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OVERVIEW OF ENHANCED DISTILLATIONS

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ABSTRACT

The separation of azeotropic mixtures is an interesting and important topic for academic research and industrial application.Of all available liquid separation techniques, distillation stands as the most widely applied technique. In chemical process industry, desired product purities areobtained using separation processes, and distillation is by far themost widely used one of these processes. The ordinary distillation process, that utilizes the difference in volatilities between the constituent components of the mixture to separate them, is ineffectual for mixtures which form azeotropes where the difference between the volatility approaches to zero. Enhanced techniques are therefore employed for separation of azeotropic mixtures which include pressure swing distillation, extractive and azeotropic distillation, liquid-liquid extraction, adsorption, pervaporation using membrane, salt additionetc. All of them have their own advantages and disadvantages. This article presents an overview covering all the enhanced separation techniques mentioned here.

Keywords: Azeotropic mixtures, Enhancedseparations, Extractive distillations, Membrane technology, Pressure Swing distillations.

I. INTRODUCTION

Distillation is a widely used separation technique and has broadly been used in most chemical and petrochemical industries.Distillation is based on differences in compositions between liquid and vapor phases. Thus, conventional distillation processes are used for mixtures with idealor near-ideal vapor–liquid equilibrium behavior. If the mixturehas a non-ideal vapor–liquid equilibrium behavior, it may form anazeotrope, which is a mixture of chemical components with identical compositions in liquid and vapor phases at equilibrium. The separation of azeotropes by distillation is especially energy-intensive. As distillation still remains the major separation technique in process industries, it is imperative to improve its energy efficiency, especially when employed for the separation of azeotropic mixtures in a distillation process.At thispoint, some special distillation techniques, including pressure swing distillation [1], extractive and azeotropic distillation [2], liquid-liquid extraction [3], adsorption [4], pervaporation using membrane [5], salt addition [6] etc. has to be used to separateazeotropes.Extractive distillation is a method where the relative volatilitiesof components to be separated are altered by using an additionalcomponent (called solvent or entrainer) with a higher boiling point.Literature is available on design, synthesis and optimizationof extractive distillation for different azeotropic systems [7,8,9,10,11]. On the other hand, pressure-swing distillation is based on the fact that at a simple change in pressure can alter the composition of the azeotrope, and two columns operating at two differentpressures can achieve separation. Design, modeling and optimization of pressure-swing distillation

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processes have been studied in severalarticles[12,13,14,15].The pervaporation technique usually uses a membrane for azeotropeseparation, which has the advantage of low energy consumption compared with conventional distillation technology [16,17,18,19]. However, the technique requires a balance between permeability and selectivity of solvent molecules, which limits the wide application of membrane technology.

Fig.1 shows some of the currently available technologiesfor separation of azeotropic mixtures, which can be classified into three main categories:

i) Enhanced distillation,

ii) Membrane processes and

iii) Process intensification.

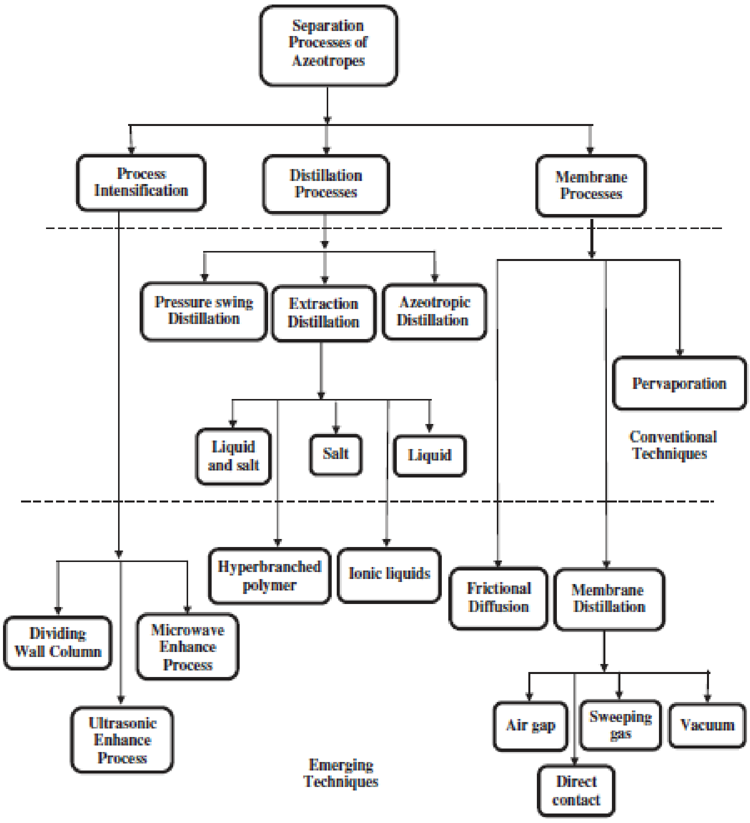

Figure 1: Schematic diagram of various techniques for separation of Azeotropic mixtures

