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Effectively Break Azeotropes

Homogenous and heterogeneous varieties require different methods

By Tom Schafer and Alan Erickson, P.E., Koch Modular Process Systems, LLC.

An azeotrope is a complex formed by two or more chemicals and has the same composition in the liquid and the vapor phase. This interesting property means that the compound mixture distills without separating. Some common well-known binary azeotropes are water (95.4%) and ethanol (4.6%) as well as diethyl ether (33%) and halothane (66%), formerly used in anesthesia. However, as sometimes happens in chemical processing, an azeotrope may be formed unexpectedly or, even if recognized, may make downstream processes additionally challenging.

This article will discuss some methods used to "break" azeotropes that may exist in binary or ternary forms and their applications, with a focus on breaking azeotropes using various distillation methods. Solvent recovery often necessitates breaking azeotropes when substances are required in a purer form, either downstream or in other areas of the chemical process. Water removal may motivate others. Situational and contextual factors also may impinge on process optimization. Several basic types of processes to break azeotropes using distillation and real-world examples are described.

DISTILLATION AND DECANTATION

The easiest azeotrope to break is a heterogeneous azeotrope. Unlike homogeneous azeotropes, heterogeneous azeotropes' two compounds are not totally miscible. The combination of distillation and decantation works with heterogeneous azeotropes whereby condensation of the two liquids results in two phases that then

can be decanted. That is, each of the two phases can be fed to separate stripping columns. Examples of mixtures typically separated this way include the minimum boiling azeotrope of n-butanol and water or dichloromethane (methylene chloride) and water.

In the example of n-butanol and water, after condensation, the water-rich phase goes to a stripping column where butanol-free water comes out the bottom and the butanol-rich phase goes to another column where dry butanol comes out the bottom and the distillate of each column approaches the azeotropic composition. Generally, chlorinated hydrocarbons and water or any of the aromatic or paraffinic solvents and water can be separated that way.

PRESSURE SWING DISTILLATION

When two substances are totally miscible, as in homogenous azeotropes, other factors can come into play. Pressure swing distillation is effective when the azeotrope's composition is a reasonably strong function of pressure. An azeotrope distilled at a low pressure subsequently is fed to a second distillation column operating at a higher pressure where the azeotropic composition is substantially different. Acetonitrile and water and tetrahydrofuran (THF) and water are two typical azeotropes broken using this method.

At atmospheric pressure, the azeotrope formed between THF and water is 95% THF. However, at 95 psig, the mixture is closer to 88% THF. By operating two columns at the different pressures, dry THF can be retrieved from the bottom of the 95 psig column and the azeotrope emerging at the top, recycled to the atmospheric column.

AZEOTROPIC DISTILLATION

This distillation process is used to break homogeneous azeotropes by introducing an additional component called an entrainer, which forms a lower boiling decantable ternary azeotrope. The ethanol and water azeotrope (95.6:4.4) mentioned above is a classic example of this type of process whereby benzene (or the more commonly seen cyclohexane) is used as the entrainer. Similarly, an isopropanol and water azeotrope can be broken using di-isopropyl ether as the entrainer. The lower boiling azeotrope then is condensed and decants.

Typically, this process requires three separate distillation columns. The first column distills the alcohol to the azeotrope with water removed as the bottom product. The second column is the azeotropic column, in which the alcohol is removed at the bottom and the ternary azeotrope is removed as the distillate product. This distillate then is decanted with entrainer-rich phase and returned to the azeotropic column and the water-rich phase is sent to the third column to remove entrainer and alcohol from the water. Sometimes, columns one and three can be combined.

In the case of ethanol and water, ethylene glycol may be used to change the behavior of the two substances and allow distillation to be effective.

Obviously, the use of specific entrainer substances will not be applicable to all industries. Introduction of a known toxin or carcinogen such as benzene, for example, is a nonstarter for a pharmaceutical process.

EXTRACTIVE DISTILLATION

In contrast to azeotropic distillation, in extractive distillation an additional high boiling component is introduced. The added component, which basically is a diluent, changes the original binary pair's behavior such that the azeotrope can be broken. Azeotropes of ethanol and water or methanol and acetone can be broken this way. Azeotropes of refrigerants also are amenable to breaking using this method.

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ALTERNATE TECHNIQUES FOR BREAKING AZEOTROPES

Liquid-liquid extraction (LLE) can be used if the difference in the solubility of a solute between two liquid phases breaks azeotropes. Pyridine-water and THF-methanol are examples of azeotropes that can be broken via LLE.

Newer membrane technologies — in which the membrane material is robust enough to withstand attack by the substances being separated and the pore size can distinguish the complexes formed by a mixture's different components — also can break azeotropes. However, membranes also are subject to clogging. Over time, even trace amounts of solvents or particles, such as minute amounts of catalyst, can compromise the polymeric material used in membrane filtration.

DETERMINING THE BEST APPROACH

Breaking azeotropes or even recognizing when they are present is not always straightforward. Most undergraduate chemical engineering curricula do not spend much time on nonideal separations in their mass transfer classes. Turning to companies with expertise in mass transfer and separations is critical, particularly when there is a suspicion that azeotropes may be in play.

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Pilot plant testing often is required to test the actual feedstock and show that the conceptual design first offered will meet required specifications. The drums of actual feedstock that customers send to companies for pilot scale testing frequently contain minute amounts of other contaminants, which differ from the ideal feedstock upon which the concept design was developed. This can affect the path chosen to break the azeotrope, and pilot testing can uncover those trace components and find solutions.

Working with or around nonideal separations, such as azeotropes, may require multiple distillation columns and several decades of chemical process design experience.

TOM SCHAFER and **ALAN ERICKSON, P.E.**, are vice presidents at Koch Modular Process Systems, LLC. They can be reached at thomas.schafer@kochmodular.com and alan.erickson@kochmodular.com.