유기물 분리용 투과증발막

(한국과학기술연구원)

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1. Introduction

(1) Liquid mixture separation in the chemical industry

In the chemical industry, in the pharmaceutical industry, and in a number of other industries separation processes are necessary to separate and purify products and raw materials [1,2]. Separation processes are also widely used in other applications such as in recycling valuable materials from waste streams.

Unit operations for separation processes can be classified in phase separation techniques and component separation techniques based on the nature of the feed mixtures to be separated. The former techniques are used for the separation of heterogeneous mixtures, in which the feed is already present in two or more separated phases on a micro-scale. The latter are suitable for the separation of homogeneous mixtures such as gaseous mixtures and mixtures of completely miscible liquids. In these cases the separation into individual components is generally achieved by utilizing the differences in physico-chemical properties of components, and is much more difficult compared to phase separation techniques. Separation processes such as distillation, evaporation, liquid-liquid extraction, and crystallization belong to this class.

For the separation of a homogeneous liquid mixture in the chemical industry, distillation is generally the preferred technique [3,4]. The basic principle in distillation is the difference in composition between a liquid phase and a vapor phase. The composition difference between two phases is due to differences in vapor pressures, or volatilities, of the components of the liquid mixture. In this process thermal energy is the driving force for separation. No additives are required here, which might cause a pollution problem of the final products or generate a need for an extra separation step to avoid this problem. The simplicity in operation is another advantage of this technique. However an adequate separation can not be performed by conventional distillation if the volatility differences are very small or do not exist at all. This is the case with close-boiling hydrocarbons, azeotropic mixtures, and various isomers. The separation of these mixtures is nowadays performed by other, generally energy-consuming, processes like extractive or azeotropic distillation and liquid-liquid extraction.

(2) Pervaporation as an alternative separation technique

The characteristic of distillation is the requirement of energy in the form of heat to accomplish a separation, and this can represent a significant cost factor. It is estimated that 40 % of the total energy consumed by the chemical processing industry is used in distillation operations. Especially since the Arab oil embargo in 1973, which caused a rapid increase in energy costs, there has been an emphasis on energy-efficient separation methods. Existing separation methods have been reviewed in terms of energy efficiency, and also there have been research efforts in developing new separation techniques with a low energy consumption. One outcome of this search is the membrane separation process. Membrane processes offer good prospects since the energy consumption is generally much lower compared to the conventional separation methods.

Pervaporation is a membrane process which can be used to separate liquid mixtures. In this process a semi-permeable membrane through which permeation occurs separates the pervaporation unit into two parts. At the upstream compartment the liquid mixture to be separated is brought into direct contact with the membrane. The permeated product is removed as a vapor phase at the other compartment by applying a low partial vapor pressure usually by means of vacuum or a carrier gas.

For the separation of liquid mixtures pervaporation can replace all distillation units in the chemical processing industries. But this option is not economically feasible for most applications. In pervaporation a part of the processed liquid mixture (the permeate) undergoes a phase change from liquid to vapor during transport through the membrane. Therefore the heat of vaporization of the permeate must be supplied. From this point of view pervaporation might not offer so much benefit over the conventional distillation techniques. However pervaporation is very attractive in removing minor components from liquid mixtures for purification or recovery purposes. This is definitely the case for the separation of azeotropic and close-boiling mixtures. Therefore the best utilization of pervaporation can be made by integrating this membrane process with distillation in a hybrid system, where pervaporation is used to replace energy-intensive separation techniques such as azeotropic distillation and liquid-liquid extraction.

Until now a number of studies have been reported to integrate pervaporation with distillation, particularly for the dehydration of organic solvents. In such cases the comparison of production cost has been performed to illustrate the advantage of the pervaporation process. Recently, for example, Pearce has carried out a study to compare the cost of production of 99 and 99.9 wt.% ethanol by distillation starting from a 50 wt.% ethanol feed mixture with water [5]. The separation costs were evaluated for two procedures: conventional distillation technology and distillation combined with pervaporation by using a composite membrane produced by Kalsep, UK. In the former case the normal distillation was used to produce the azeotrope, which was subsequently broken with a benzene entrainer. In the latter case the feed was dehydrated to an optimum sub-azeotropic composition of 92.6 wt.% ethanol by distillation. This product was then further dehydrated by pervaporation to 99 or 99.9 wt.% ethanol. From his study it was concluded that a hybrid system combining

distillation with pervaporation could reduce the overall production cost for 99 wt.% ethanol by more than 30 %, with energy savings of 60 %. In the production of 99.9 wt.% ethanol the production cost could be reduced by 10 %. Besides the above mentioned example, there have been many other studies comparing the production cost of organic solvents [6-9]. All the cost comparisons have shown that pervaporation is far more economical than the conventional separation techniques in removing the last small amounts of water from the organic solvents. Thus pervaporation is nowadays accepted as a unit operation in the chemical industry for this application: the dehydration of organic solvents.

