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DISTILLATION

Azeotropic Distillation

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Introduction

An azeotrope occurs when the composition of a vapour in equilibrium with a liquid mixture has the same composition as the liquid. Azeotropic distillation takes advantage of azeotropes that form naturally between many components. Azeotropic distillation involves the formation of an azeotrope, or the use of an existing azeotrope, to effect a desired separation.

For almost 100 years the existence of naturally occurring azeotropes has been used to purify chemicals. In 1902, Young reported using benzene as an azeotropic agent to dehydrate ethanol. This first industrial application was in a batch mode and therefore not conducive to widespread commercial use. Twenty years elapsed before a continuous commercial process was developed. In 1923, Backus, Keyes and Stevens of the United States, and Guinot of France developed continuous azeotropic distillation processes for the dehydration of ethanol. As with Young's batch process, the continuous processes relied upon the ethanol–benzene–water ternary azeotropic mixture for dehydrating ethanol. From that time, azeotropic distillation processes have grown to become an indispensable tool in today's industries.

Desirable properties for an azeotropic entrainer are:

1. Heterogeneous azeotrope for ease of entrainer recovery
2. Commercially available and inexpensive
3. Nontoxic
4. Chemically stable
5. Noncorrosive
6. Low latent heat of vaporization
7. Low viscosity to provide high tray efficiencies
8. Low freezing point to allow ease of handling and storage

Azeotropic distillation is an essential unit operation in today's processes. Applications using azeotropic distillation are readily apparent in the chemical process industry (CPI), speciality chemicals and food industries. Applications from various industries are listed in **Table 1**.

The main advantages of azeotropic distillation are in allowing the separation of chemicals that cannot feasibly be separated by conventional distillation, such as systems containing azeotropes or pinch points, and improving the economics of the separation by saving energy and increasing recovery. The main disadvantages of azeotropic distillation are the larger diameter column required to allow for increased vapour volume due to the azeotropic agent, and an increase in control complications compared with simple distillation.

A minimum-boiling azeotrope can be formed by the introduction of an azeotrope-forming compound (entrainer) to an existing azeotropic mixture or close-boiling mixture for which separation by

Table 1 Industrial applications of azeotropic distillation

Industry	*Application*	*Separation involved*	*Typical entrainers*
CPI	Acetic acid recovery or purification	Acetic acid/water	Ethyl acetate, butyl acetate
CPI	Terephthalate acid solvent recovery	Acetic acid/water	Ethyl acetate, butyl acetate
CPI	Preparation of high purity esters	Water/esters to change equilibrium	Alcohol
CPI	THF purification	THF/water azeotrope	*n*-Pentane
Speciality chemicals	Purification of 1,1,1,2-tetrafluoroethane (refrigerant)	1,1,1,2-tetrafluoroethane/hydrogen fluoride and/or 1-chloro-2,2-difluoroethylene	Components present in system
Speciality chemicals	Recovery of perchloroethylene (dry cleaning solvent)	Perchloroethylene and residue	Water
Speciality chemicals	Solvent recovery from tyre manufacturing	Contaminated solvents	Water
Food	Alcohol dehydration	Alcohol/water azeotrope	Benzene, cyclohexane
Food	Production of L-aspartyl-L-phenylalanine methyl ester (sweetener)	Acetic acid/toluene azeotrope	Water

CPI, chemical process industry.

conventional distillation is not feasible. One example is alcohol dehydration. Ethanol and water form a minimum-boiling azeotrope with ethanol as the major component and therefore ethanol cannot be completely dehydrated by conventional distillation. Benzene forms a ternary azeotrope with ethanol and water, which boils at a lower temperature and will therefore remove the water (with some ethanol) overhead, leaving dry ethanol as a bottoms product.

In some cases, an azeotrope that exists within the system can be used advantageously to purify a compound, as in the production of esters. The esterification of alcohols involves a reversible reaction. Being equilibrium limited, the reaction will not go to completion in the presence of the product. If one of the products is removed (in this case water) utilizing the water/alcohol azeotrope (almost all alcohols from C_2 to C_{20} form azeotropes with water) the reaction is driven in favour of the ester product. A comprehensive list of many azeotrope-forming compounds can be found in the publication *Azeotropic Data III*, by Horsely (see Further Reading section).

Relative volatility is a comparison of the volatilities of the components in the mixture. When the compositions of the vapour and liquid phases are the same, the volatilities of the components are the same and the relative volatility is equal to 1. The further the relative volatility is away from 1, the easier it is to separate the components of the mixture. **Figure 1** illustrates the number of theoretical stages required to separate two components to 99% purity compared with the relative volatility of the mixture. As can be seen, the number of trays required asymptotically approaches infinity and the separation becomes impossible as the relative volatility approaches unity. A relative volatility close to unity could indicate the presence of a pinch point. It is technically feasible to separate components that form a pinch point, but often not economic due to the large number of stages required to effect the separation.

