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Pervaporation-Based Separation of Methanol/MTBE Mixtures—A Review

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Abstract: Separation of Methanol (MeOH) and Methyl-*tert*-butyl ether (MTBE) is one of the most challenging processes in the chemical industry. Membrane based pervaporation is an attractive alternative to separate azeotropic and close-boiling mixtures like Methanol-MTBE. Conventional process, such as distillation, on the other hand, although feasible and in use in many industries, is accompanied by high capital and operating costs thereby rendering the separation process complex. Pervaporation (PV) is a viable alternative to azeotropic distillation both from economical and technical viewpoints. As a clean technology, this membrane separation process has provided solutions to several environmental problems. While PV-based hybrid processes have attracted industrial attention, progresses in PV separation of MeOH/MTBE suggest that this technique can handle a greater share for this particular separation. In this paper, an extensive review on the properties, production, as well as separation processes utilised for methanol/MTBE system is presented. The performance of different PV membranes applied for this separation is highlighted and emphasis on prospective membrane materials for the future is laid.

Keywords: Pervaporation, Methanol-MTBE mixtures, hybrid process

INTRODUCTION

Purely organic mixtures, such as azeotropes or isomers, have traditionally been separated mainly by distillation, extraction and adsorption processes

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that involve high capital investment and energy consumption. Recently, much attention has been paid to pervaporation (PV) process (1, 2) to separate organic mixtures because of its high separation efficiency towards close boiling and azeotropic mixtures.

The petrochemical industry has encountered lead additives in petrol as a major source of air pollution. To reduce air pollution from automobiles, it is recommended to use lead-free or low leaded gasoline. In response to the phase out of leaded components in petrol, alternative sources of octane boosters have gained due economic importance during the last couple of decades. Various oxygenated compounds like alcohols and ethers have proven to be suitable octane enhancers (3). Therefore, several fuel additives are being added to maintain an adequate octane value of gasoline. Methyl-*t*-butyl ether (MTBE), an oxygen-containing chemical is one such fuel additive mainly employed as an octane enhancer besides finding application as a reagent in fine chemical production (4).

MTBE is produced by a reaction of methanol (MeOH) with isobutylene, with excess methanol being used for higher yield. The use of excess methanol, however, causes a purification problem because methanol forms an azeotrope with MTBE at a composition of 14.3 wt% methanol (5). Separation of methanol and MTBE is difficult to achieve by conventional distillation because these components form close boiling mixtures (at different compositions in addition to the azeotrope). One promising alternative technology to distillation is the membrane based PV technique.

Pervaporation is the selective evaporation of one component of a liquid mixture through a non-porous membrane, which is in direct contact with the liquid mixture. Due to this, a much more energy efficient process can be obtained compared to distillation, wherein all components are evaporated. Moreover, separation of azeotropic mixtures takes place in one step because 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 (6). Thus, the (partial) replacement of distillation with pervaporation or a hybrid process combining the two will have important benefits with respect to energy consumption, yield, and product quality (7).

The goal of this review is to provide a concise information on the techniques involved in separating this type of organic mixtures. This review covers the properties of the two components, and their production techniques. A considerable amount of information pertinent to the applicability of distillation, pervaporation and the hybrid process involving both PV and distillation in separating MeOH/MTBE mixtures is provided. The types of various membrane materials used and the influence of operating parameters on the separation performance are also dealt with.

PROPERTIES OF METHANOL AND METHYL-*t*-BUTYL ETHER (MTBE)

Methanol (methyl alcohol) with the chemical formula CH_3OH, is produced from the distillation of wood and is a clear, colorless, volatile liquid with a weak odor that is somewhat sweeter than ethanol. Methanol (MeOH) is a clean burning alcohol fuel, containing no sulfur or nitrogenous materials. Methanol biodegrades easily in water and soil and is widely distributed both globally and regionally as a commercial product. Its chemical structure is shown in Figure 1 and the representative physical properties are given in Table 1 (9–12). It is non-corrosive to most metals at ambient temperatures; exceptions include lead, magnesium and platinum. Methanol being a liquid at normal conditions, can be handled much the same way as conventional fuels like gasoline or diesel. Methanol is also the starting material to produce an ether, Methyl-*t*-Butyl Ether (MTBE), which is blended with gasoline to enhance octane and to create oxygenated gasoline. Methanol forms azeotropic mixtures with a fairly large number of organic components, for example, aliphatic and aromatic hydrocarbons, ketones, ethers and esters (Ethyl acetate, dimethylcarbonate, methylmethacrylate) (Table 2) (9, 13). In contrast to aqueous–organic azeotropes, non azeotropes of methanol also exist (Table 3).

MTBE is a chemical compound that is manufactured by the chemical reaction of methanol and isobutylene. At room temperature, MTBE is a volatile, flammable and colorless liquid that dissolves partially in water. Table 4 gives the physical properties and the chemical structure is shown in Figure 1 (10). MTBE is produced in very large quantities and is almost exclusively used as a fuel additive in motor gasoline. It is one of a group of chemicals commonly known as "oxygenates" because they raise the oxygen

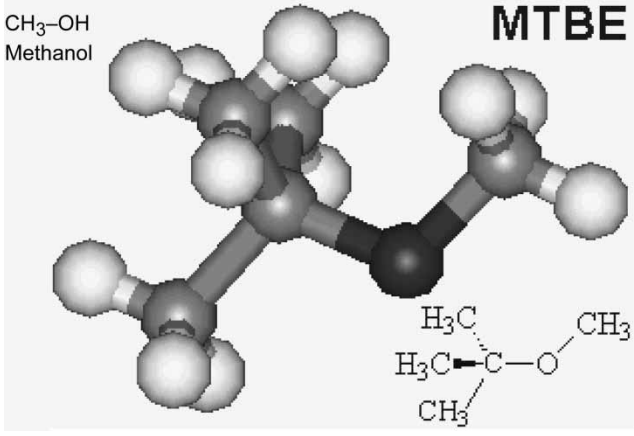

Figure 1. Chemical structures of Methanol and Methyl-*t*-Butyl Ether.

Table 1. Physical properties of pure methanol (9–12)

Molecular weight	32.04 g mol^{-1}
Critical temperature	512.5 K (239°C; 463°F)
Critical pressure	8.084 Mpa (78.5 atm)
Critical density	0.2715 gcm^{-3}
Specific gravity	
Liquid	
(25°/4°C)	0.7866
(20°/4°C)	0.7915
(15°/4°C)	0.796
Vapour	1.11
Vapour pressure	
20°C (68°F)	12.8 kPa (1.856 psia) (96 mmHg)
25°C (77°F)	16.96 kPa (2.459 psia) (127.2 mmHg)
Boiling Point @760 mmHg (101.3 kPa)	64.6°C (148.3°F)
Freezing point	−97.6°C (−143.7°F)
Reid vapour pressure	32 kPa
Refractive index	
15°C (59°F)	1.33066
20°C (68°F)	1.32840
25°C (77°F)	1.32652

content of gasoline (14, 15) and helps gasoline burn more completely, thereby reducing harmful tailpipe emissions from motor vehicles. In one respect, the oxygen dilutes or displaces gasoline components such as aromatics (e.g., benzene) and sulfur. In another, oxygen optimizes the oxidation during combustion.