(3) Liquid mixture separation by pervaporation

The pervaporation process is a potential option for the separation of liquid mixtures. In principle this process can be applied to separate all kinds of organic liquid mixtures in the chemical industry. It can also be used in other areas such as the concentration of heat-sensitive products in the pharmaceutical and food industries and the removal of volatile organic contaminants from waste water. Such possible applications can be classified as intermediates in between aqueous and non-aqueous mixtures. The former category includes liquid mixtures containing water as one component, while the latter refers to organic-organic mixtures.

The pervaporation application in the separation of aqueous mixtures can be represented by the dehydration of organic solvents [10-13]. A well-known example is the dehydration of ethyl alcohol. The aqueous solution of ethanol has satisfied human needs for a beverage for thousands of years. It also has been used as solvent and medicine. In addition, there is an increasing interest in anhydrous ethanol as motor fuel produced by fermentation of biomass. Distillation techniques are widely used to concentrate the fermentation ethanol. In order to obtain anhydrous ethanol, an additional separation step is necessary because of an azeotropic composition at 4.43 wt.% water at 760 mmHg. Azeotropic or extractive distillation are generally used for this purpose. However the high energy consumption and operational complexity of these processes make pervaporation optional as an alternative. In this case pervaporation can be used to break the azeotrope and to remove the last part of the water presence in ethanol. During the last two decades this area has been studied intensively. As a result pervaporation is now applied for the dehydration of organic solvents on technical scales with capacities of up to 120,000 l of 99.8 % ethanol/day [12,13].

Besides the dehydration purpose, pervaporation can also be used to remove organic solvents from their dilute aqueous solutions [14,15]. Alcohols can be removed from fermentation broths, and traces of volatile organic contaminants can be removed from waste water. The pervaporation application in this area is expected to reach the commercial stage in the near future.

In the chemical and petro-chemical industries the separation of organic-organic mixtures is a major separation problem. In measures of bulk quantity it is much

more important than the aqueous systems. In the early 1960s when systematic studies on pervaporation were started, the separation of non-aqueous liquid mixtures was a major target to solve. Binning and his colleagues carried out a series of investigations for the separation of hydrocarbon mixtures [16-18]. Since then a number of studies have been reported in this area. Despite these research efforts the commercial application of pervaporation for the separation of organic-organic mixtures is still in an embryonic stage. This is mainly due to the fact that membranes developed for this purpose have shown rather unsatisfactory results. Also the lack of membrane modules which can withstand the relatively severe conditions required for this separation is hindering the commercial application of pervaporation in this sector.

In recent years, however, the pervaporation process for this separation area is actively studied. This is partially encouraged by the successful application of pervaporation in dehydrating organic solvents. Separation problems related to newly emerging processes in the chemical industry, recycling of organics, and more severe restrictions on environmental protection are also stimulating the use of pervaporation. If problems associated with membrane and module stability can be solved, the organic-organic mixture separation by pervaporation will be a major membrane application around the year 2000 [19].

2. Potential of Pervaporation Process

i) Distillation : limited by Vapor-Liquid Equilibrium (VLE)
ii) Pervaporation : not limited by VLE
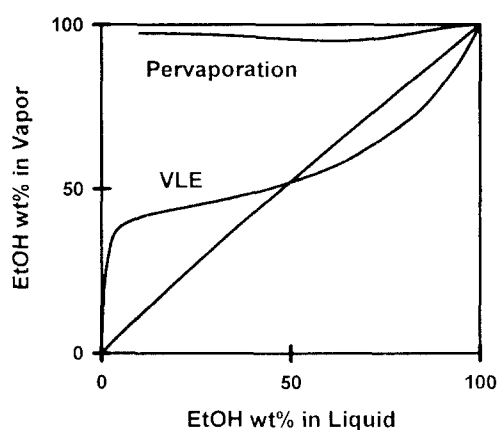only dependent on membrane property

