

Review Article

Review on Pervaporation: Theory, Membrane Performance, and Application to Intensification of Esterification Reaction

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The esterification reaction is reversible and has low yield. In order to increase the yield of reaction, it is required to simultaneously remove the product of reaction. For this membranes are the viable approach. Pervaporation membranes have success in removal of components in dilute forms. Membrane performance is represented in terms of flux, sorption coefficient, separation factor, and permeance. These factors are related to the thickness of membrane, temperature, and feed concentration. Higher flux is observed at lower membrane thickness and higher feed concentration of water and lower selectivity is observed at higher temperatures due to increased free volume, lower viscosity, and higher feed side pressure. Different factors affect the pervaporation aided esterification reactor setup such as effect of initial molar ratios of the reactants, effect of catalyst concentration, effect of membrane area, and effect of temperature. Large membrane size could provide higher surface for the transfer of acid, though the challenges of membrane rupture do surround the studies. In the present review work, we tried to collaborate the works in totality of the pervaporation design starting from the membrane behavior to the process behavior. Different prospective fields are also explored which need investigation.

1. Introduction to Pervaporation

Separation of liquid mixtures by partial vaporization through a membrane (nonporous or porous) is the separation principle in pervaporation. This results in collection of permeating component in vapor form, which may be either removed by flowing an inert medium or applying low pressure on the permeant side. The driving force for pervaporation process is the difference in chemical potential, corresponding to the concentration gradient between phases on the opposite sides of the interfacial barrier. Sorption diffusion model is used to describe the transport on the basis of difference in the molecular size instead of volatility as in the case of distillation. Thus, it could be effectively utilized as economical substitute azeotropic separations. In addition to this the no use of third component and requirement of low energy consumption (due to energy integration) are the add-on benefits [1, 2]. In the last two decades, pervaporation is finding wide range of areas for its application such as liquid hydrocarbons separations (petrochemical application, alcohol/ether separations) [3–5],

removal of volatile organic compounds (VOCs) from water [6, 7], removal of water from glycerin [8], and dehydration to intensify esterification reaction [9, 10].

Pervaporation can be integrated with either distillation or a chemical production step to provide intensification and energy integration. Pervaporation-distillation hybrid system leads to a clean technology and offer potential savings in energy because of reduced thermal and pressure requirements. When integrated with reactions such as esterification process, it offers the opportunity to shift the chemical equilibrium by removing the product of the reaction. Reactor-pervaporation hybrid method overcomes the inhibition of the chemical equilibrium of the process and therefore leads to an increased productivity. This process also allows one to use heat of the chemical reaction to increase the efficiency of the pervaporation process and leads consequently to potential savings in energy costs.

Membranes are successfully used in separation industries as selective barriers to prevent unwanted solutes from permeating through. Thus the impurity is separated from the target.

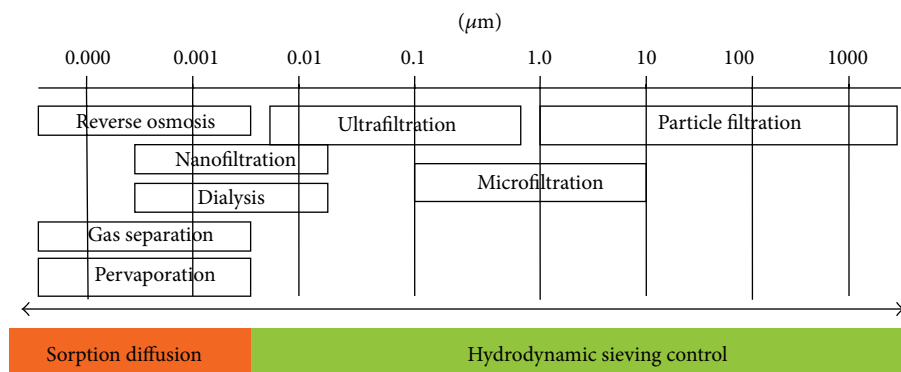


FIGURE 1: The choice of membrane with respect to the size of particles encountered.

Separation is based on pore sizes and hence the membranes got their characteristic names as microfiltration, ultrafiltration, and nanofiltration membranes (Figure 1). Membranes are either porous or nonporous and in the separation based on sizes, usually porous membranes are used. Pervaporation is the distinction class among above membranes as the separation criteria are different. Pervaporation membranes are nonporous and have been widely employed for separating liquid mixtures. The separation feature is based on affinity with membrane materials and hence the molecule having higher affinity is adsorbed and diffuses through the membrane while the membrane retains molecules having low affinity.

2. Membrane Materials for Pervaporation

For pervaporation, the hydrophilic membranes were the first one to achieve the industrial applications and were used for the organic solvent dehydration. The main industrial applications in pervaporation even today are almost the same as before, which is the dehydration of organic liquids. By modifying the active layer of these membranes with different chemical compositions and structures, these membranes are enabled to extract water with broad ranges of flux and selectivity [11, 12]. Commercially available hydrophilic membranes are made of polymeric membrane materials such as polyvinyl alcohol (PVA), polyimides, polymaleimides, Nafion, and polyacrylonitrile (PAN).

Presently there have been a number of investigators concerning R&D of the hydrophilic membrane, which can be cataloged into organic, inorganic, and organic-inorganic hybrid membranes. Inorganic membranes such as zeolite and silica are generally used [13, 14]. Inorganic membranes are very suited for high temperature applications (harsh environments) and generally these membranes are prepared by sol-gel method, which was appropriate to elaborate thin and porous layers with controllable porosity on a wide range of chemically resistant macroporous substrates [15]. While these inorganic membranes showed high dehydration efficiency, their industrialization process may be slow-paced due to the complicated large-scale preparation and high manufacturing cost. In addition to this, several kinds of commercial organic

membranes including PERVAP 2201 [16, 17], PERVAP 1005 (GFT) [18], and GFT-1005 [19] have been introduced to the pervaporation-esterification coupling process. Few studies on cross-linked poly(vinyl alcohol) membranes have also been investigated, such as PVA with catalyst $Zr(SO_4)_2 \cdot 4H_2O$ and Amberlyst [20, 21], cast on polyethersulfone [22, 23] and on poly(acrylonitrile) [24]. However, the inherent instabilities of these organic membranes severely limit their applications.

Organic-inorganic hybrid materials have been proposed to be the best choice for having both the functionality of the organic moiety and the stability of inorganic moiety. Budd et al. [25] employed zeolite/polyelectrolyte (chitosan/poly(4-styrene sulfonate)) multilayer pervaporation membranes to enhance the yield of ethyl lactate. Adoor et al. [26] prepared aluminum-rich zeolite beta incorporated sodium alginate pervaporation membranes. Organic-inorganic hybrid membranes showed improved performance of pervaporative dehydration of solution, with better flux and retention.