Homogeneous azeotropes exist when the vapour is in equilibrium with a single liquid phase. In a homogeneous azeotropic system, the entrainer must be recovered by additional fractionation or extraction. **Figure 2** illustrates the homogeneous azeotropic

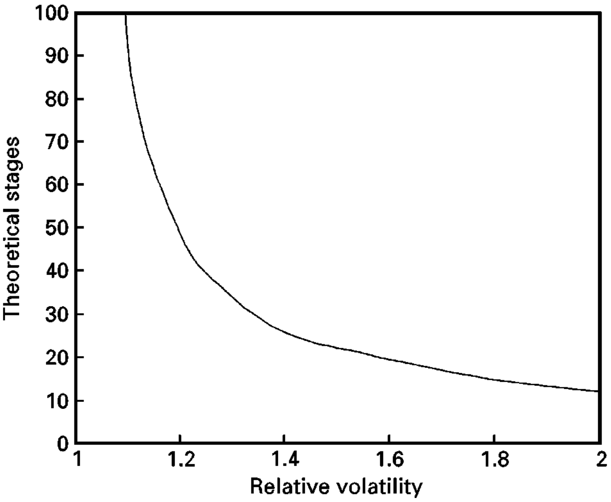

Figure 1 Relative volatility versus theoretrical stages required to separate two components to 99% purity.

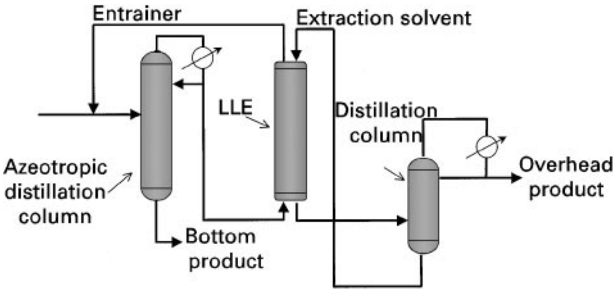

Figure 2 Typical homogeneous azeotropic distillation system utilizing a liquid–liquid extraction (LLE) column to separate the overhead product from the entrainer.

distillation system. Heterogeneous azeotropes exist when the vapour is in equilibrium with two liquid phases. Heterogeneous azeotropic distillation is widely used for the separation of azeotropic or close-boiling mixtures by forming a minimum-boiling azeotrope and taking advantage of the liquid–liquid immiscibility to recover the entrainer. **Figure 3** illustrates a typical azeotropic distillation system of a heterogeneous azeotrope.

Acetic Acid Recovery

There are many industrial processes where acetic acid and water coexist and must be separated. One such process is the production of terephthalic acid. Terephthalic acid (TA) is a polyester raw material used to produce fibres, films and bottles. Terephthalic acid production is important because of the phenomenal growth of this product in the market. The worldwide purified terephthalic acid (PTA) production is currently 15 million tonnes per year, with a growth rate of 12% per annum expected well into the twenty-first century. Let us examine the operational advantage of using azeotropic distillation in the production of purified terephthalic acid.

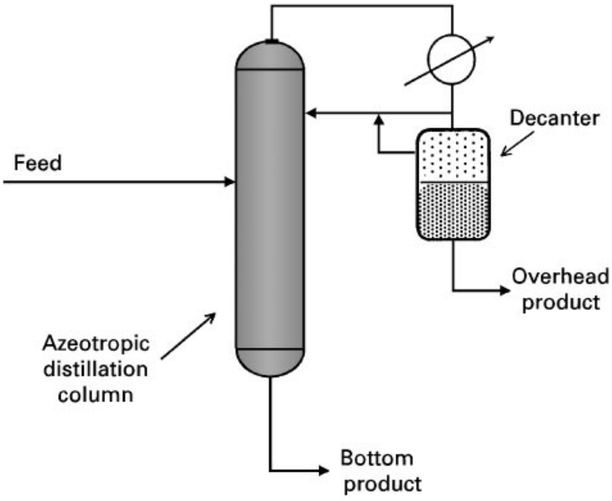

Figure 3 Typical heterogeneous azeotropic distillation system.

The production of PTA includes two main sections, oxidation and purification. Within the oxidation unit, *p*-xylene is catalytically oxidized to produce crude TA. **Figure 4** shows a PTA oxidation section block diagram. Acetic acid is present in the oxidation reactor as a solvent and has also been found to be beneficial in the oxidation reaction itself.

