

# Advances in Chemical Engineering

## Chapter 5

### State of the Art Technologies for Separation of Azeotropic Mixtures

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#### Abstract

Azeotropic separation technologies have been classified broadly into two major categories, i.e., distillation and membrane processes. Because normal distillation has limitations for azeotropic mixtures, enhancements have been proposed that either introduce a third component serving as an entrainer in extractive and azeotropic distillation processes or apply a pressure swing distillation system. Among the membrane processes, pervaporation was reported to be most promising for azeotropic separations. 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. This paper reviews the state of the art technologies covering all the above mentioned separation techniques. Existing techniques are appraised, and technology gaps are identified. Based on these insights, areas for further development are suggested, aiming at satisfying the process objectives by inherently safer, environmentally benign and economically more attractive techniques.

**Keywords:** Separation Technologies; Azeotropic Mixtures; Special Distillation Processes, Pervaporation; Intensified Processes

**List of symbols:** A: Light component; B: Heavy component; C: Concentration; D: Diffusivity; F: Feed flow; D: Diffusivity; F: Feed flow; VLE: Vapor liquid equilibria; VLLE: Vapor liquid liquid equilibria; CAMD: Computer aided molecular design; PSD: Pressure swing distillation; THF: Tetra hydrofuran; HP: High pressure; LP: Low pressure; PV: Pervaporation; MTBE: Methyl tertiary-butyl ether; ETBE: Ethyl tertiary-butyl ether; ILs: Ionic liquids; EtOH: Ethanol; DWC: Dividing wall column; FricDiff: Frictional diffusion; AD: Azeotropic distillation; ED: Extractive distillation; R: Gas constant; S: Selectivity; Ncol: Number of columns; Np: Number of pure component; NB: Number of boundaries crossed; P<sub>io</sub>: Vapor pressure of component i; T: Temperature; y: Concentration of component in vapor phase; x: Concentration of component in liquid phase; i<sub>l</sub>: Components i in the upper liquid phase; x<sub>ill</sub>: Components i in the lower liquid phase; J: Diffusion flux; J<sub>p</sub>: Permeate flux; J<sub>o</sub>: Pre-exponential factor; z: Position [length];  $\theta$ : Correction factors for high pressure;  $\gamma$ : Activity coefficients;  $\Gamma$ : Activity coefficients in the lower liquid phase;  $\alpha_{ij}$ : Relative volatility of components i and j;  $\alpha$ : Overall selectivity of membrane;  $\alpha_s$ : Sorption selectivity

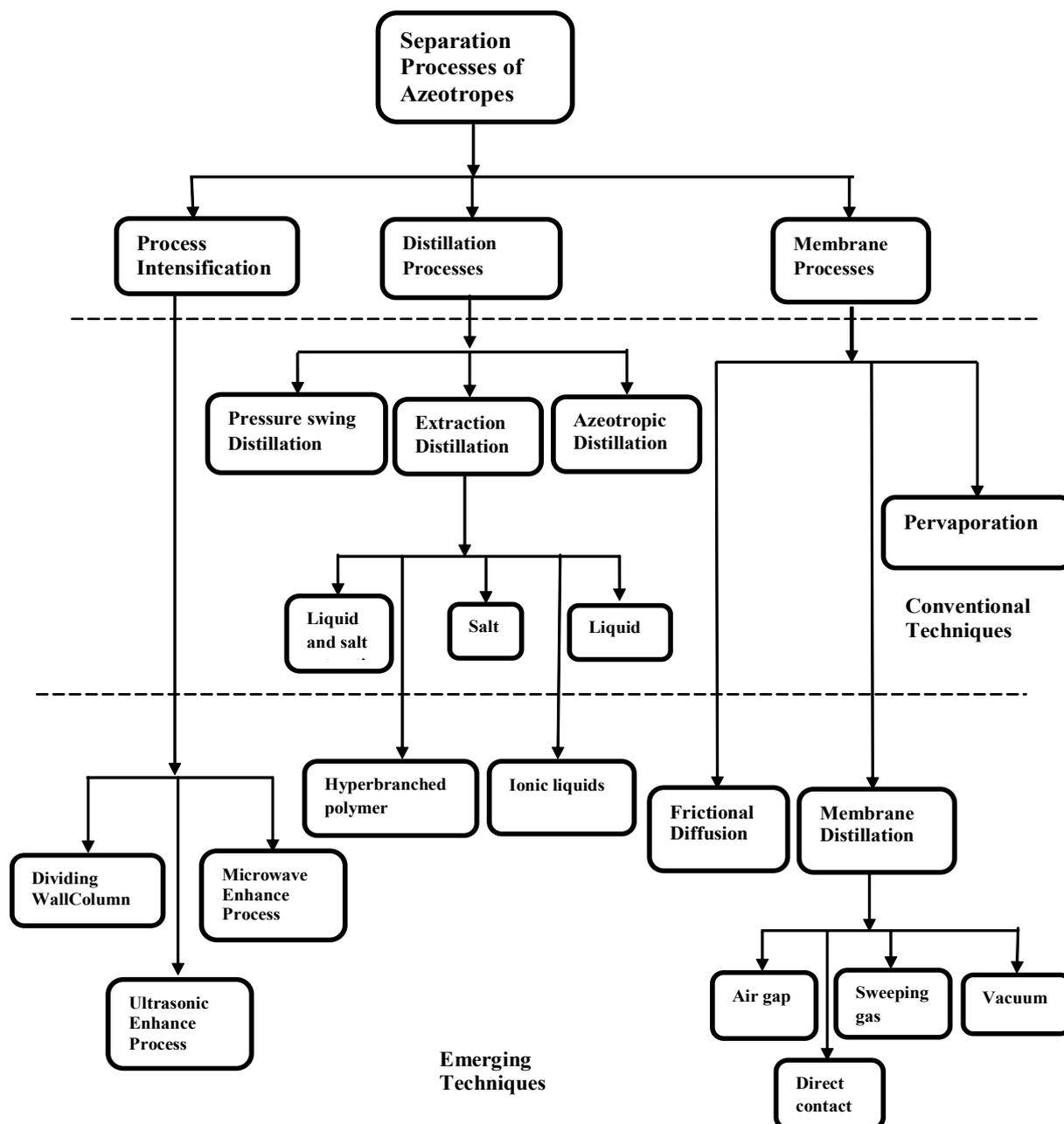
## 1. Introduction

The separation of liquid mixtures is an important task in the process industry, and much research has been carried out to meet the requirements of the industry. Of all available liquid separation techniques, distillation stands as the most widely applied technique. Distillation is typically achieved in columns of various sizes with heights ranging from 6 to 60 meters and diameters that range between 0.65 and 6 meters [1]. Despite its widespread use, distillation consumes large amounts of energy that are estimated to be more than 95% of the total energy used for separation processes in chemical process industries [2]. Nevertheless, because distillation offers many processing advantages and is well understood, it remains the preferred process whenever possible.

Distillation is, however, limited in its use when the mixtures to be separated exhibit complex phenomena. An example of these situations is when the mixtures involved form azeotropes, a point at which the vapor phase has the same composition as a liquid phase. There are two types of azeotropic systems: i) a minimum boiling azeotropic system, and ii) a maximum boiling azeotropic system. For such systems, a higher purity product beyond the azeotrope point cannot be achieved using a conventional distillation process. Therefore, alternative methods have been developed to satisfy the separation requirement.

**Figure 1** shows some of the currently available technologies for separation of azeotropic mixtures, which can be classified into three main categories: i) enhanced distillation, ii) membrane processes and iii) process intensification. 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 apparatuses 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.



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

Due to the importance of the subject, there have been several review articles in various journals and chapters in books dealing with the separation of azeotropic mixtures, elaborating their fundamental theories and applications. For example, the work of Widagdo and Seider [3] concentrated on methods used for analyses, entrainer selection, column design and control of azeotropic distillation. Lei et al. [4] discussed various combinations of extractive distillation and other separation processes. Li et al. [5] addressed the entrainer selection and proposed a mathematical model for the process. Huong et al. [6] published a review on extractive distillation for bio refining of hemicelluloses and added chemicals from fermentation hydrolysates. More

recently, Pereiro et al. [7] reviewed methods utilizing ionic liquids as azeotrope breakers and compared the performance of the new system with conventional extractive distillation.

Similarly, Villaluenga and Mohammadi [8] reviewed the performance of the membrane pervaporation process for separation of benzene and cyclohexane mixtures. The applications of pervaporation and vapor permeation in environmental protection were reviewed by Kujawski [9]. The scientific and technological factors governing the separation of organic mixtures by pervaporation were also reviewed by Smitha et al [10]. Despite the significant number of review articles, a comprehensive coverage that addresses the overall technologies is not available and has therefore become the motivation for this paper. In this article, a comprehensive review of the available technologies is provided with elaboration of advantages and disadvantages of each method. Based on these insights, technological gaps are identified and future work is recommended with special emphasis on developing processes that are more energy efficient, environmentally benign and inherently safe.

## **2. Enhancement of Distillation Process for Separation of Azeotropic Mixtures**

Separation of azeotropic mixtures can be achieved by enhancing the separation mechanisms involved in the distillation process to overcome its limitations. The most common strategy is to introduce a third component to alter the thermodynamic equilibrium. By choosing a suitable candidate component, along with the determination of thermodynamic properties such as residue curve maps, optimal values of distillation parameters such as the entrainer amount, reflux ratio and boiler duty and the number of stages can be fixed [11], setting the foundation of the azeotropic and extractive distillation processes. Another approach to enhance the distillation is to manipulate the operating pressure as in the case of pressure swing distillation.

### **2.1. Distillation processes using an entrainer**

Azeotropic and extractive distillation processes have the same common features that basically consist of *two* distillation columns to separate compounds with close boiling points or mixtures that form azeotropes. 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, thus enabling the new three-part mixture to be separated by normal distillation [12].

