Dehydration of Isopropyl Alcohol Using Hybrid Separation Technique

Parin D.Shah*

**Semester –II, P.G. Student, Chemical Engineering Department, Nirma University of Science & Technology, E-mail: pdshah75@hotmail.com*

ABSTRACT

Isopropyl alcohol (IPA) – water mixture exhibits a homogeneous minimum-boiling azeotrope (at 80.3–80.4 ^{0}C, 87.4–87.7 wt. %). Some methods of enhanced distillation of this mixture have been developed, such as azeotropic distillation, reactive and extractive distillation, and membrane separation either in the form of membrane distillation or pervaporation. This paper is a basic study of a state of the art of technology, called fixed adsorptive distillation, in which distillation and adsorption are applied simultaneously. Fixed adsorptive distillation consists of two raschig ring-packing distillation columns, which are equipped with an inter-bed of adsorbent filled of silica gel. First column (I) distils the mixture to produce distillate at slightly below the azeotropic composition. Silica then adsorbs selectively one of the components (water), so that IPA rises in purity passing the azeotropic point. Finally, the second column (II) distils it to achieve higher composition or pure. This paper aims to investigate the possibility of fixed adsorptive distillation in application of enhancement of azeotropic IPA–water solution.

INTRODUCTION

At atmospheric condition, a binary mixture of IPA–water forms a homogeneous minimum-boiling azeotrope at 87.4–87.7 mass% and 80.3–80.4 ^{0}C [1]. It is required to break this point to obtain very high purity or pure IPA. An azeotropic distillation with an entrainer of cyclohexane (CyH) has been done [2], to investigate the steady-state and dynamic behavior of IPA–CyH–water heterogeneous azeotropic column both theoretically and experimentally. The results also showed that the addition of CyH be able to break azeotropic point of IPA–water and yielded IPA with the purity of 99–100 wt. % Some investigations have reported that IPA–water azeotrope can also be broken with other azeotropic distillations to form heterogeneous azeotropic

systems by adding one of the following entrainers: isopropyl ether, benzene, methyl ethyl ketone, and isopropyl acetate. Sometimes, ethyl ether is used as entrainer at pressures substantially above atmospheric [1].

A modification technique, which is a combination of reactive and extractive distillation by using the mixture of ethylene glycol ($C_2H_6O_2$) and glycolic potassium ($C_2H_5O_2K$) as additional components has been investigated [3]. By this way, with a volume ratio of feed and solvent of 1:1, IPA produced has purity over 96.0 mass%. A novel method, sweep gas membrane distillation, which is similar to sweeping gas pervaporation has also been examined to purify the same system [4]. Another type of membrane separations, pervaporation, which is originally applied in dehydration of high concentration of organic compounds, was found potential to break IPA–water azeotropic as well and can be applied by combining with distillation [5].However, pervaporation itself still encounters some challenges in particular to the membrane productivity and membrane stability [6]. In addition, investigations of general azeotropic systems have also been studied by some researchers by applying the currently developed methods, such as azeotropic distillation [7], extractive distillation [7–10], reactive distillation [11,12], and adsorptive distillation slurry system [13,14]. In principle, those common methods require other specific components to be mixed directly together with the solution that will be separated.

The fixed bed distillation method applies simultaneously distillation and adsorption in which the regular form of adsorbent used in the adsorption process is placed in a separated fixed bed. The application of hybrid method which combines together distillation and adsorption has actually been studied [15], and a pressure swing adsorptive distillation has been enforced in industrial scale as well, but both used a molecular sieve adsorbent, a more complicated form of adsorbent. One thing that distinguishes the fixed adsorptive distillation from other common methods of azeotropic distillation is that the additional component is not mixed directly together with the solution to form a well-mixed solution or a slurry system, but is placed separately. By this circumstance, further separation between additional component and solution is not needed. This work utilized two raschig ring-packing distillation columns, which were equipped with an inter-bed of adsorbent filled of silica gel. The first column distilled the mixture of IPA–water to achieve the purity slightly below the azeotropic point, after that the condensate was split into two streams, one was passed through the bed of adsorbent (silica gel) and the other was bypassed. Because of its surface's polarity, silica then adsorbed selectively the more polar existing

component, in this case, water. As a result, IPA underwent rise in purity passing the azeotropic composition. This higher purity mixture was then fed to the second column and be distilled to obtain very high purity or pure product. As a minimum boiling homogeneous azeotrope, over the azeotropic point IPA became less volatile than water so that the main product was taken out from the bottom. The distillate of the second column, which its concentration has been above azeotropic point was recycled to the first column to maintain feed composition of the first column.

