the feeds were at room temperature. Flow rates were measured by rotameters volumetrically. Reflux ratio was adjusted manually. Temperatures were controlled by thermometers. The column was operated under atmospheric pressure. The experimental device was shown in Figure 1.

Analysis

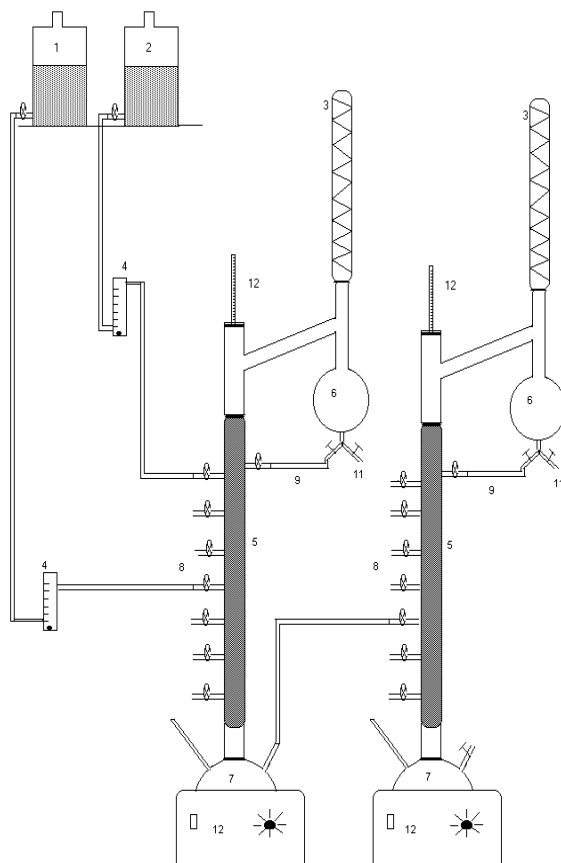
The acetic acid concentration was measured by volumetric titration with NaOH and phenolphthalein as indicator. The solvent concentrations were computed by using gas chromatographic analysis with a 15 m 0.25 mm inner diameter DB-FFAP (Free Fatty Acid Phase) capillary column with nitrogen as the carrier gas and flame ionisation as detector.

Experimental method

The acetic acid solution was fed to the column at two different rates of 3 mL/min and 5 mL/min at a location 80 cm from the column top, while the solvents were charged at a rate of 10 mL/min at a location 30 cm from the column top. Thus the solvent feed rate/acetic acid solution feed rate ratios (S/F) were chosen as 3.33 and 2. The column reflux ratio was adjusted to 4. The analysis of the ternary mixtures was carried out at intervals of 10 min in the head of the column and overhead compositions were determined. Furthermore, the bottom product of the extractive distillation column was fed to the second distillation column (solvent recovery column) to separate acetic acid from the entrainer.

Results and discussion

The experimental results obtained for adiponitrile at two different solvent feed rate/acetic acid solution feed rate ratios are given in Figure 2 and Figure 3. The experimental results obtained for sulfolane at two different solvent feed rate/acetic acid solution feed rate ratios



- | | |
|------------------------|----------------------------|
| 1. Solution feed tank | 7. Reboiler |
| 2. Solvent feed tank | 8. Feed valves |
| 3. Condenser | 9. Reflux |
| 4. Rotameter | 10. Thermometer |
| 5. Distillation column | 11. Overhead product valve |
| 6. Overhead product | 12. Heater |

Figure 1 Experimental device

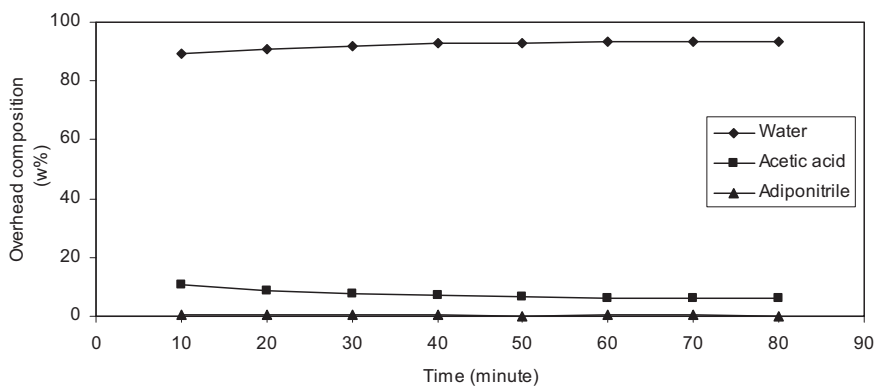


Figure 2 Overhead composition of extractive distillation column versus time for adiponitrile (S/F = 2)

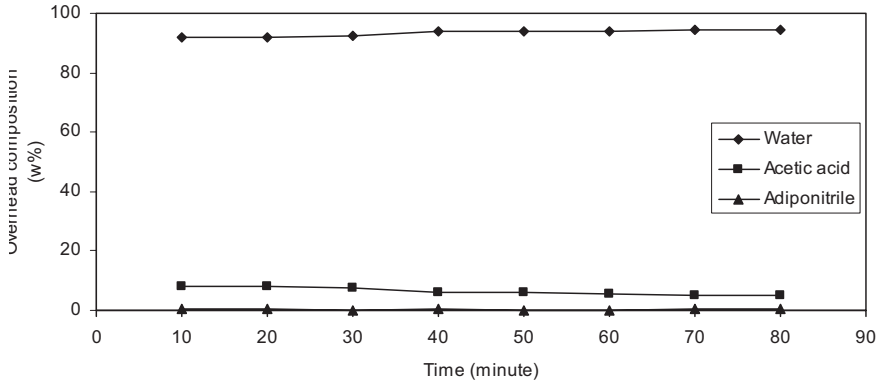


Figure 3 Overhead composition of extractive distillation column versus time for adiponitrile (S/F = 3.33)

are given in Figure 4 and Figure 5. Comparison of solvent type according to the solvent feed rate/solution feed rate ratios (S/F) is given in Figure 6.