#### **2.1.1. Rules of Entrainer selection**

The entrainers to be used in the azeotropic and extractive distillation processes are chosen

based on selectivity. Typically, solvents considered are ranked based on their potential to affect the relative volatility of the components, and the solvent that gives the highest relative volatility and the lowest operating costs is selected [13]. The relative volatility of separation of a given mixture of key components  $i$  and  $j$  occurs in two phases (vapor-liquid) at equilibrium, as illustrated in Eq. 1:

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i P_i^o}{\gamma_j P_j^o} \quad (1)$$

Here,  $x_i$  and  $y_i$  are the molar fractions in the liquid and vapor phase of component ( $i$ ), respectively. The parameter  $\gamma_i$  is the activity coefficient, and  $P_i^o$  is the vapor pressure of the pure component. In some cases, for large changes in operating pressure and temperature, the value of  $\alpha_{ij}$  is significantly affected, and the azeotrope is eliminated [4]. For small temperature changes, the ratio of  $P_i^o/P_j^o$  is almost constant, and the relative volatility can only be affected by introducing a solvent that changes the ratio  $\gamma_i/\gamma_j$ . This ratio, in the presence of the solvent, is called selectivity,  $S_{ij}$ .

$$S_{ij} = \left( \frac{\gamma_i}{\gamma_j} \right)_s \quad (2)$$

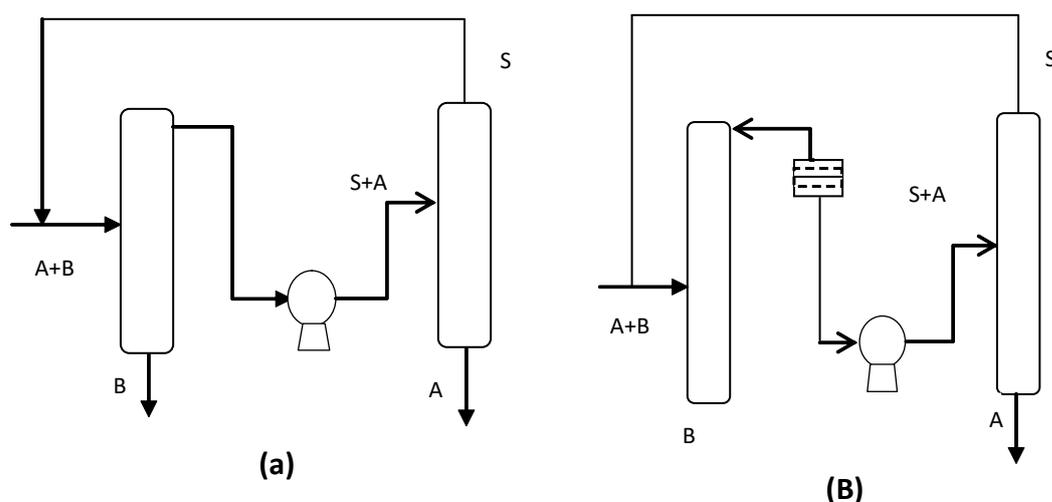
There are several other constraints to be considered in choosing the entrainers. These constraints include the requirement that the entrainer should have a boiling point significantly different from the other components to facilitate an easier separation in the second column. Moreover, the entrainer selection should also consider safety, environmental effect, corrosiveness, costs and availability [14].

Ewell et al. [15] studied the relationship between hydrogen bonding and azeotrope formation and classified entrainers into groups according to their molecular interactions. These authors also developed guidelines to identify chemical classes suitable as entrainers for heteroazeotropic and extractive distillations. Based on these guidelines, Berg [16] classifies organic and inorganic mixtures by making use of the molecular structure to identify promising entrainers and suggests that the successful entrainers for extractive distillation should be highly hydrogen-bonded liquids (e.g., water, amino alcohols, amides, phenols alcohols and organic acids). Although it is impossible to choose the best entrainer entirely through experimental work, a large number of computation approaches appear to fit the purpose. These methods include the Pierotti-Deal-Derr method, the Parachor method, the Weimer-Prausnitz method and Computer-Aided Molecular Design (CAMD). Among these methods, CAMD is the most recent and preferred method [17].

## 2.1.2. 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 [18]. Most of the solvents are highly volatile compared to the components to be separated so that the solvent is taken off from the overhead of the column. Azeotropic distillation processes basically utilize 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 heavies are 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 [12], as illustrated in Figure 2. In the case of homogeneous process, phase split does not appear in the liquid along the whole column, unlike the heterogeneous counterpart, in which the two liquid phases exist in some regions of a composition space. A decanter is used in heterogeneous azeotropic distillation to collect the condensed vapor from the condenser and permits the separation of the two liquid phases. Commonly, these two liquids are the entrainer and the lighter component where the entrainer phase is refluxed back to the column. The other phase is fed to the second column where it is fractionated to remove the dissolved entrainer. The case of heterogeneous mixtures without the use of a decanter at the top of the azeotropic distillation column can be considered as a homogeneous mixture, and at the same time, the liquid composition on a tray or a section of the packing is replaced by the overall liquid composition [19].



**Figure 2:** Schematic diagram of an azeotropic distillation, where A and B are light and heavy components of the feed mixture respectively, S is an entrainer component; a) homogeneous process, b) heterogeneous process.

Relative volatility is an important physical quantity as it reflects the influence of the entrainer on the vapor-liquid equilibrium [20]. In the case of heterogeneous azeotropic distillation, the entrainer and the two components  $i$  and  $j$  being separated form three phases

on trays of the column, (i.e., vapor-liquid-liquid) and two liquid phases in equilibrium with a vapor phase. For the three-phase equilibrium, the solubility of components  $i$  and  $j$  in the upper liquid phase is denoted by  $x_i^l$  and  $x_j^l$ , respectively. The solubility of components  $i$  and  $j$  in the lower liquid phase is denoted by  $x_i^ll$  and  $x_j^ll$ , respectively, and the corresponding activity coefficients are denoted by  $\gamma$  and  $\Gamma$  in the upper and lower liquid phases, respectively. The relative volatility of components  $i$  and  $j$  is related to the overall composition  $x_i$  by Eq. 3 [3]:

$$\alpha_{ij} = \frac{\gamma_i \Gamma_i p_i^o \theta_i (x_i^{ll} - X_i) \Gamma_j + (X_i - x_i^l) \gamma_j}{\gamma_j \Gamma_j p_j^o \theta_j (x_j^{ll} - X_j) \Gamma_i + (X_j - x_j^l) \gamma_i} \quad (3)$$

where  $\theta_i$  and  $\theta_j$  are correction factors for high pressure. At low or moderate pressure, the values can be approximated as  $\theta_j = \theta_i \approx 1$ . Eq. 3 represents the relative volatility of components  $i$  and  $j$  in a three-phase (vapor-liquid-liquid) at equilibrium.

The key feature of feasible heterogeneous azeotropic distillation is that entrainers and top tray vapor compositions are selected to generate liquid-liquid tie lines, which straddle at least one of the distillation boundaries dividing the two regions containing the two components to be separated. Heterogeneous azeotropic distillation is often preferred industrially over homogeneous azeotropic distillation due to the ease of recovery of the entrainer and the transition across a distillation boundary in the decanter [21]. However, heterogeneous azeotropic distillation suffers from some disadvantages associated with the high degree of nonlinearity, multiple steady states, distillation boundaries, long transients, and heterogeneous liquid-liquid equilibrium, limiting the operating range of the system under different feed disturbances [22]. Moreover, it is difficult to find a model that represents both the vapor-liquid and liquid-liquid equilibrium data accurately for heterogeneous systems. Unstable saddle azeotropes are also difficult to identify experimentally. Furthermore, the examinations based on the rate-based model are necessary, but the studies with the rate-based model for design and analysis of a heterogeneous azeotropic distillation process are quite insufficient [23].

Homogeneous and heterogeneous azeotropic distillation corresponds to the real state of the mixture, consisting of the components to be separated as high purity products. Forming a homogeneous azeotrope neither means that the separation method becomes a homogeneous process nor that it is forming a heterogeneous azeotrope, because the separation method becomes heterogeneous while depending on the physical property of the entrainer used [24]. In addition, for both types of azeotropic distillation, the entrainer must be vaporized through the top of the column, thus consuming much energy. Some of the recent studies on the application of azeotropic distillation as a separation method are listed in **Table 1**.