EXPLORATORY STUDY

Basic concept and approach

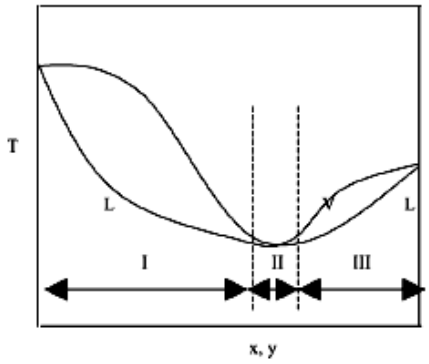

Fig.1. Three zone operation of fixed adsorptive distillation in minimum bi\oiling azeotrope: distillation (I), adsorption (II), and distillation (III)

Fixed adsorptive distillation is an integration of conventional techniques to overcome the separation problem in azeotropic solution. In theory, conventional distillation cannot pass azeotropic point even using infinite number of equilibrium stage or height of packing because of the existence of pinch point. This study tried to apply a hybrid separation technique to break or to pass the azeotropic point. One of conventional techniques that is considered to be able to handle this problem is adsorption. This technique changes only a little bit difference in concentration of component in the mixture. Hence, it is suitable to carry out this purpose, breaking azeotropic point. Therefore, in simply, fixed adsorptive distillation comprises three-zone operations: distillation–adsorption–distillation, as described in VLE diagram of Fig. 1.

Fig. 2 is, especially to illustrate this method in behalf of enhancement of minimum-boiling homogeneous azeotrope. However, it can also be modified to treat the maximum boiling one by recycling the bottom product of the second column to the first column and take out the

distillate as the main product. Based on Figs. 1 and 2, there are essentially three approaches used in the fixed adsorptive distillation method:

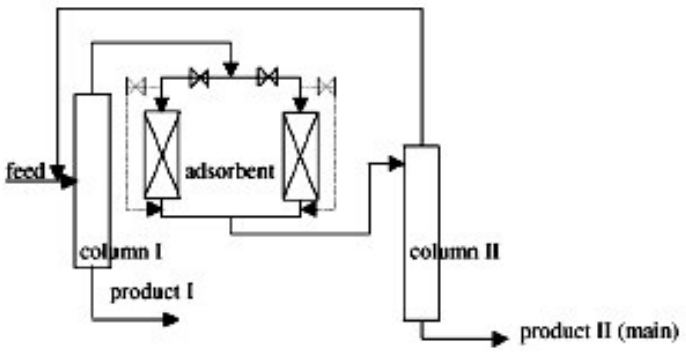

Fig.2. Scheme of enhanced distillation of azeotropic solution using fixed adsorptive distillation

1. Application of two separation techniques in three-zone operations: (a) distillation from range of feed concentration of zero to slightly below azeotropic point; (b) adsorption from slightly below to slightly above azeotropic point; (c) distillation from slightly above azeotropic point to 100%.
2. Application of two streams in adsorption operation, one passed through adsorbent and the other is bypassed to optimize the adsorption process.
3. Application of recycle of side product to maintain the feed concentration.

The approach (2) in this method is considered as the most distinctive application from other adsorptive distillation methods. Fixed adsorptive distillation uses a specified adsorbent located between the two distillation columns to apply separation based on adsorption. Adsorption is separation of components in fluid phase (liquid or gas) in which the component will be adsorbed onto the active surface of solid [16]. Because one of components is adsorbed selectively or more strongly, the unadsorbed component will increase in its composition in fluid phase. This is basically the principle of fixed adsorptive distillation, an attempt to pass the azeotropic point by adsorbing the undesired component. Even though adsorbent has ability to capture all components existing in the mixture, the adsorbates are adsorbed in different proportion due to their different polarities. In this case, the desired component in the main product is hopefully the least captured component.

