A review on the separation of benzene/cyclohexane mixtures by pervaporation processes

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Abstract
Separation of benzene (Bz) and cyclohexane (Chx) is one of the most challenging processes in the chemical industry. On account of the only 0.6°C difference in volatilities of the two components, conventional distillation processes are not practical. Azeotropic distillation and extractive distillation, on the other hand, although feasible and in use in many industries, are accompanied by high capital and operating costs and also are complex processes in nature. Membrane pervaporation (PV) is a viable alternative to the conventional techniques both from economical and technical points of view. While extractive distillation/PV hybrid has attracted industrial attention, progresses in PV separation of Bz/Chx suggest that this technique can handle a greater share in the process.

In this paper, an extensive review is presented on the properties, production, conventional and alternative separation processes of benzene and cyclohexane. Special emphasis is given to the performance of membrane PV processes. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Separation of benzene/cyclohexane; Pervaporation processes; Permselectivity

1. Introduction
Separation of benzene (Bz) and cyclohexane (Chx) is among the most important and most difficult processes in the petrochemical industry. Cyclohexane is produced by catalytic hydrogenation of benzene. The unreacted benzene is present in the reactor’s effluent stream and must be removed for pure cyclohexane recovery. Separation of benzene and cyclohexane is difficult by a conventional distillation process because these components form close boiling point mixtures at the entire range of their compositions. Presently, azeotropic distillation and extractive distillation are used for this separation. These two processes, however, suffer from complexity and high energy consumption. For all these reasons, the industry has always been eager to look for a viable alternative to the conventional Bz/Chx separation processes.

In the recent years, pervaporation (PV) separation has emerged as an economical and simple alternative to many organic/organic separation applications. This process is especially attractive in azeotropic and close boiling point separation applications. That is so because, unlike distillation processes, the separation mechanism in PV is not based on the relative volatility...
of components, but on the difference in sorption and diffusion properties of the feed substances as well as permselectivity of the membrane.

2. Properties of benzene and cyclohexane

Benzene is an aromatic hydrocarbon with the chemical formula C₆H₆. It is a non-polar, volatile, colorless, flammable liquid, with a characteristic odor and great thermal stability. The chemical structure of benzene is shown in Fig. 1 and its representative properties are given in Table 1 [1]. Benzene has a stable planar structure with a six-member Kekule ring. The carbon bonds have equal lengths of 1.39 Å and bond angles of 120°.

Cyclohexane, with the chemical formula C₆H₁₂, is a volatile, colorless, flammable, water-insoluble, non-corrosive, non-polar liquid having a pungent odor. It is less toxic than benzene. The most stable chemical structure of cyclohexane, known as ‘chair conformation’, is shown in Fig. 1. Table 3 gives its physical properties. Cyclohexane is used in paints and varnishes, as a solvent in the plastic industry.

The principal use of benzene is as a chemical raw material in the synthesis of compounds such as styrene (polystyrene plastics and synthetic rubber), phenol (phenolic resins), cyclohexane (Nylon), aniline, maleic anhydride (polyester resins), alkylbenzenes (detergents), and chlorobenzenes. Benzene is also used in the production of drugs, dyes, insecticides, and plastics. Benzene, toluene, and xylenes (BTX) can be found in motor gasoline as light high-octane aromatic hydrocarbons. Benzene was also used as a solvent, but safer solvents have replaced it in the recent years. Table 2 shows selected applications of benzene [2]. An extensive application of benzene in different chemical products can be found in the same reference.

Cyclohexane is used in paints and varnishes, as a solvent in the plastic industry, and in the production of nylon. It is also used as a solvent in the manufacture of synthetic rubber.
Table 3

Physical properties of cyclohexane

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>fp (°C)</td>
<td>6.554</td>
</tr>
<tr>
<td>bp (°C)</td>
<td>80.738</td>
</tr>
<tr>
<td>Density at 25°C (g/mol)</td>
<td>0.77855</td>
</tr>
<tr>
<td>Refractive index, nD25</td>
<td>1.42623</td>
</tr>
<tr>
<td>Viscosity (absolute) at 20°C (cP)</td>
<td>0.980</td>
</tr>
<tr>
<td>Surface tension at 25°C (dyn/cm)</td>
<td>25.3</td>
</tr>
<tr>
<td>Critical temperature (°C)</td>
<td>281.0</td>
</tr>
</tbody>
</table>

particularly for resins used in wire coating, and for the extraction of essential oils. However, the importance of cyclohexane lays mainly in its conversion to the intermediate cyclohexanone, a feedstock for Nylon precursors such as adipic acid, ε-caprolactam and hexamethylenediamine [2,3].

Cyclohexane forms binary, tertiary, and quaternary azeotropes with a variety of chemicals. Table 4 shows the three most well known binary azeotropes formed with cyclohexane. More details of the cyclohexane azeotropes can be found in [4].