When compared to alcohols, MTBE offers low water solubility, low reactivity and low volatility—characteristics that enable refiners to avoid the handling problems associated with alcohol oxygenates. So most refiners have confined their choice to use MTBE over other oxygenates primarily for its blending characteristics and for economic reasons. In terms of solubility parameters of two components, methanol is rather polar while MTBE is a much non-polar component, attributed by the difference in dispersive (δ_d), hydrogen (δ_h), and polar (δ_p) contributions to the overall solubility parameter (16).

APPLICATIONS OF METHANOL AND MTBE

The primary uses for methanol are the production of chemical products and use as a fuel. Roughly three-quarters of all methanol is used in the production of formaldehyde, acetic acid and a variety of other chemical intermediates which form the foundation of a large number of secondary derivatives (17). These secondary derivatives are used in the manufacture of a wide range of products including plywood, particleboard, foams, resins, and plastics. The

Table 2. Some binary azeotropes of methanol (9, 13)

Component	Pure boiling point of component (°C at 760 mmHg)	Constant boiling point of mixture (°C at 760 mmHg)	Methanol content of azeotrope (wt%)
Acetonitrile	81.6	63.45	19
Acrylonitrile	77.3	61.4	61.3
Acetone	56.15	55.5	12
Benzene	80.1	57.5	39.1
Butyl Methyl Ether	71	56.3	35.4
2-Butanone	79.6	64.5	70
CCl_4	76.8	55.7	20.7
Chloroform	61.2	53.5	12.5
Cyclohexane	80	54	38
Cyclohexene	82.75	55.9	40
Cyclopentane	49.4	38.8	14
Dichloromethane	41.5	39.2	8
Ethyl acetate	77.1	62.25	44
Ethyl formate	54.15	50.95	16
Ethylene Dichloride	83.5	59.5	35
Furan	31.7	$<$30.5	$<$7
n-Hexane	68	50	21.5
Methyl acetate	57.1	53.9	17.7
Methyl acrylate	80	62.5	54
Methylmethacrylate	99.5	64.2	82
Methyl propionate	79.8	62.45	47.5
n-Octane	125.6	63	72
n-Pentane	36.15	30.85	7
Tetrahydrofuran	66	60.7	31.0
Thiophene	84	$<$59.55	$<$55
Toluene	110.6	63.5	72.5
Trichloroethylene	87	59.4	38.0

This table shows the proportion of methanol in some binary mixtures

remainder of methanol demand is in the fuel sector, principally in the production of MTBE. Methanol is considered to be one of the most promising fuels for fuel cell applications (18). Methanol is more environmentally benign than conventional liquid fuels. It has fewer potential environmental impacts and offers a greater degree of environmental protection.

Gasoline is one of the key ingredients that drives the combustion engine and prior to 1979 gasoline had lead as an additive. The oil refineries stopped using lead after discovering that the lead in gasoline was causing health problems and replaced it with MTBE. MTBE is the second largest end use of methanol, consuming approximately 7.3 million tonnes of methanol in 1999 (an estimated 29% of global demand) (14). This additive was

Table 3. Non-azeotropes of methanol

Some Non-azeotropes of Methanol (13)	Acetaldehyde	Ethane	Propyl acetate
	Acetone (@ < 100 mmHg)	Ethanol	Pyridine
	Chloroethane	Diethyl ether	Triethylamine
	Cumene	Ethylene Oxide	Water
	Diethylamine	Isopropanol	*m*/*o*/*p*-Xylenes

Table 4. Physical properties of MTBE (10)

Molecular weight	88.15
M.P (°C)	−109
B.P (°C)	55.2
Specific gravity	0.744
H_2O solubility (mg/l)	48,000
Vapor pressure (mg Hg, 25°C)	245

designed to reduce smog forming anti toxic pollutants and also increase the octane content to prevent engines from knocking (15). MTBE is a special ether that contains an oxygen atom in every molecule. Oxygenating gasoline promotes more complete combustion of the gas in the engine by increasing the temperature at which gas burns; thus, decreasing the amount of carbon monoxide (CO) produced during combustion. The oxygen atom in MTBE helps provide extra oxygen for complete combustion, and helps to give it an Octane rating of 116 (19).

PRODUCTION OF METHANOL AND METHYL-*t*-BUTYL ETHER

Production of Methanol

Methanol is a primary liquid petrochemical made from renewable and non-renewable fossil fuels containing carbon and hydrogen. There are many roots to the production of methanol (20, 21). Figure 2 is a schematic of the basic methanol production method.

- From Water Gas: Methanol is mostly manufactured from Water Gas (Steam is passed through red hot coke to form water gas) (Figure 3). A mixture of water gas and hydrogen is compressed to 300 atmospheres and is then passed through zinc oxide-chromium oxide catalyst at 300°C to produce methanol vapors that are then condensed.
- From Natural Gas: Methanol is obtained from methane present in natural gas. A mixture of methane and oxygen (9:1) is passed over copper catalyst at 250°C under pressure to yield methyl alcohol.

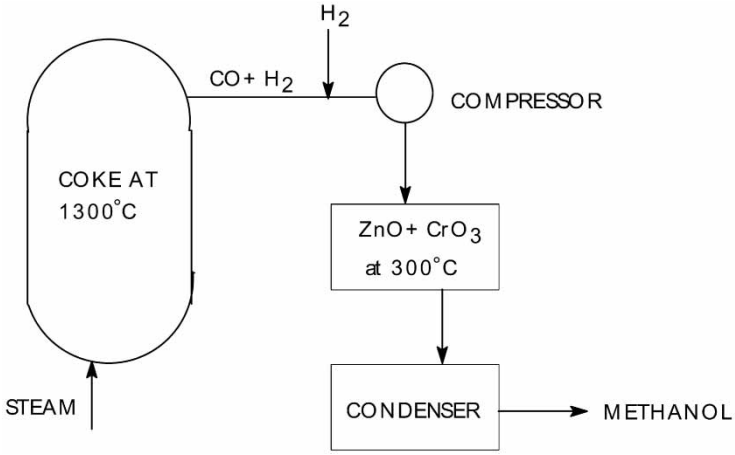

Figure 2. Methanol production from water gas. Reproduced from reference (20).

- From Wood: In the past, methanol was produced from wood. Wood is heated to 400°C in iron retorts in the absence of air to produce pyroligneous acid which is an aqueous mixture of 5% MeOH, 0.5% acetone, 10% acetic acid, from which MeOH can be separated.
- From Synthesis Gas: Synthesis gas is usually produced from the methane(CH_4) in natural gas rather than from coal. At moderate pressures (10–20 atm) and high temperatures (around 850°C), methane reacts with steam on a nickel catalyst to produce syngas according to the chemical equation:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The carbon monoxide (CO) and hydrogen (H_2) then react on a second catalyst to produce methanol. Today, the most widely used catalyst is a mixture of copper, zinc oxide, and alumina first used by ICI in 1966. At 50–100 atm and 250°C, it can catalyze the production of methanol from carbon monoxide and hydrogen with high selectivity

$$CO + 2H_2 \rightarrow CH_3OH$$

It is worth noting that the production of synthesis gas from methane produces 3 moles of hydrogen for every mole of carbon monoxide, while the methanol synthesis consumes only 2 moles of hydrogen for every mole of carbon monoxide. One way of dealing with the excess hydrogen is to inject carbon dioxide into the methanol synthesis reactor, where it, too, reacts to form methanol according to the chemical equation