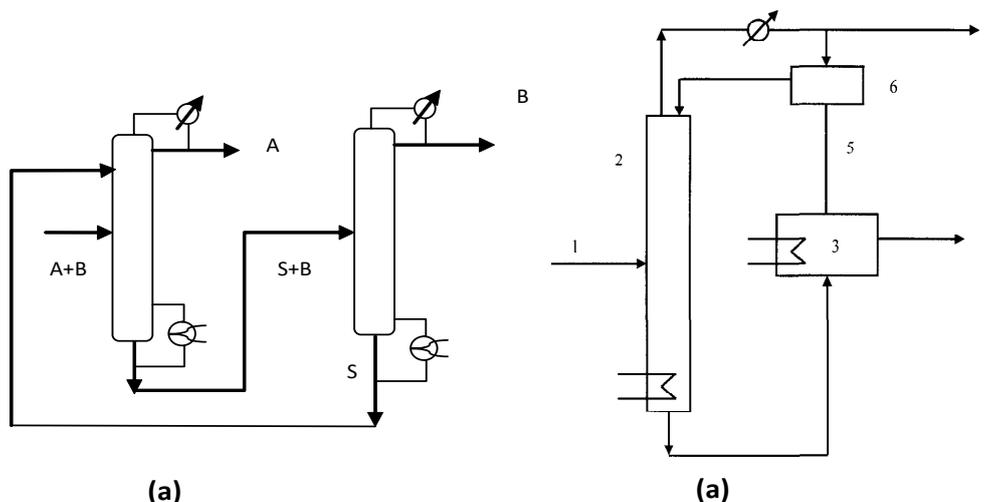
**Table 1:** Summary of the latest azeotropic distillation cases with minimum-boiling binary azeotropes

Components to be separated (A+B)	Type azeotropic distillation	Entrainers	Azeotrope B.P. °C	B wt% in Azeotrope	References
Cyclohexane + benzene	Homogeneous	Chlorobenzene	77.8	45.0	[25]
Ethanol + water	Heterogeneous	Cyclohexane	78.2	95.6	[26]
Ethanol + water	Homogeneous	Methanol	78.2	95.6	[27]
Acetic acid + water	Heterogeneous	Butyl acetate	76.6	3.0	[28]
Isopropanol + water	Heterogeneous	Benzene	80.4	87.8	[29]
Isopropanol + water	Heterogeneous	Benzene	80.4	87.8	[30]
Isopropanol + toluene	Homogeneous	Acetone	80.6	58.0	[19]
Acetone + heptanes	Homogeneous	Toluene	---	---	[31]
ethyl acetate + <i>n</i> -hexane	Heterogeneous	Acetone	64.8	65.7	[32]
Tetrahydrofuran + water	Heterogeneous	<i>n</i> -Pentane	65	95	[33]
Acetontrite + water	Homogeneous	butyl acetate	76.5	83.7	[34]
Acetone + heptane	Homogeneous	Benzene	55.6	93.5	[35]
Acetone + water	Heterogeneous	Toluene	---	---	[36]
1,2Dichlor ethane + water	Heterogeneous	Chlorinated	72.0	80.5	[37]
Phenol + water	Heterogeneous	Toluene	99.76	97.8	[38]
Formic acid + water	Heterogeneous	Propyl Formate	107.1	77.5	[39]
Dichloromethane + acetone	Heterogeneous	Water	---	---	[40]
Ethylene Diamine + water	Heterogeneous	Benzene	119.0	81.6	[40]
1,4-dioxane + water	Heterogeneous	Benzene	87.8	81.6	[41]
Isopropanol + ethanol	Homogeneous	1,3-Dioxolane	---	---	[42]
Ethyl acetate + ethanol	Homogeneous	Ethyl ether	71.8	69.0	[42]

### 2.1.3. Extractive distillation Process

Extractive distillation involves a relatively nonvolatile 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 high amount 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 [43]. Figure 3a 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 [5]; a) double column process where A and B are light and heavy components of the feed mixture respectively, S is a solvent component. b) single column process with salt: 1- feed stream, 2- column of extractive distillation, 3- equipment for salt recovery, 4- bottom product, 5- the salt recovered, 6- reflux tank and 7- overhead product.

Extractive distillation is more frequently used compared to azeotropic distillation due to better availability of entrainers. Extractive distillation is also better in terms of energy consumption, unlike the azeotropic distillation that is required to vaporize both the solvent and the component into the top of the column [44]. However, extractive distillation cannot produce highly pure product compared to azeotropic distillation because the solvent coming from the bottom of the solvent-recovery column most likely contains impurities that may affect the separation process [45]. Another drawback of the extractive distillation is the number of degrees of freedom when compared with a simple distillation setup. In a simple distillation setup, the degrees of freedom are the reflux ratios and the number of stages of the distillation columns, while in extractive distillation, the entrainer type and its flow rate comprise additional degrees of freedom [46].

**Table 2:** 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
Purity of products	Less	More
Flexible selection of solvents	Less	More

Some of the latest examples of the single liquid solvents commonly used in the extractive distillation technique are listed in Table 3. Interested readers can compare the entrainers used in practice with the rules of selecting entrainers. This table shows that there is a difference in the azeotropic percentile of the component and different boiling points in an azeotropic mixture.

**Table 3:** Summary of the latest studies on extractive distillation for separation of azeotropic mixtures

Mixtures of solvent (A+B)	Entrainer	Type	Azeotrope B.Pt. °C	B wt.% in Azeotrope	reference
Benzene + cyclohexan	<i>N,N</i> -dimethyl acetamide (DMAC)	Close-boiling and minimum-boiling azeotropes	77.8	45.0	[47]
Tetrahydrofuran + water	Propylene glycol	Minimum-boiling azeotropes	65	95	[48]
Ethyl acetate + chloroform	2-Chloro-butane	Maximum-boiling azeotropes	---	---	[49]
Ethanol + water	DMF	Minimum-boiling azeotropes	78.2	95.6	[50]
Hexane + ethanol	[mmim] [MeSO <sub>4</sub> ]	Minimum-boiling azeotropes	58.7	79.0	[51]
Isopropyl ether + acetone	3-Pentanone	Minimum-boiling azeotropes	53.3	43.5	[52]
Propanone + <i>di</i> -isopropyl ether	Putyl ether	Minimum-boiling azeotropes	61	---	[53]
Ethanol + water	Ethylene glycol	Minimum-boiling azeotropes	78.2	95.6	[54]
Ethyl acetate + ethanol	Diethylene triamine	Close-boiling and minimum-boiling azeotropes	71.8	69.0	[55]
Acetone + methanol	Water	Minimum-boiling azeotropes	55.7	88.0	[26]
Methyl acetate + methanol	Dimethylformamide	Minimum-boiling azeotropes	119.0	81.6	[56]
Propylene + propane	Acetonitrile	Close boiling	---	---	[57]
Acetonitrile + water	Ethylene glycol	Minimum boiling azeotrope	76.5	83.7	[34]
C <sub>4</sub> material/ 1,3-butadiene	DMF	Close boiling	126	45	[58]
Acetic acid + water	Tributyl amine	Minimum boiling azeotrope	76.6	3.0	[59]
Di- <i>n</i> -propyl ether + <i>n</i> -propyl alcohol	2-Ethoxyethanol	Minimum boiling azeotrope	50	66.5	[60]
Chloroform + methanol	Water	Minimum boiling azeotrope	53.5	13.0	[61]
Ethyl benzene + <i>p</i> -xylene	5-Methyl-2-hexanone	Close boiling	136.1	60	[62]
Isobutyl alcohol + isobutyl acetate	<i>n</i> -Butyl propionate	Minimum boiling azeotrope	107.4	55.0	[63]
Methyl acetate + cyclohexane	Carbon tetrachloride	Minimum boiling azeotrope	---	---	[64]

### 2.1.3.1. Types of entrainers used in extractive distillation

The selection of a separating agent influences the economics of the extractive distillation process. This separating agent can be a liquid solvent, dissolved salt, mixture of liquid solvents, mixture of dissolved salts, ionic liquids and hyperbranched polymers. Based on the type of separating agent, the extractive distillation process can be further divided into five categories that will be discussed in the following sub-sections.

#### (i) Extractive distillation with a liquid solvent

A schematic diagram of an extractive distillation with liquid solvents is shown in Figure 3a. In this case, a high solvent ratio (i.e., mass ratio of solvent to feed) with values typically in the range of 5 to 8 is used, thus leading to high energy consumption. However, because the solvent can be recovered effectively under normal operating conditions, this scheme remains a preferred choice in industry rather than schemes using any other agents and attracts the interest of many researchers [34,55,58,61,63].

#### (ii) Extractive distillation with solid salt

In this case, a separating agent in a form of a solid salt is fed at the top of the column, dissolved into the liquid phase, and recovered from the column by evaporation [65]. A schematic diagram of this process is shown in Figure 3b. To suit the process requirements, the solid salt must be soluble in the feed components, nonvolatile and able to flow all the way down the column. The salt extracted from the bottom of the column is then recycled.

The so-called “salt effect in Vapor-Liquid equilibrium (VLE)” refers to the ability of a solid salt that has been dissolved into a liquid phase consisting of two or more volatile components to alter the composition of the equilibrium vapor without itself being present in the vapor. The feed component in which the equilibrium vapor is enhanced is said to have been “salted out” by the salt, while the other feed component is “salted in.” This phenomenon can be described by the following equation which is known as the Setschenow equation and expresses the solubility of a nonelectrolyte in a solid salt solution with a low salt concentration.

$$\log \frac{S_o}{S} = K_s C \quad (4)$$

Here,  $S_o$  is the solubility of the salt in pure solvent,  $S$  is the solubility of the salt in a salt solution of concentration  $C$  (mol/L), and  $K_s$  is the salting coefficient, which has a characteristic value for a given salt-nonelectrolyte pair. A positive value of  $K_s$ , corresponds to salting out ( $S_o > S$ ); if  $K_s$  is negative, salting in is observed ( $S_o < S$ ). Species which lower the dielectric constant should be salted out by all electrolytes [4].

Solid salt is a more effective separating agent when compared to the liquid agent, and

requires a much smaller salt ratio, thus leading to a high production capacity and a low energy consumption [66]. Furthermore, because solid salt is not volatile, the product at the top of the column is free from salt impurities and is therefore more environmentally friendly. However, when solid salt is used in industrial operation, dissolution, reuse and transport of the salt that has been introduced causes corrosion of equipment, thus limiting the application of salt in the process industry [5].

### **(iii) Extractive distillation with the combination of liquid solvent and solid salt**

The extractive distillation using a combination of liquid solvent and solid salt has a configuration similar to the system with liquid solvent as shown in Figure 3a. This process is advantageous due to the easier operation offered by the liquid solvent scheme and the high separation ability offered by a solid salt scheme. This process is also suitable for separating both polar and non polar systems. Lei et al. [67] examined the use of N, N-dimethylformamide (DMF) as a solvent to separate a C4 mixture. By adding a small amount of solid salt to DMF, considerable improvement in the relative volatilities of C4 was achieved. These authors also concluded that NaSCN and KSCN are among the best salt additives when criteria such as relative volatilities, price, erosion and availability are considered. However, because solid salts tend to cause corrosion in the equipment and decay easily at high temperatures, a narrow range of suitable solid salts is available for selection.