3. Production of benzene and cyclohexane

3.1. Benzene

On account of the increasing demand for plastics, detergents, and organic chemicals, the production of benzene has increased rapidly since 1950. There are many roots to the production of benzene, including

- Extraction from crude oil or coal
- Dehydrogenation of cycloparaffins
- Dealkylation of chain alkyl aromatics, e.g., toluene and xylenes
- Transalkylation of toluene
- Reforming-separation
- Extraction from coal

Some expensive processes such as dealkylation of toluene, xylenes, or longer chain alkyl aromatics were considered only in the past couple of decades when the high price of benzene justified the process. The above processes are described briefly in this paper. More details could be found in [1,2,5–14].

Benzene can be practically found in all crude oils in small amounts. However, its separation becomes attractive only when its concentration in the petroleum fraction is increased. Another source of benzene is the light gas produced from coal. Benzene is one of the principal compounds present in the light oil recovered from coal carbonization gases. The composition of light oil depends mainly on the temperature of the evolved gases. A higher proportion of benzene is found at high temperatures.

Dehydrogenation of cycloparaffins was developed prior to 1950. In this process, a naphtha-range petroleum fraction is catalytically reformed to produce a high-octane product for use in gasoline blending. Then, solvent extraction and fractional distillation of the extract removes benzene and other aromatic hydrocarbons.

In the dealkylation process, methyl radical in a toluene molecule is replaced by hydrogen atom to produce benzene [1].

More recently, benzene has been produced from toluene by transalkylation, also called toluene disproportionation. In this process, the methyl group from one toluene molecule is transferred to another toluene molecule to produce benzene and mixed xylenes [13,14]. The high value of p-xylene has made, at times, this process more profitable than dealkylation. Mobil is presently using this method in its TransPlus™ as well as MTDP-3 technology [15,16].

The production of benzene by reforming-separation processes is associated with the production of toluene and xylene (BTX plants) ([2] and references therein; [5]). In reforming-separation processes, the aromatic fraction of crude oil is reformed catalytically to produce BTX compounds. Benzene, toluene, and xylenes are then recovered by extractive distillation. A novel example of this technology is Chevron’s Aromax reforming process, which uses a zeolite catalyst to convert light naphtha to benzene and toluene [17–19].

3.2. Cyclohexane

The production of cyclohexane is of special interest to us because it is directly related to the sub-

Table 4

Binary azeotropes of cyclohexane [4]

<table>
<thead>
<tr>
<th>Second component</th>
<th>Cyclohexane (wt.%)</th>
<th>bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>91.6</td>
<td>69.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>45</td>
<td>77.5</td>
</tr>
<tr>
<td>Methanol</td>
<td>39</td>
<td>54.2</td>
</tr>
</tbody>
</table>
Fig. 2. Top: multistage reactor, vapor phase process, (a) reactors; (b) separator drum; (c) compressor; (d) stabilizer. Bottom: liquid and vapor phase reactor process. (a) Liquid phase reactor; (b) vapor phase reactor; (c) separator drum; (d) compressor; (e) stabilizer.
ject of this paper. Although cyclohexane was first obtained by direct fractionation of crude gasoline cuts, two major factors pushed for the introduction of new processes. One was the increasing demand for cyclohexane, which could not be met by the amount of natural occurrence of this substance, and the other was the low purity of product by direct distillation (85–98%). The demand for cyclohexane mainly comes from the plastic industry where cyclohexane is used as a feedstock for Nylon 6 and Nylon 6,6. Presently, virtually all cyclohexane is produced by the hydrogenation of benzene (ca. 80–85%) [3,4].

Benzene is hydrogenated catalytically to cyclohexane in liquid or vapor phase in the presence of hydrogen. Several cyclohexane processes, which use nickel, platinum, or palladium as the catalyst, have been developed [4]. Hydrogenation proceeds readily and is highly exothermic \(\Delta H_{500K} = -214\text{ kJ/mol}\). Temperature and pressure control is essential in shifting the equilibrium in favor of benzene or cyclohexane [20,21]. Typical set-points are 300°C and 300–450 psi. High purity cyclohexane can only be obtained under a complex process control. Therefore, economical and efficient heat removal has been the subject of many reactor designs [22–24]. Fig. 2 shows the schematics of typical liquid phase and vapor phase benzene hyrogenation reactors.

Cyclohexane can also be distilled directly from naphtha. The starting concentration of cyclohexane in the naphtha fraction of crude oil is in the range of 0.5–5.0 vol%. The presence of several hydrocarbons boiling in the same range, such as \(n\)-hexane, isohexanes, methylcyclopentane, benzene, and dimethylpentanes, makes the recovery of cyclohexane from petroleum by fractional distillation or recrystallization difficult and uneconomical. However, cyclohexane at 85 wt.% purity is manufactured in commercial quantities by fractionating the naphthas from natural gasoline. The C5 naphtha produced, then, contains 10–14% cyclohexane. This stream is finally treated in high efficiency distillation towers, which further concentrates the cyclohexane to 85% purity. The difficulty of separating cyclohexane from naphtha is underscored by the fact that only one company, Phillips Petroleum, produces cyclohexane by distillation.