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

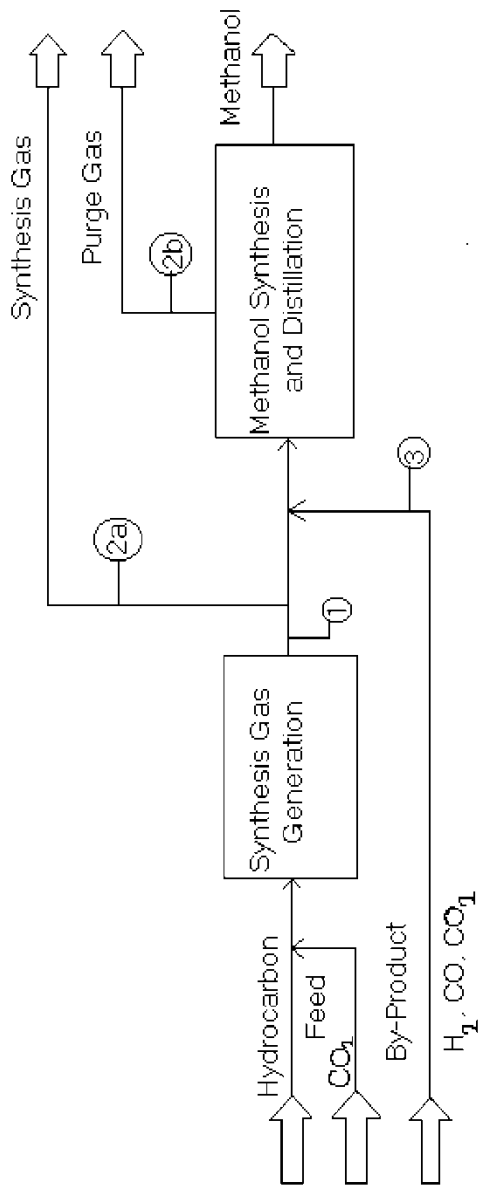

Figure 3. Production of methanol from synthesis gas.

Although natural gas is the most economical and widely used feedstock for methanol production, other feedstocks can be used. Where natural gas is unavailable, light petroleum products or coal can be used in its place.

MTBE Production

Methyl *tert*-butyl ether (MTBE) is one of the largest growing chemicals in the last 10 years and will probably be in the next 10 years (22).

There are three types of MTBE production plants:

- Refinery/Petrochemical plants: Isobutylene, produced as a by-product in refinery catalytic crackers and in petrochemical ethylene plants, is reacted with methanol to produce MTBE. These are the smallest and the least expensive MTBE plants.
- Merchant plants: Merchant plants isomerize normal butane to isobutane, dehydrogenate isobutane to isobutylene, and then react the isobutylene with methanol to produce MTBE. The merchant plants are the most expensive.
- TBA plants: Tertiary butyl alcohol (TBA) is a by-product of the propylene oxide production process. TBA is reacted with methanol to produce MTBE. Very few plants use this process.

The marginal source of MTBE supply comes from the large merchant plants that involves synthesis of MTBE with isobutene and methanol as reactants and n-butane as inert. The reactive mixture is composed of methanol, isobutene, n-butane and methyl *tert*-butyl ether (MTBE) and the chemical reaction is assumed to be homogeneous and takes place in the liquid phase. In the early 1990s MTBE was considered one of the most promising clean burning octane enhancers, being expected to be the second largest organic chemical produced in United States by the year 2000, especially promoted by the increased demand for premium-grade fuels and the elimination of lead gasolines (23). MTBE synthesis via reactive distillation represents a major development in the field and an open door to novel and innovative processes (24). MTBE is produced from methanol and isobutene in an equilibrium-limited liquid-phase reaction catalyzed heterogeneously by a strong acid ion-exchange resin (e.g., Amberlyte 15) or homogeneously by sulfuric acid according to the following expression,

$$\underset{\text{isobutene+methanol}}{C_4H_8 + CH_3OH} \longrightarrow \underset{\text{MTBE}}{C_5H_{12}O}$$

The production process of methyl *tert*-butyl ether (MTBE) involves the separation of MTBE, mixed C4's and non-reacted methanol from the reactor effluent to achieve a high MTBE purity. Methanol forms azeotropes with both MTBE and C4's in this mixture (25). In the conventional MTBE

process the reactor effluent was separated into an MTBE-bottom product and an azeotropic mixture of methanol and C4 components as top product by distillation. Methanol was separated from the C4's by water wash combined with distillation or separation using molecular sieves.

CONVENTIONAL SEPARATION PROCESSES FOR METHANOL/MTBE

For the process industries, choosing the right separation process is essential to ensure the desired product quality, and to reduce costs. Most separations carried out during operations in the chemical process industries (CPI) are achieved by classical separation methods, such as distillation, solvent extraction, precipitation, and filtration. Others require novel technologies, such as supercritical fluid extraction, liquid and catalytic membranes, liquid chromatography, and electrophoresis. Chemical feedstocks, solvents, and products of (chemical) reactions in the liquid phase are very often a complex mixture of organic components that are difficult to separate. The separation is mostly performed by various distillation techniques sometimes combined with the use of entrainers, which are hazardous to the environment. Distillation is an energy intensive process mainly due to the need to evaporate liquid for generating reflux in addition to the liquid taken off at the column head as top product (26). This disadvantage becomes most pronounced in the separation of close boiling mixtures (example: Methanol-MTBE), where the reflux stream is far larger than the tops product stream and in the case of azeotropes where multiple distillation steps are required.

Several methanol–organic systems have been tested in pilot plants, and the first industrial plants are in operation. The first approach and application investigated was the separation of the methanol-methyl tertiary butyl ether (MTBE) system. The excess MeOH in the MTBE reaction mass must be removed for recycle to the reactors and for high purity ether products and C_4 to C_7 raffinates. The effluent of the reactor contains mainly, the product, MTBE and the untreated excess of MeOH. The effluent mixtures are first split in the debutanizer into a bottom MTBE product and a near azeotropic mixture of MeOH and MTBE, the composition of which is 14.3 wt% MeOH at 760 mmHg. This mixture is then separated by water washing, after which MeOH and the water mixture are distilled to recycle MeOH to the reactor (27, 28). However, this conventional process is both expensive and energy intensive.

PV SEPARATION OF METHANOL/MTBE

Distillation is the dominant separation method for organic mixtures in the chemical and petrochemical processing industries. However, around 40% of

the total energy consumed by the chemical processing industries can be attributed to distillation due to its energy intensive nature. Pervaporation is proven to provide a high potential separation alternative because it is less energy consuming than distillation (10).

Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. It is considered an attractive alternative to other separation methods for a variety of reasons (29–31). With the low temperatures and pressures involved in pervaporation, it often has cost and performance advantages for the separation of constant-boiling azeotropes (32). Characteristics of the pervaporation process include (33–35):

1. Low energy consumption
2. No entrainer required, no contamination
3. Permeate must be volatile at operating conditions
4. Functions independent of vapor/liquid equilibrium

In a PV process, components of a liquid feed permeate through the membrane and evaporate into the downstream at different rates (36–38). The fact that feed components undergo phase change makes PV unique among membrane processes. The driving force behind the PV process is the difference in chemical activity of components in the feed and the permeate (39, 40). 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 (41, 42). 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 (43). Figure 4 is a schematic of a laboratory PV set-up.