Hydrophobic membranes used as pervaporation membranes are used to separate volatile organic compounds from the body of water. Hydrophobic membrane systems utilize molecules made from proprietary polymeric hollow fiber membranes. The membrane only permits the volatile organic compound and rejects water molecule due to its hydrophobic nature. Hence, pervaporation integrated with membrane separation technology serves as an interesting subject for the separation of organic compounds such as pollutants and high-value products like aroma compounds. Here the membranes employed are polymeric in nature [27–29]. Rarely, ceramic membranes [30–34] can also be used. However, when it comes to recovering volatile polar organics from their very dilute solutions in water [35], the selectivity exhibited by polymeric membranes, as well as ceramic membranes, is not high [36–38].

One of the most applied polymeric materials for organic separation is polydimethylsiloxane (PDMS). PDMS exhibits high selectivity and permeability towards organic substances because of the flexible structure and therefore is preferred for the removal of organic compounds from water [39]. Organic liquid membranes of oleyl alcohol (OA) were found to demonstrate high selectivity for recovering species like n-butanol and acetone [40] from simulated fermentation

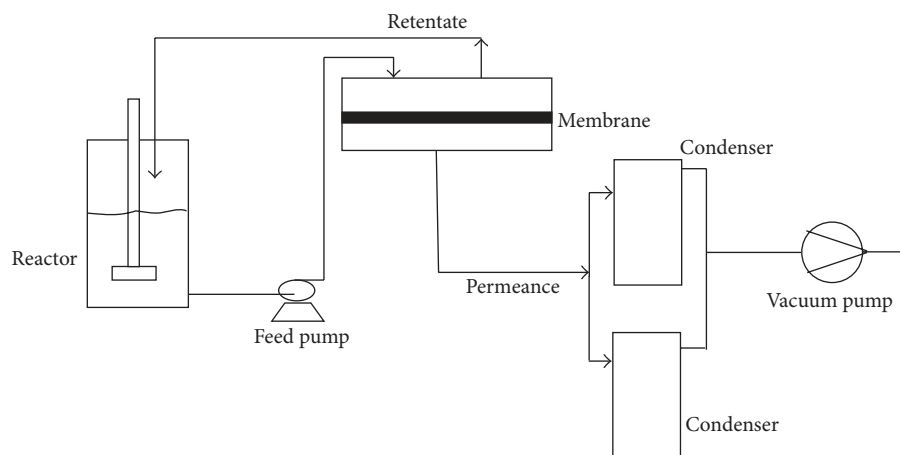


FIGURE 2: Schematic diagram of pervaporation-chemical reactor integrated system.

broths. Employing tri-*n*-octylamine (TOA) as a supported liquid membrane (SLM), Thongsukmak and Sirkar [41] prepared liquid membrane of trioctylamine (TOA) in the coated hollow fibers and demonstrated high selectivity of as much as 275, 220, and 80 for *n*-butanol, acetone, and ethanol from a very dilute solution representative of an acetone-*n*-butanol-ethanol (ABE) fermentation broth (1.5 wt% *n*-butanol, 0.8 wt% acetone, and 0.5 wt% ethanol).

In hybrid configuration as the pervaporation membrane reactor, esterification is a typical example in which pervaporation is used for removal of the product or the byproduct of a reaction (Figure 2). Esterification reactions are typically reversible and equilibrium limited processes with ester and water as products. Pervaporation-membrane reactors (PVMR) have a selective membrane for removal of water from the esterification reaction mixtures and hence achieve a higher yield of ester. In pervaporation-esterification coupling systems, several types of commercial membranes are used including GFT-1005 [19], polydimethylsiloxane [42], PERVAP 2201 [16, 43], and PERVAP 1005 [44, 45]. Table 1 shows the various membranes employed for the pervaporation-esterification integrated system for the synthesis of several esters such as methyl acetate, ethyl acetate, isobutyl acetate, ethyl acrylate, and ethyl lactate.

Zhang et al. [46] employed three types of composite membrane, namely, glutaral cross-linked chitosan (GCCS)/carbomer (CP)/polyacrylonitrile (PAN), glutaral cross-linked gelatin (GCGE)/PAN, and glutaral cross-linked hyaluronic acid (GCHA)/hydrolysis modification- (HM-) PAN, to study esterification of lactic acid and ethanol. In GCCS/CP/PAN composite membrane, the content of the CP is 0.5 wt% and the molar ratio of the CS repeating unit to GA is 60. For GCGE/PAN composite membrane, the content of the GE is 2 wt% and the mass ratio of the GA to GE is 2.5 and in the case of GCHA/HM-PAN membrane, the content of the HA is 0.8 wt% and the cross-linking degree is 0.3. Korkmaz et al. [47] employed ester-permeable polydimethylsiloxane (PDMS) and the water-permeable poly(vinyl alcohol) membranes to study the esterification of acetic acid with isobutanol. They prepared the membranes in laboratories

which are composed of the respective polymer and a cross-linking agent. Zhang et al. [48] employed a catalytically active pervaporation membrane to enhance the conversion of esterification reaction of acetic acid and *n*-butanol. The membrane used consists of three layers: a support layer (commercial PES porous membrane), a separation layer (PVA pervaporation membrane), and a porous catalytic layer with the loading of catalysts.

Currently it is great deal of interest in pervaporation assisted production of enzymatic esters by lipase-catalysed chemical esterification reaction, because higher selectivity can be achieved by the biotechnological way, as milder reaction conditions should be applied; thus, energy demand, cost of production, and byproduct formation can be simultaneously reduced and the conversion or yield of biodiesels can be enhanced [49, 50]. Krishna et al. [51] studied the esterification of isoamyl alcohol with acetic acid in *n*-heptane solvent using immobilized lipase from *Mucor miehei*. They presented relationship between esterification variables (substrate and enzyme concentrations and incubation period) and ester yield to determine optimum conditions for the synthesis of isoamyl acetate catalyzed by Lipozyme IM-20 (immobilized lipase from *Mucor miehei*). They observed that conversion over 95% achieved at even very low enzyme concentrations. Ziobrowski et al. [50] presented the enzymatic production of glycerol monostearate in different high polar organic solvents to remove water produced during the esterification process using pervaporation. Shieh et al. [49] investigated a commercial immobilized lipase from *Rhizomucor miehei* (Lipozyme IM-77) to catalyze the transesterification of soybean oil and methanol. They developed relationships between the variables (reaction time, temperature, enzyme amount, substrate molar ratio, and added water content) and the response (percent weight conversion) and obtained the optimum conditions for biodiesel synthesis using central composite rotatable design (CCRD) and RSM analysis. Koszorz et al. [45] studied the kinetics of enzymatic esterification of oleic acid and *i*-amyl-alcohol (main compound of fusel oil). In the experiments an immobilized lipase enzyme, Novozym 435 (Novo Nordisk, Denmark), which was taken as a catalyst and

TABLE 1: Pervaporation membranes employed for various esterification reactions.