**4. Conventional separation processes for Bz/Chx**

Separation of Bz/Chx mixtures is among the most complicated processes in the petrochemical industry. As the difference in the boiling points of benzene and cyclohexane is only 0.6°C, and the interaction parameter between them is small, the liquid–vapor equilibrium curve of their binary liquid mixture, as shown in Fig. 3, is nearly a close-boiling system. Also, benzene and cyclohexane form azeotrope at 45 vol% cyclohexane, as shown in Table 4. Consequently, fractional distillation becomes expensive and cumbersome for Bz/Chx separation. The most common separation techniques developed for aromatic/aliphatic mixtures are listed in Table 5 [3]. The separation problems and the requirements for the technological or economical operation of the individual processes are also summarized in Table 5.

Distillation processes such as azeotropic distillation and extractive distillation are the main technologies presently available to separate Bz/Chx mixtures. The selectivity of these processes is limited by the vapor–liquid equilibrium. Also, these processes are partly carried out by adding a third component to the Bz/Chx mixtures. Removal of the third component from distillate or residue adds to the complexity and cost of the process.

*Fig. 3. Bz/Chx vapor–liquid equilibrium curve.*
Table 5

Processes for aromatic recovery [31]

<table>
<thead>
<tr>
<th>Process</th>
<th>Separation problem</th>
<th>Requirements for basic or economical operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azeotropic distillation</td>
<td>BTX separation from pyrolysis gasoline</td>
<td>High aromatic content (&gt;90%)</td>
</tr>
<tr>
<td>Extractive distillation</td>
<td>BTX separation from pyrolysis gasoline</td>
<td>Medium aromatic content (65–90%)</td>
</tr>
<tr>
<td>Liquid–liquid extraction</td>
<td>BTX separation from reformate gasoline</td>
<td>Lower aromatic content (20–65%)</td>
</tr>
<tr>
<td>Crystallization</td>
<td>Isolation of p-xylene from m/p-mixtures</td>
<td>Distillative pre-separation of o-xylene and ethylbenzene from C₈ aromatic fractions</td>
</tr>
<tr>
<td>Adsorption on solids</td>
<td>Isolation of p-xylene from C₈ aromatic fractions</td>
<td>Continuous, reversible and selective adsorption</td>
</tr>
</tbody>
</table>

In azeotropic distillation, the separation process is facilitated by addition of strongly polar auxiliary agents such as amines, alcohols, ketones, and water. The auxiliary agent forms azeotrope with one of the two components and alters the vapor–liquid equilibrium curve. This mixture is collected at the overhead of the distillation column. The second component is then recovered at high purity from the bottom. The new azeotrope is separated in a secondary stage, where the auxiliary agent is recycled to the first distillation column and the second component is recovered at high purity. Azeotropic distillation is economical when the aromatic content is greater than 90%, i.e., only a small amount of non aromatics is to be separated, such as with the pyrolysis of gasoline or crude benzene from coal coking [2,4].

In the case of Bz/Chx separation, azeotropic distillation is practical only at high benzene concentrations, e.g., >90%. The separation is facilitated by the addition of acetone [25], as shown in Fig. 4 [26]. This is a hybrid process consisting of azeotropic distillation and extraction. In this process, two entrainers are used. The first is acetone to mix with cyclohexane and replace Bz/Chx azeotrope. Acetone forms a minimum azeotrope with cyclohexane at approximately 77% cyclohexane, with a boiling point of 53.1°C [26]. The second entrainer is water, which recovers the acetone in the extraction column. As shown in Fig. 4, the border distillation line runs from Bz/Chx azeotrope to acetone/cyclohexane azeotrope. In the first distillation tower, acetone/cyclohexane azeotrope is collected from the overhead, and benzene from the bottom. The azeotrope is fed into the extractor where acetone is washed with water. As cyclohexane is insoluble in water, nearly pure cyclohexane is produced. Finally, the water/acetone mixture is distilled in the second distillation tower. Acetone is recycled to the first distillation column as entrainer, and water is recycled back to the extractor for acetone wash.

Extractive distillation is similar to azeotropic distillation in the sense that they both use an auxiliary agent to facilitate the separation. In extractive distillation, however, the additive is used to decrease the volatility of one component. The other component is distilled overhead in pure form, and the bottom mixture is fed into a stripping column for separation. Extraction distillation is particularly economical for the isolation of aromatics from pyrolysis gasoline (approximately 65–90% aromatics).

Extractive distillation is widely used by the industry to separate benzene and cyclohexane. An example of this process is shown in Fig. 5 [27]. In this process, furfural, which is highly benzene selective, is added to the mixture to shift the vapor–liquid equilibrium. Highly pure cyclohexane is distilled overhead. The benzene/furfural mixture is fed into a second column where benzene is collected from the overhead and furfural is recycled back to the first distillation column. A major problem with this system is that the production of high purity cyclohexane, i.e., >98.5%, is accompanied by rapidly increasing energy consumption [27].