The removal of methanol by means of the pervaporation method would be a promising alternative, provided that a suitable methanol-selective membrane is available. Methanol forms a minimum-boiling azeotrope with MTBE at a composition of 14.3 wt% of the alcohol at atmospheric pressure. Pervaporation has therefore been used to break this azeotrope (31, 32). Pervaporation could be employed beneficially, most likely in combination with existing distillation processes (28), which is dealt in detail later.

Parameters Affecting the Separation of MeOH/MTBE by PV

There are two major factors which determine the degree of sorption of a given liquid in a polymer membrane, i.e., the solubility parameter and the free volume. The solubility parameter mainly determines the extent of interaction between the permeating liquid and the functional groups of the polymer

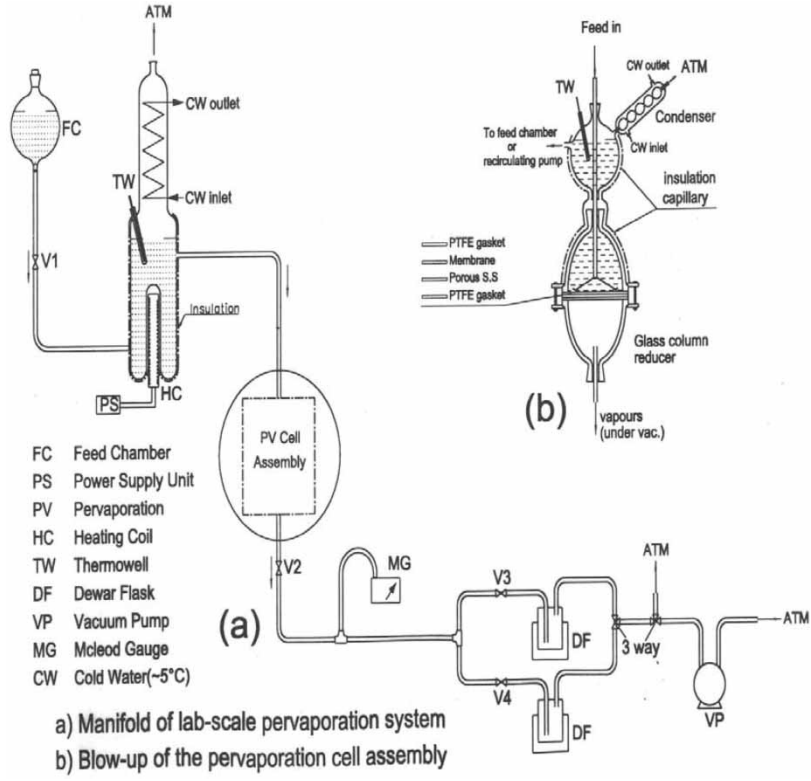

Figure 4. Schematic of laboratory pervaporation set-up.

whereas the free volume provides information on the void space available for absorption. The influence of both these factors are discussed in detail next.

The solubility parameter is an intrinsic physicochemical property of a substance that is used to explain the structure-activity relationship. Hansen divided the conventional solubility parameter into three partial parameters: dispersion δ_d, dipole δ_p and hydrogen bonding δ_h (44). The solubility parameters of methanol, MTBE listed in Table 5, indicate that the hydrogen bonding component (δ_h) of methanol solubility is stronger than that of

Table 5. Three partial solubility parameters ($Mpa^{1/2}$) of Methanol, MTBE

Component	δ_d	δ_p	δ_h
Methanol	15.13	12.27	22.29
MTBE	15.48	3.63	5.22

MTBE. It is expected that the alcohol would interact with polar groups present in the membrane matrix through hydrogen bonding (45). The solubility values of MTBE in the polar membrane are much lower than MeOH because pure MTBE is moderately hydrophobic.

In general, selection of polymers compatible with the organic mixtures which need to be separated, is based on the Hansen solubility parameter (Δ) and Flory-Huggins interaction parameter (χ). The compatibility among components, *1* and *2*, which are the organic liquids in major and minor quantities respectively and polymer, *3* is indicated by the relationship (46)

$$\Delta_{i,3} = \sqrt{[(\delta_{d,i} - \delta_{d,3})^2 + (\delta_{p,i} - \delta_{p,3})^2 + (\delta_{h,i} - \delta_{h,3})^2]} \qquad (1)$$

where δ_d, δ_p, and δ_h are the dispersive, polar and hydrogen bonding contributions and Δ is the magnitude of the vectorial distance, as shown in 3-dimensional diagram of δ_d, δ_p, δ_h on *x, y*, and *z* axes, respectively (Figure 5), '*i*' represents 1 or 2. The greater the compatibility between any two components the smaller will be the magnitude of Δ.

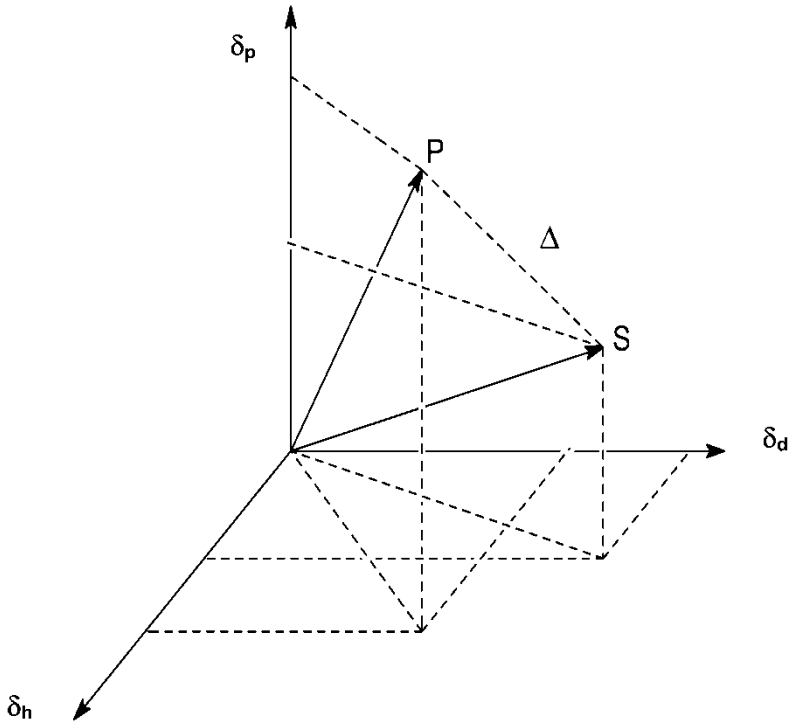

Figure 5. Schematic representation of polymer (P) and solvent (S) vectors (δ_p, δ_d, δ_h) in space; Solubility parameter Δ is the distance between end points of vectors.

The Flory-Huggins interaction parameter (χ) also signifies the compatibility of feed components with the polymer. The binary interaction parameters, $\chi_{1,3}$ and $\chi_{2,3}$ between the components and the polymer can be determined from

$$\chi_{i,3} = \frac{-[\ln(1 - v_p) + v_p]}{v_p^2} \tag{2}$$

where *i* represents component *1* or *2* and v_p is the volume fraction of the polymer *3* determined individually for each liquid component. Again the smaller the value of χ (close to 0.5 but not below), the greater will be the interaction.