Critical to the efficient and economical operation of a PTA plant is the recovery and recycling of the acetic acid solvent. The acetic acid must be separated from the water that is produced as a product of oxidation. Water and acetic acid exhibit a pinch point at high water concentrations making it very difficult to recover the pure acid. **Figure 5** illustrates the water/acetic acid pinch point on a graph of the fraction of water in liquid phase versus the fraction of water in the vapour phase.

In this process, a clean separation of acetic acid from water is vital. If the acetic acid recycled to the reactor contains too much water, the oxidation reaction will be inhibited, resulting in a decrease in overall yield. If the water being disposed as waste contains acetic acid, the acid must be treated within a wastewater treatment facility. Therefore, any acid losses count against the process economics both as increased make-up solvent required and increased wastewater treatment costs.

The acetic acid recovery unit separates the acetic acid to be recycled to the reactor, from water that can be polished for disposal. A conventional acetic acid recovery unit in a PTA process consists of the low and high pressure absorbers and the acid dehydration column. The low pressure absorber uses water to absorb acetic acid and methyl acetate (reaction by-product) from the TA drier gas. The high pressure absorber uses water to absorb acetic acid and methyl acetate from the reactor off-gas. These streams generally make up 25% of the feed to the dehydrator and contain less than 30% concentration of acetic acid. The remaining feed to the dehydrator column comes

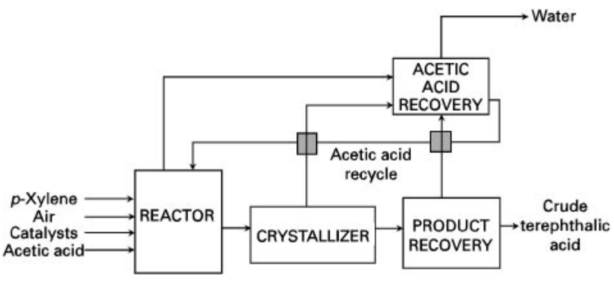

Figure 4 PTA oxidation section block diagram.

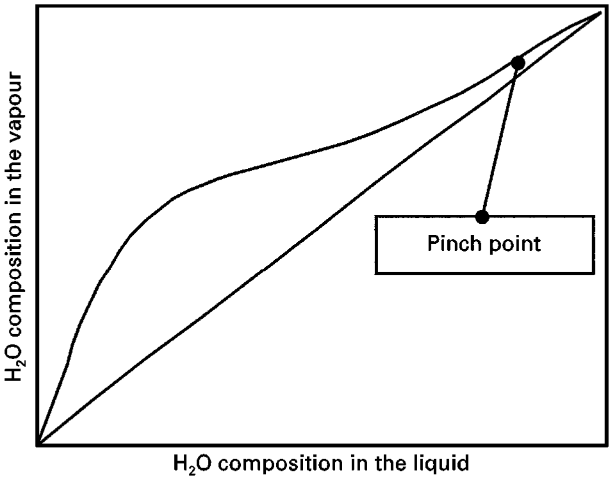

Figure 5 Diagram illustrating acetic acid/water pinch point on a graph of the fraction of water in the liquid phase versus the fraction in the vapour phase.

from the crystallizers. **Figure 6** shows a conventional acetic acid recovery unit using azeotropic distillation in a PTA process.

Typically the acetic acid/water separation of the acid recovery unit is accomplished by either conventional distillation or azeotropic distillation. Separation of acetic acid and water by conventional distillation requires a very tall column, containing 70 to 80 trays.

Preferably, the acid dehydration column in the solvent recovery unit can be operated as an azeotropic distillation column. As an example, let us assume the azeotropic agent used is *n*-butyl acetate. *n*-Butyl acetate and water exhibit limited miscibility and therefore form a heterogeneous azeotrope which boils at 90.2°C. *n*-Butyl acetate is added in sufficient quantities to form an azeotrope with all the water being fed to the dehydration column. The *n*-butyl acetate/water azeotrope can then be distilled as an overhead stream, leaving the pure acetic acid as the bottoms product. The heterogeneous azeotrope forms two phases upon condensation, with the top layer containing almost pure *n*-butyl acetate saturated with water. The bottom phase contains almost pure water saturated with *n*-butyl acetate. The top (entrainer) phase is recycled back to the dehydration column. The bottom phase (aqueous) is fed to a stripping column where the relatively small amount of entrainer is removed as an azeotrope with the overhead back to the dehydration column and water is removed as the bottom product.