Fig. Distillation and pervaporation characteristics for an ethanol-toluene mixture at 30°C. (Pervaporation carried out through a PAA-PVA (10 wt.% PVA) blend membrane)

3. Pervaporation of Liquid Mixtures

(1) Separation of Aqueous Mixtures

- dehydration of organic solvents
  ethanol (120,000 L of 99.8% ethanol/day), propanol, etc.
  anhydrous acetic acid
  * dehydration of gases (air, etc.)
- removal of organic solvents from aqueous solutions
  alcohols from fermentation broth
  volatile organic contaminants from water
  * organic vapors from gas streams

(2) Separation of Organic-Organic Mixtures

- separation of polar/non-polar solvent mixtures
  methanol/toluene, methanol/benzene
  methanol/methyl acetate, methanol/methyl acrylate
  methanol/methyl t-butyl ether
- separation of aromatic/aliphatic hydrocarbon mixtures
  benzene/cyclohexane, toluene/heptane
- separation of aliphatic hydrocarbons
  - steric effect :   chain length & cross-sectional area (branch, cyclic)
  - olefin/paraffin: ethylene/ethane, propylene/propane, etc.
- separation of aromatic isomers
  o-, m-, p-xylene mixtures, styrene/ethyl benzene

4. Energy Consumption in Distillation

40 % of total energy consumed by chemical processing industry
(2 quads (2 * 10^5 Btu) / year)
(* F.E. Rush, Jr., "Energy Saving Alternatives to Distillation", Chem. Eng. Progress (1980))

5. 10 Most Energy-Intensive Distillations in U.S. Industry

Separation	Energy Consumptions 1981 (quads/year)
Crude Oil	0.32
Intermediate Hydrocarbon Liquids	0.29
Light Hydrocarbons	0.22
Vacuum Oil	0.08
Sour Water	0.024
Ammonia/Water	0.023
Styrene/Ethylene Benzene	0. 0115
Ethylene Glycol/Water	0. 0109
Methanol/Water	0. 0107
Oxygen/Nitrogen	0. 0103

* J.L. Bravo et al., "Assessment of Potential Energy Savings in Fluid Separation Technologies: Technology Review and Recommended Research Area", DOE Report # DOE/I.D/12473, 1 (1984)

6. Distillation

   (a) Separation based on the volatility difference
   (b) Azeotropic or close boiling mixtures
       High pressure distillation
       Vacuum distillation
       Catalytic distillation
   (c) Entrainer ➜ additional separation step

7. Pervaporation

   (a) Separation Factor :   evaporation separation factor
                              membrane separation factor
   (b) Removal of more volatile components
   (c) Pervaporation / Distillation Hybrid Process :   best economics

   * separation of temperature sensitive mixtures

8. Pervaporation/Distillation Hybrid

 • breaking azeotropes
 • removing a single-component, high-purity side stream from
   a multicomponent distillation stream

9. Potential Configurations for Pervaporation/Distillation Hybrid Processes

 (a) Break an azeotrope that is concentrated in one component (>90%)
 (b) Break binary azeotropes that contain appreciable concentrations of
       both components (20:80 to 80:20)
 (c) Unload a distillation column
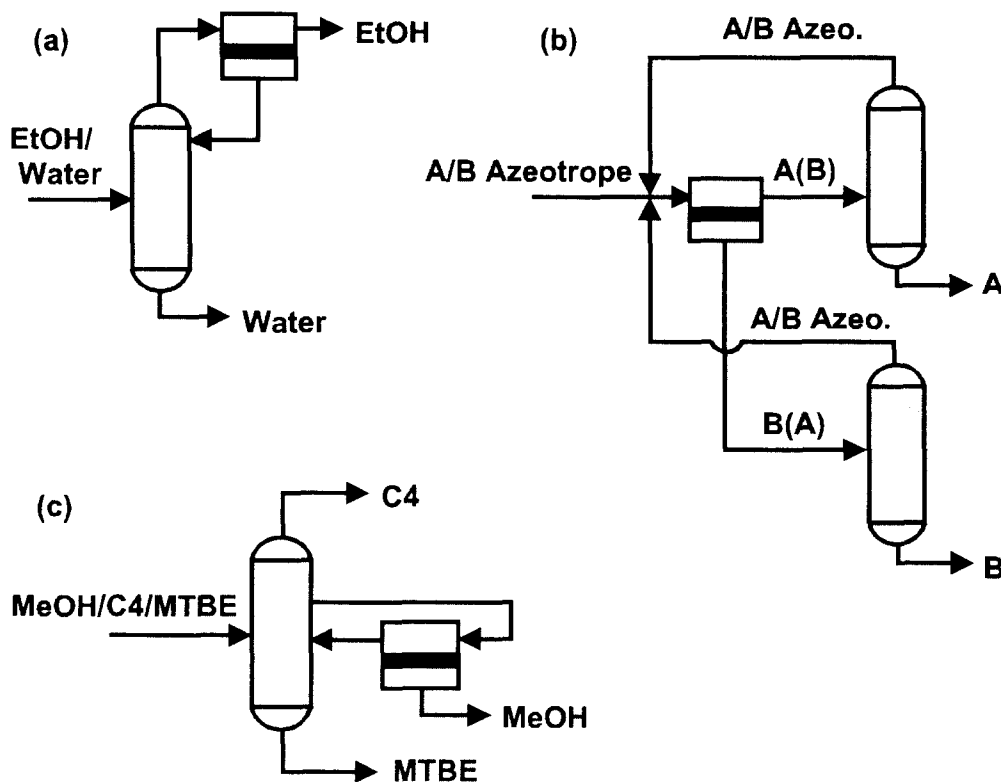
10. 10 Prime Energy-Saving Candidates by Hybrid Membrane Systems