On the other hand, the free volume is a parameter, which is purely physical in nature. Linear chain polymers such as polyethylene and polypropylene are rigid and possess lower free volume compared to polymers with branched chains such as poly (methylmethacrylate) or polymers with aromatic backbone.

During crosslinking, the polymer chains are drawn closer thereby reducing the free volume as well as the number of groups available for interaction with the feed liquid. This results in a reduction in solubility, diffusivity, and subsequently the permeation rate of a liquid through the polymer. For pure MeOH, the solubility decreases with an increase in the degree of cross-linking of the membranes (47).

Factors Affecting Membrane Performance

According to the solution-diffusion model (48), an increase in the thermal motion of the polymer chains and the diffusing species result in higher flux. Properties of the polymer that affect diffusion include the nature of its "backbone" material, and degree of cross-linking. In addition to the specific characteristics of the feed components and the membrane, operating parameters such as feed temperature, feed concentration and downstream pressure also influence the overall performance of a PV process.

i. Feed composition and concentration: A change in the feed composition directly affects the sorption phenomena at the liquid membrane interface, as proved by the solution-diffusion principle and as the diffusion of the components in the membrane is dependent on the concentration of the components (or the solubility of the components), the permeation characteristics are hence dependent on the feed concentration as well.
ii. Feed and permeate pressure: The main driving force in pervaporation is the activity gradient of the components in the membrane. The permeate pressure is directly related to the activity of the components at the downstream side of the membrane, which strongly influences flux and

selectivity. The maximum gradient can be obtained for zero permeate pressure and thus for higher permeate pressures, the feed pressure influences the pervaporation characteristics by favoring permeation of the more volatile constituent of the feed (49).

iii. Temperature: Solubility and diffusivity of feed mixture component are generally dependent on operating temperature and so is the permeate flux. When the temperature of the feed increases, the permeation rate generally follows an Arrhenius-type law (50, 51)

$$J = J_0 \exp(E_p/RT)$$

The permeation rates may increase many times for each 10°C temperature increment. Also, since diffusion rates increase with increasing temperature, permeation rates also increase consequently. Unlike the flux, the selectivity is not greatly influenced by temperature. In general, a marginal decrease in selectivity is observed with increasing temperature (50).

iv. Concentration polarization (CP): When a binary liquid mixture is permeating through a semi-permeable membrane, at different individual component rates, an increase of the less permeable component in the boundary layer near the membrane surface results. This concentration gradient between the more concentrated boundary layer solution and the less concentrated bulk is termed as concentration polarization (CP). Generally, it has been assumed that CP does not play an important role in pervaporation but some researchers have dealt with the concentration polarization problems in PV (52–55b).

Besides process conditions, nature of organic feed constituents can also greatly influence the performance levels of the membranes. This is probably due to anomalous swelling of the polymer materials by the organic solvents, or to cracks that are formed in the membrane top layer; the so-called activated diffusion. The specific interaction of solvent and membrane material also plays an important role.

Types of Membranes Used For MeOH/MTBE Separation

Extensive research has been done in finding the optimal membrane material that has special interactions with a specific component to maximise performance such as selectivity, flux, and stability (56, 57).

The first studies to separate this mixture were made by Muzzarelli et al. (58). The applicability of using chemically modified chitin and chitosan membranes in separating this mixture by pervaporation was attempted by a few researchers (59–61). Earlier the usage of chitosan was predominant in biomedical applications (62–64). Farnand and Noh (65) in 1989, tested a series of polymers as pervaporation membranes for MeOH/MTBE separation.

Amongst the polymers tested they found that Nafion and a cellulose based material exhibited similar separation performance. Pasternak et al. (66) explored the possibility of using poly (vinyl alcohol) (PVA) membranes by conducting a study on the pervaporation performance of PVA on MeOH/MTBE separation and compared the results with Nafion membranes. However, all the attempts resulted in poor flux and relatively lower selectivity towards methanol.

In 1994, the application of modified poly (phenylene oxide) membrane for the separation of this mixture was studied by Doghieri et al. (67) under various operating conditions. A flux of 3–4.8 (kg μm/m^2-hr) and a selectivity of 5.4–7.8 was obtained. Process optimization was performed by considering the influence of both permeate side pressure and methanol concentration in the feed mixture. Park et al. (68), in 1995 synthesised a blend membrane of PVA and poly (acrylic acid) for the separation of methanol/MTBE mixture. This membrane yielded good flux with better selectivity. In order to separate methanol from MTBE (69) and attain high flux and extremely high selectivity, the focus of researchers was shifted to using inorganic silicalite based membranes keeping in view that these types of composites have stability to the liquid in which the native polymer is completely soluble.

A number of researches reported the characteristics of polyelectrolyte complex materials and crosslinked membranes for several mixtures (70–74). Pervaporation of ionically surface cross-linked chitosan composite membranes was studied for the separation of methanol/MTBE mixture by Sang Yong Nam et al. (75). Pervaporation behaviours were controlled by varying the cross-linking time and surfactant content in the membrane (76).

Cellulose acetate membrane (77) was noted to have good permeation flux but lower methanol concentration in permeate when compared to other membranes. Cellulose sulfate-surfactant complex membranes also exhibited high separation factor with respect to methanol.

Asymmetric tubular alumina-supported poly (vinyl acetate) (PVAc) and poly (vinyl pyrrolidone) (PVP) membranes were synthesized, characterized, and tested by pervaporation for the separation of binary mixtures of methanol and methyl *tert*-butyl ether (MTBE)(78–80). The active separation layer was created by free-radical graft polymerization of PVAc and PVP onto a vinylsilane-modified alumina substrate with an average native pore diameter of 50 Å (81). The methanol separation factors for the PVP and PVAc grafted pervaporation membranes reached values of 26 and 100, respectively, at the lower range of methanol concentrations (1–5% v/v) (82). The separation impact of the grafted polymer chains was apparent given that the native (unmodified) and vinylsilylated alumina membranes lacked selectivity for the MTBE/methanol system. Total permeate flux attained with the PVAc and PVP-based membranes ranged from 2.5–31 kg μm/m^2-hr and 0–7.5 kg μm/m^2-hr, respectively. A trade-off between separation and

permeate flux was attained from a decrease in permeation flux with increasing separation factor.

Conducting polymer composite membranes with a separation layer of polypyrrole doped with hexafluorophosphate (PF_6^-) and *p*-toluenesulfonate ($CH_3C_6H_4SO_3^-$), were examined by Zhou et al. (83) for the removal of methanol from MTBE by pervaporation. Both membranes displayed preferential permeation of methanol. An acceptable methanol flux was obtained with the membrane doped by PF_6^-.

Pervaporation experiments with ceramic membranes did not show a major breakthrough, but selectivities measured were about 19 with fluxes of about 41 $g/m^2/h$ (84–86). The polar and dispersive forces could probably be the main influence that contributed to the selectivities measured. In comparison with polymeric membranes, ceramic membranes are expected to withstand higher temperatures and show greater chemical resistance to different solvents without serious degradation of the material. The main problem with ceramic dense membranes is to produce and maintain a defect free top layer. Polycrystalline silicalite membrane was prepared on a porous sintered stainless steel support and its pervaporation performance was investigated by Sano et al. (87) using MeOH/MTBE mixture. MeOH selectivity in pervaporation was considerably higher than the relative volatility value of distillation, indicating that the membrane behaves as a third component by allowing preferential permeation of methanol. With a feed methanol concentration of 50 vol%, the permeation rate, flux increased slightly with an increase in the methanol concentration and the values were between 0.08 and 0.12 kg/m^2hr. The separation factor (α) decreased with an increase in the feed temperature, since the component flux of MTBE increased with temperature while the MeOH flux remained constant. The silicalite membrane shows high hydrophobic property (88) and because MTBE is more hydrophobic than MeOH, the improved sorption of MTBE takes place in the voids between silicalite crystals to cause a reduction in selectivity. This view was supported by Flanigen et al. (88).