Like azeotropic distillation, extractive distillation suffers from disadvantages such as high capital and operating cost, complexity of the process, need for a secondary distillation of the auxiliary agent, and limited range of feed concentration. The sum of these disadvantages became the driving force for research into alternative separation processes including the emerging membrane PV. Proper membranes must show affinity towards aromatic substances reflected by a distinctly higher permeability for aromatics than for aliphatic organics.
Fig. 4. General flowsheet for azeotropic distillation. The process consists of a first distillation stage to remove lower boiling fraction with the aid of an auxiliary agent. The agent is then water washed from the distillate and recovered in a second distillation process. Top: flowsheet, bottom: triangular phase diagram for the distillation process.
5. PV separation of Bz/Chx

5.1. PV processes

PV is derived from combining permeation and evaporation, the two mechanisms involved in the process. In a PV process, components of a liquid feed permeate through a membrane and evaporate into the downstream at different rates. The fact that feed components undergo phase change makes PV unique among membrane processes. The driving force behind the process is the difference in chemical activity of components in the feed and the permeate. The separation occurs because of the different rates of sorption and diffusion of the feed components through the membrane. The main advantage of PV over distillation is that PV is independent of relative volatilities of components, and therefore, it is not limited by the vapor–liquid equilibrium. This characteristic makes PV an attractive alternative to separate azeotropic and close-boiling point mixtures. PV processes cover a wide range of applications including organic dehydration, organic removal from aqueous solutions, and organic/organic separation.

Separation performance of a membrane is characterized by two parameters: flux and selectivity. Flux is defined as the rate of permeation of feed components through unit area of membrane at unit time. Two commonly used flux units in PV processes are kg/m² h, and g/cm² s.

Two types of selectivities are defined for a membrane: ideal selectivity and actual selectivity. The ideal selectivity is simply the ratio of fluxes of pure substances through the membrane. The actual selectivity of a membrane in a binary system is defined as the ratio of concentrations of components in the permeate to that in the feed:

\[ \alpha = \frac{y_a}{y_b} \]

where \( \alpha \) is selectivity (separation factor), \( x \) and \( y \) are concentrations of components in feed and permeate, respectively, and ‘a’ and ‘b’ subscripts denote the two components to be separated. Selectivity of a membrane is strongly influenced by two factors: affinity of the membrane towards one (or more) component(s) of the feed, and ease of diffusion of the permeating molecules through the membrane matrix. The overall selectivity of a membrane is defined as the product of sorption selectivity, \( \alpha_s \), and diffusion selectivity, \( \alpha_D \):

\[ \alpha = \alpha_s \times \alpha_D \]

Either or both of these selectivities contribute to the preferential permeation of feed component(s) through a given membrane. However, in most cases, selectivity of a membrane is mainly governed by the sorption component of the selectivity. Studies by Aptel et al. [28], Néel [29] and Binning et al. [30] suggested that the unswollen fraction of the skin layer in a PV membrane controls the permselectivity of the membrane.
Therefore, the choice of proper membrane material is a crucial factor for a specific separation. On one hand, a polymer with great affinity towards one component of the feed is preferred because it leads to higher selectivity. On the other hand, if this affinity exceeds a certain level, the membrane gets swollen by the compound and loses its integrity and therefore its selectivity. Consequently, in the preparation of a proper membrane, it is important to suppress or control its degree of swelling.

In addition to the specific characteristics of the feed components and the membrane, the operating parameters influence the overall performance of a PV process. These parameters include feed temperature, feed concentration, and downstream pressure. It is generally believed that feed pressure has insignificant effect on the permeability and selectivity of PV membranes.

5.2. Parameters affecting the separation of Bz/Chx by PV

The effects of both sorption selectivity and diffusion selectivity of benzene and cyclohexane have been studied extensively. Table 6 [31,32] compares the molar volumes, collision diameters, and solubility parameters of benzene and cyclohexane. Benzene’s smaller size, smaller collision diameter, and planar shape enhance its diffusivity. Many researchers have realized the domination of diffusion selectivity or sorption selectivity in different membranes. Huang and Lin [33] reported that the permeation and separation of Bz/Chx are significantly influenced by their molecular sizes. Also, Inui et al. [34] showed that the membrane selectivity decreased with increasing molecular size of aromatic hydrocarbons in an aromatic/cyclohexane separation study. The later group, in a series of separate studies [35,36], emphasized that the diffusion selectivity dominates the overall selectivity of the membranes under study.

However, in most cases, the experimental evidences indicate that the separation of benzene and cyclohexane is mainly governed by sorption selectivity due to the chemical interaction between benzene molecule and membrane [32,37–41]. The domination of sorption selectivity is due to the affinity between the double bonds of benzene molecule and the polar groups of the polymeric membrane. That is, benzene has π electrons, which show stronger affinity to polar molecules. Therefore, a polymer possessing polar groups facilitates the permeation of benzene through the membrane. The solubility parameters, reported in Table 6, indicate that the hydrogen bonding component (δ_H) of benzene solubility is stronger than that of cyclohexane. It is expected that the high hydrogen bonding interacts with free polar groups in a membrane. An interesting study to support the above explanation was done by Yamasaki et al. [39]. They compared the retention time of benzene, n-hexane, and cyclohexane through a column filled with PVA polymer, and observed that the retention time of benzene was considerably higher than that for the other two components. They concluded that the difference in retention time was due to the stronger interaction between benzene and PVA. Tanihara et al. [32] compared the overall selectivity of a membrane with its diffusivity selectivity component to show that the latter has an insignificant effect on the separation process. Sun and Ruckenstein [41] also showed that the swelling of different membranes was mainly due to the sorption of benzene than cyclohexane.