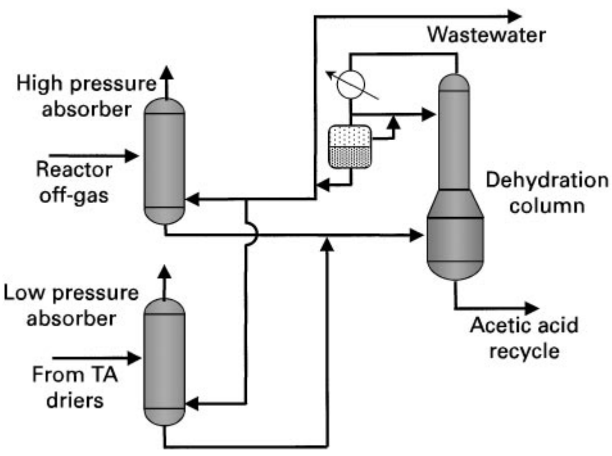

Figure 6 Conventional acetic acid recovery unit using azeotropic distillation in a PTA process.

The use of azeotropic distillation in the PTA process has economic and environmental advantages over conventional distillation for acetic acid recovery. Due to the lowered heat of vaporization of the azeotrope compared with that of water alone, azeotropic distillation can save one-third the energy of conventional distillation. Since azeotropic distillation results in a cleaner separation, the amount of acetic acid lost in the aqueous discharge can be reduced by almost 40%. **Table 2** shows the substantial advantages of using azeotropic distillation in this commercial application.

Production of PTA is just one illustration of azeotropic distillation being used in the commercial separation of acetic acid and water. Azeotropic distillation is also used in the production of acetic acid. The most popular methods for producing acetic acid are methanol carbonylation, butane or naphtha catalytic liquid-phase oxidation (LPO) and acetaldehyde oxidation. Methanol carbonylation is used for more than 90% of all new acetic acid capacity worldwide. In methanol carbonylation methanol and carbon monoxide are reacted over a rhodium catalyst under gentle operating conditions to produce acetic acid. The reaction produces low boiling by-products which are flash distilled to recover the rhodium catalyst. The remaining acid is dehydrated by azeotropic distillation much the same way as described in the PTA acetic acid recovery unit.

Butane/naphtha catalytic liquid-phase oxidation was once the most favoured method for the production of acetic acid. Along with acetic acid, a host of other components are produced such as

Table 2 Comparison of distillation methods for PTA production

Parameter	*Conventional distillation*	*Azeotropic distillation*
Energy, J h^{-1}	139	92
Acetic acid in WW, t yr^{-1}	400	250

WW = wastewater.

formic, propionic and butyric acids. Azeotropic distillation is used to separate the formic acid and water from the aqueous reactor product.

In acetaldehyde oxidation, ethanol is dehydrogenated oxidatively to acetaldehyde using a silver, brass or bronze catalyst. Acetaldehyde is oxidized in the liquid phase over cobalt and manganese catalysts to produce acetic acid. The final purification process uses ethyl acetate to azeotropically remove formic acid and water. The acetic acid product is removed as a side stream from the azeotropic column.

Alcohol Dehydration

Azeotropic distillation for alcohol dehydration has the longest history of use within the industry. Beginning with the work of Young, who demonstrated the first industrial application, azeotropic distillation is still used today in the production and dehydration of alcohol. Alcohol production is present in the CPI, speciality chemicals and food industries, and although the end use and perhaps the alcohol purity requirements vary, the method of production using azeotropic distillation is similar.

Prior to Young's work, absolute alcohol was prepared by distilling the alcohol with a dehydrating agent such as freshly ignited lime. This method required the major component (alcohol) to be boiled overhead leaving the minor component (water) at the bottom. Young's objective was to find a method of removing the minor component as the overhead product. When two different chemicals are distilled together, often a minimum boiling point occurs where a mixture of the two chemicals will distil off first, with the last portion being the compound in excess. Since ethanol is a hydroxyl compound like water and yet an organic compound, it should exhibit analogies to both water and hydrocarbons. Therefore, ethanol should form azeotropes with water and organic compounds. If an azeotroping agent such as benzene is used (in Young's time benzene and heptane were preferred due to their availability), the fractions would come off as follows: ternary water/benzene/alcohol azeotrope; alcohol and benzene azeotrope; and water and benzene azeotrope. At this point, all the water should be removed, leaving anhydrous alcohol. Young performed his azeotropic dehydration of alcohol by a batch method. While popular for distilling strong spirits, this batch method did not catch on commercially. It was not until Backus *et al.* and Guinot developed continuous azeotropic distillation processes that it became a commercial success.