Based on Flory-Huggins theory and the solution-diffusion model, several experiments were performed on pervaporation of methanol-MTBE mixtures through cellulose acetate (CA) and triacetate (CTA) glassy polymeric membranes by Jae Shick Yang et al. (89). MTBE showed a higher flux with CTA (2–4 $kg\,\mu m/m^2$-hr) than with CA (0.05–2 $kg\,\mu m/m^2$-hr), whereas the selectivity with CTA (90–300) was lower than with CA (400–2000). This is probably due to a looser structure of CTA, which has bulkier side groups and a relatively weak dipole-dipole interaction without hydrogen bonding as compared with CA.

Masakazu Yoshikawa et al. (90) investigated the pervaporation separation of MeOH/MTBE by using natural polymer, agarose (91), as a membrane material, which permeated MeOH from the MeOH/MTBE mixture. Permselectivity with respect to MeOH reached a value above 9×10^5. From

pervaporation and sorption data, the permselectivity was attributed to both solubility selectivity and diffusivity selectivity. Table 6 deals with the performance of various membranes applied for MTBE/methanol separation (67–101).

Commercial Membrane for MeOH/MTBE Separation

To the best of our knowledge, there is only one example for industrial applications of PV for separation of this mixture. The only organoselective membrane commercialised by Sulzer Chemtech for extracting methanol from methanol/methyl ester or methyl ether mixtures is PERVAP 2256. However, its chemical structure is confidential. Developments in this field have already shown that this membrane could be a very specific answer to key separation problems, especially in the petrochemical industry.

Effect of Operating Parameters

The performances of membranes can be largely influenced by changes in process conditions like concentration and temperature. With an increase in the methanol concentration in the feed mixture, the swelling of the membranes is due to the increasing sorption of MeOH. The other component, MTBE, penetrates into the upstream swollen membrane portion, which is in a plasticized state. Hence, the flux increases with an increase in wt% of methanol in the feed and the selectivity decreases. This phenomenon has been reported by various researchers (78, 90, 93–95) and is the result of the swelling characteristics of the membrane, as observed by Cao et al. (92) and Luo et al. (96).

For a given feed of MeOH (wt.%), the total flux increases when the feed temperature rises. This is because at high temperature, the sorption ability will be improved as the polymer chains become more flexible. The intermolecular distances will increase and the diffusion coefficients of the components will be greatly enhanced.

The selectivity decreases drastically when the MeOH concentration in the feed increases. This is because the mobility of MTBE is facilitated by preferential increasing membrane swelling caused by preferential adsorption of excess methanol present in the feed.

To this day, the study on pervaporation is mainly concentrated on binary mixtures; while in contrast most products to be separated are multiple component mixtures especially in the petrochemical industry, such as methanol/MTBE/C_4 and cyclohexane/cyclohexanol/cyclohexanone are encountered. There is a large difference of pervaporation characteristics between ternary and binary mixtures because of the more complicated coupling effects in case of ternary mixtures. It is necessary to investigate the

Table 6. Summary of separation performance of various membranes for the separation of MeOH/MTBE mixtures

System	Membrane material	Selectivity (α)	Flux (kg μm/ m^2h)	Temp. (°C)	Ref.
Methanol (21%)/MTBE	Modified PPO	5.4–7.8	3–4.8	40	Doghieri et al. (67)
Methanol (9%)/MTBE	Ceramic silica	19	0.41	—	Dogihieri et al. (67)
MeOH (50%)/MTBE	Silicalite membrane	10	10	30	Sano et al. (69)
Methanol (20%)/MTBE	Chitosan composite modified with H_2SO_4	9.33	1.5	25	Nam et al. (75)
Methanol (20%)/MTBE	Chitosan composite modified with and surfactants	231.29	7.05		
MeOH (12.3%)/MTBE	Polyelectrolyte surfactant complex	349	10.4	50	Schwarz et al. (76)
MeOH (1%–5%)/MTBE	PVP and PVAc grafted	26–0 (PVP) 100–0 (PVAc)	2.5–31 0–7.5	25	Yoshida et al. (82)
MeOH (5%–100%)/Methyl-tert butylether (MTBE)	PPY-PTS	100–25	0.25–9.5	50	Zhou et al. (83)
MeOH (10%–30%)/MTBE	CA CTA	20–4 ($\times 10^2$) 3–0.9 ($\times 10^2$)	0.05–2 2–4	—	Shick Yang et al. (89)
MeOH (20%)/MTBE	Naturally occurring agarose	9×10^5	low	30	Yoshikawa et al. (90)
MeOH (5%–35%)/MTBE	CTA	1200–20	0.1–6	—	Cao et al. (92)

(*continued*)

Table 6. Continued

System	Membrane material	Selectivity (α)	Flux (kg μm/ m^2h)	Temp. (°C)	Ref.
MeOH/MTBE (5%–50%)	CA	—	Very low	25	Lin Zhang et al. (93)
MeOH (22%)/MTBE MeOH (5%–20%)/MTBE	CTA	65	16	50	Niang et al. (95)
		9480–82	0–6.575	30	
MeOH (5%–30%)/MTBE	CA blended with CAHP	92–99.8	47–1	—	Niang et al. (96)
MeOH/MTBE (67%–95%)	PIC membrane of SA and Chitosan	∞	>2.4	40–55	Sang-Gyun Kim et al. (97)
MeOH (14.3%–5%)/MTBE	PSS–Na/Al_2O_3	2–1 ($\times 10^{-4}$)	0.06–0.01	25	Chen et al. (99)
	PSS–Mg/Al_2O_3	1.4–0.66 ($\times 10^{-4}$)	0/09–0.02		
MeOH (Azeotrope) (5%–35%)/ MTBE	Blends of PVA/PAA	4000	1.0	50	Rhim et al. (100)
		6800–1500	1.0–2	30	
MeOH (Azeotrope) (5%–35%)/ MTBE	Blends of PVA/SSA	1300–1200	1.6–2	50	
		low	—	30	
Methanol (10%–100%)/MTBE	CTA hollow fiber	60–2000	1.3–0.4	25	Cai et al. (101, 102)

influence of such effects on pervaporation. The pervaporation performances for methanol/MTBE/C_4 ternary mixtures and corresponding binary mixtures through the CA membrane were studied by Lin Zhanga et al. (93). In addition, the methanol flux model with "accompany effect" was also developed.

Ethanol Replacing MTBE in Reformulated Gasoline

In the early 1990s MTBE was mandated to be in all gasoline sold in California (by far the largest consumer of gasoline of any state). When blended with gasoline, MTBE dramatically reduced exhaust emissions and contributed greatly to cleaning the air in California. A 15% blend of MTBE and gasoline was found to increase octane levels and enhance combustion.