Membranes	Nature of membrane	Esterification reactions studied	Reference
Chitosan-tetraethoxysilane hybrid membrane	Hydrophilic organic-inorganic hybrid membrane	Lactic acid + ethanol	[73]
Nafion membrane	Hydrophilic catalytically active membrane	Acetic acid + methanol	[94]
		Acetic acid + butanol	[94]
GFT-1005 and T1-b membrane	Hydrophilic organic membrane	Lactic acid + ethanol	[19]
		Succinic acid + ethanol	[19]
Polydimethylsiloxane membrane [PDMS]	Hydrophobic cross-linked membrane	Acetic acid + isobutanol	[95]
		Acetic acid + ethanol	[42]
PERVAP			
[2201]	Hydrophilic polymeric membrane	Lactic acid + ethanol	[16]
[2201]		Lactic acid + ethanol	[9]
[2201]		Lactic acid + ethanol	[96]
[2216]		Lactic acid + ethanol	[96]
[1000]		Acetic acid + ethanol	[97]
[2201]		Acetic acid + isopropanol	[43]
[2201]		Propionic acid + isopropanol	[98]
[1005]		Oleic acid + i-amyl alcohol	[45]
[1005]		Acetic acid + ethanol	[18]
[1005]		Acetic acid + benzyl alcohol	[44]
Polyetherimide- γ alumina composite membrane	Hydrophilic composite polymeric-inorganic membrane	Acetic acid + ethanol	[99]
Silica membrane [Pervatech BV]	Hydrophilic inorganic membrane	Lactic acid + ethanol	[13]
Polyetherimide composite membrane	Polymeric/ceramic membrane	Acetic acid + ethanol	[100]
PVA membrane	Hydrophilic polymeric/ceramic composite membrane	Acetic acid + n-butanol	[89]
			[87]
			[101]
PVA membrane cross-linked with catalyst $Zr[SO_4]_2 \cdot 4H_2O$	Polymeric composite catalytic membrane	Acetic acid + butanol	[20]
PVA membrane [Amberlyst coated]	Polymeric/ceramic composite membrane	Acetic acid + butanol	[21]
PVA membrane [cast on polyethersulfone]	Hydrophilic polymeric composite membrane	Oleic acid + methanol	[22]
		2,2,2-Trifluoroethanol + methacrylic acid	[23]
Zeolite membrane [aluminum rich zeolite beta incorporated sodium alginate]	Hydrophilic mixed matrix membrane	Acetic acid + ethanol	[26]
Zeolite T membrane	Hydrophilic membrane	Acetic acid + n-butanol	[102]
		Acetic acid + ethanol	[103]
Zeolite NaA membrane	Hydrophilic membrane	Lactic acid + ethanol	[14]
		Propionic acid + isopropanol	[98]
Poly[ether block amide] membrane	Organophilic membrane	Acetic acid + n-butanol	[104]
Poly[2,6-dimethyl-1,4-phenylene oxide] [PPO] and thin layer fluoroplastic	Hydrophobic composite membrane	Acetic acid + methanol	[105]
Tubular hydroxy sodalite [SOD] membrane	Hydrophilic membrane	Acetic acid + ethanol	[106]
		Acetic acid + butanol	[106]
HZSM-5 membrane	Hydrophilic catalytic active membrane	Acetic acid + ethanol	[107]
Poly[2,6-dimethyl-1,4-phenylene oxide] [PPO] and fullerene C_{60}	Hydrophobic composite membrane	Acetic acid + ethanol	[108]

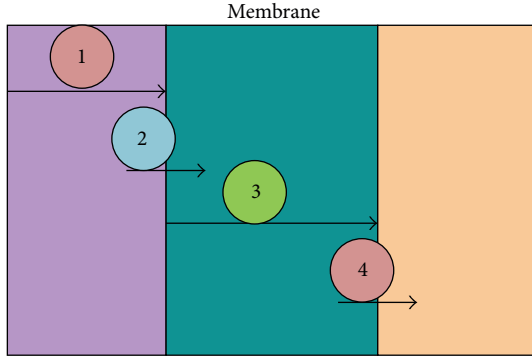


FIGURE 3: Steps involved in transport of component through a pervaporation membrane.

proved to be very sensitive for the presence of water and alcohol in the reaction mixture.

3. Theory of Pervaporation

The transport of component across the membrane in pervaporation is described by solution desorption model that results from these processes in series: (i) diffusion of the component through the liquid boundary layer to the membrane surface, (ii) sorption/diffusion into the membrane, (iii) transport through the membrane, and (iv) diffusion through the vapor phase boundary layer into the bulk of the permeate (Figure 3). In modeling the transport model for pervaporation, it is assumed that the resistance offered by the boundary layer at the vapor phase is negligible and that the concentration of the solute is zero at the permeant side, since the permeant side is maintained at a low vacuum. At increased permeant pressure, however, the resistance to transport on the vapor side will increase and become significant.

Transport through the boundary layer on the liquid feed side of the membrane is given by

$$J_a^{bl} = k_l \rho (x_f - x_{i,l}), \quad (1)$$

where k_l is the boundary layer mass transfer coefficient on the liquid side and $x_{i,l}$ and x_f are the organic concentration at the liquid-membrane interface and feed side, respectively.

Membrane transport is given by

$$J_o^m = k_i \rho (x_{m,l} - x_{m,g}), \quad (2)$$

where k_i is membrane mass transfer coefficient, t is membrane thickness, and $x_{m,l}$ and $x_{m,g}$ are the organic concentration at the membrane in liquid phase and vapor phase, respectively.

Overall organic flux is described by

$$J_i = K_{ov} \rho (x_f - x_p), \quad (3)$$

where the subscripts f and p refer to feed and permeance. It can also be expressed in terms of partial vapor pressure, concentration of i , or fugacity as [52, 53]

$$J_i = Q_{ov,i} A (p_{l,i} - p_{g,i}) = K_{ov,l} A (C_{l,i} - C_{g,i}^*), \quad (4)$$

$$J_i = K_{ov,i} (f_i^{\text{feed}} - f_i^{\text{permeate}}), \quad (5)$$

where J_i is the flux of i across the membrane, $Q_{ov,i}$ is the overall mass transfer coefficient of i in terms of vapor pressure, A is the membrane area, $p_{l,i}$ and $p_{g,i}$ are partial vapor pressures of i in the liquid side and in the permeant (or gas) side, respectively, $K_{ov,l}$ is the overall mass transfer coefficient of i in terms of liquid concentration, $C_{l,i}$ is the concentration of i in the liquid, and $C_{g,i}^*$ is the concentration of i in the liquid which would be in equilibrium with the gas. In pervaporation, the partial vapor pressure is preferred as a measure of the driving force since the effects of temperature on the driving force and on the mass transfer coefficients are separated more clearly.

The partial vapor pressure of i in the liquid side is related to the concentration in the liquid side ($C_{l,i}$) by the expression given by [54]

$$p_{l,i} = \frac{C_{l,i} \gamma_i P_i^0}{\rho_l}, \quad (6)$$

where γ_i is the activity coefficient of i in the liquid side, P_i^0 is the saturation vapor pressure of pure i at the liquid temperature, and ρ_l is the molar density of the liquid. The partial vapor pressure of i in the gas side is related to the concentration in the gas side ($C_{g,i}$) by the expression

$$p_{g,i} = \frac{C_{g,i} P_T}{\rho_g}, \quad (7)$$

where P_T is the total pressure in the gas side and ρ_g is the molar density of the gas. $K_{ov,i}$ in (5) is the apparent mass transfer coefficient and f_i is fugacity. The fugacity of component in the feed and in permeance can be expressed as follows:

$$f_i^{\text{feed}} = \gamma_i x_i^{\text{feed}} P_i^o (T^{\text{feed}}), \quad (8)$$

$$f_i^{\text{permeate}} = \gamma_i P_p,$$

where P_i^o is the vapor pressure of compound i , γ_i is activity coefficient, T^{feed} is the feed temperature, and P_T is total pressure.

