

An overview of Dehydration of Ethanol by Azeotropic Distillation using various entrainer

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Abstract- The fermentation of biomass represents a promising means of obtaining biofuels – one that involves lower emissions of polluting gases into the atmosphere. Bioethanol is one of the most widely used of these biofuels, and the manufacture thereof from raw materials requires several rounds of treatment, including milling, fermentation and distillation, before a water-ethanol azeotrope can be obtained. A dehydration step usually follows at this point, for which there are many different available techniques. , azeotropic distillation was the most commonly used method to obtain pure ethanol using benzene , cyclohexane , hexane , toluene , isoctane ... as entrainers. In this paper, a study of azeotropic distillation using different entrainers is carried out.

Index Terms- Azeotropic distillation, Entrainer, Dehydration, Ethanol

I. INTRODUCTION

Normally, we use distillation to isolate materials as the ideal solutions with one part normally more volatile than the other. However, in an azeotropic mixture, since the vapour and liquid concentrations will be the same this approach will prevent their separation.

Two, three and more azeotropes can be either uniform or heterogeneous (more than a phase). Azeotrope usually happens when a mixture is heated in order to produce vapour with the same liquid composition.

If the mixture deviates from Raoult's Law then azeotropes are formed and for azeotropes bubble point and dew points is the same. Mixtures of non-azeotropic liquids under any circumstances are referred to as azeotropic.

Azeotropic mixtures with a higher boiling point in their constitutions are maximum boiling azeotropes. Water boils at 373 K and hydrochloric acid boil at about 188 K, while azeotropes boil at around 383 K which is a boiling point greater than its constituents. Consider, for example, hydrochloric acid consisting of a weight concentration of approximately twenty per cent and 79 per cent of water.

Examples:

- Separation of water and isobutanol.
- Dehydration of ethanol.
- Separation of cyclohexane and benzene.

Similarly, an azeotropic mixture that has a boiling point lesser than its constituents is known as minimum boiling azeotropes. Consider, for example, ethanol consisting of a weight concentration of approximately ninety-five per cent and four per cent of water. Water boils at 373 K, and ethanol boils at about 351.5K, while azeotropes boil at around 351.15 K, suggesting a boiling point lower than its constituents.

Azeotropic distillation in today's processes is an integral unit activity. In the chemical process industry (CPI), chemical specialities and the food industry, applications of azeotropic distillation can be easily seen. The main advantages of azeotropic distillation are to allow the separation and re-energization of chemicals which can not be effectively separated by conventional distillation systems such as the azeotropic or pinch point systems. The key drawbacks of azeotropic distillation are the overall column diameter required to increase the volume of steam and the sophistication of the controls in comparison with the simple distillation of the azeotropic agent.

A minimum-boiling azeotrope may be produced by adding a compound forming an azeotrope (trainer), which can not be differentiated by the conventional distillation, in an established azeotropic or closely boiling mixture. The oxidation of alcohol is one example. A minimum boiling azeotrope is produced by ethanol, which means that ethanol can not fully be dehydrated by modern distillation. Benzene produces ethanol and a water ternary azeotrope that boils at a lower temperature to remove the surface water (with ethanol) and so leaves dry ethanol to the floor.

In some situations, as in the processing of esters, an azeotrope that occurs within the system can be beneficially used to purify a compound. Alcohol esterification is a reversible reaction. The reaction will not be completed in the presence of the product as the equilibrium is reduced. If one of the components is extracted (in this case water) using water/alcohol

azeotrope (nearly all alcohols form azeotropes with water from C2 to C20) the reaction is guided in favour of the ester component.

Relative volatility reflects a difference between the mixture variable volatility. When the vapour and liquid phase compositions are the same, the factor volatility is the same and the relative volatility is the same as 1. The further away from 1 is the relative volatility, the simpler it is to distinguish the mixture components.

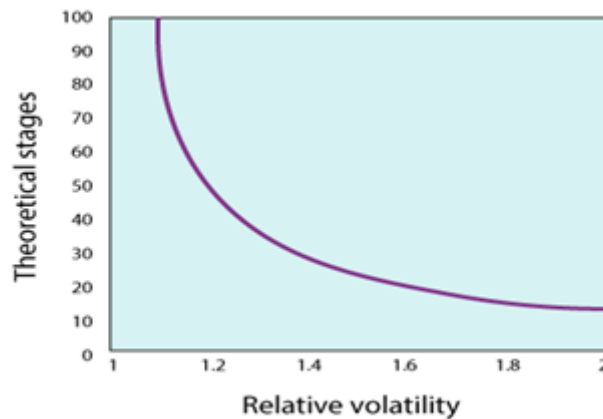


Fig -1: Effect of relative volatility on theoretical stages

As can be seen, infinity approaches the number of trays needed asymptotically and separation becomes impossible as unification approaches relative volatility. The existence of a pinch point contributes to relative unity uncertainty. Due to numerous separation phases, pinch forming components are technically feasible but often not economical.