A few years ago it was discovered that gasoline, containing MTBE, was leaking from old service station storage tanks and finding its way into creeks, rivers, reservoirs, etc. Although it is not very toxic, it is not very biodegradable either, and has a strong taste and odor, noticeable at 15 ppm level. Ethanol being a safe, biodegradable and renewable oxygenate that does not harm drinking water resources could successfully replace MTBE nationwide in the coming years, with negligible effects on gasoline prices and no disruption in supply (96, 97). Recent reports have determined that no negative impact on air quality, water quality, or health is expected from ethanol's use as an oxygenate. However, until this substitution takes place, the separation of MeOH/MTBE will be of great significance (98–102).

HYBRID PROCESS

PV as a single process has often to compete with conventional processes such as distillation, liquid-liquid extraction, adsorption, and stripping. Generally, in many cases, PV alone may not supply products suitable for further processing or waste disposal in accordance with environmental standards (103, 104). Thus, hybrid processes are regarded as one means of overcoming these limitations. However, only two types of PV based hybrid processes, viz., PV-distillation or PV combined with a chemical reactor, have been realized on an industrial-scale. The position of the PV unit is determined by the predefined task of the hybrid process. Nevertheless, in general terms, consideration should be given to the possibility of positioning pervaporation in front of a distillation column to overcome an azeotropic point. The different options for the incorporation of a PV unit within an MTBE production process are reviewed below.

Chen et al. (106, 107) proposed two alternative layouts, the so called "total recovery improvement for MTBE" or TRIM process, which was a combination of organophilic (methanolphilic) PV and distillation.

In the first layout, shown in Figure 6, the PV unit was used to decrease the methanol concentration of the effluent from about 5 to 2 wt.%. The

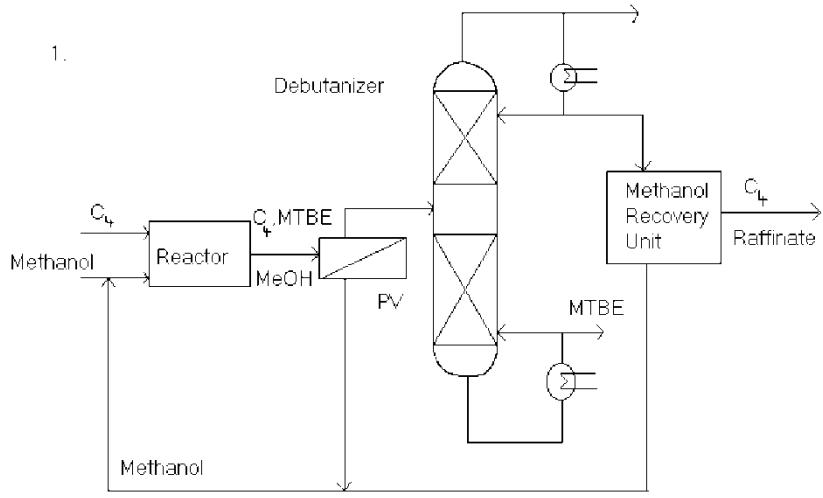

Figure 6. MTBE Production: Process layout (1) of the TRIM process integrated in the MTBE production. Reproduced from reference (103).

methanol-rich permeate of the PV unit was recycled to the reactor to improve the MTBE conversion by 5% per cycle. The treatment of the retentate by a de-butaniser and a methanol recovery at the end of the process will be unaffected by the improved conversion. Therefore, this method could be integrated into a conventional process without modifying the overall process. An economic comparison indicated that TRIM could reduce investment costs from 10% to 15% by replacing a second reactor-debutaniser stage. Even the integration of the TRIM process into an existing process was found to be economically desirable as it could increase production by 5%.

The alternative layout of the TRIM process is shown in Figure 7. The PV unit treats a side stream from the de-butaniser to remove the methanol (107, 108). The methanol-rich permeate was recycled to the reactor and the retentate was recycled to the de-butaniser. This process layout led to an increased performance of the column by reducing the methanol concentration in the top product. The costs of the methanol recovery could, thus, be decreased by minimising or even eliminating the need for the methanol recovery unit. This side-stream approach led to an increased driving force for membrane permeation and, consequently, reduced the required membrane area. In comparison with a high conversion plant it was found that the side-stream approach could save up to 20% on investment costs (107). The PV unit was used to separate a side stream from the distillation column. An economic comparison by the Institut Francais du Petrol for a reactive distillation process revealed that the investment costs for the conventional process were similar to that of the hybrid, but the hybrid process was found to be of economical

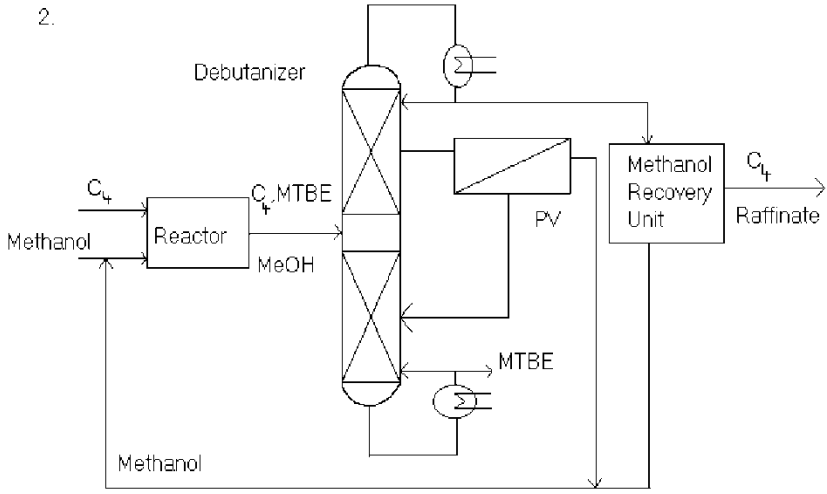

Figure 7. The alternative layout of the TRIM process. Reproduced from reference (104).

interest due to its reduced energy requirement. The side-stream approach was further compared by Hommerich (109) with the removal of methanol from reactor effluent by a PV unit functioning prior to distillation. In his work the side-stream approach was more attractive because of a 50% reduction of the feed quantity going to the PV unit, high feed methanol concentration, and a low amount of methanol to separate. This led to a reduced membrane area requirement (109). An economic comparison between the conventional Huls-process, consisting of two high-pressure columns between 6 and 12 bar, and a hybrid process, combining a 6 bar distillation process with side-stream separation and pervaporation, revealed that the hybrid process may reduce annual operating costs by about 10% to 20% (108, 110).

FUTURE PROSPECTS

With respect to the aforementioned discussions, it can be noted that even though researchers have attempted to synthesize/use different varieties of membranes for effective MeOH/MTBE separations on a commercial level, some restrictions for its applications are still encountered. Here are a few prominent cases and potential routes to overcome these drawbacks:

Development of Appropriate Membrane Material

As discussed earlier, flux and selectivity of a membrane are deciding factors in pervaporation mass-transport. Therefore, development of a new polymer

material is a key research area in membrane technology. The aim in the development of new pervaporation membranes is either to increase the flux, keeping the selectivity constant or aiming for higher selectivities at constant flux, or both. Three approaches are:

1. Development of completely new polymers (111)
2. Functionalisation of membrane polymers (112)
3. Integration of adsorber agents into polymer material such as zeolite (113, 114).