The membrane mass transfer coefficient (k_i) includes sorption to, diffusion through, and desorption from the membrane. It is equivalent to the relation between the permeability coefficient (P_i) and the thickness of the active layer of the membrane (l) as shown in

$$k_i = \frac{P_i}{l}, \quad (9)$$

$$P_i = S_i D_i, \quad (10)$$

where the permeability coefficient (P_i) is equal to the product of the solubility coefficient of the permeance in the membrane (S_i) and the diffusion coefficient (D_i) of the permeance in the membrane.

As stated earlier, for pervaporation, the permeant concentration can be neglected when vacuum is used on the permeant side. Therefore, the overall mass transfer coefficient is estimated from the organic flux data obtained by varying feed concentration. Combining the above equations results in the resistance-in-series model that is typically applied to describe components transport by pervaporation [54, 55]:

$$\frac{1}{K_{ov}} = \frac{1}{k_l} + \frac{l}{P_m} \quad (11)$$

or

$$\frac{1}{Q_{ov}} = \frac{1}{Q_m} + \frac{1}{Q_l} = \frac{l}{P_m} + \frac{\gamma p^0}{\rho_l k_l}. \quad (12)$$

It is assumed that the diffusion coefficient remains constant and that there is negligible resistance offered by the vapor phase boundary layer. It is generally known that permeant pressures of 1–15 Torr are a valid assumption. The liquid phase mass transfer coefficient for a driving force expressed in terms of vapor pressure (Q_l) is related to the liquid phase mass transfer coefficient for a driving force in terms of concentration (k_l) as follows:

$$Q_l = \frac{\rho_l}{\gamma p^0} k_l. \quad (13)$$

The factor $\gamma p^0 / \rho_l$ is the conversion factor from a concentration driving force to a partial vapor pressure driving force. It is useful to note this conversion factor since values for Q_l are not generally available, and it is k_l which is normally found in correlations which relate mass transfer coefficient to physical and hydrodynamic conditions. Similarly, to convert the overall mass transfer coefficient from a vapor pressure driving force (Q_{ov}) into a concentration driving force (K_{ov}),

$$Q_{ov} = \frac{\rho_l}{\gamma p^0} K_{ov,l}. \quad (14)$$

Ganapathi-Desai and Sikdar [56] reported that flux increased linearly with increasing feed concentration as expected from (3). The slope of the line yields the overall mass transfer coefficient (K_{ov}). The determination of liquid side mass transfer coefficient (k_l) is obtained using correlations. For laminar flow through a flat channel Leveque's correlation (15) is used. For turbulent flow (16) is used [57, 58].

Leveque's correlation for laminar flow in open channels is given as

$$k_l = 1.6 \left[\frac{D_i}{d_h} \right] [\text{Re}]^{1/3} [\text{Sc}]^{1/3} \left[\frac{d_h}{L} \right]. \quad (15)$$

For turbulent flow through open channels, k_l may be predicted as

$$k_l = 0.026 \left[\frac{D_i}{d_h} \right] [\text{Re}]^{0.8} [\text{Sc}]^{1/3}, \quad (16)$$

where $\text{Re} = u \rho d_h / \eta$ is Reynolds number, L is length of cell, d_h is hydraulic diameter, A is cross-sectional area, u is velocity, and D_i is diffusivity.

Upon determination of k_l from correlations, the resistance-in-series model is applied to the data (K_{ov} and k_l) and membrane resistance (or permeability) is calculated from the intercept of the plot of $1/K_{ov}$ versus $1/k_l$ from (11). This approach yields a quick measure of membrane permeability but cannot be relied upon if the k_l estimates are approximate. Ganapathi-Desai and Sikdar [56] studied the separation of volatile organic compounds (VOCs) such as 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE) from dilute aqueous solutions using composite membrane and reported the permeability by the above method as 5.7×10^{-9} and 1.1×10^{-8} m²/s for TCA and TCE, respectively. They reported the permeability values for other systems also.

3.1. Solution Diffusion Theory. The transport of gas, vapor, or liquid through a dense nonporous membrane is described as [59]

$$\text{Permeability } (P) = \text{solubility } (S) \times \text{diffusivity } (D). \quad (17)$$

Solubility for gases is described by Henry's law. For ideal systems, solubility is independent of concentration and hence sorption isotherm is linear and concentration inside the polymer is proportional to applied pressure. For liquids, as they are not ideal, Henry's law is not applicable. In addition the affinity between liquid and polymer is much greater; hence, sometimes cross-linking is necessary to prevent polymer dissolution. High solubility implies high permeability as this influences diffusivity by making the polymer chains more flexible. Sorption isotherm is nonlinear and behavior is described by free volume models and Flory Huggins thermodynamics. Diffusion coefficients increase with the temperature, while sorption is usually exothermic [59–61]. For the effect of temperature on the permeability of organic compounds through a membrane, different results have been reported in the literature, in some cases permeability decreases with temperature [60, 61], in others, permeability increases with temperature [53], and for some cases permeability is unaffected by temperature within the range studied [52, 55].

Diffusivity depends on geometry of penetrant (as molecular size increases, diffusion coefficient decreases) and concentration. Dependence on size is determined by Stokes-Einstein equation, which is the relation between frictional resistance and the radius of the diffusing component

$$f = 6\pi\eta r. \quad (18)$$

And diffusion coefficient is inversely proportional to frictional resistance as

$$D = \frac{KT}{f}. \quad (19)$$

Large molecules having ability to swell the polymer can have large diffusion coefficient. Diffusivity is determined by

permeation method or time lag method. The amount of penetrant (Q_t) passing through the membrane in time t is given by

$$Q_t = \frac{Dc_i}{l} \left[t - \frac{l^2}{2D} \right]. \quad (20)$$

Instead of Q_t , pressure (p) can also be monitored and this plot of p versus time (t) will give time lag as intercept and permeability as slope from the steady state part of this permeation experiment. Since $P = S \times D$, hence S can be found once D and P are known.

Alternatively, keeping the polymer in closed volume and applying pressure to the chamber can determine diffusivity. Due to sorption, the pressure decreases with time and equilibrium is reached.