The vapour is mixed in a single liquid phase with homogeneous azeotropes. The trainer should be recovered through further fractionation or extraction in a homogeneous azeotropic environment.

The vapour is in harmony with two phases of air. There are heterogeneous azeotropes. Heterogeneous azeotropic distillation is widely used for insulation of azeotropic or closed boiling mixtures by producing a minimum boiling azeotropic and reclaiming the equipment by using fluid immiscibility.

II AZEOTROPIC DISTILLATION USING DIFFERENT ENTRAINER

a. Using Benzene as entrainer[1]

For ethanol dehydration process we use three columns, which we can see in below figure. First column is **Dehydration Column**, second is **Benzene Recovery Column** and third is **Water Removal Column**. Therefore, we can divide whole process in three main steps as below.

ETHANOL DEHYDRATION STAGE

In Dehydration Column, we feed the azeotropic mixture of ethanol and water, which contain 89% ethanol and 11% water on mol basis. In other words, we know this mixture as RS or Rectified Spirit also, which is the final product of a distillery.

So, from dehydration column top ternary azeotrope of benzene with water and alcohol goes to condenser. The boiling point of this azeotrope is 64.9 °C. Subsequently, this ternary mixture after condensation forms two layers. Moreover, for the composition of ternary azeotrope vapor and both the layers, you can refer below table.

The vapor from benzene recovery column also mix with the vapor of dehydration column. After condensation liquid goes to a decanter. From decanter water rich layer contains small amount of benzene goes to benzene recovery column. While, benzene rich layer is a reflux stream for the anhydrous alcohol column.

The bottom stream of ethanol dehydration column is 99.99% ethanol, which is anhydrous or absolute alcohol.

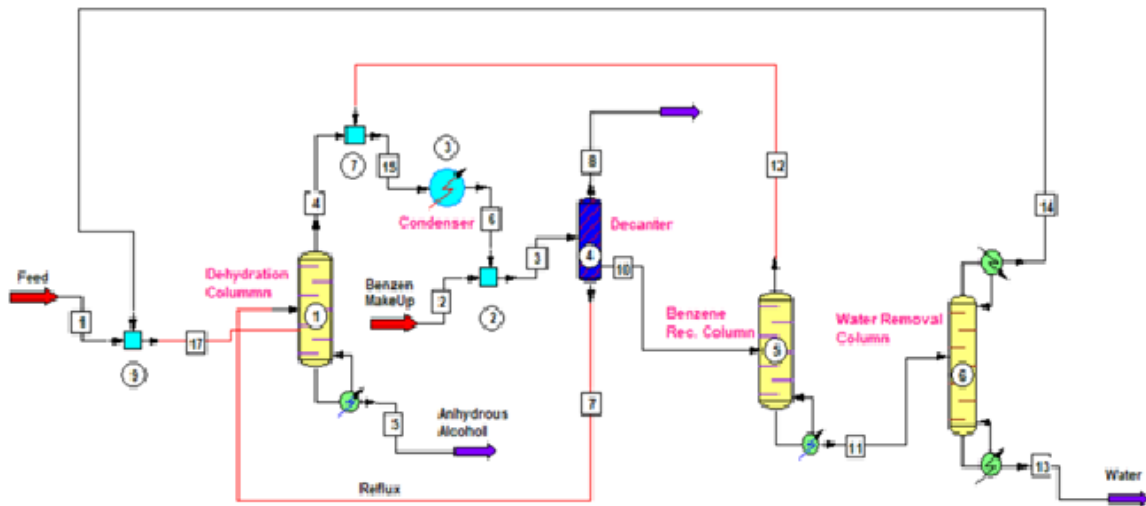


Fig -2: dehydration of ethanol using benzene as entrainer

RECOVERY OF BENZENE

For benzene recovery, we use benzene recovery column from the water rich layer. So, from decanter water rich layer stream goes into the benzene recovery column. This column is just like a stripper, which strip out all the benzene from coming feed. The bottom product of this column is free from benzene and this way we recover benzene to reduce the benzene consumption norm. Therefore, reducing anhydrous alcohol manufacturing cost also.

The top stream from this column goes into the anhydrous column condenser. This stream contains more than 50% benzene and balance is ethanol and water. While, the bottom stream of this column is free from benzene and contains ethanol and water only. So, from benzene recovery column bottom, stream goes into the water removal column or ethanol recovery column.