For the development of polymers incorporating the aforesaid approaches, a few suggestions follow. Development of sulfonated membranes, obtained by modifying hydrophobic aromatic polymers such as Poly(phenylene oxide) (PPO), Polysulfone (PSF), and Poly(ether ether ketone) (PEEK) with sulfonating agents. These membranes are partially hydrophilic in nature and hence can preferentially absorb polar molecules such as MeOH.

On the other hand, ionically cross-linked acid-base blends of sulfonated polymers (as acid polymers) and chitosan, poly(ethylene imine) as basic polymers can be synthesized, which can prove to be suitable membranes for polar–non-polar separations such as MeOH/MTBE mixtures. The ionic cross-linking occurring on blending the two polymers causes a salting out effect for non-polar compounds such as MTBE. The structures of a few acidic and basic polymers are given in Figure 8.

Fouling of the Membrane

Fouling refers to the deposition of impermeable substances, present in the feed, on the membrane surface. In PV, fouling is generally caused by scale formation rather than clogging or blocking of pores. The suitability of a membrane material for a specific separation problem is also limited by possible interaction with aggressive components in the feed. This can cause reduction in the flux and ultimately renders the membrane useless. Fouling can be prevented by:

1. Using a highly turbulent flow regime
2. Cleaning the membrane semi-continuously
3. The integration of a filtration step before the pervaporation unit.

Fouling is relatively less rampant in pervaporation separation when compared to the other membrane separation processes such as reverse osmosis, electrodialysis, and nanofiltration.

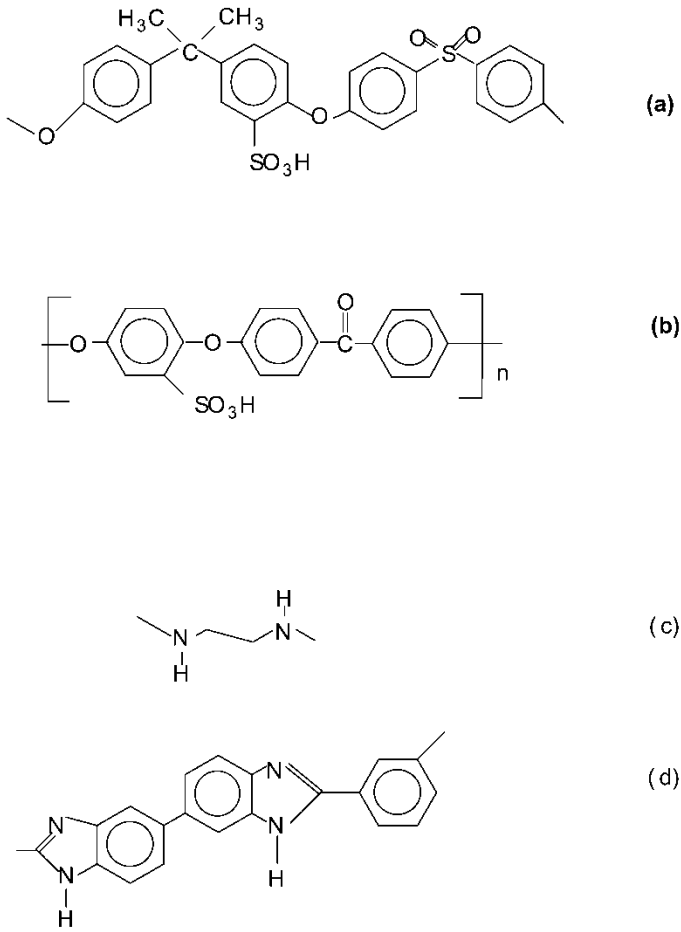

Figure 8. Structures of (a) Sulfonated PSF (b) Sulfonated PEEK (c) poly(ethylene imine) and (d) poly(benzimidazole).

Lack of Comprehensive Understanding of Pervaporation Technique

Membranes are viewed as fragile materials prone to damage by unexpected conditions. Pervaporation for separation of organic mixtures such as MeOH/MTBE is less familiar to the industry in comparison with well-established mass exchange processes and is perceived to be expensive. The industrial applications of pervaporation are thus far mainly confined to dehydration of alcohols and to the extraction of volatile trace organics contained in effluents. To widen the scope for commercialization of specialty/novel membrane modules, emphasis could be laid on coating

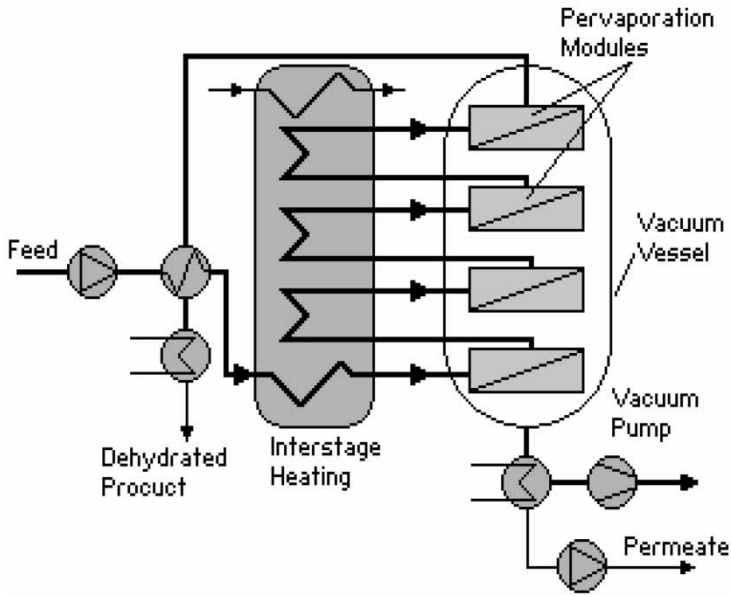

Figure 9. Cascades in pervaporation. Reproduced from reference (110).

techniques of hollow fibres/UF sheet membrane substrates. The coated sheet membranes could then be converted to modular configuration such as plate-and-frame or spiral-wound. It is a well-known fact that operation in series/parallel modes can be performed for obtaining complete separation. But the calculations for this are based on the assumptions that concentration polarization in the modules can be neglected (2), which tends to make the multi-stage process (Figure 9) open for further research. In addition, adequate attention needs to be given to process design and simulation.

Furthermore, for economic analysis, a membrane life cycle is an important factor. Though the economic estimation plays a vital role for any industrial viability of a membrane system it cannot be dealt with in detail here. The reader can refer to books for further information.

CONCLUSION

The attractiveness of PV systems in MeOH/MTBE separation is evidenced by the increasing number of papers appearing in the scientific journals on the subject. The PV technology is competitive with other separation or extraction processes and it particularly holds well for the energy-intensive distillation process. In addition to sometimes providing a unique way of solving really difficult separation problems, PV offers very significant savings in energy

and raw materials. Many studies have proved the technical feasibility of PV processes in MeOH/MTBE separation. However, lack of a more recent economical evaluation can be felt in this field. Such a study is an essential factor to encourage the industry to invest in researches focusing on establishing pilot plants and commercial scale PV units for this application. Sulfonated membranes and ionically crosslinked acid-base blends show potential for separation of polar/non-polar organic mixtures such as MeOH/MTBE. Development of these membranes in an asymmetric form could further improve the feasibility of PV for separation of MeOH/MTBE on a commercial scale.

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