4. Parameters in Membrane Performance

The effectiveness of a pervaporation membrane can be determined by mainly two parameters, namely, the separation factor and the permeant flux. The flux was determined by weighing the permeant mass and then dividing by the product of the interval time and membrane area. In dilute solutions, the fluxes are equal to the product of $D_i S_i$ for each component, where D_i is the diffusion coefficient in the membrane material and S_i is the sorption coefficient defined as

$$S_i = \frac{w_{i,\text{Memb}}}{w_{i,\text{Feed}}}, \quad (21)$$

where $w_{i,\text{Memb}}$ and $w_{i,\text{Feed}}$ are the weight fractions of component i in the membrane material and the liquid feed solution in solubility equilibrium with the membrane phase.

The solubility of a compound is the amount sorbed by the membrane under equilibrium conditions and hence a thermodynamic parameter, in contrast to the diffusivity (D_i), which is a kinetic parameter quantifying the rate of permeation through the membrane. D_i is depended on the geometry of the membrane as well as its state (glassy, rubbery, swollen, etc.). A small molecule will more easily diffuse through a membrane than a larger one.

Separation factor determines the overall separation performance of a membrane system. The value of separation factor may vary from unity to infinity. High value of separation factor specifies amplified selectivity. The separation factor α_i for a given compound i is defined as the follows:

$$\alpha_i = \frac{w_i^{\text{permeate}} / (1 - w_i^{\text{permeate}})}{w_i^{\text{feed}} / (1 - w_i^{\text{feed}})}, \quad (22)$$

where w_i is the weight fraction of the compound i in the feed (w_i^{feed}) and in the permeance (w_i^{permeate}).

Following the solution-diffusion mechanism, the basic transport equation for pervaporation can be written as

$$J_i = \left[\frac{P_i}{l} \right] (x_i \gamma_i p_i^{\text{sat}} - y_i p^p), \quad (23)$$

where P_i is the membrane permeability, which is a product of diffusivity and solubility coefficients, l is the membrane thickness, y_i is the permeant mole fraction, and p^p is the permeant pressure. The term $[P_i/l]$ is known as permeance that can be determined by rearranging the above equation:

$$\left[\frac{P_i}{l} \right] = \frac{J_i}{(x_i \gamma_i p_i^{\text{sat}} - y_i p^p)}. \quad (24)$$

The ideal membrane selectivity β is defined as the ratio of the permeability coefficients or the permeances:

$$\beta_{i/j} = \frac{P_i}{P_j}. \quad (25)$$

Overall performance of the membrane was evaluated in terms of pervaporation separation index (PSI), as given in the following [62]:

$$\text{PSI} = J(\alpha - 1), \quad (26)$$

where J is permeation flux ($\text{kg}/\text{m}^2\text{h}$); when $\alpha = 1$, no separation occurs; PSI of zero means either zero flux or zero separation. Table 2 and Figures 4–6 summarize the performance parameters of different types of membranes for several systems obtained in the pervaporation studies of research articles. It presents the values of important parameters including permeation flux and selectivity of membrane at different operating temperatures.

4.1. Effect of Membrane Thickness. According to Fick's equation and the solution-diffusion model, permeability of a penetrant through a membrane should be independent of membrane thickness, but the flux is inversely proportional to membrane thickness [63]. Hasanoglu et al. [64] studied hydrolysis reaction of ethyl acetate (EAc), water, ethanol (EOH), and acetic acid (AsAc) using polydimethylsiloxane (PDMS) and discussed the effect of membrane thickness. 250 μm and 300 μm membranes thickness were employed. It was found that fluxes through 250 μm membranes are higher than those through the 300 μm membranes.

Hyder et al. [65] studied the influence of selective layer thickness on separation factors of dehydration of ethanol-water mixture using poly(vinyl alcohol) and poly(sulfone) (PVA-PSf) cross-linked composite membrane with varying selective PVA layer thickness and concluded that, with a change in thickness from 52 to 4 μm (92% decrease), the selectivity change was not significant (only 17% decrease), compared to the change in flux (193% increase) that was dependent on the bulk thickness of the membrane.

Raisi and Aroujalian [66] investigated the effect of membrane thickness on the performance behavior of the pervaporation membrane PDMS (polydimethylsiloxane) and POMS (polyoctylmethylsiloxane) in the binary and ternary model solution of pomegranate aroma compounds. It was observed that results were in agreement with the fact that the permeation rate is inversely proportional to membrane thickness because permeation resistance enhances as membrane thickness increases.

TABLE 2: Overview of membrane performance parameters of different pervaporation systems.

System	Membrane	Parameters			Reference
		Temperature (°C)	Flux (kg/m ² h)	Selectivity	
Water/isobutyl acetate	PDMS	70	4.429	1.421	[47]
Water/isobutyl acetate	PERVAP 1201	70	0.712	686.5	[47]
Water/ethyl acetate	Hydrophilic	40	0.448 (mol/m ² h)	—	[109]
Water/ethyl acetate	Hydrophobic	40	7.505 (mol/m ² h)	—	[109]
Water/ethyl lactate	Glutaral cross-linked chitosan (GCCS)/carbomer (CP)/polyacrylonitrile (PAN)	80	1.247	256	[46]
Water/ethyl lactate	Glutaral cross-linked gelatin (GCGE)/PAN	80	1.08	298	[46]
Water/ethyl lactate	Glutaral cross-linked hyaluronic acid (GCHA)/hydrolysis modification (HM)-PAN	80	1.634	233	[46]
Water/ethyl oleate	PERVAP 1000	25	0.215	120	[110]
Water/n-butanol	PVA/PES	75	0.14	135	[48]
n-Butyl acetate/methanol	PERVAP 2255-50	41	—	3.5	[111]
Isobutyl acetate/water	Cross-linked PDMS	60	3.7	1.4	[95]
Water/ethanol	Polyvinyl alcohol	90–100	0–2	50–2000	[112]
Water/ethanol	Polyamide-6	80	1.15	2	[113]
Water/dioxane	Polyamide-6	35	0.04	45	[114]
Water/acetic acid	Polyamide-6/PAA	15	0.005	82	[115]
Water/isopropanol	PESS Li+	25	0.087	40	[116]
Water/isopropanol	PESS K+	25	0.026	60	[116]
Acetone/water	Polypropylene	116	0.1–1.2	3	[117]
Isopropanol/water	Silicone rubber	25	0.03–0.11	9–22	[118]
Butanol/water	Silicone rubber	30	<0.035	45–65	[119]
Butyl acetate/water	PDMS	50	0.55	370	[120]
Ethanol/water	Zeolite NaA	95	3.35	5100	[121]
Water/acetic acid	Pervatech	75	2.5	150	[122]
Water/isopropanol	Pervatech	100	4.0	250	[122]
Ethanol/water	Polyacrylonitrile	70	0.03	12500	[123]
Ethanol/water	Polyvinyl alcohol	70	0.38	140	[123]
Ethanol/water	Polyhydrazide	70	1.65	19	[123]
Methanol/isopropanol	Polypyrrole	58	0.004	2	[124]
Water/n-butanol	PVA membrane	70–90	0.154–0.184	12.2–16.5	[125]
Water/n-butyl acetate	PVA membrane	70–90	0.15–0.196	432–441	[125]
Water/acetic acid	PVA membrane	70–90	0.176–0.192	9.0–10.8	[125]
Water/methanol	CS-TEOS	60–80	0.005–0.29	450–1150	[73]
Ethanol/water	Tri-n-octylamine (liquid membrane)	54	0.0598	100	[75]
Ethyl acetate/water	Surface modified alumina membrane	40	0.254	66.9–78.9	[76]
Ethyl propionate/water	Surface modified alumina membrane	40	0.343	106.5–97.3	[76]
Ethyl butyrate/water	Surface modified alumina membrane	40	0.377	120.5–122.8	[76]
Water/ethanol	Modified porous glass	79	0.1	1630	[126]
Water/ethanol	Polyimide	75	0.01	850	[127]