This column is also a packed column and has structured packing. And, the MOC for column and reboiler is SS304. Moreover, piping, valves and other fittings are also made of SS304.

ETHANOL RECOVERY AND WATER REMOVAL

The purpose of this column is to remove water and recover ethanol from the benzene recovery column bottom stream. This is also a packed column having structured packing inside. Also, the MOC for column, reboiler, condenser and all associated piping, valves and fittings is of SS304.

Bottom stream of this column is as good as pure water and may contain traces of ethanol. This we can recycle inside the plant after suitable treatment. While the top stream is azeotropic mixture of ethanol, which we recycle back into the dehydration column feed tank.

b. With iso octane[2]:

The viability of an azeotropic distillation process using 2,2,4-trimethylpentane (isooctane) as an entrainer to dehydrate ethanol and obtain a mixture of ethanol + isooctane without water is analyzed utilizing both an experimental procedure and an equilibrium-model-based simulation. The direct manufacture of this mixture of ethanol + isooctane for use as gasoline should avoid the additional cost of dehydrating ethanol in an earlier process. Experimental results indicate that azeotropic distillation allows obtaining mixtures of isooctane + ethanol with water concentrations lower than 50 ppm. The results indicate that the most critical parameter for this process is the reboiler heat duty. Low values of this parameter (<2.2 kJ/g of feed ethanol) produce mixtures of ethanol + isooctane with excessive water contents. At high heat duty values (>3.6 kJ/g of feed ethanol) the azeotropic distillation column does not function properly, as the top stream condenses giving only one liquid phase. Results of the equilibrium-model-based simulation of the process yield results having a similar trend to the experimental ones. However, significant discrepancies are observed in some values, which could be attributed to the calculation of the liquid-liquid equilibrium. It is therefore necessary to improve the correlation of experimental equilibrium data of determined regions on the ternary system diagram.

2.3 Using Toluene[3]

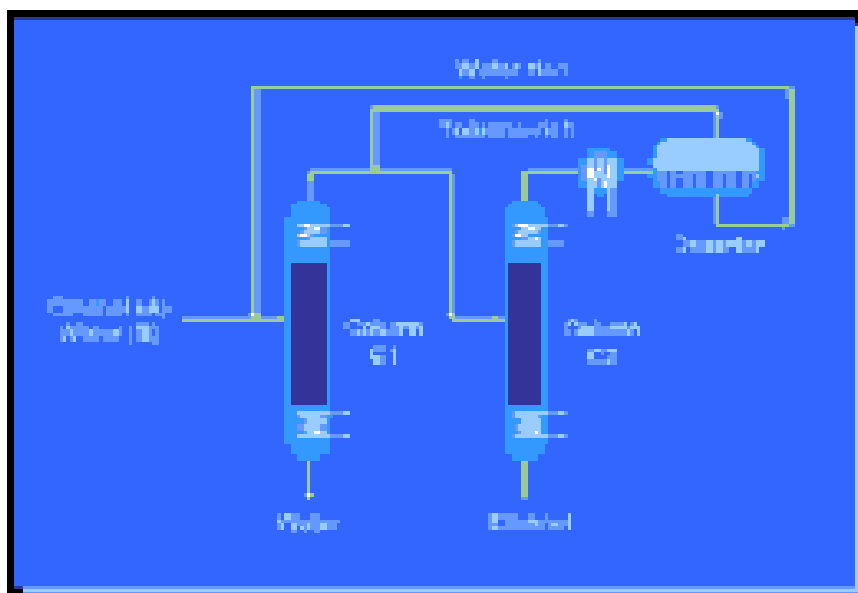


Fig -3: dehydration of ethanol using toluene as entrainer

The feed is introduced to column C1 where water is removed as bottoms. The overhead product is a near azeotrope of ethanol- water. It is mixed with a toluene rich phase acting as source of entrainer before entering column C2. An alternative arrangement is to have the toluene rich phase entering C2 directly. Ethanol is removed from the bottom of column C2, while the overhead is a vapour of ternary azeotrope of ethanol-water-toluene(74.6°C). When condensed and cooled, it forms two liquid phases that are separated in the decanter. The toluene rich phase serves as the source of entrainer that is recycled to column 2, while the water rich phase is re- circulated to column 1 for mixing with the feed.

c. With gasoline fractions[4]:

Experiments and simulation shows that it is viable both technically and economically to manufacture a ready-to-use ethanol-hydrocarbon fuel blend by azeotropic distillation. Starting from an azeotropic mixture of water and ethanol, and with several different hydrocarbons acting as entrainers (hexane, cyclohexane, isooctane and toluene), we have demonstrated the technical viability of this process in a distillation column at the semi pilot-scale. This is based on the fact that the ethanol-hydrocarbon fuel blend obtained as final product contains less water than is stipulated by the EU legislation currently in force. The various experiments carried out in this study show that, at a given feed rate, as the reboiler heat duty rises, the amount of water in the ethanol-hydrocarbon blend falls until the heat duty reaches a maximum value at which the distillation column ceases to operate correctly. Conventional thermodynamic models exhibit departures from observed behavior when used to correlate experimental data, and particularly in the case of liquid-liquid equilibria in the vicinity of the plait point, which also happens to be in the vicinity of the operating range of the column. To avoid such departures, other methods of interpolating equilibrium data are required, as otherwise we would not find maximum reboiler heat duty values that result in distillation column malfunction. A simulation of the process in Chemcad with the above considerations taken into account produces results that agree well with experiment. The simulation results of the proposed process indicate that there is a threefold reduction in heat duties compared to heteroazeotropic distillation, which produces pure ethanol.

d. Using cyclohexane[5]

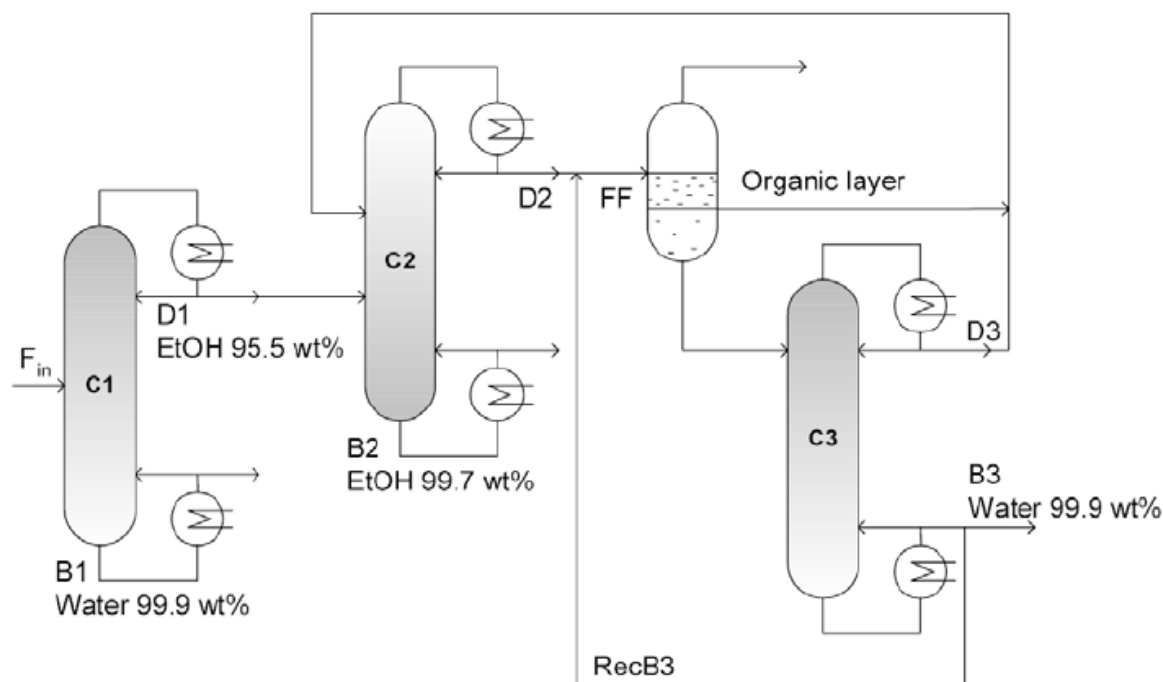


Fig -4: dehydration of ethanol using cyclohexane as entrainer

III. CONCLUSION

A common historical example of azeotropic distillation is its use in dehydrating [ethanol](#) and [water](#) mixtures. For this, a near azeotropic mixture is sent to the final column where azeotropic distillation takes place. Several entrainers can be used for this specific process: [benzene](#), [pentane](#), [cyclohexane](#), [hexane](#)[6], [heptane](#), [isooctane](#), [acetone](#), and [diethyl ether](#) are all options as the mixture. Of these benzene and cyclohexane have been used the most extensively. However, because benzene has been discovered to be a carcinogenic compound, its use has declined. While this method was the standard for dehydrating ethanol in the past, it has lost favor due to the high capital and energy costs associated with it. Another favorable method and less toxic than using benzene to break the azeotrope of the ethanol-water system is to use [toluene](#) instead.

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