The first category involves enhancement of the distillation process by modifying the process conditions and configurations. These modifications include extractive distillation, azeotropic distillation, and pressure swing distillation. The second category involves utilization of membrane separation technologies such as the pervaporation process. The pervaporation process is advantageous as it offers low energy consumption and better safety and is more environmentally friendly than conventional processes. Nevertheless, the pervaporation process is still limited in terms of applications because it is yet to be proven in large scale applications. Another class of process intensification consists of the development of novel equipment and techniques, compared to the present state-of-art in the chemical process industry. The aim of intensification is to optimize capital, energy, environmental and safety benefits by radical reduction of the physical size of the plant. This technology includes dividing wall column, microwave and ultrasonic techniques. The former introduces changes in column internals, whereas the two latter techniques employ microwave and sonication effects to alter the thermodynamic properties of the mixture.

II. DISTILLATION PROCESSES USING AN ENTRAINER

Azeotropic and extractive distillation processes have the same common features that basically consist of twodistillation columns to separate compounds with close boiling points or mixtures that formazeotropes. This separation is normally accomplished by adding a third component known as an entrainer as a separating agent, to increase the relative volatility and alter the vapor liquid equilibrium data of the components that are the most difficult to separate.Added in the liquid phase, the new component alters the activity coefficient of various compounds in different ways, thus affecting the relative volatility of the mixture, thusenabling the new three-part mixture to be separated bynormal distillation [20].

2.1 Azeotropic Distillation Process

Azeotropic distillation can be defined as a distillation in which a relatively small amount of the added entrainer forms an azeotrope with one or more of the components in the feed based on differences in polarity [21].Most of the solvents are highly volatile compared to the components to be separated so that the solvent is taken off from the overheadof the column. Azeotropic distillation processes basicallyutilize two columns. The first column serves as the main column, and the second column is used for entrainer recovery. In this process, an entrainer leaves the first column from the column overhead with the lighter component, while the heavierare collected as a bottom product. The entrainer and the lighter component are then fed to the second column to produce a high purity product at the bottom while the recovered entrainer is recycled back to the first column. Azeotropic distillation is usually classified into two classes based on the type of mixtures to be separated:
i) Homogeneous and ii) Heterogeneous azeotropic distillation [20]as illustrated in Fig.2.

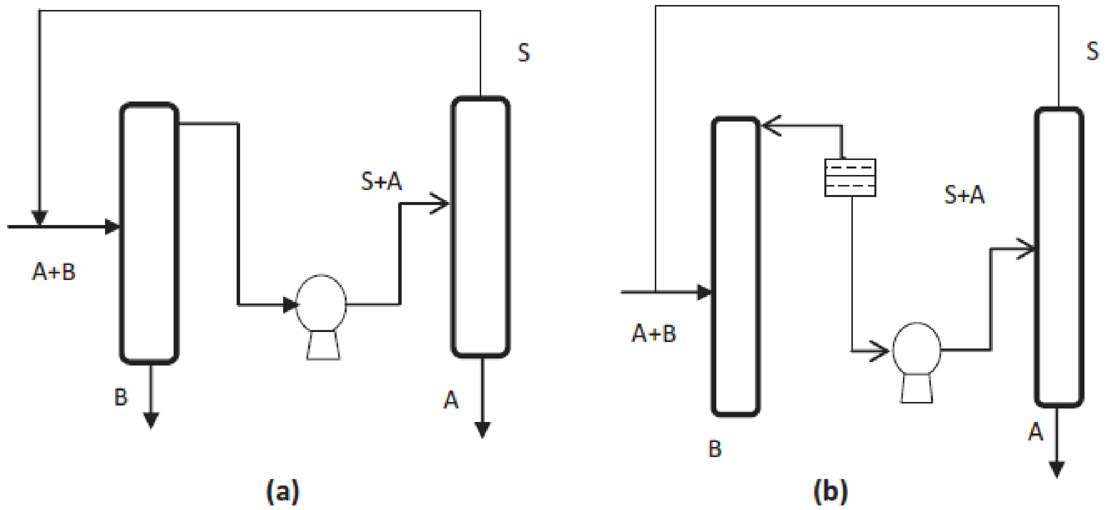

Figure 2: Schematic Diagram of an Azeotropic Distillation, a) Homogeneous Process and b) Heterogeneous Process.