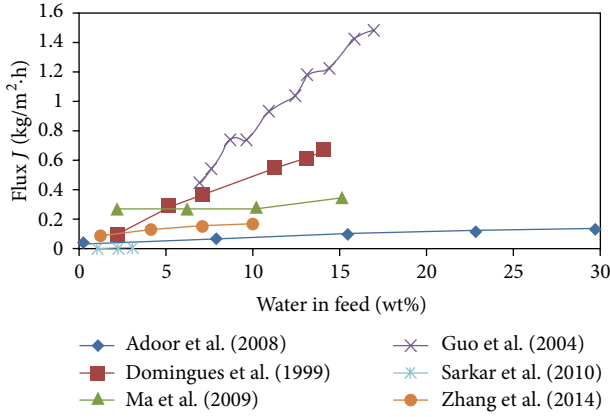


FIGURE 4: Effect of feed water concentration (wt%) on flux of water-organic pervaporation system.

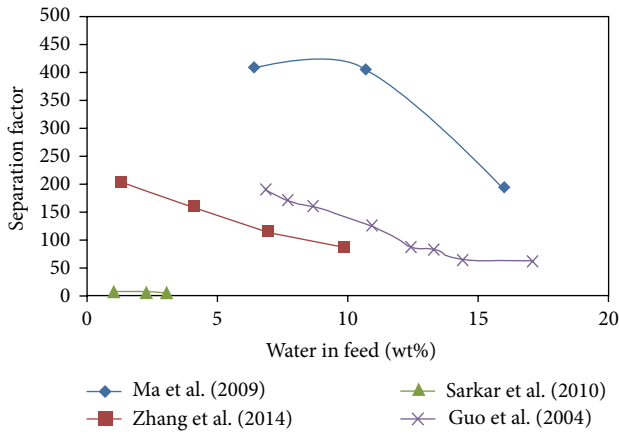


FIGURE 5: Effect of feed water concentration (wt%) on separation factor of water-organic pervaporation system.

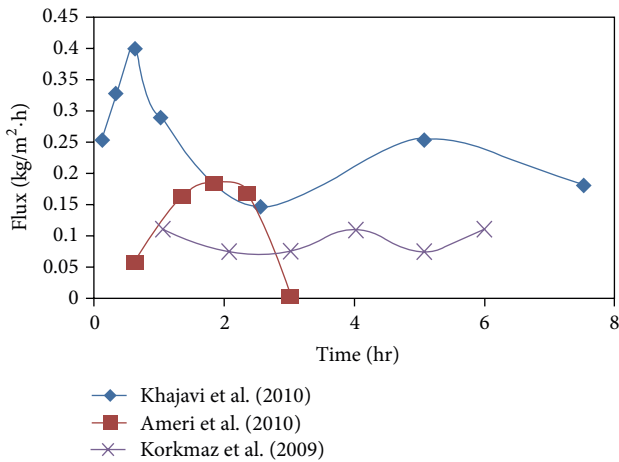


FIGURE 6: Obtained trend of flux with time for different pervaporation systems.

4.2. *Effect of Temperature.* Temperature has a significant effect on the transportation rate. The effect of temperature can be expressed by an Arrhenius type function. Since $P = S \times D$, both S and D contribute to the effect of temperature. For small noninteracting gases, D is the more dominating, as S does not change much with temperature. For the larger molecules, the situation is more complex since two effects, diffusion and solubility, are opposing, and further both are concentration dependent.

S dependence on temperature can be described as

$$S = S_o \exp\left(-\frac{\Delta H_s}{RT}\right), \quad (27)$$

where S_o is the temperature-independent constant and ΔH_s is heat of solution. Similarly temperature effect on diffusion is described as

$$D = D_o \exp\left(-\frac{E_d}{RT}\right), \quad (28)$$

where D_o is the temperature-independent constant and E_d is activation energy for diffusion or it is a preexponential factor. Using $P = S \times D$ and using the above expression for S and D , we get

$$P = D_o S_o \exp\left(-\frac{\Delta H_s + E_d}{RT}\right) = P_o \exp\left(-\frac{E_p}{RT}\right). \quad (29)$$

Chang et al. [67] represent the temperature dependence of flux using the following relationship:

$$J_w(T, P) = J_w(T^o, P^o) \exp\left[\left(\frac{E_w}{R}\right)\left(\frac{1}{T^o} - \frac{1}{T}\right)\right] \cdot \frac{RT \ln(x_w \gamma_w P_w^o / \gamma_w P)}{RT \ln(x_w \gamma_w P_w^o / \gamma_w P^o)}, \quad (30)$$

where $J_w(T^o, P^o)$ is the water flux measured at a feed side temperature of T^o and permeant side pressure of P^o .

The term on the influence of permeant pressure on water flux in (30) is derived from the fact that the driving force for transport originates from the difference in chemical potential between feed and permeance in the pervaporation [68]. The difference in chemical potential can be approximated as a difference in partial vapor pressures of the permeating component in the liquid feed and the gaseous permeance. Empirical equations for partial water permeation flux and permeation water composition are given by the following equations:

$$J_w = 3.935C_w^f, \quad (31)$$

$$C_w^p = \frac{12C_w^f}{0.055 + 12.84C_w^f - 7.7C_w^{f2}}. \quad (32)$$

The data on saturation vapor pressure required for calculating (32) were obtained by using the coefficients as tabulated by Daubert and Danner [69] and the activity coefficient by using the coefficients for the Van Laar equation as tabulated by Gmehling and Onken [70]. The equations and coefficients are given in the following equations:

$$P_w^o = \exp\left(A + \frac{B}{T} + C \ln T + DT^E\right),$$

$$A = 7.3649 \times 10, B = -7.2582 \times 10^3, C = -7.3037, D = 4.1653 \times 10^{-6}, E = 2, \quad (33)$$

$$\ln \gamma_w = A_{12} \left[\frac{A_{21}(1-x_w)}{\{A_{12}x_w + A_{21}(1-x_w)\}} \right]^2, \quad A_{12} = 1.7769, A_{21} = 0.94, \quad (34)$$

where P_w^o and γ_w are the saturated vapor pressure and the activity coefficient of water, respectively, and x_w is the mole fraction of water in an ethanol/water mixture.