As an example of an alcohol dehydration process, let us examine ethanol dehydration. Dilute water/ethanol solutions can be rectified to produce an ethanol-rich stream containing a maximum of about 89.4 mol% ethanol at atmospheric pressure. The introduction of benzene as a heterogeneous azeotropic entrainer to the top of the column, which is fed with an 89.4 mol% aqueous ethanol feed, produces the ternary ethanol/benzene/water azeotrope. This ternary azeotrope boils at 64.9°C and is easily separated from ethanol (b.p. = 78.4°C), which is removed as the bottom product. The ternary ethanol/benzene/water azeotrope forms two liquid phases with the benzene-rich phase fed back to the column. The aqueous phase contains nearly equimolar proportions of ethanol and water which is rectified to produce water as the bottom product and the binary ethanol/water azeotrope as the overhead product. The concentrated ethanol/water azeotropic stream is recycled back to the feed for the dehydration column. **Figure 7** illustrates a typical ethanol dehydration process.

Production of Esters

Esters are produced by reacting alcohols with organic acids. The reaction is reversible and therefore unless one of the products is removed, the ester yield is limited. Assuming the reaction is equilibrium-limited and not rate-limited, higher conversions can be obtained by removing one of the products. For instance, if during the reaction the water is removed, the reaction will be driven by equilibrium to produce more ester product. High purity esters can be produced with azeotropic distillation to simultaneously remove water and alcohol from the esters using aromatic and aliphatic hydrocarbons as entrainers.

Mato Vazquez *et al.* found isobutyl acetate, *n*-butyl acetate and *iso*amyl acetate could be purified using an entrainer such as *n*-heptane, methyl cyclopentane or various other hydrocarbons to simultaneously remove the water and alcohol. The reaction products are fed to an azeotropic column where the entrainer is used to remove the alcohol and water as overhead

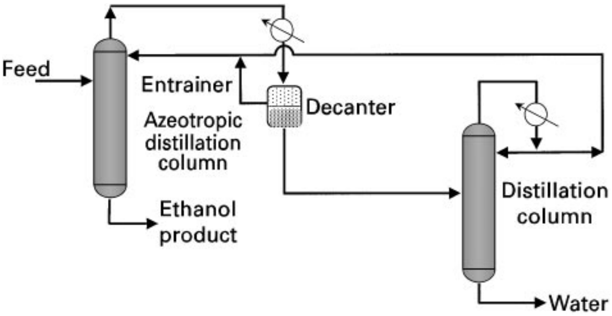

Figure 7 Typical ethanol dehydration process using azeotropic distillation.

products. Final purification of the ester product is carried out in a rectification column with only a few stages. The entrainer is recovered using a one-step liquid–liquid extraction (LLE) column with water as the extractant.

Wuest *et al*. found they could prepare ethyl chloroacetate by addition of ethanol to a melt of chloroacetic acid and *p*-toluene sulfonic acid and purify the ester product using azeotropic distillation. The ester and water form a minimum boiling binary azeotrope and therefore affect the ester/alcohol separation. Water and ethyl chloroacetate are removed overhead and the product is decanted. In this manner the ester is practically alcohol-free. This process avoids formation of the ternary ester/alcohol/water azeotropes which are difficult to separate.

Hills *et al*. found that azeotropic distillation is useful in the purification of esters produced using an enzymatic route. For example, isopropyl myristate can be prepared with lipase or immobilized lipase from myristic acid and propane-2-ol. The water produced in the reaction is removed by azeotropic distillation.

Conclusion

For almost 100 years azeotropic distillation has been an essential tool in the separation of purification of many industrial chemicals. There are distinct advantages to using azeotropic distillation, including energy savings, increased recovery and ability to separate components contained in close boiling, pinch point and azeotropic mixtures. Azeotropic distillation will undoubtedly remains a viable alternative for simplifying difficult separations found in industry.

See also: **I/Distillation. II/Distillation:** Energy Management; High and Low Pressure Distillation; Historical Development; Instrumentation and Control Systems; Modelling and Simulation; Multicomponent Distillation; Theory of Distillation; Vapour–Liquid Equilibrium: Correlation and Prediction; Vapour–Liquid Equilibrium: Theory.

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Batch Distillation

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Introduction

The interest in batch distillation has been steadily increasing in the last few years. This is a natural reflection of a change in industrial trends. In fact, the shift towards the production of high value-added and low volume speciality chemicals and biochemicals has been much more marked in the last decade than in the past. Within firms producing specialized chemicals and biochemicals, batch distillation is a ubiquitous method for separating products from process inventories, for recovering components that are used in one of the process steps (like solvents, for example), and for removing undesired components