Furthermore, the swelling effect of benzene was noticed in a number of studies [38,42,43]. Suzuki and Onozato [42] compared the ideal selectivity and actual selectivity of benzene and cyclohexane through poly(γ-methyl l-glutamate) (PMLG) membrane and

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molar volume (cm³/mol)</th>
<th>Collision diameter (nm)</th>
<th>Solubility parameter ((MPa)²)</th>
<th>δ_P</th>
<th>δ_H</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>89.4</td>
<td>0.526</td>
<td>18.4</td>
<td>0</td>
<td>2.0</td>
<td>18.6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>108.7</td>
<td>0.606</td>
<td>16.8</td>
<td>0</td>
<td>0.2</td>
<td>16.8</td>
</tr>
</tbody>
</table>

*δ: Hansen solubility parameter, δ_P: dispersive forces contribution component, δ_H: polar component, δ_H: hydrogen bonding component. δ² = δ_P² + δ_H².
realized that the selectivity reduced from an ideal value of 370 to between 5 and 12 when a mixture of benzene and cyclohexane was used as the feed. They attributed this observation to the swelling of the membrane by benzene, which resulted in enhanced permeation of cyclohexane through the membrane. In another study, Ray et al. [44] measured flux and selectivity of 5% benzene in cyclohexane mixture through three copolymers of polyacrylonitrile with styrene, methyl methacrylate (MMA), and vinyl acetate. They observed that the membrane’s selectivity decreased with increasing content of active monomer in the copolymer. The selectivity loss was attributed to the plasticization effect of benzene in the monomer moieties of the membrane.

The above evidences indicate that, because of small difference between diffusion of benzene and cyclohexane, the key to the choice of a proper membrane is the benzene/membrane chemical affinity. A proper membrane for Bz/Chx separation must possess both polar groups to facilitate the sorption of benzene and a rigid molecular structure resistive to swelling to retain the membrane’s integrity. For example, it is evidenced that the solubility of benzene in water is one order of magnitude larger than that of cyclohexane [45]. Therefore, benzene selectivity may improve by using membranes having hydrophilic groups in their polymer structure. Such separation studies using hydrophilic membranes were reported by Yamasaki et al. [39].

5.3. Types of membranes used for Bz/Chx separation

The first attempts to separate benzene and cyclohexane by membranes were not successful [33,46] because of low selectivity of membranes. Kucharski and Stelmaszek [46] slightly enhanced the selectivity of polypropylene towards benzene by modifying the orientation of polymers. Huang and Lin [33] proposed that the polymer’s functional groups are major contributors to the benzene selectivity of membranes. A successful attempt was performed by McCandless et al. [47] who obtained a selectivity of 20 using polyvinylidene fluoride membrane. However, they were not successful in increasing the permeability by adding solvents to the feed mixture.

These preliminary studies lighted the road to many membrane preparation techniques to obtain reasonable selectivity and flux. In the recent years, polymer alloy membranes became popular for PV separation of Bz/Chx. The concept of alloy membranes refers to the preparation of membranes by mixing a benzene-soluble polymer with a benzene-non-soluble one. The insoluble polymer forms the backbone of the polymeric membrane, while the soluble one provides affinity for benzene. Selectivity of these membranes was enhanced by techniques such as cross-linking, graft-polymerization, microphase separation, concentrated emulsion polymerization, and copolymerization.

Cabasso et al. [43,48] tried out alloy membranes of polyphosphonates (PPN) and acetyl cellulose (AC). They succeeded in preparing membranes with selectivities between 12 and 40, and fluxes between 800 and 1000 ml/m² h.

More recently, methacrylate family of polymers has become popular because of its favorable characteristics towards Bz/Chx separation. Examples of this type of polymers include MMA and ethyl methacrylate (EMA). This family has been used as common starting materials for many membrane alloys. Terada et al. [49] alloyed methyl acrylate (MA) with 2-hydroxyethyl methacrylate (HEMA). Yamaguchi et al. [50] tried graft copolymerization of MA/high-density polyethylene (HDPE). Inui and his coworkers have focused on polymethyl methacrylate (PMMA) in a number of studies. They prepared PMMA alloyed membranes with polyethyl methacrylate (PEMA) [34], dimethyl acrylamide–methyl methacrylate (DMMA) [35], and polymethyl methacrylate–methacrylic acid (MMA–MAA) [36]. Finally, Ray and coworkers prepared polyacrylonitril (PAN)–PMMA alloy membrane for Bz/Chx separation [44]. All these membranes showed moderate to high selectivity and flux. Also, a non-alloy use of polymethacrylic acid (PMA) is given by Sakohara et al. [51] who used PMA in porous silica membrane.