Effect of temperature on membrane mass transfer coefficient (k_f) can be derived from changes in the physical properties of the solution, mainly its viscosity. For the same flow rate, the Reynolds number increases sharply with temperature. From 30°C at a constant liquid flow rate, the Reynolds number increased from 7930 to 11469 at 50°C and to 15573 at 70°C in the studies by Oliveira et al. [54] Their studies were on monochlorobenzene (MCB) transport using silicone rubber (70% polydimethylsiloxane (PDMS) + 30% silica filler) tubing as membrane.

Burshe et al. [71] studied the effect of temperature on flux and selectivity of water in glycerine-water mixtures using Nafion (NA), cellulose triacetate (CA), carboxylated polyvinyl chloride (CPVC), and polyimide and polyethersulfone (PES) membranes. Temperature was varied from 30°C to 70°C. Increasing temperature was found to increase flux. Though amount sorbed decreased with temperature yet, this is offset by an increase in the diffusion coefficient of the solute because of increased temperature. NA has the lowest energy of activation for diffusion and hence efficiently transports water through it. Increasing temperature however decreases selectivity. The reason behind this is that the thermal motion of polymer chains randomly produces free volumes through which permeating molecules can diffuse. With increasing temperature, thermal agitation increases, thus enlarging the diffusive free volume. Thus, more solute can diffuse through the membrane. At water content > 60% very little difference in selectivity was observed at all temperatures.

Domingues et al. [44] pointed out that the flux is practically linear for small variations in the water concentration and that it increases with an increase in temperature and membrane selectivity for water remains constant and equal to 96%. Guo et al. [72] reported that water flux increases with an increase in temperature. The reason is that increase in motions of the polymer chains thermally induced and the expansion of the free volume. In addition, the increased thermal motions of the permeant molecules also promote their diffusion. However, water permeance does not increase with an increase in temperature. The relatively negative dependence of water permeances on temperature may arise from the fact that permeance is defined as permeant flux divided by permeant driving force. The driving force combines two temperature-dependent factors, γ_i and p_{sati} , which are external factors outside the membrane. The values of water activity coefficients of different butanol water systems (1-butanol/water; 2-butanol/water; isobutanol/water;

and tert-butanol/water) are quite close at different temperatures for each of four butanol systems. Thus, p_{sati} plays a more important role than the water activity coefficient in these four systems. The higher temperature results in a higher p_{sati} , a larger denominator, and consequently a smaller permeance.

Ma et al. [73] presented the effect of operating temperature ranging from 60°C to 80°C on the pervaporation properties of the CS-TEOS membrane. The reaction system was lactic acid-ethanol and Amberlyst 15 ion exchange resin was used as a catalyst. Total flux increased notably, while the separation factor decreased with increasing temperature. When operating temperature is increased, vapor pressure of permeating components in the upstream side of the membrane increases. Vapor pressure difference between the upstream and downstream side of the membrane enhanced the transport driving force. Moreover, increasing temperature brought about higher molecular diffusivity [74]; therefore, the mass transport was faster, and the total flux increased. In addition, as temperature is increased, polymer chains became more flexible and accommodated larger available free volume of the polymer matrix for diffusion, which allowed easier water and ethanol transfer across membrane and eventually the selectivity decreased.

Thongsukmak and Sirkar [75] studied alcohol-water separation for feed alcohol concentrations of 5–10% in the presence of a small amount of n-butanol in the feed varying between 0.5 and 2.5 wt% over a feed temperature range of 30–54°C. In single organic solvent species in solution, three feed concentration levels, the values for 1.5, 5, and 10 wt% were taken. As the temperature was increased from 25 to 54°C, the n-butanol-water selectivity went up from 60 to as high as 162 at 54°C; the permeant mass flux of n-butanol reached 11.0 g/(m²h) at 54°C (for a n-butanol wt% of 1.5 in feed). In mixtures of n-butanol and ethanol, the selectivity and mass flux of solvents were increased significantly at elevated temperatures. For a constant air flow rate, the beneficial effect of increasing temperature on the mass transfer of monochlorobenzene (MCB) across the membrane silicone rubber (70% polydimethylsiloxane (PDMS) + 30% silica filler) tubing (3.0 mm i.d. with 1 mm wall thickness) was reflected in an increase of the MCB concentration in the air stream leaving the membrane module [54]. For an increase in temperature from 30°C to 50°C, the MCB concentration in the gas outlet of the membrane module (at standard temperature and pressure) increased by a factor of 1.3, from 3.2 to 4.2 gm⁻³. From 30 to 60°C, the increase was by a factor of 1.6.

Song et al. [76] studied the pervaporation of ester (ethyl acetate, EA; ethyl propionate, EP; ethyl butyrate, EB) with

hydrophobic membranes. Effect of temperature (30–50°C) on different esters (ethyl acetate, EA; ethyl propionate, EP; and ethyl butyrate, EB) was studied. For EB and water permeation through a hydrophobic alumina membrane, the E_a values are 34.1 and 45.7 kJ/mol for EB and water, respectively, whereas their corresponding E_p values are -2.2 and -5.1 kJ/mol. The negative value of E_p for EB means that the increasing rate of ester flux reduces with increasing temperature. Activation energy of penetrant increased as the penetrant size increased in the order: EA < EP < EB. Activation energy (E_a) is the sum of the activation energy of diffusion (E_D) and the enthalpy of sorption (ΔH). While E_D is usually positive, ΔH is negative for the exothermic sorption process. When the positive E_D dominates over the negative ΔH , the positive value of E_a occurs, indicating that the membrane permeability coefficient increases with increasing temperature [60]. In this study, the activation energy (E_p) of esters was negative and that of water was positive values. The ester flux decreased and water flux increased with increasing temperature, which shows that the activation energy of sorption (ΔH) dominates over diffusion. The activation energy of EB was greater than EA and EP, which means that permeation flux of EB was most sensitive to the temperature change. It was observed that all ester compound and water fluxes increased exponentially with temperature. The reason for this is the flux expression which is expressed as follows:

$$J_i = K_i (C_i x_i^{\text{feed}} P_i^o (T^{\text{feed}}) C_2). \quad (35)$$

Since vapor pressure (P_i^o) increases with increasing temperature, this results in the increase of flux (J_i). The fluxes of EB increased with increasing temperature, and the concentration of EB in permeance decreased with increasing temperature. This result might be explained by the negative value of E_p for ester as described earlier. All esters (EA, EP, and EB) exhibited similar behavior regarding permeant concentration with feed temperature.

Transport of volatile organic compounds (VOCs) such as 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE) from dilute aqueous solutions through composite membrane constructed on a porous ceramic support from a block copolymer of styrene and butadiene (SBS) was studied by Ganapathi-Desai and Sikdar [56]. An increase in feed temperature causes changes in the feed viscosity and VOC diffusion coefficients and yields higher fluxes for all components. Arrhenius plot of flux versus temperature was used to calculate the activation energy for the transport of the VOCs through the SBS composite membrane. These activation energies for TCA and TCE were found to be 4.4 and 5.3 kcal/mol, respectively. In an earlier work by Dutta and Sikdar [77], activation energy of 5.6 kcal/mol was reported for TCA transport through the SBS membrane.