| System	Potential Energy Saving (trillion Btu per year)
Propane/propylene separation	13
Natural gas dehydration	10-12
Deasphalting of oil	10
Ethane/ethylene separation	6
Sour-water stripping	6
Inorganic acid dehydration	5
Acetic acid dehydration	3
Ammonia manufacture	2
Methyl t-butyl ether manufacture	1-2
Urea manufacture	1-2

*D.E. Gottschlich, D.L. Roberts (SRI International), "Energy Minimization of
Separation Processes Using Conventional/Membrane Hybrid Systems", DOE Report
DE91-004710, Sep. 28, 1990.*

11. TRIM process (Total Recovery Improvement for MTBE)

Separex (Cellulose Acetate Membrane)
    (Air Products & chemicals Inc. ➔ Hoechst Celanese Corporation)
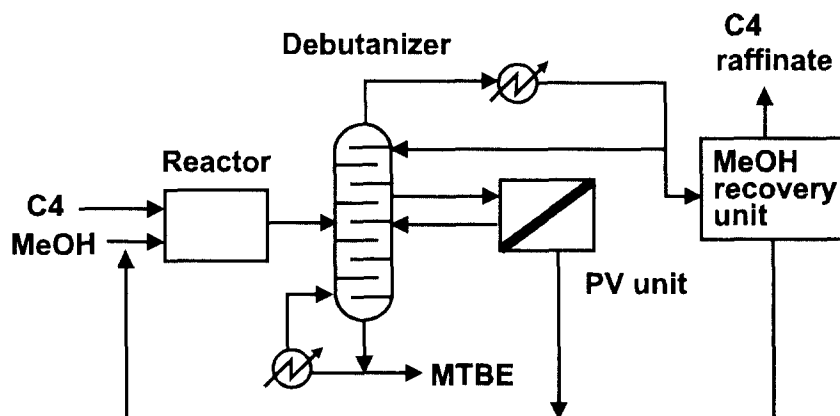
(a) Pervaporation process before debutanizer

    retrofitting plants being installed
    pay-back period of 18 month or less
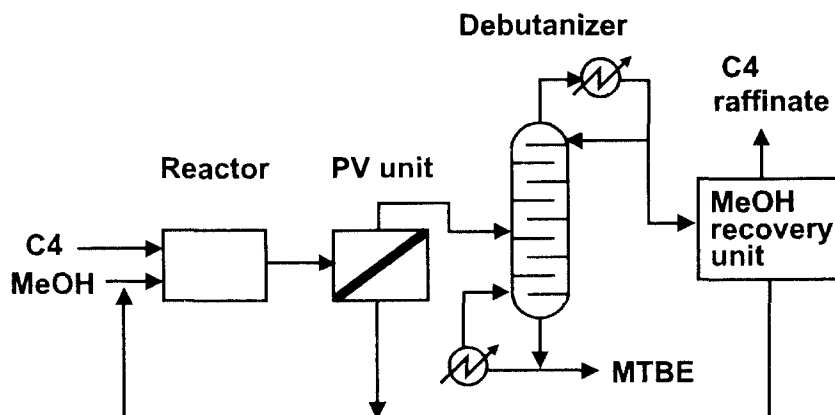
(b) Pervaporation on debutanizer sidedraw