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2.2 Extractive Distillation Process

Extractive distillation involves a relatively non-volatile entrainer compared to the components to be separated. Therefore, the entrainer is charged continuously near the top of the fractionation column, so that an appreciably highamount of entrainer is maintained on all plates in the tower below its entry. Thus the solvent is removed from the bottom of the tower. An extractive distillation process is more commonly applied in the chemical and petrochemical industries than the azeotropic distillation [22].Fig.3 shows the principle of this technology, where components A and B are fed to the first column that acts as an extractive column where the solvent (S) is introduced at the top stage. In this process, the lighter component (A) is withdrawn at the top of the first column, while the solvent with other component exits at the bottom. The bottom products of the first column are then fed to the second column, in which the heavier component (B) is withdrawn at the top and the entrainer is separated from the bottom and recycled back to the first column. The separation in the second column is often easier because of the larger boiling point difference between the high-boiling entrainer and the existing second component, and because the solvent does not form an azeotrope with the second component.

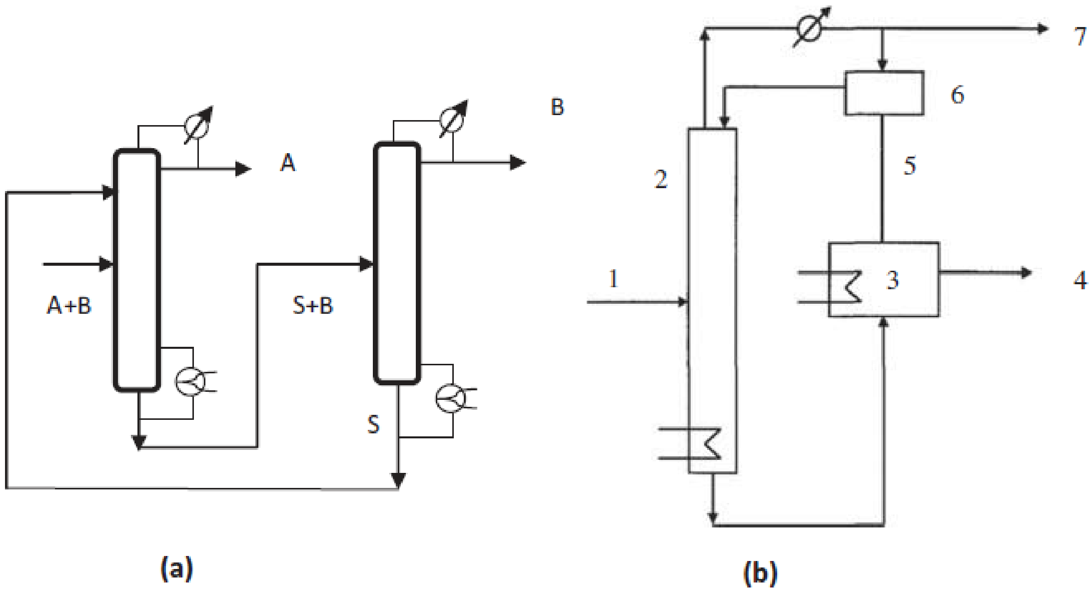

Figure 3: Schematic Diagram of an Extractive Distillation, a) Double Column Process b) Single Column Process with Salt

Table 1 illustrates a comparison between Azeotropic and Extractive distillation in terms of different parameters.

Table 1. Comparison between Azeotropic distillation and Extractive distillation

Parameters	Azeotropic distillation	Extractive distillation
Common use	Less	More
Energy consumption	More	Less
Solvent coming out	Top	Bottom
Flexibility of solvents	Less	More

III. PRESSURE SWING DISTILLATION

Pressure swing distillation (PSD) is a process alternative tothe broadly applied azeotropic and extractive distillations. The principle of pressure swing distillation (PSD) is based on the fact that a change in pressure can alter the relative volatility of a liquid mixture, even for liquid mixtures with a close boiling point or those that form an azeotrope. If the operating pressure is increased, the azeotropic point shifts to lower composition values of the light component. The significant positive change in the azeotrope point and enlargement of the relative volatility of azeotropic mixtures allow the separation to take place without any need for a separating agent [23].The general set up of a PSD for minimum-boiling homogeneous binary azeotrope is shown in Fig. 4.