### **(iv) Extractive distillation with ionic liquid**

The use of Ionic Liquids (ILs) as separating agents in the extractive distillation process is a recent strategy that has been adopted and is often used in processes involving chemical reactions [68]. This process has a configuration similar to the configuration of extractive distillation with solid salt as shown in Figure 3b. The features of this process include salts consisting completely of ions, which are in the liquid state at room temperature. The salts of ionic liquids therefore do not need to be melted by an external heat source [69]. The most outstanding reason for interest in these solvents is the negligible vapor pressure at room temperature [70], leading to a lower risk of worker exposure and minimal loss of solvent to the atmosphere. ILs can be tailored for a specific application by accurate selection of the cations and anions [71]. ILs also have the advantages of liquid solvents in promoting high separation ability. ILs are also suitable for both polar and non polar solvent systems. In addition, extractive distillation with the IL technique has the following advantages [72]:

- 1) Absence of product impurities at the top of the column, because ionic liquids are not volatile.
- 2) Suitability for use over a wide temperature range from room temperature to above 300°C, which corresponds to the typical operating conditions of extractive distillation due

to the inherently high volatility of ILs.

- 3) Suitability of ionic liquids for treatment with a wide variety of materials including organic, inorganic and even polymeric materials.
- 4) Facile recovery and reuse of ionic liquids.
- 5) High stability of ionic liquids under the operating conditions of extractive distillation in terms of thermal and chemical conditions.

Taking all of these features into account, the ILs are considered good candidates for application as extracting solvents or entrainers in the separation of azeotropic mixtures, and ILs have demonstrated capabilities to separate many mixtures [73,74]. However, despite the increase in publications addressing azeotropic separations with ILs, these studies are limited to analysis of the liquid-liquid equilibria [75] and vapor-liquid equilibria [76] or simulation of the extractive distillation process with ILs [77].

Extractive distillation with ILs also suffers from some disadvantages such as the long time required to prepare the ionic liquids and the high cost of synthesis of such specialty components [5]. The separation of viscous solutions using this technique is very difficult to manage [7] and the ILs demonstrate moisture sensitivity [72]. Such disadvantages have slowed down the application of this process in industry [5].

#### **(v) Extractive distillation with hyperbranched polymers**

A class of highly branched polydisperse macromolecules with a tree like topology with large number of functional groups and three-dimensional polymers such as hyperbranched polymers [78] or dendrimers [79] have recently found a variety of applications in the field of chemical engineering. Most of the applications are related to the absence of chain entanglements and presence of a large number of functional groups within a molecule. Furthermore, the functional groups of hyperbranched polymers allow tuning of their thermal, rheological, and solution properties. This tuning provides the opportunity to design entrainers for a wide variety of applications [80,81]. Unlike the conventional linear polymers, hyperbranched polymers not only show a remarkable selectivity and capacity, but because of a lack of chain entanglements, also show a comparatively low solution and melt viscosity as well as an enormous thermal stability [77].

Recently, Seiler et al [77] suggested the use of hyperbranched polymers as entrainers for extractive distillation for the separation of azeotropic mixtures. In another study, these authors studied the separation of the Tetrahydrofuran (THF)/water and ethanol/water mixtures using different hyperbranched polyesters as entrainers in extractive distillation [82]. Their experimental results illustrated the potential of such entrainers in breaking the azeotropic phase

behavior and concluded that the use of hyperbranched polyesters provides cost savings compared to conventional separation processes. Comparing between dendrimers and hyperbranched polymers, the tedious and complex multistep synthesis of dendrimers results in expensive products with limited use for large-scale industrial applications. For many applications that do not require structural perfection, hyperbranched polymers can circumvent this major drawback of dendrimers. Therefore, a wide variety of applications, which originally seemed conceivable only for dendrimers, were investigated for the statistically branched hyperbranched polymers in the past decade [83].

## 2.2. Pressure Swing Distillation

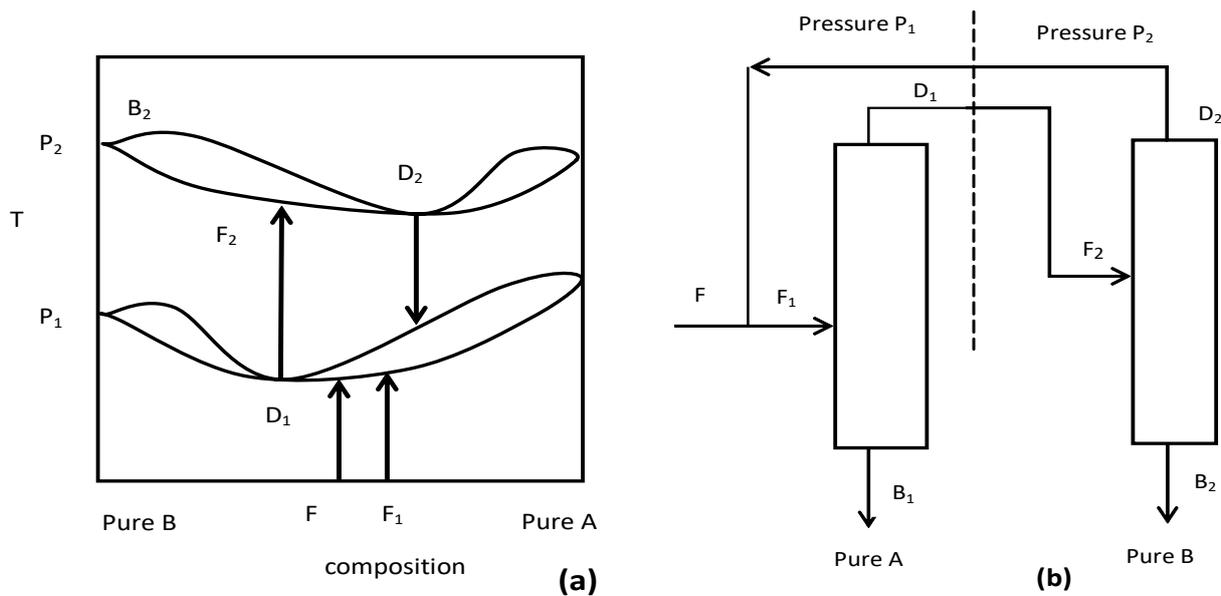
Pressure swing distillation (PSD) is a process alternative to the broadly applied azeotropic and extractive distillations. The principle of pressure swing distillation (PSD) is based on the fact that a change in pressure can alter the relative volatility of a liquid mixture, even for liquid mixtures 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. Following the early work in 1928 by Lewis [84] and further developments that followed [85-87]. Table 4 shows some of the recent studies on the separation of azeotropic mixtures using PSD.

**Table 4:** Summary of the latest studies using pressure swing distillation for separation of azeotropes

system	Type	LP(bar)	HP (bar)	Process type	Reference
Acetonitrile + water	Minimum	1.013	2.78	Continuous	[88]
Acetonitrile + water	Minimum	1.013	3.02	Batch	[89]
THF + water	Minimum	1.013	7	Continuous	[87]
THF + water	Minimum	1.013	10	Semicontinuous	[86]
Acetone + methanol	Minimum	1.013	4	Continuous	[90]
Acetone + methanol	Minimum	1.013	10	Batch	[91]
Ethyl acetate + ethanol	Minimum	4	25	Continuous	[92]
Ethyl acetate + ethanol	Minimum	1	10	Batch	[93]
Isobutyl acetate + isobutyl alcohol	Minimum	0.2	1.013	Continuous	[63]
Diamine-ethylene + water	Maximum	1.013	8	Batch	[94]
Ethanol + toluene	Minimum	0.1	1.1	Batch	[29]
di- <i>n</i> -propyl ether + <i>n</i> -propyl alcohol	Minimum	0.3	1.01	Continuous	[60]
Acetone + <i>n</i> -pentane	Minimum	1.013	10	Batch	[94]
Ethanol + water	Minimum	1.013	10	Continuous	(95)

PSD can be operated in three different modes: i) continuous [3, 85], ii) batch [96] and iii) semi-continuous [97]. The dependence of the azeotropic concentration on the system pressure is used for the separation of the mixture. If the feed has a lower light component concentration than the azeotropic point, the feed is introduced into the Low Pressure (LP) column, otherwise the feed has to be fed into the High Pressure (HP) column.

**Figure 4** illustrates the separation of a binary mixture with a homogeneous minimum-boiling azeotrope in a continuous PSD. Because the feed stream  $F1$ , which is a combination of the fresh feed  $F$  with the recovery stream  $D2$ , has a mole fraction of light component A greater than the azeotropic point,  $F1$  is fed into the low-pressure column (LP). The objective of this column is to concentrate component B near an azeotropic point of the mixture and to remove pure component A in the column bottom stream. The azeotropic mixture  $D1$  that leaves the top of the column serves as the feed stream  $F2$  to the second high-pressure (HP) column to produce pure heavy component B in the bottom stream. The remaining products are recycled from the top to be mixed with fresh feed  $F$  to the first column. Both columns operate at different pressures that suit the intended separation requirement.



**Figure 4:** Schematic diagram for continuous pressure-swing distillation: (a) pressure-sensitive minimum-boiling azeotrope and (b) column sequence [90].