high concentration of MeOH
better productivity of pervaporation unit

12. Cost Comparison for DMC/MeOH Azeotrope Separation

	High pressure distillation	Hybrid pervap./distil.
Capital cost x 10⁻⁶, $	1.5	1.0

Annual Utility Requirement		
1. Steam x 10⁻⁶, kg		
a) Membrane Unit (138 kPa)	---	1.1
b) Distillation column		
(1) 1.38 MPa	---	2.9
(2) 4.14 MPa	14	---
2. Electricity x 10⁻⁹, kJ for refrigeration	---	1.1
3. Cooling water x 10⁻⁶, m³	0.3	0.1
Utility cost x 10⁻⁶, $	0.171	0.045

* V.M. Shah, C.R. Bartels, "Engineering considerations in pervaporation application",
Proc. 5th Int. Conf. On Pervap. Processes in Chem. Ind., R. Bakish Ed., Bakish Material
Corp., Englewood, NJ, 1989; pp.321-331

13. Propylene/Propane Separation

- ● 95% purity propylene :   Pervaporation process
- ● 99.5% purity propylene :   Pervap./Distillation hybrid process

D.E. Gottschlich, D.L. Roberts, "Energy Minimization of Separation Processes Using Conventional/Membrane Hybrid Systems", DOE Report #DOE/ID-10301 (1990)

14. Development of Membrane materials

(a) Commercially available polymers and polymer films

(b) New Materials

- synthesis of new polymers
    - • polymerization and copolymerization
    - • radiation grafting
    - • plasma grafting
    - • new monomer
- modification of existing polymers
    - • introduction of specific groups
    - • polymer bulk
    - • surface of a polymer membrane
- polymer blending
    - • a range of materials with properties in between or completely different from homo-polymers
    - • low development costs

15. Survey of pervaporation research in organic/organic separation

The separation of organic-organic mixtures is potentially a major application area of pervaporation in the chemical processing industries. The number of possible applications is very large. It may be roughly classified as follows:

- * separation of polar/non-polar solvent mixtures
- * separation of aromatic/aliphatic mixtures
- * separation of aliphatic hydrocarbons
- * separation of aromatic isomers

The research which is carried out until now is surveyed and discussed following the classification given above.

(1) Separation of polar/non-polar solvent mixtures

Interactions between polymeric membranes and penetrants play an important role in liquid separation. If there is a large difference in chemical nature between mixture components, a satisfactory separation will be obtained by using polymer membranes which interact preferentially with one of the mixture components. This is the case with polar/non-polar solvent mixtures. This type of mixture was intensively studied by Aptel et al. by using poly(tetrafluoro ethylene) membranes grafted with Lewis base groups: poly(N-vinyl pyrrolidone) [20-22] and poly(4-vinyl pyridine) [20,23] (table 1). Because a Lewis base is a proton-acceptor, the membranes can possess nucleophilic groups. It implies that these membranes can preferentially interact with electrophilic molecules such as alcohols, but not with non-polar hydrocarbons. With these membranes a number of liquid mixtures have been tested for pervaporation. The component of a mixture which is able to form hydrogen bonds with the polymer showed a higher permeation rate than the other component.

Table 1. Pervaporation through poly(tetrafluoro ethylene) (PTFE) membranes grafted with Lewis base.

Membrane	Liquid mixture
PTFE grafted with poly(N-vinyl pyrrolidone) [20-22]	methanol/benzene, methanol/acetone, methanol/methyl acetate, methanol/ethyl acetate, methanol/methyl acrylate,
	ethanol/hexane, ethanol/cyclohexane, ethanol/benzene, ethanol/toluene, ethanol/chloroform, ethanol/1,2-dichloroethane, ethanol/ethyl acetate, ethanol/ethyl acrylate, ethanol/triethylamine,
	propanol/cyclohexane, propanol/benzene, propanol/diethyl ketone, iso-propanol/cyclohexane, iso-propanol/ethyl acetate,
	butanol/cyclohexane, butanol/pyridine,
	acetic acid/1,2-dichloroethane, acetic acid/dioxane, acetic acid/pyridine, acetic acid/N,N-dimethyl formamide, formic acid/pyridine, propionic acid/pyridine,
	chloroform/pentane, chloroform/hexane, chloroform/cyclohexane, chloroform/benzene, chloroform/acetone, chloroform/methyl ethyl ketone
PTFE grafted with poly(4-vinyl pyridine) [20, 23]	chloroform/pentane, chloroform/hexane, chloroform/cyclohexane, chloroform/ethyl ether

Table 2. Pervaporation of polar/non-polar solvent mixtures.