A technique to prepare composite membrane was suggested by the Ruckenstein group by late 80’s and is known as concentrated emulsion polymerization [41,55,56]. In this method, the membrane is prepared using two incompatible polymers. One polymer is soluble in one feed component, e.g., benzene. The other is insoluble and preserves the integrity of the membrane. The soluble polymer is emulsified and dispersed in the insoluble one. Benzene preferentially swells this polymer and permeates through the membrane, while
cyclohexane permeation is retarded. Sun and Ruckenstein report a selectivity of around 25 at a flux of \( \approx 2 \text{ kg} \mu\text{m}^2/\text{m}^2 \text{h} \) with a feed concentration of 10 wt.% benzene in cyclohexane at 20°C [41].

Other examples of polymer alloy membranes include polyethylene glycol (PEG)/Nylon 6 [52], and PEMA/Nylon 6 [53], and grafted polyglycidyl methacrylate (GMA) [38]. In addition, some researchers examined polymer mixing and hybrid polymers. An example is the study done by Kusakabe et al. [54] who prepared polyurethane (PU)/silica and PU/tetraethylorthosilicate (TEOS) to separate Bz/Chx. They observed a flux of 0.1 kg/m² h and a selectivity of 19 for a 50% mixture of benzene in cyclohexane.

Besides alloy membranes, a number of studies examined other types of membranes for this separation. For example, Inui et al. used benzoylchitosan [37] at different degrees of benzoylation. The same group also tried nematic and smectic liquid crystalline polymers (n-LCP and s-LCP) [40,57]. Also, Bryant et al. explored the possibility of facilitated transport with Ag(I) ions in a polyvinyl alcohol (PVA) holder [58]. Finally, Darkow et al. [59] synthesized polycrylonitril-co-butadien-co-styrene-co-diaryltetrazolyl (ABSV) membrane, a new type of polymer containing a photosensitive moiety. The functionalization and cross-linking were initiated by photoradiation. The PV results showed that although the photochemical treatment enhanced the permselectivity of the membranes, the separation factor was still low \((\alpha = 2.46)\).

5.4. Flux and selectivity of membranes

Table 7 compares the flux and selectivity of a number of membranes for Bz/Chx separation. All flux values in Table 7 were converted to kg \(\mu\text{m}/\text{m}^2 \text{h} \). These values are also presented graphically in Fig. 6.

It can be observed in Table 7 that both flux and selectivity vary in a wide range. Flux deviates between as low as 0.03 kg \(\mu\text{m}/\text{m}^2 \text{h} \) and as high as 64.6 kg \(\mu\text{m}/\text{m}^2 \text{h} \). Similarly, selectivity starts from almost no separation, e.g., 1.3, to perfect separation, e.g., \(\infty\). However, a majority of the experimental fluxes lay in the vicinity of 1–10 kg \(\mu\text{m}/\text{m}^2 \text{h} \), at selectivities of 5–20. These flux and selectivity values are comparable to those obtained in most industrial applications of PV processes.

Most membranes used in the laboratory experiments were of homogeneous type. Only few studies were performed using asymmetric membranes. Three examples are shown in Table 7 for comparison [34,39]. In one case, Yamasaki et al. [39] compared the performances of homogeneous and asymmetric PVA membranes for Bz/Chx separation and observed a selectivity of 10 for an asymmetric membrane compared to 3 for a homogeneous one. The authors explained this unusual phenomenon by the density difference in the skin layer of an asymmetric membrane and a homogeneous one: the asymmetric membrane probably had denser polymer packing, resulting in smaller free volume for the diffusion of permeating molecules. Therefore, sorption selectivity dominated the overall selectivity, and because benzene had greater affinity towards PVA, the overall selectivity increased with increasing polymer density.

5.5. Effects of operating parameters

Few researchers studied the effects of temperature on the permselectivity of membranes in Bz/Chx separation [36,41,46–48,65]. All the experimental evidences confirm an increase in permeability and decrease in selectivity of membranes with increasing temperature. Fig. 7 represents the general trend in the effects of temperature on the flux and selectivity of PV membranes. Acharya et al. [65] and Inui et al. [36] show that the permeability of PV membranes decrease linearly with reciprocal of temperature following an Arrhenius type relation of the form

\[ Q_i = Q_0^i \exp \left( -\frac{E_p}{RT} \right) \]

where \(Q_0^i\) is a constant, \(E_p\) is activation energy for permeation, \(R\) is universal gas constant, and \(T\) is absolute temperature.

The effect of temperature on the selectivity of membrane was explained by Sun and Ruckenstein [41] by considering two parallel effects of temperature on the membrane. One is increasing polymer chain mobility and facilitating the diffusion of both components. The other is weakening the interaction between benzene molecule and the membrane lowering the sorption of benzene.