In this study the effects of solvent type and S/F ratios were investigated. When Figure 5, in which the comparison of solvent type according to the S/F ratios is given, is investigated, adiponitrile was seen to be a more effective entrainer than sulfolane. As the S/F ratio is increased, the overhead composition of acetic acid was decreased from 8.38% to 7.84% with sulfolane, while this composition was decreased from 6.22% to 4.84% with adiponitrile. So

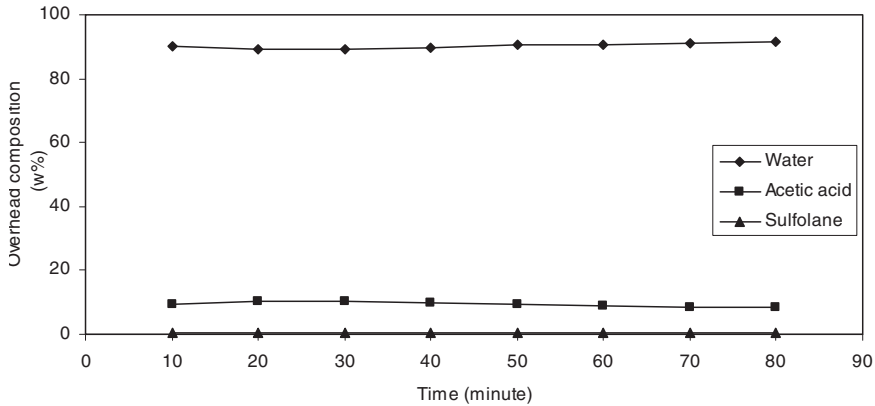


Figure 4 Overhead composition of extractive distillation column versus time for sulfolane (S/F = 2)

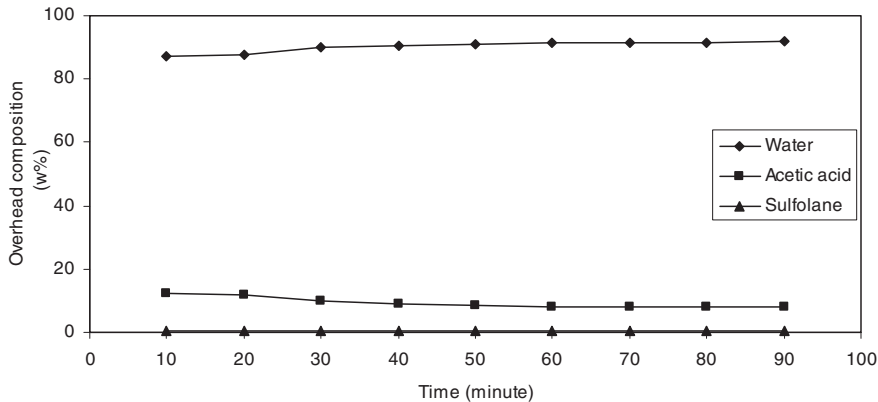


Figure 5 Overhead composition of extractive distillation column versus time for sulfolane (S/F = 3.33)

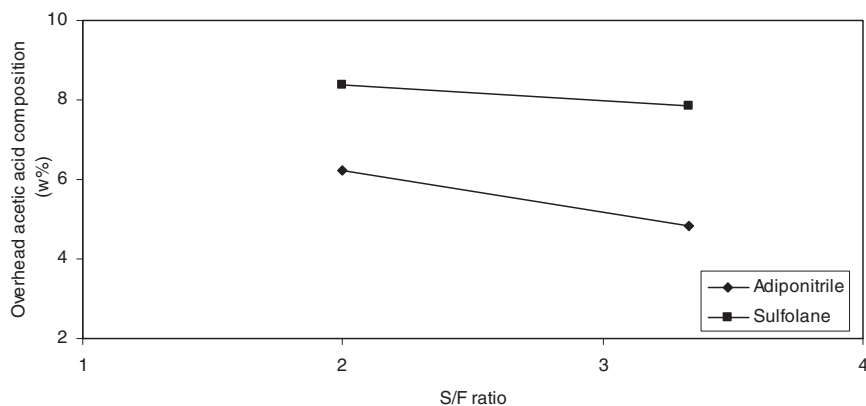


Figure 6 Comparison of solvent type according to the S/F ratios

adiponitrile is better than sulfolane as an entrainer. Furthermore the S/F ratio is an important parameter for extractive distillation. According to the experimental results, the S/F ratio was seen to be effective on acetic acid composition of the overhead. Increasing the S/F ratio, the percentage of acetic acid in overhead product was decreased. As the amount of acetic acid in overhead is decreased, the concentration of acetic acid in bottom product is increased. The bottom product consists of contained entrainer and acetic acid mixture. Acetic acid is separated from the entrainer in a second distillation column. As a result, extractive distillation is a convenient method for recovery of acetic acid from waste streams.

Conclusion

At the separation of a mixture of water and acetic acid, adiponitrile and sulfolane can be utilized as an extractive distillation solvent. The ratio of S/F has an appreciable effect on extractive distillation. In extractive distillation, other important operating variables are reflux ratio, solvent temperature, state of the feed and distillation pressure. In this study the effect of these variables were not investigated. By examining these parameters, the operation of extractive distillation can be made more productive.

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