Liquid mixture	Membrane material

methanol/aliphatic hydrocarbon
    poly(vinyl alcohol) [24, 25]; poly(phenylene oxide) [26]; Nafion* [24, 26];
    polyether sulphone [24]; blend of poly(acrylic acid) with Nylon 6 [24, 27];
    alloy of phosphonate polymer with cellulose acetate [26];
methanol/aromatic hydrocarbon
    cellulose triacetate [16]; polyethylene [16, 28, 29]; polypropylene [29];
    Nitrile rubber [30]; perfluorosulfonic acid [31]
methanol/methyl tert-butyl ether
    cellulose acetate [32, 33]; Nafion [24, 34]; poly(vinyl alcohol) [34];
    cellulose base material MT [24]
methanol/dimethyl carbonate
    Nafion [34]; poly(vinyl alcohol) [34, 35]
ethanol/aliphatic hydrocarbon
    poly(vinyl alcohol) [25]; cellulose acetate [36, 37]; cellophane [37, 41];
    perfluorosulfonic acid [31]; poly(hexamethylene adipamide) [36];
    polyethylene, polypropylene, and rubber hydrochloride [37];
    polyester, natural rubber, ethylene-vinyl acetate copolymer,
    ethyl acrylate-chloroethylvinyl ether copolymer,
    and natural rubber-methyl methacrylate graft copolymer [38]
ethanol/aromatic hydrocarbon
    polyethylene [39]; polyphenylquinoxaline [40];
    perfluorosulfonic acid [31]; natural rubber and polyester [38];
iso-propanol/hydrocarbon
    poly(vinyl alcohol) [25]; perfluorosulfonic acid [31];
    polyethylene [28, 42]; polypropylene [43]
butanol/toluene
    polypropylene [44]
aromatic alcohol/benzene
    polyethylene and modified polyethylene [45]
acetic acid/aromatic hydrocarbon
    polypropylene [43]
acetone/hexane
    polyethylene, polypropylene, poly(vinyl chloride), cellophane,
    and vinylidene chloride-vinyl chloride copolymer [37]
aniline/benzene
    polyethylene and modified polyethylene [45]

* Nafion: copolymer of polysulfonyl fluoride vinyl ether and poly(tetrafluoro ethylene)

The best separation was obtained for the azeotropic mixtures of alcohols with aliphatic hydrocarbons; for instance, a selectivity value of 24 for the azeotrope of propanol and cyclohexane. And relatively good selectivities were observed for the chloroform/hydrocarbon systems. In contrast, the azeotropic mixtures of the type alcohol/ester, alcohol/ketone, and carboxylic acid/pyridine showed a poor

separation performance. This may be due to the hydrogen bonding ability between the components of these mixtures. Moreover it appeared that the weak interaction force between the hydroxyl functionality of an aliphatic alcohol with the * electrons of an aromatic ring was sufficient to hinder the efficiency of separation of aliphatic alcohol/aromatic hydrocarbon mixtures by these grafted membranes.

Besides the above mentioned studies, a number of investigations have been reported which were mainly applied to the pervaporation of mixtures of aliphatic alcohols with hydrocarbons (table 2). From these investigations it was observed that generally polar molecules permeated faster through polar membranes than non-polar molecules, and vice versa. Polar polymers such as poly(vinyl alcohol), Nafion, and cellulose acetate were found to be selectively permeable for alcohols over hydrocarbons. But aliphatic and aromatic hydrocarbons always permeated preferentially through polyethylene, polypropylene and natural rubber with respect to alcohols.

(2) Separation of aromatic/aliphatic mixtures

The mixture of benzene with cyclohexane is a representative of this class of liquid mixtures. The difference in boiling points between benzene and cyclohexane is only 0.6 °C. The vapor liquid equilibrium curve of this mixture shows the typical feature of close-boiling mixture system. Furthermore they form an azeotrope at 52.2 wt.% benzene. This means that it is very difficult to separate by conventional separation techniques such as distillation. Therefore much attention has been given to the separation by pervaporation (table 3).