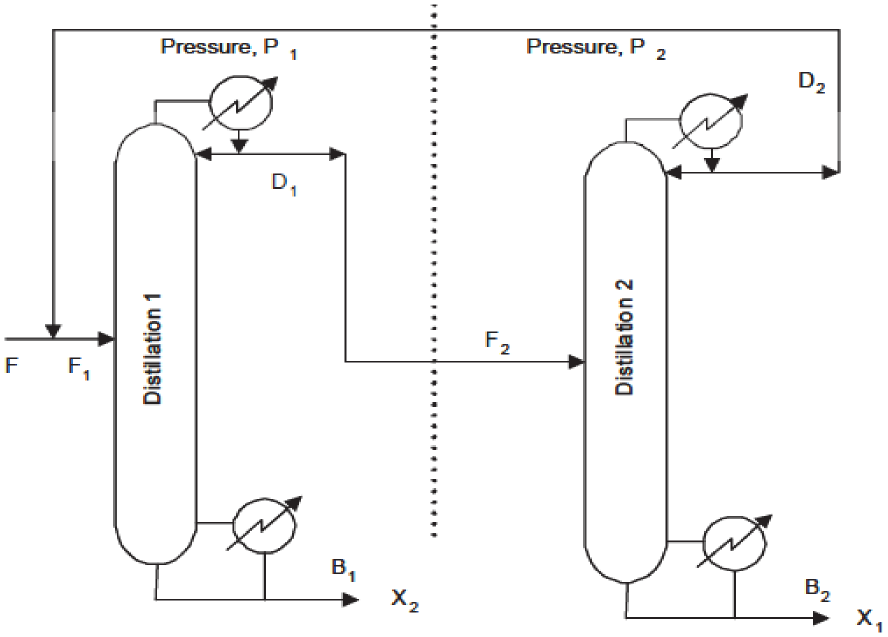

Figure 4: General Set Up of PSD Column for Minimum-Boiling Azeotrope

IV. SEPARATION OF AZEOTROPIC MIXTUREUSING MEMBRANE TECHNOLOGY

A higher energy requirement and a limited choice of entrainers to be used in azeotropic and extractive distillation processes have led to the development of alternative processes such as membrane-based processes [24,25].Membrane processes may be regarded as “clean technology” due to the lower energy demand and the fact that membrane processes do not require the use of additional chemicals [26].Within this class of techniques, pervaporation (PV) is most prominent [27,28],and accounts for 3.6% of the total membrane separation applications in chemical and petrochemical operations [29]. Some of the PV applications in industry include removal of water from organic solvents (e.g., dehydration of alcohols, ketones and esters) [30],removal of organic compounds from water [31],and separation of organic-organic azeotropes and isomers [32].

V. PROCESS INTENSIFICATION

More recently, an approach known as process intensification has been proposed for combining multiple processes into single units such as a dividing wall distillation column or exploiting sonication phenomena to break an azeotrope in an ultrasonic distillation system.Process intensification is a process design approach that leads to substantially smaller, cleaner, safer and more energy-efficient process technology [33].Within the realm of the separation processes discussed in this paper, process intensification can be used to increase the functionality of the process as in the case of the dividing wall distillation column, or process intensification can be used to introduce selected process phenomena into the conventional separation [34].

VI. CONCLUSIONS

This article provides anoverviewon the conventionaland emerging technologies for the separation ofazeotropic mixtures. The research areas to be emphasized forfurther development are also elucidated. Conventional separationprocesses such as azeotropic and extractive distillationsare observed to be the main technologies used at presentand in the near future, with opportunities for improvementsby introducing new entrainers with desirable properties. While the Azeotropic and extractive distillation use an Entrainer, which may pose environmental concerns, Pressure Swing Distillation provides an advantage over these distillation techniques as it does not require any additional component. However, the effective cost to maintain high pressure in the column may be the only limitation of Pressure Swing Distillation technique.Since, membrane processes offer good efficiency,simplicity of operation and low energy consumption, membraneprocesses are limited by the surface area requirementand thus may only be suitable for small-scale applications.To extend the applicability, hybrid processes combiningmembranes with other process technologies mightbe needed.Another potential approach is to exploit the process intensification concept in developing new separation techniques. In summary, we can conclude that while some workable solutions are readily available, the challenges are numerous, with a wide horizon of opportunities for improvement. The search for better processes should be intensified to expedite countermeasures for environmental and safety threats continually imposed by the process industries on human livelihood.

VII. NOMENCLATURE

Symbol	**Description**
A	Light Key Component
B	Heavy Key Component
S	Entrainer
1	Feed stream
2	Extractive distillation column
3	Equipment for salt recovery
4	Bottom product
5	Salt recovered
6	Reflux tank
7	Overhead product

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