In addition, the Cabasso group observed irregularities in the sorption behavior of AC/PPN membrane.
Table 7
Results on the separation of Bz/Chx mixtures by PV

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Benzene in feed (wt.%)</th>
<th>Temperature (°C)</th>
<th>Q1 (kg·m⁻²·h⁻¹)</th>
<th>α</th>
<th>Reference</th>
<th>Reference #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified CE</td>
<td>53</td>
<td>80</td>
<td>50.3</td>
<td>5.2</td>
<td>Martin</td>
<td>[60]</td>
</tr>
<tr>
<td>PP (oriented)</td>
<td>55</td>
<td>25</td>
<td>54.4</td>
<td>1.3</td>
<td>Kucharski</td>
<td>[46]</td>
</tr>
<tr>
<td>PP (double oriented)</td>
<td>55</td>
<td>25</td>
<td>64.6</td>
<td>2.4</td>
<td>Kucharski</td>
<td>[46]</td>
</tr>
<tr>
<td>LDPE</td>
<td>50</td>
<td>25</td>
<td>10.8</td>
<td>1.6</td>
<td>Huang</td>
<td>[33]</td>
</tr>
<tr>
<td>PVDF</td>
<td>53</td>
<td>60</td>
<td>1.6</td>
<td>6.2</td>
<td>McCandless</td>
<td>[61]</td>
</tr>
<tr>
<td>PVDF</td>
<td>53</td>
<td>56</td>
<td>1.5</td>
<td>5.4</td>
<td>McCandless</td>
<td>[47]</td>
</tr>
<tr>
<td>PE</td>
<td>10</td>
<td>35</td>
<td>30.0</td>
<td>2.5</td>
<td>Raubenhan</td>
<td>[62]</td>
</tr>
<tr>
<td>MA-g-HEMA</td>
<td>50</td>
<td>25</td>
<td>7.4</td>
<td>∞</td>
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<td>[49]</td>
</tr>
<tr>
<td>PMG</td>
<td>50</td>
<td>25</td>
<td>3</td>
<td>7</td>
<td>Suzuki</td>
<td>[42]</td>
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<tr>
<td>CA</td>
<td>50</td>
<td>77.8</td>
<td>0.34</td>
<td>19</td>
<td>Cabasso</td>
<td>[43]</td>
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<tr>
<td>CA/PPN</td>
<td>50</td>
<td>77.8</td>
<td>13.6</td>
<td>40</td>
<td>Cabasso</td>
<td>[43]</td>
</tr>
<tr>
<td>PEU (asymmetric)</td>
<td>50</td>
<td>30</td>
<td>1.5</td>
<td>3.8</td>
<td>Enneking</td>
<td>[63]</td>
</tr>
<tr>
<td>PSP/CA</td>
<td>55</td>
<td>78</td>
<td>0.8</td>
<td>13.3</td>
<td>Néel</td>
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<tr>
<td>CA/PE/MA</td>
<td>50</td>
<td>25</td>
<td>2.3</td>
<td>11.9</td>
<td>Park</td>
<td>[66]</td>
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<tr>
<td>BP–3MPD/EPD</td>
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<td>70</td>
<td>2.7</td>
<td>14</td>
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<tr>
<td>BP–3MPD/PD</td>
<td>50</td>
<td>70</td>
<td>0.4</td>
<td>27</td>
<td>Tanihara</td>
<td>[32]</td>
</tr>
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<td>BP–PEO</td>
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<td>25–70</td>
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<td>2.6</td>
<td>22.5</td>
<td>Ray</td>
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<td>0.057</td>
<td>4.5</td>
<td>Yoshikawa</td>
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<tr>
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<td>50</td>
<td>0.16</td>
<td>&gt;10³</td>
<td>Yoshikawa</td>
<td>[52]</td>
</tr>
<tr>
<td>DSDA–DDBT</td>
<td>60</td>
<td>78</td>
<td>0.93</td>
<td>32</td>
<td>Hao</td>
<td>[68]</td>
</tr>
<tr>
<td>DSDA–DDBT</td>
<td>60</td>
<td>78</td>
<td>2.4</td>
<td>20</td>
<td>Hao</td>
<td>[68]</td>
</tr>
<tr>
<td>PU–TEOS</td>
<td>50</td>
<td>50</td>
<td>0.65</td>
<td>19</td>
<td>Kusakabe</td>
<td>[54]</td>
</tr>
<tr>
<td>PGMA grafted</td>
<td>60</td>
<td>40–70</td>
<td>8.7</td>
<td>22</td>
<td>Wang</td>
<td>[38]</td>
</tr>
<tr>
<td>PS/PAA</td>
<td>50</td>
<td>20</td>
<td>48.4</td>
<td>9.6</td>
<td>Sun</td>
<td>[41]</td>
</tr>
<tr>
<td>PEMMA–EGDM</td>
<td>10</td>
<td>40</td>
<td>8.7</td>
<td>6.7</td>
<td>Inui</td>
<td>[34]</td>
</tr>
<tr>
<td>MMMA–EGDM</td>
<td>10</td>
<td>40</td>
<td>55.1</td>
<td>3.9</td>
<td>Inui</td>
<td>[34]</td>
</tr>
<tr>
<td>PVA (asymmetric)</td>
<td>25</td>
<td>50</td>
<td>0.002²b</td>
<td>10</td>
<td>Yamasaki</td>
<td>[39]</td>
</tr>
</tbody>
</table>