Commercially available polymers were first tested as membrane materials, and new polymers were carefully designed and tested for this separation problem. For all membranes reported in published works, benzene permeated preferentially over cyclohexane, but to a different extent. For a 1/1 by wt mixture, high fluxes were obtained by using polyethylene and polypropylene, but selectivities were very low, less than 2. On the other hand, polar membranes such as cellulose acetate and cellulose acetate butyrate showed higher selectivities although fluxes were much lower than in the case of polyethylene and polypropylene. Some new polymeric materials were finely designed for the separation of this mixture. These include graft copolymer of methacrylate with 2-hydroxyethyl methacrylate, copolymer of 2-hydroxy-3-(diethylamine) propyl methacrylate with styrene, and alloys of phosphonate and phosphate polymers with cellulose acetate. These new membranes showed a large enhancement both in permeation rate and selectivity.

Because of the very similar physical properties of benzene and cyclohexane, a low selectivity was obtained through chemically inert membranes such as polyethylene and polypropylene. However both components exhibit different chemical properties. Benzene, the principal representative of aromatic hydrocarbons, has * electrons which to a certain extent endows benzene with hydrogen bonding ability and polarity. However cyclohexane is totally non-polar. Therefore higher separation factors could be achieved through polar polymer membranes than through non-polar ones. Furthermore specific membranes could be designed based

on the difference in properties like the one mentioned.

Pervaporation was also investigated for the separation of other aromatic/aliphatic hydrocarbon mixtures (table 3). In all cases reported the aromatic hydrocarbon permeated faster than the aliphatic hydrocarbon, but low selectivities were obtained.

Table 3. Pervaporation of aromatic/aliphatic liquid mixtures.

Liquid mixture	Membrane material
benzene/ cyclohexane	polyethylene [29, 46-48]; polypropylene [29, 43, 48, 49]; Neoprene rubber [30]; polyphenylquinoxaline [40]; cellulose ester and ether [25]; cellulose acetate [26]; cellulose acetate butyrate and modified cellulose acetate butyrate [18, 50]; poly(γ-methyl L-glutamate) [51]; poly(bis(2,2,2-trifluoroethoxy)phosphazene) [52]; modified poly(vinylidene fluoride) [53, 54]; graft copolymer of methacrylate and 2-hydroxyethyl methacrylate [55]; ethylene-carboxylic acid copolymer [48]; copolymer of 2-hydroxy-3-(diethylamine)propyl methacrylate with styrene [56]; alloys of phosphonate and phosphate polymers with cellulose acetate [26, 57-59]
benzene/ other paraffins	NBR and SBR [62]; polyethylene [43, 47, 60, 61]; polyethylene grafted with polystyrene [61]; cellulose acetate butyrate [63]; Membrane F XII [25]; ethylene-carboxylic acid copolymer [48]
benzene/olefins	alloy of phosphonate polymer with cellulose acetate [58]
toluene/paraffins	Neoprene rubber [30]; polyethylene [61, 64, 65]; polyethylene grafted with polystyrene [61]; polyurethane [67]; modified poly(vinylidene fluoride) [53]; cellulose acetate butyrate [63, 66]; cellulose ester and ether [25]; ethyl cellulose [66]; modified ethyl cellulose [18]
ethyl benzene/ ethyl cyclohexane	modified poly(vinylidene fluoride) [53]

(3) Separation of aliphatic hydrocarbons

This type of mixture consists of molecules being very similar in chemical nature. For instance, in the case of a hexane/heptane mixture there is no apparent difference in the nature and strength of interactions between a membrane and individual permeants. Therefore permselectivity is largely governed by the steric effects of permeants: diffusional cross section and molecular length. A survey of pervaporation studies for this class of liquid mixtures is given in table 4.

In the pervaporation of the binary mixtures of paraffins, the component with the smaller molecular weight permeates faster than the other one because of a smaller diffusional cross section. In the case of methyl cyclohexane/iso-octane mixture, however, methyl cyclohexane permeates preferentially although it has a larger diffusional cross section. This discrepancy may be caused by the abnormally long

Table 4. Pervaporation of mixtures of aliphatic hydrocarbons.