In general, vapor-liquid equilibrium calculations can be divided into two types. The starting point for both is the equality of fugacities of a component ( $i$ ) in the vapor and liquid phases, as shown in Eq. [5]. The two types differ in the description of the component fugacities in the vapor ( $f_i^v$ ) and liquid ( $f_i^l$ ) phases [87].

$$f_i^v(T, P, y_i) = f_i^l(T, P, x_i) \quad (5)$$

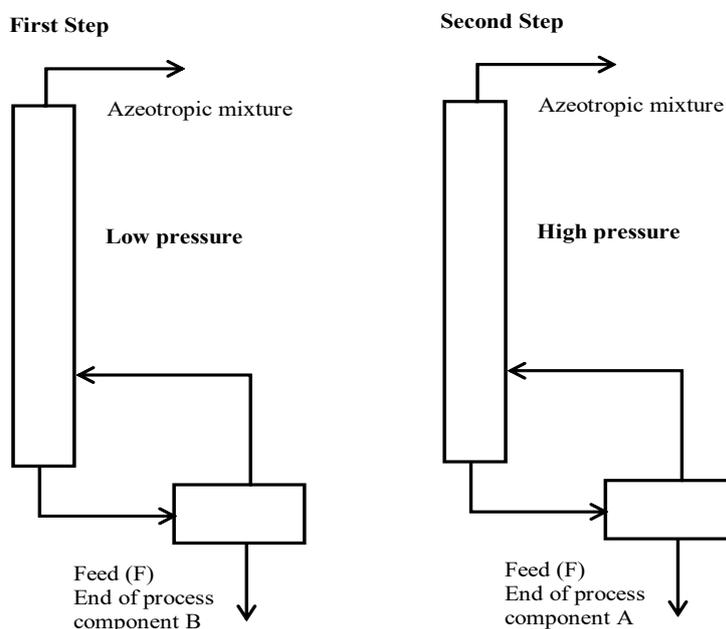
The correlations of the first types involve a “two-model” approach: one model is used to estimate the vapor phase ( $\phi_i$ ) nonidealities while another model is used for the liquid phase ( $\gamma_i$ ). The starting equations are:

$$f_i^v(T, P, y_i) = \phi_i y_i P \quad \text{for the vapor phase} \quad (6a)$$

$$f_i^l(T, P, x_i) = \gamma_i x_i P_i^{vap} \quad \text{for the liquid phase} \quad (6b)$$

where  $\gamma_i$  is the activity coefficient, and  $\phi_i$  is the fugacity coefficient (for more details, see [85]).

In a batch operation, only a single column is used for the separation. Component A is supposed to be the ultimate product in a mixture consisting of components A and B. This process includes two steps: in the first step, the column is initially charged with the feed mixture F into a bottom tank (for a regular batch) and operates at low pressure, as shown in Figure 5. Component B is removed from the bottom of the tower while a mixture close or equal to the azeotropic composition is accumulated at the top. This step runs until the target composition of component B is achieved in the bottom tank. On completion, the process is switched over to the second step, in which the column is recharged with the azeotropic mixture and is operated at high pressure. Thus, component A is obtained from the bottom while the mixture approaches the azeotropic composition at the top. If the initial feed concentration is higher than the azeotropic point, then the first step becomes the high pressure step, and component A is produced at the bottom. To provide high recovery, this cycle may be repeated many times [89].



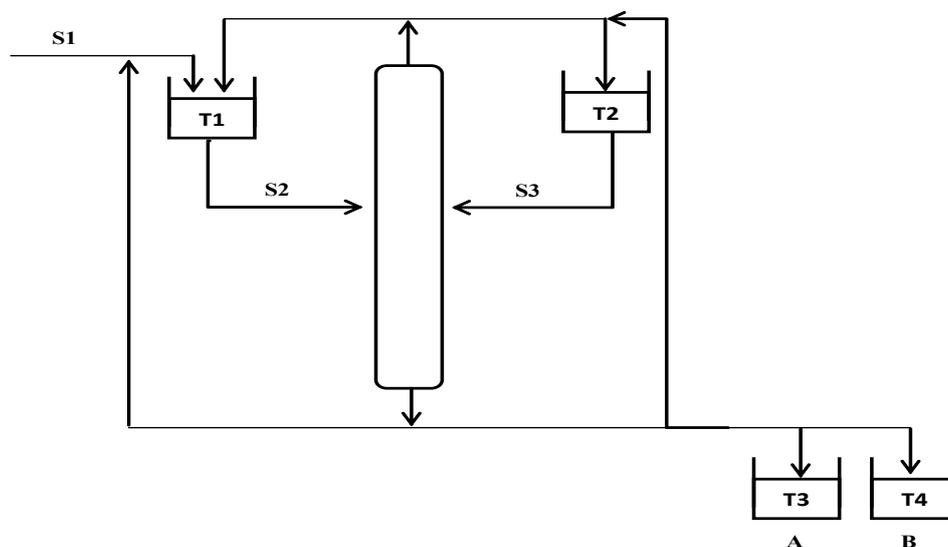
**Figure 5:** Schematic diagram for regular batch operation of PSD [89].

More recently, a number of novel batch column configurations have been introduced. These novel batch column configurations include an inverted batch process for separation of an acetonitrile/water mixture [89], a middle vessel configuration for separation of the ternary azeotropic mixture of acetone, benzene, and chloroform [98] and multi-vessel design for separating a mixture of methanol–ethanol–propanol–butanol [99].

In semicontinuous operation, only a single distillation column is involved. However, the column operates continuously or periodically. Liquid levels are maintained on the trays or packing, a stream is fed continuously to the reboiler, and cooling water is fed continuously to the condenser. The column operates in two modes, with tanks T1 and T2 alternating as the feed source, and the distillate and bottoms products are also sent to alternate tanks, as shown in **Figure 6**. Operation begins in mode 1, after startup, during which on-specification products (nearly pure A as a bottoms product and distillate near the azeotrope at a low pressure) are achieved. T1 is recharged periodically with fresh feed from S1. The column operates continuously but not at a steady state.

The column alternates between the modes defined as follows: Mode 1: S2 feeds the column. The condensed overhead and off-specification bottoms product is fed to tank T2. S1 has a zero flow rate. The operating mode is low pressure. Mode 2: S3 feeds the column. The overhead and off-specification bottom product is fed to tank T1. S1 feeds tank T1. The operating pressure is high. Product is fed to tank T3 or tank T4 when the bottom composition exceeds high purity in A or B, respectively. The process switches between modes when tank T1 or tank T2 is empty. In each mode, the column has a fixed pressure, reflux and reboil ratio. Modes 1 and 2 operate at low and high pressure, respectively [86].

Compared with continuous processing, semicontinuous PSD has several advantages, including greater plant flexibility and lower investment costs, because the product can be obtained without the need for additional equipment. When semicontinuous operation is compared with batch PSD, the downtime due to liquid holdups is sharply reduced because the compositions near the top of the column approach the azeotropic compositions in the distillate and consequently do not vary greatly as the tower shifts between low- and high-pressure operation [86].



**Figure 6:** Schematic diagram for semi-continuous operation of PSD [86].

The minimum number of columns required for a given separation can be calculated from Eq.(7), below [86]:

$$N_{col} = N_p + N_B - 1 \quad (7)$$

Here,  $N_{col}$  is the minimum number of columns required,  $N_p$  is the number of pure component products,  $N_B$  is the number of boundaries crossed for PSD (which does not include boundaries that disappear as the pressure changes). For example, for an extractive distillation to separate a ternary mixture,  $N_B$  is equal to unity and the number of columns needed is 3 ( $N_{col} = 3 + 1 - 1 = 3$ ). Consequently, it is unlikely that PSD will be advantageous as the azeotropic point for homogeneous azeotropes may vanish as the pressure decreases to some extent. Thus  $N_B = 0$  and the column number is therefore reduced to 2 for PSD.

However, the PSD process has a number of disadvantages, including a higher complexity of operation, resulting in the need for more sophisticated automation and more complex process control. There is also a gap in the experimental data in the literature because industrial applications are seldom published. In spite of the available theoretical knowledge [85], reliable experimental studies are scarce, partly because the operation tends to be limited to atmospheric conditions because operations under nonatmospheric conditions are difficult to establish and generation of such data is expensive [100]. This drawback limits the application of the PSD *process* in industry. Among the limited applications reported is the work of Knapp and Doherty [90] on the separation of tetrahydrofuran and water by continuous PSD

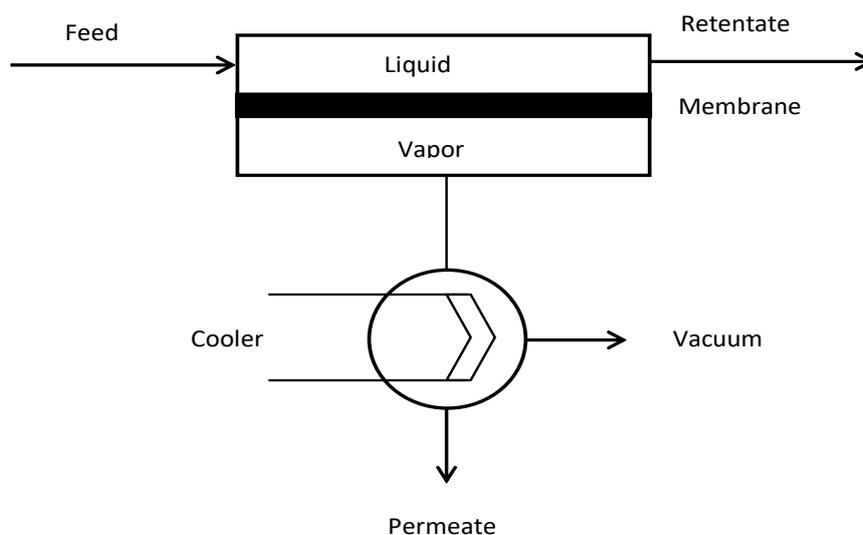
### 3. Separation of Azeotropic Mixture Using Membrane Technology

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 [8,101]. 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 [102]. Within this class of techniques, pervaporation (PV) is most prominent [10,103], and accounts for 3.6% of the total membrane separation applications in chemical and petrochemical operations [104]. Some of the PV applications in industry include removal of water from organic solvents (e.g., dehydration of alcohols, ketones and esters) [105], removal of organic compounds from water [106], and separation of organic-organic azeotropes and isomers [107].