a 3MPD: 2,4,6-trimethyl-1,3-phenylenediamine; BP: 3,3’,4,4’-biphenyltetracarboxylic dianhydride; CA: cellulose acetate; CE: cellulose ester; DDBT: dimethyl-3,7-diaminobenzothiophene-5,5’-dioxide; DSDA: 3,3’,4,4’-diphenilsulfone tetracarboxylic dianhydride; EGDM: ethyleneglycol dimethacrylate; HPDE-g-MA: high density polyethylene graft methacrylate; LDPE: low density polyethylene; MA-g-HEMA: poly(methylacrylate) graft 2-hydroxyethyl methacrylate; PAA: polyalyl amine; PAS: polycrystalline polythiophene; PD: 1,3-phenylenediamine; PE: polyethylene; PEMA: polyethyl methacrylate; PEOD: polyethylenoxide; PEU: polyurethane; PGMA: polyglycidyl methacrylate; PMG: poly γ-methyl-α-glutamate; PMMA: polymethyl methacrylate; PP: propylene; PPOBrP: polybromophenylene oxime dimethylphosphonate ester; PVA: polyvinyl alcohol; PVDF: polyvinylidene fluoride; TEOS: tetraethylorthosilicate.

b Unit for asymmetric membrane flux is kg/m²·h.

[48], which was later confirmed by Acharya et al. [65] through PV experiments. Cabasso realized that rate of sorption of benzene depended on the thermal history of the membrane. That is, the sorption increased with decreasing temperature. Reversing the direction also reversed the sorption behavior. However, when the temperature started from low values and then increased, the sorption increased again, until the starting temperature of the first experiment was reached. At this point, reversing the temperature direction did not reverse the sorption behavior, but caused it to increase along the same curve as in the first experiment. Also, Acharya et al. [65] realized that flux was higher during cooling than when heating the feed within similar temperature limits. Their observations can be explained by the ‘temperature history effect’ proposed by Cabasso.

Permeability and selectivity of membranes are also functions of feed concentration [32,34,35,37,43,44,47,63,65,67,69]. Fig. 8 shows that permeability increases...
and selectivity decreases sharply, with increasing benzene content of the feed. The decline in the selectivity is explained by the plasticization effect of benzene on the membrane. With increasing benzene content, the membrane is swollen and the relaxed polymer chains allow for enhanced permeation of cyclohexane. As evidenced in Fig. 8, the permeability of cyclohexane was enhanced more profoundly compared to benzene when the benzene concentration of the feed increased.

6. Economy

Membrane processes have not been used in the industry for Bz/Chx separation yet. Therefore, not much economical evaluation and comparison with other separation technologies are available in the open literature. Acharya et al. [65] compared two membrane processes, namely, PV and perstraction to suggest that the earlier is advantageous because of smaller membrane area requirements.

Rautenbach and Albrecht [27,70] did a thorough economical comparison between a conventional extractive distillation process alone, a PV system alone, and a hybrid system consisting of the two processes. The hybrid system was designed to separate a 1:1 Bz/Chx mixture to 99.5 mol% benzene and 99.2 mol% cyclohexane. The extractive distillation used furfural as carrier in a two-stage distillation process. In the first stage, furfural was added to break the Bz/Chx azeotrope. The product from this stage was a cyclohexane rich stream and a mixture of benzene/furfural. The benzene impurity in the cyclohexane rich stream was removed using a PV system. Finally, The benzene/furfural mixture was distilled in the second stage to recover furfural and produce highly pure benzene.

The authors’ analyses indicated that a hybrid system is more economical than either of the two processes alone. That is especially true when high purity products are required. The cost of production using an extractive distillation process is mainly determined by the cost of heating steam (~58%), followed by the investment cost on the sieve tray column (~19%), and evaporator/heat exchanger (~14%). On the other hand, similar cost using a PV system is governed by the membrane replacement cost (~51%), followed
by steam (~17%) and cooling water (~15%). Also, the overall cost of production using a PV system is more than twice as much as that using an extractive distillation.

A comparison of the numbers given above show that the two processes complement each other in a hybrid system. The production cost using a hybrid system is 74.51 DM/t (10.55 DM/t for PV + 63.96 DM/t for distillation). Which is 20% less than that using an extractive distillation alone (93.65 DM/t). This saving comes from a reduced cost of membrane replacement on one hand, and reduced energy consumption compared to the conventional process on the other.

7. Final remarks

The attractiveness of PV systems in Bz/Chx separation is evidenced by the increasing number of papers appearing in the scientific journals on the subject. Many studies have proved the technical feasibility of PV processes in Bz/Chx separation. However, lack of a more recent economical evaluation can be felt in this field. Such study is an essential factor to encourage the industry to invest in researches focusing on the pilot plant and large scale studies of the process.

References