Membrane material	Liquid mixture
polyethylene	hexane/heptane [39, 68]; hexane/octane [43]; hexane/neohexane [47]; cyclohexane/heptane [64]; cyclohexane/neohexane [47]; heptane/iso-octane [69]
polypropylene	heptane/iso-octane [69]
cellulose acetate butyrate [63]	3-methyl pentane/2,3-dimethyl pentane, heptane/iso-octane, methyl cyclohexane/iso-octane, 1-hexene/hexane, 2-heptene/heptane, cyclohexene/cyclohexane
ethyl cellulose and modified ethyl cellulose	heptane/iso-octane [18, 70]; methyl cyclohexane/iso-octane [18]
cellulose ester and ether [25]	hexane/iso-octane, hexene/hexane
alloy of phosphonate polymer with cellulose acetate [26]	cyclohexene/cyclohexane
P(AA-St)* [56]	cyclohexene/cyclohexane
NBR [71, 72]	1,3-butadiene/iso-butene
aromatic polyimide [73]	1,3-butadiene/trans-2-butene

* P(AA-St): copolymer of 2-hydroxy-3-(diethylamine)propyl methacrylate with styrene

molecular length of iso-octane compared with cyclohexane. This suggests that diffusion occurs by a snake-like motion preferentially along the direction of the greatest length of permeating molecule.

In the binary mixtures of olefins with paraffins, however, there is a relatively large difference in chemical nature of both components. Therefore good separation results may be expected if there is any specifically designed membrane material. This had been proved by copolymerizing 2-hydroxy-3-(diethylamine)propyl methacrylate with styrene. This copolymer was highly selective for olefins over paraffins. For instance, a complete rejection of cyclohexane was observed in the pervaporation of cyclohexene/cyclohexane mixture.

(4) Separation of aromatic isomers

This class of mixtures is one of the most difficult to separate. The industrial separation of C8-aromatics (o-xylene, m-xylene, p-xylene and ethyl benzene) is now performed by super-fractionation, fractional crystallization, adsorption, or a combination of these methods. These processes are very complex and, in general, energy intensive. Therefore this mixture system has been considered as one of the most interesting mixtures for which the pervaporation process could be applied, and many investigations have been reported (table 5 and 6).

Pervaporation separation through commercially available polymeric films and polymers was first carried out, and new polymers such as polymer alloys were synthesized and tested. As was expected, the separation was very poor because of very similar size, shape and chemical nature of the aromatic isomers. Although xylene isomers have almost the same molecular volume, all tested membranes showed the order of selective permeation of p-xylene > m-xylene > o-xylene. This is

Table 5. Pervaporation of aromatic C8 isomers through commercial polymer films [74].

Liquid mixture:	p-xylene/o-xylene, p-xylene/m-xylene, p-xylene/ethyl benzene
Membrane:	Polyethylene, 125A101, DuPont
	Polypropylene, Clysar* 350P-1A3, DuPont
	Saran Wrap*, Dow
	Teflon* FEP, 200A, DuPont
	Polyimide, Kapton*, 100H, DuPont
	Poly(vinyl fluoride), Tedlar*, 100AG30UT, DuPont
	Parylene C and N, Union Carbide
	Cellulose acetate, 100CA-43, DuPont
	Nylon, Allied Chemical, Capron* 77C
	Poly(vinylidene fluoride), Kynar*, Pennwalt

consistent with the order of decreasing diffusional cross-section area of these isomers [75]. However polymers containing specific functional groups showed a different order of permeation rate. The order of permeation rate of m-xylene > o-xylene > p-xylene was observed through membranes prepared from a copolymer of 2-hydroxyethyl acrylate with 2-hydroxyethyl methacrylate modified by 3,4- or 3,5-dinitrobenzoyl chloride.

Table 6. Pervaporation of aromatic isomers.

Liquid mixture	Membrane
C8-isomers*	polyethylene [75, 76]; cellulose tripropionate and cellulose acetate butyrate [77]; Methocel HG* [80]; modified poly(vinylidene fluoride) [78]; P(HEA-HEMA)* and modified P(HEA-HEMA) [79];
dichlorobenzene isomers	Methocel HG* [80]
nitrochlorobenzene isomers	Methocel HG* [80]
nitrotoluene isomers	Methocel HG* [80]
benzene/toluene	poly(ethylene terephthalate) [81]
toluene/o-xylene	Nitrile rubber [30]
styrene/ethyl benzene	ethylene-carboxylic acid copolymer [48]; alloy of phosphonate polymer with cellulose acetate, poly(phenylene oxide), and Nafion [26]

* binary or ternary mixtures of o-, m-, and p-xylene and ethyl benzene
* hydroxypropylmetyl cellulose membranes containing Schardinger cyclodextrin
* copolymer of 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate

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