#### 3.1. Pervaporation (PV)

Pervaporation involves permeation of feed components through a membrane, followed by evaporation into the downstream in various rates. A schematic diagram of the PV process is shown in Figure 7. PV separates the liquid feed mixture by partial vaporization through a

dense nonporous membrane. The feed mixture is usually in direct contact with one side of the oleophilic membrane, whereas permeate is removed in a vapor state from the opposite side into a vacuum or sweeping gas and then condensed [108]. The driving force for the separation is the difference in the partial pressures of the components on the two sides of the membrane, and the driving force is not affected by the relative volatility of the mixtures. This driving force for transport is the difference between the liquid feed/retentate and vapors permeated on each side of the membrane. The retentate is the remainder of the feed leaving the membrane feed chamber, which did not permeate through the membrane [109]. However, the use of PV to break azeotropes is restricted because the mass transportation through a thick dense polymer membrane is a slow process [110].



**Figure 7:** Schematic diagram of pervaporation process.

The main advantages of PV separation technology are that it is not limited by the vapor–liquid equilibrium because it is independent of relative volatilities. This property makes PV a good alternative technique to separate azeotropic and close-boiling point liquid-liquid mixtures [111]. However, because the feed mixtures are in direct contact with the surface of the polymeric membranes, the feed mixtures affect the swelling or shrinking of the membrane materials. Uragami and coworkers [112] proposed an improvement to overcome this disadvantage by vaporizing the feed solution and permeating it through the membrane. In this manner, the swelling or shrinking of the polymeric membrane can be prevented. A polymer with great affinity with one component in the feed is preferred for making PV membranes to obtain higher selectivity. However, the membrane becomes swollen if this affinity exceeds a certain level in a way that makes the membrane lose its integrity, thus necessitating higher selectivity. Aptel et al. [113] and Binning et al [114] proposed that the control of the membrane selectivity prevents the swollen fraction of the skin layer in a PV. Therefore, the choice of the proper membrane material is a crucial factor for a specific separation. In practice, separation by PV is achieved with a small amount of feed mixture as a result of the low permeation rate and therefore a large surface area for the membrane is needed. Increasing the membrane surface area for a larger-scale application is required, and several heat exchangers must be available

to vaporize the permeating component of the feed stream [110]. The PV process is limited by the boiling point of the feed mixture and the temperature sensitivity of the feed components [115].

### 3.1.1. Factor Influencing PV performance

The separation performance of the PV process is dependent on flux and selectivity. Flux is affected by the operating conditions, while selectivity involves a design decision. The maximum separation potential is provided when a suitable membrane is selected. In a binary system, the selectivity of a membrane is defined as the ratio of the concentrations of components in the permeate to the concentrations of the components in the feed [116]:

$$\alpha = \frac{y_a/y_b}{x_a/x_b} \quad (8)$$

where  $\alpha$  is the selectivity, and  $x$  and  $y$  are the concentrations of the components in the feed and the permeate, respectively. The 'a' and 'b' subscripts refer to the two components to be separated. The selectivity of a membrane is strongly dependent on the membrane affinity for one (or more) component(s) of the feed and the diffusion of the permeating molecules through the membrane matrix. The expected selectivity of a membrane therefore decreases with the increase in the molecular size of the components [117]. The overall selectivity of a membrane can be computed by multiplying the selectivity of sorption,  $\alpha_s$ , by the selectivity of diffusion,  $\alpha_D$ :

$$\alpha = \alpha_s * \alpha_D \quad (9)$$

Flux is defined as the rate of permeation of the feed components through a unit area of the membrane at a unit time. Flux is governed by the mass transfer process described by Fick's law of diffusion, as defined by Eq.10, below,

$$J = -D \frac{dC}{dz} \quad (10)$$

where  $J$  is the diffusion flux (mole/m·s),  $D$  is the diffusivity (m<sup>2</sup>/s),  $C$  is the concentration (mole/m<sup>3</sup>) and  $z$  is the position [length] (m). The negative sign indicates that  $J$  is positive when movement is down the gradient, i.e., the negative sign cancels the negative gradient along the direction of positive flux.  $D$  is proportional to the squared velocity of the diffusing particles, and the value of  $D$  depends on the temperature, the viscosity of the fluid and the size of the particles according to the Stokes-Einstein relationship. The driving force for the one-dimensional diffusion is the quantity  $-dC/dz$  that is the concentration gradient for ideal mixtures. In chemical systems other than ideal solutions or mixtures, the driving force for diffusion of each species is the gradient of the chemical potential of these species [118]. According to Fick's law, the rate of transfer by diffusion is proportional to the concentration gradient in the area of the interface over which the diffusion takes place [119].

The mass transfer in the PV process is also influenced by the operating conditions, including the concentration and composition of the feed, the feed permeate pressure and the temperature. This allows manipulation of the operating variables to suit the process constraints and to find the optimal operating conditions for the maximum mass transfer.

### 3.1.2. Membrane material selection in PV technology

The work on membrane separations began in 1960 with a wide range of membrane materials including dense metals, zeolites, polymers, ceramics and biological materials. The first manufactured polymeric membranes that found applications for organic solvent dehydration [120], including hydrophilic PV membranes, are still in use in the industry [121]. Recently, ceramic membranes have also been used as selective barriers in PV [122]. Such ceramic membranes are used in a wide range of applications, including separation of mixtures in acid and alkaline environments, which require high thermal and chemical stability [123].

The selection of the membrane polymeric materials for PV applications depends on three important factors, including capacity of sorption, chemical resistance, and mechanical strength. To separate a liquid mixture by the PV process, one of the components of the feed solution must have good interaction with the membrane materials to provide the swelling needed. Table 5 summarizes the performance and design limitations of the various membranes currently available for the separation of azeotropic mixtures.

**Table 5:** Summary of the latest studies of the pervaporation process for separation of azeotropic mixtures

Binary mixtures (A/B)	Membrane materials	Content of A in feed [wt. %]	Temperature [°C]	Selectivity $\alpha_{A/B}$	Flux [Kg/m <sup>2</sup> .h]	References
Water/ethanol	Phosphorylated chitosan	10.23-52.3	70	213	0.58	[124]
Water/1,4-dioxane	Chitosan and Nylon-66	18	40	865	0.09045	[125]
Water/acetic acid	Polymide-6 /PAA	8.7	15	82	0.005	[126]
Isopropanol/water	Chitosan	87.5	70	472	0.39	[127]
Butanol/water	Silicone rubber	0-8	30	45-65	<0.035	[128]
MTBE/water	PDMS	2	50	280	1.2	[129]
Methanol/toluene	Cellulose	5-90	45	1200	15	[130]
Methanol/ ETBE	CAB PEG600DMA	20	40	21	1.4	[131]
Methanol/MTBE	Poly(ether ether ketone)	1-87	30	254-3.2	0.015-0.113	[132]
Methanol/benzene	PFSA on Teflon	31	45	9.6	100.28	[118]
Ethanol/cyclohexane	Polyelectrolyte	12.1	50	106.7	8.7	[133]
Methanol/cyclohexane	PAN-g-MA	5-80	50	<200	<80	[134]
Methanol/MTBE	Chitosan with H <sub>2</sub> SO <sub>4</sub>	20	25	9.3	1.5	[135]

Ethanol/ETBE	PERVAP 2256	30	50-70	14.2	2.3	[136]
Benzene/ cyclohexane	LDPE	50	25	1.6	10.8	[137]
Toluene/cyclohexane	PS and PAM	75	30	7.9	1400	[138]
Toluene/ <i>n</i> -hexane	Polyurethane	10-70	25	2.8-5.8	1.1-3.5	[139]
Toluene/ <i>n</i> -octane	Polyesterimide	50	50	70	10	[140]
Styrene/ ethylbenzene	Polyurethane	20-80	60	1.1-5.7	0.3-1.2	[141]
Ethanol/ethyl acetate	Polydimethylsiloxane PDMS	60	30	3.61	1.397	[142]
Ethanol/cyclohexan	Poly(vinyl pyrrolidone)	25-100	54	7.5-47.4	0.05	[143]
Methanol/dimethyl carbonate	Poly(acrylic acid)/poly (vinyl alcohol)	10-90	60	1-6	0.577	[144]
Methanol/methyl acetate	Pervap 2255-30	30	60	-	7.4	[145]
Water /ethanol	Sodium alginate	5.2-38.6	30	2182	0.035	[146]
Toluene/ <i>n</i> -heptane	MSE-modified	10	85	4.985	4.61	[147]
Dimethyl carbonate/ methanol	Hydrophobic nano-silica/ polydimethylsiloxane	30	40	3.97	0.702	[148]
Toluene/iso-octane	3,5-Diaminobenzoic	50	100	90	-	[149]
Methanol/MTBE	Poly(lactic acid)	10	30-50	30	15	[150]
Methanol/dimethyl carbonate	Chitosan	10	60	-	0.276	[151]
Methanol/toluene	PVAHII	1.8-18.6	30	0.759-2.88	16-622	[152]
Methanol/TAME	Poly(vinyl alcohol)	97	50	4	175	[153]
Water/ethyl acetate	Polyvinyl alcohol	5.1	60	129	$2.83 \times 10^{-4}$	[154]
Ethanol/ethyl acetate	Na Y	30	130	27-82	2.9	[155]