The adsorbent is set fixedly in a bed, so, as the process runs the adsorbent will be dense with the adsorbed component, and in a certain time it will be saturated. In this condition, the

adsorption process does not work, and will disturb the whole process. To avoid the adsorbent undergoing saturated in short time, it is needed to minimize the flow passed through the adsorbent, or in other word to maximize the bypass flow. As consequently, fixed adsorptive distillation utilizes two streams around the condenser and bed of adsorbent. The ratio of flow has significant role to optimize the adsorption process. If the flow flown through the adsorbent is too high, it will produce better mixture composition, or in other word, adequate far above azeotropic point. However, the adsorbent will be fast saturated or non-durable use so that regeneration must be frequently done and more energy is required to activate the saturated adsorbent. In contrast, if the flow is low enough, the adsorbent will be durable in use but the composition of the mixture entering the second column might be still below the azeotropic point.

As abovementioned, the use of two streams around adsorbent bed mainly deals with an effort to optimize the operation of adsorption. It is not urgent to flow all condensates of the first column through the adsorbent because the major purpose of this approach is to attain a mixture entering the second column with composition at least slightly above the azeotropic point. The application of this approach, however, cannot eliminate the saturation of adsorbent. As a result, to ensure the continuity of the whole process, the utilization of two parallel adsorbent beds is still needed as the common adsorption operation. When one adsorbent part undergoes saturation, the other one is then used, while the saturated one is being regenerated. In principle, some methods of regeneration including thermal and pressure are able to be applied due to no strict requirements in this regular adsorbent re-activation which is placed separately from the mixture system. Thermal regeneration will probably be more interesting to be used because at the same time the vapor mixture from the top of the first column releases amount of heat to condense. This mixture's latent heat can cover partially or completely the heat required to desorb the adsorbates from the surface of adsorbent. A combination of thermal and pressure swing will be more effective, but it will of course be more costly.

This laboratory study can be run in a batch operation. However, basically fixed adsorptive distillation can also be operated continuously as many applications in industries. The feed of the first column and the bottom products of both the first and the second columns can be fed and put out continuously. The saturation of adsorbent that disturbs the whole process can be anticipated by the application of two parallel adsorbent bed as above mentioned.

ADVANTAGES

In comparison with the currently applied methods, fixed adsorptive distillation has some advantages as follows:

1. ***Selection of additional component* (*adsorbent*):** The selection of the type of adsorbent is easier than that of the entrainer, solvent, catalyst, or inert. In general, there are two kinds of adsorbents, i.e. hydrophobic and hydrophilic adsorbents [17]. Hydrophobic, or non-polar surface adsorbent including active carbon and polymer materials, will prefer to adsorb the non-polar component than the polar one, whereas hydrophilic including silica gel and active alumina is in vice versa. The selection of adsorbent will strongly depend on the polarity of component that will be adsorbed. The strength of polarity of some components can be easily known from the functional chemical compounds existing in the component. Even though adsorbent has capacity to adsorb all components existing in the mixture, the components will be captured in different proportion due to their various polarity.
2. ***Addition of component*:** Both in batch and continuous processes, the addition of adsorbent is enforced only once in the early stage of process. The saturation of adsorbent can be anticipated by the use of two parallel adsorbent beds in which adsorption and regeneration are operated simultaneously.
3. ***Design of equipment*:** The design of equipment is simpler because there are no changes in equilibrium-phase curve due to the addition of adsorbent. In other word, the addition of adsorbent does not convert a binary system into multi-system distillation. Distillation process at the two columns of fixed adsorptive distillation is intrinsically similar to the conventional distillation and the performance as well.
4. ***Cost requirement*:** In general, total annual cost of a process is affected by two main cost components, i.e. investment and operating expenses. In case of a large and long-life production, operating cost usually gives more contribution to the total annual cost rather than investment cost. Based on rough estimation and assumption that the latent heat released by the vapor mixture of the first column could provide energy for thermal regeneration, using adsorbents rather than other additional chemicals (entrainer, solvent, or catalyst) is a potential way to reduce operating cost because of the cheapness of adsorbents.

CONCLUSION

From this preliminary study, we can conclude that fixed adsorptive distillation method is having potential ability in enhanced distillation of azeotropic IPA–water solution. The most important thing emphasized in this hybrid method is an attempt to break or pass azeotropic point by applying an optimized adsorption process in which not all condensates from the first column are flown through the adsorbent bed. More efforts can be performed with respect to enhancement of the product purity by improving the performance the second distillation column, such as the addition of equilibrium stage or height of packing as well as the increase of reflux ratio. Finally, deeply economical analysis is required in considering the feasibility of this method.

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