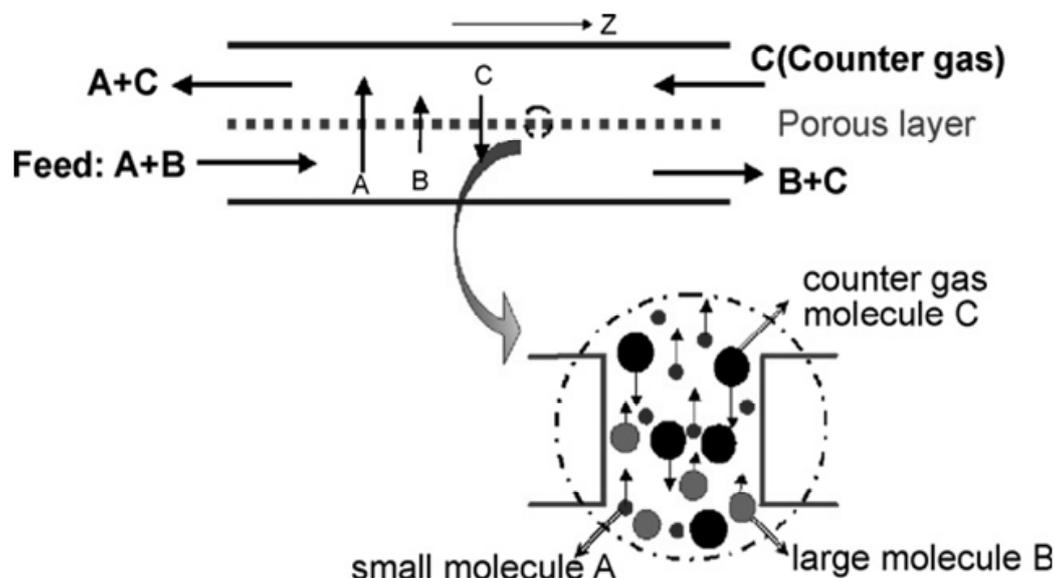
An efficient and economical membrane separation process can be established by correctly choosing membrane materials with desirable qualities including high selectivity and stability, good permeability, resistance to fouling, and lengthy lifetime [156]. The PV permeability coefficient represents the product of the solution coefficient and the diffusion coefficient. Fouling, which is generally caused by scale formation rather than clogging or blocking of pores, poses a challenge to the economy of the PV together with the membrane life cycle.

### 3.2. Frictional Diffusion

Frictional Diffusion (also called friction difference, FricDiff) is a separation technology based on differences of diffusivities in a mass separating sweep gas or vapor mixtures. A FricDiff module consists of flows of a target gas mixture (feed side) and a mass separating agent (sweep side) separated by a nonselective porous layer (barrier). FricDiff has been shown

to allow for the breaking of azeotropes in mixtures [157,158]. Development of frictional diffusion (FricDiff) technology for azeotropic mixture separations aims for increasing the energy-efficiency and reducing the use of hazardous solvents in the separation section of a chemical process [159]. As implied by the name, the separation principle that governs FricDiff is the membrane separation method [160].

Figure 8 depicts the mechanism at the molecular level. When considering the diffusion of molecules A and B through a third species C, the smaller molecule A experiences, in terms of diffusion, less hindrance from the so-called sweep gas (counter gas) C than the larger molecule B, resulting in a higher diffusive velocity of A compared to B, which can be exploited to achieve separation of the two gases. The FricDiff apparatus consists of two channels that are separated by a porous layer. The feed mixture A + B enters a side of the device. The sweep gas C enters the other side. In this setup, a counter-current flow pattern is chosen, but the concept works for co-current flow patterns as well. If the pressure gradient needed for convective flow through the channels can be neglected, FricDiff works both isothermally and isobarically on both sides of porous barrier. The separation in FricDiff is based on diffusional processes only [157].



**Figure 8:** Schematic presentation of the principle of the FricDiff separation technique [157].

Similar to other membrane processes, the driving force for mass transport in FricDiff is the gradient in the chemical potential, which reduces to a gradient in the partial vapor pressure for ideal gases. However, the mechanism for separation between FricDiff and these membrane processes is different. The separation principle in membrane separation processes depends on the type of selective membrane that is used, while in the FricDiff process, separation is based on the difference in transport velocities of the components of the feed mixture in the sweep gas [161].

### 3.3. Hybrid process distillation/pervaporation

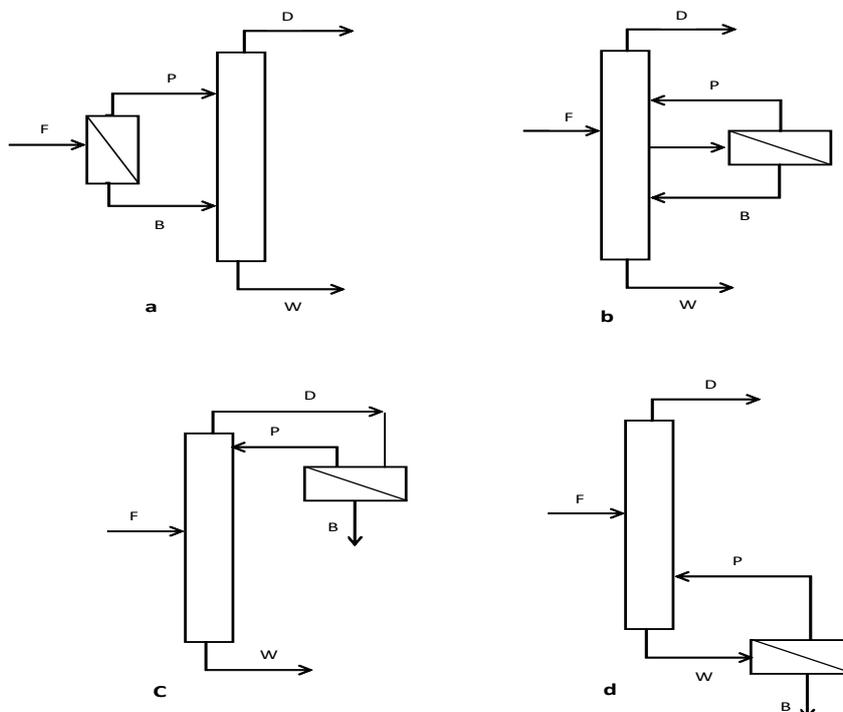
The PV process alone is not sufficient to separate some of the azeotropic mixtures. Thus,

hybrid processes combining distillation and membranes, known as Membrane Distillation (MD), is highly attractive to overcome these limitations [162]. Hybrid MD processes have drawn attention on various occasions [30,163]. However, only a few studies deal with optimization aspects of such a hybrid process with different approaches.

In the MD process, a liquid solution at a high temperature is brought into contact with one side of a porous hydrophobic membrane that acts as a barrier to separate the warm solution (called the feed side) from the permeate in either a liquid or a gaseous phase, which enters a cooling chamber called the permeate side. The hydrophobic nature of the microporous membrane prevents liquids/solutions from entering its pores due to the surface tension forces. As a result, a fixed interface is formed at the pore entrance. If the solution contains at least one volatile component, the temperature difference at the two ends of the pores produces a vapor pressure gradient within the pores. By the driving force, the vapor molecules of the volatile component that is produced by evaporation from the feed solution at the vapor-liquid interface migrate from the feed side to the permeate side of the membrane. At the permeate side, the migrated molecules that depend on the configuration of the membrane used are either condensed or removed in a vapor form from the membrane module. Flowing this way, the solution from the feed side is concentrated [5].

MD is advantageous due to its low cost and low energy consumption but suffers from some drawbacks such as low permeate flux (compared to other separation processes, such as RO), high susceptibility of the permeate flux to the concentration and temperature of the feed conditions due to the concentration and temperature polarization phenomena. The trapped air within the membrane also introduces a further mass transfer resistance, which also limits the MD permeate flux. The amount of heat lost by conduction is quite large [164].

A distillation column and a membrane module can generally be combined in various different configurations. Figure 9 (a-d) shows a schematic diagram for some configurations for a membrane/distillation hybrid process. The membrane module can be placed in the column feed stream as shown in Figure 9a, and this design is called parallel configuration. A series configuration is also available and is considered a special case of the more general solution (**Figure 9b**), in which the membrane feed stream is taken as a side draw from the column and permeate as well as the retentate streams are fed back into the column. In Figures 9c and 9d, the membrane is located, respectively, on the head and bottom of the column performing the final product stream purification [164].



**Figure 9:** Schematic diagram for various configurations for a membrane/distillation hybrid process [164].

Daviou et al [165] carried out studies on the optimal design of hybrid distillation pervaporation systems for the separation of a methanol/methyl *tert*-butyl ether mixture. Their simulation results using rigorous models show that significant cost reduction can be achieved. Working on isopropanol–water and propylene–propane mixtures, Naidu and Malik [166] illustrate the structural and parametric optimization of a continuous hybrid distillation-pervaporation process with different configurations such as series, parallel, and series-parallel arrangements of pervaporation modules in the network. Their findings proved that the purity of products can be obtained without violating the composition constraints of products and the heat exchange policy that minimizes the required membrane area by increasing the flux through the membrane. Kookos [167] carried out studies on optimal design of hybrid processes for membrane/distillation column using the structural and parametric optimization procedures. The results proved that the economic potential for using hybrid systems is significant.

#### 4. Process Intensification

Process intensification is a process design approach that leads to substantially smaller, cleaner, safer and more energy-efficient process technology [168]. Within the realm of the separation processes discussed in this review, 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 [169]. In the following sub-sections, some examples are illustrated.

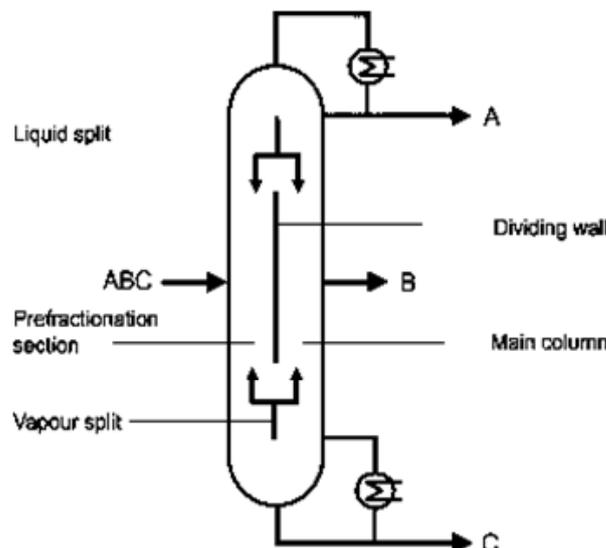
##### 4.1. Dividing Wall Distillation Column

When more than two products are to be obtained in a distillation process from a multi

component feed, the number of columns required to isolate products at the specified quality is equal to the number of components. Accordingly, plants with multiple products require a large number of possible column sequences, and it is important to determine the optimal number of separation columns in a sequence to reduce operation costs. To overcome such challenges, a distillation column with one longitudinal partition wall welded to the column wall, known as a dividing wall column (DWC), is introduced to reduce the number of columns required. In this case, the middle section of the vessel is split into two sections by inserting a vertical wall at an appropriate position [170].

DWC has found a great appeal in the chemical process industry because it offers significant energy saving along with substantial capital and space reductions. These advantages can be further enhanced by using a recently introduced non-welded wall technology, which allows the use of multiple columns within a shell. Several reviews and research papers have been published on this topic, covering the design [171], simulation [172], control [144, 173], optimization [174] and applications of DWC [175, 176]. However, because this process defines a single operating pressure, the boiling point in the reboiler becomes higher leading to a higher pressure drop and a higher temperature difference [177].

The separation of a ternary mixture of components A, B and C by a DWC is illustrated in Figure 10, with A being the lightest and C the heaviest. In the first half (pre-fractionator) of the DWC, a crude separation is carried out between components A and C. Component A is concentrated at the top of the second half (main column), and C is concentrated at the bottom with component B distributed between the top and the bottom. A liquid from the top section refluxes to the top of both the pre-fractionator and the main fractionator, while the vapor from the bottom section similarly strips the bottom of the pre-fractionator and the main fractionator. Under steady state conditions, the DWC yields the lightest component (A) at the top of the column and the heaviest component (C) at the bottom. The middle component B is withdrawn at a selected stage of the main fractionator where its concentration is at a maximum [175].



**Figure 10:** Schematic diagram for a dividing wall column [175].

The DWC technology can also be used in azeotropic separations (A-DWC) [178, 179], extractive distillation [180], and even reactive distillation [181]. However, industrial application for the separation of azeotropic mixtures is yet to be realized, and publications are still more focused on theoretical and simulation studies. For example, Briones-Ramírez et al. [182] report an Aspen-Plus simulation of an A-DWC system for isopropanol-water–acetone and isopropanol-water–methanol mixtures and obtain results claiming energy savings of up to 50% compared to a system with a two-column sequence. Sun et al [178] also carry out Aspen-Plus simulation of A-DWC for an ethanol dehydration process with cyclohexane as an entrainer. The results revealed that the proposed A-DWC system managed to save 42.17% of the energy consumption and 35.18% of the overall annual operating costs, along with reduction in greenhouse gas emissions. Kiss and David [183] used a DWC to enhance the bioethanol dehydration in both extractive distillation and azeotropic distillation and obtained energy savings of 10–20% for the novel process intensification alternatives based on DWC, while using fewer equipment units compared to the conventional extractive and azeotropic distillation configurations.

## 4.2. Microwave Enhanced Process

A microwave heating process is a molecular-level process that has gained substantial attention in academia and industry, including chemical process applications. However, while microwave technology has been introduced for reaction intensification [184], its use in separation processes is currently limited to a few applications such as extraction [185], desorption [186] and drying [187].

In recent years, several studies have focused on understanding of the microwave technology to enhance evaporation and improve the performance of the distillation process, and promising results have been reported [188]. Altman et al. [189] studied the effects of microwave on distillation of a binary system and concluded that the improvements offered by the microwave field occur only when the microwave field interacts directly with the vapor–liquid interface. On azeotropic mixtures, Gao et al. [190] studied the separation of a benzene/ethanol system at 101.33 kPa under various operating conditions and concluded that the azeotropic point is shifted upward from the standard curve when a microwave field is introduced.

The influence of a microwave field on the vapor–liquid equilibrium varies based on the components involved due to the variation in absorption of microwave energy. For example, ethanol is a good microwave absorber, whereas benzene is a poor microwave absorber. Thus, for a benzene/ethanol mixture, the OH groups of ethanol become rotationally excited, and heat is generated, leading to an increase in the overall internal energy of the ethanol molecule. The VLE is shifted because the microwave energy dissipated rapidly into the ethanol, and the heat transfer rate between ethanol and benzene in the vapor–liquid interface is slower than the

interaction of the microwave field with ethanol [190]. As a result, the vapor phase is richer in the high microwave irradiation absorption medium for the binary system, and the liquid phase is exactly the opposite, opening up opportunities for exploiting microwave irradiation in overcoming azeotropic separation.

### 4.3. Ultrasonic Enhanced Process

The application of ultrasonic waves can be found in various areas of application including biology, medicine, material forming, and the chemical industry [191, 192]. In the process industry, this sonication phenomenon has been exploited in enhancing cleaning, separation and reaction processes [193,194]. Heating, acoustic streaming and ultrasonic cavitation are widely believed to be the main causes for the enhancement [195]. Recently, employment of the potential of the sonication phenomenon for the separation of liquid mixtures has been reported [196,197].

Ultrasonic waves have also been found to be useful in enhancing the distillation process, particularly for the separation of azeotropic mixtures. Ripin et al. [198] and Mudalip et al. [199] studied the effect of ultrasonic waves on the Vapor Liquid Equilibrium (VLE) using typical binary mixtures. These authors also found that ultrasonic waves can positively change the VLE and alter the relative volatility of azeotropic mixtures. The changes in the relative volatility and VLE data for the binary mixtures are caused by the cavitation activity during the transmission of ultrasonic waves in a liquid medium. When the ultrasonic intensity is increased, greater energy enters the liquid medium, producing microbubbles, and this effect is coupled with the creation of vacuum effects inside the liquid. Because sonication is a fast transient process that occurs in microseconds, during this short period, heat and mass transfer processes are very rapid. Although the use of ultrasonic waves does not produce significant net changes in the operating conditions of the distillation process, use of ultrasonic waves does impact the thermodynamics significantly by altering the VLE of the system.

The main advantage of ultrasonic technology is the fact that the azeotrope point can be eliminated by correctly choosing the sonication parameters and other operating conditions. The separation of azeotropic mixtures can be carried out in a single column without the need for a separating agent. The ultrasonic technology is therefore attractive from the perspective of energy requirements and environmental protection. Because ultrasonic technology may also offer a reduction in the equipment size as it reduces the separation requirement by altering the VLE, the technology also offers safety features. Although previous studies [198-200] have illustrated the success on a single stage system, these studies are too sketchy, and the use of a complete ultrasonic-assisted distillation system with the typical industrial separation requirements is yet to be realized. A number of issues must be addressed that include design, safety, operability, control and efficiency.

## 5. Future Work

Research and development, along with knowledge generation and its adaptation to the chemical process industry, will continue to be driven by individual interests or availability of funding. Due to the importance of the chemical and petrochemical industry to the world economy, studies on even old technologies such as chemical separation continue to be relevant. Considering the separation of azeotropic mixtures, various studies taking different approaches have been reported. However, more studies are needed to improve the economic efficiency and ease of operation while ensuring safety to personnel and the environment.

Because pragmatic practitioners would prefer to stay with conventional processes because they are well-understood and established, azeotropic and extractive distillations would still be the main technologies used for large scale applications in the near future. The search for “perfect” entrainers should therefore be continued by examining existing options or synthesizing new ones aiming at entrainers that are effective in separation, highly selective, energy efficient, and environmentally friendly with minimal safety and health hazards. In this regard, the use of ionic liquids (ILs) and hyperbranched polymers has shown promising potential.

Considering the membrane separation technology routes, because the available surface area and durability play pivotal roles in process operability, research in these areas is likely to continue, as indicated by the increasing number of patents and publications on this subject. The separation community should either develop such processes for small-scale specialty applications or embark on the development of hybrid processes to overcome the surface area limitations.

Process intensification is a fast growing approach in the chemical process industry, offering a wide horizon of options. Because distillation is still considered the preferred process, intensification of the distillation process through a variety of frontier technologies should be explored. For example, by applying sonication to the liquid mixture, the properties of the mixture can be altered, thus opening opportunities for further process development. Some recent studies on ultrasonic distillation have been found to be promising and require additional efforts to formulate workable solutions for industrial applications. Further developments needed in this area include basic thermodynamic studies and the development of process technology involving the formulation of optimal design and operation strategies, the performance of safety and control studies and the development of complete system prototypes.

## 6. Concluding Remarks

This paper provides a state-of-the-art-review on the conventional and emerging technologies for the separation of azeotropic mixtures. The research areas to be emphasized for

further development are also elucidated. Conventional separation processes such as azeotropic and extractive distillations are observed to be the main technologies used at present and in the near future, with opportunities for improvements by introducing new entrainers with desirable properties. Similarly, while membrane processes offer good efficiency, simplicity of operation and low energy consumption, membrane processes are limited by the surface area requirement and thus may only be suitable for small-scale applications. To extend the applicability, hybrid processes combining membranes with other process technologies might be needed. For the Frictional Diffusion process, although it offers high thermodynamic efficiency and energy reduction and is an inherently irreversible process, it suffers low selectivity and thus requires further improvement. Another potential approach is to exploit the process intensification concept in developing new separation techniques. While some ideas have been implemented (including dividing wall column, microwave and ultrasonic assisted distillation), many issues remain unresolved and therefore require further scrutiny.

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. In line with the call for sustainable process development, research in this field should be given sufficient attention by the research community.

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