4.3. Effect of Feed Concentration. D can be related as an exponential function of volume fraction of penetrant as

$$D = D_o \exp(\gamma\phi), \quad (36)$$

where ϕ is the volume fraction of penetrant, γ is exponential constant (plasticizing constant, indicating the plasticizing

action of the penetrant on segmental motion), and D_o is the diffusion concentration at zero concentration. D_o is related to molecule size and D_o is large for small molecules and small for large molecules. However, ϕ and γ are greatly dominating factors as they are in exponential terms. For gases that hardly show any interaction with polymer, $\gamma = 0$; hence $D = D_o$.

Free volume theory describes the concentration dependence of the diffusion coefficient. Polymer has two states, namely, glass and rubber. Below glass transition temperature, there is glassy state and mobility of chain segment is limited. Above T_g , mobility increases, frozen microvoids no longer exist, and the number of the parameters changes, one of which is the specific volume, expressed as

$$V_f = V_T - V_o, \quad (37)$$

where V_o is the volume occupied by molecules at 0 K (estimated by group contribution method).

Fractional volume is defined as

$$v_f = \frac{V_f}{V_T}, \quad (38)$$

where v_f or V_T is obtained from polymer density. For glass polymer, the fractional free volume is 0.025 and hence below T_g it is constant and is equal to v_{f,T_g} . Above T_g

$$v_f = v_{f,T_g} + \Delta\alpha (T - T_g), \quad (39)$$

where $\Delta\alpha$ is the difference between the value of thermal expansion coefficient above T_g and below T_g . Molecule can diffuse only if there is sufficient space or free volume. If the penetrant size increases the amount of free volume must also increase. The probability of finding hole whose size exceeds the critical value is proportional to $\exp(-B/v_f)$; B is local free volume needed for a given penetrant; v_f is fractional free volume. Thus, the mobility of penetrant depends on the probability of finding a hole of appropriate size. Mobility can be related to thermodynamic diffusion coefficient:

$$D_T = RTA_f \exp\left[-\frac{B}{v_f}\right], \quad (40)$$

where A_f is dependent on the size and shape of penetrant molecule and B is in relation to minimum local free volume necessary to allow a displacement. Thus, from the above equation, D increases as temperature increases and D decreases as the size of penetrant molecule increases since B increases.

For noninteracting systems, A_f and B are independent of the polymer type; hence diffusivity of given gas molecule can be determined from density measurement alone. If A_f and B are function of the polymer type, v_f as function of both temperature and concentration in needed

$$v_f(\phi, T) = v_f(0, T) + \beta(T)\phi, \quad (41)$$

where $v_f(0, T)$ is the free volume of the polymer at temperature T in the absence of penetrant; $\beta(T)$ is constant

characterizing the extent to which the penetrant contributes to the free volume; and ϕ is the volume fraction of penetrant.

Diffusion coefficient at zero penetrant concentration can be given as

$$D_0 = RTA_f \exp \left[-\frac{B}{v_f(0, T)} \right]. \quad (42)$$

Combining the equations,

$$\ln \frac{D_T}{D_0} = \left[\frac{B}{v_f(0, T)} - \frac{B}{v_f(\phi, T)} \right] \quad (43)$$

or

$$\left[\ln \frac{D_T}{D_0} \right]^{-1} = \left[\frac{v_f(0, T)}{B} - \frac{v_f(0, T)^2}{B(T)B \cdot \phi} \right]. \quad (44)$$

Thus the LHS is related linearly to ϕ^{-1} . The relationship between measured diffusion coefficient (D) and thermodynamic diffusion coefficient (D_T) is

$$D_i = D_T \left[\frac{d \ln a_i}{d \ln \phi_i} \right]. \quad (45)$$

The factor in bracket is obtained from Flory Huggins thermodynamics. The activity of penetrant inside the polymer is

$$\ln a_i = \ln \left(\frac{P_i}{P_o} \right) = \ln \phi_i + \left(1 - \frac{v_i}{v_p} \right) \phi_p + \chi \phi_p^2, \quad (46)$$

where χ is the interaction parameter; if χ is greater than 2, the interaction is small; if χ lies between 0.5 and 2, strong interaction exists and high permeability is expected. Thus,

$$\left[\frac{d \ln a_i}{d \ln \phi_i} \right] = 1 - \left(2\chi + 1 - \frac{v_i}{v_p} \right) \phi + 2\chi \phi_p^2. \quad (47)$$

Component diffuses not a single molecule but in dimer or trimer form. Size of diffusing component increases with the diffusion coefficient decreases. The presence of clustered component can be determined by the cluster integral G_{11} (Zimm Lindbergh theory):

$$\frac{G_{11}}{V_1} = \left(\frac{1}{\phi_1} - 1 \right) \left[\frac{d \ln a_i}{d \ln \phi_i} \right] - \frac{1}{\phi_1}, \quad (48)$$

where V_1 is the molar volume. For an ideal system, $[d \ln a_i / d \ln \phi_i] = 1$; hence LHS of the above equation is 1 and hence no clustering is there. If LHS is greater than -1 , clustering will occur.

Chang et al. [67] studied the pervaporation of ethanol in the pilot plant and found that the water content in permeance is still high even with low water content in the feed. Membrane selectivity was found to be hardly altered by permeant pressure change. Permeation fluxes increase linearly with the water content in the feed and decrease with permeant pressure. Temperature influence is described by Arrhenius law and activation energy was found to be $E_w = 7.84$ kcal/mol.

Burshe et al. [71] studied the effect of water concentration on flux and selectivity of water in glycerine-water mixtures using Nafion (NA), cellulose triacetate (CA), carboxylated polyvinyl chloride (CPVC), polyimide (PI), and polyether-sulfone (PES) membranes. Increasing water in feed increases flux of water and following trend was observed $NA > CA > PES > CPVC > PI$. The reason for this is the plasticization of NA membrane because of increased water concentration in the membrane phase, which increases the free volume and results in increasing the sorption. Selectivity decreases with an increase of water in the feed in the trend $PES > PI > NA > CA > CPVC$.

Guo and Hu [78] studied on ethanol-water transport in novel silicone copolymer consisting of PDMS segments and ladder-like phenylsilsesquioxane segments and found that the concentration of ethanol in the permeance is always higher than that in the corresponding feed. The separation factor decreases as the ethanol concentration in feed increases. High separation factor can be obtained for the separation of dilute aqueous solution of ethanol through the membrane. The flux of ethanol increases proportionally with increasing ethanol concentration in the feed, whereas the flux of water is almost constant for various feed compositions. The magnitude of separation factor and flux for the pervaporation increases in the following order: methanol $<$ ethanol $<$ 2-propanol $<$ acetone $<$ THF. This order just corresponds with the decreasing order of the solubility parameters of these organic components.

Wolińska-Grabczyk et al. [79] employed three types of membranes, PUU-PES-1, PUU-PES-2, and PU-PET-1 for separation of both high and low concentrations of benzene in benzene/cyclohexane mixture. Polyester-based polyurethanes (PUU-PES-1, PUU-PES-2) exhibited an acceptable selectivity and permeability and excellent stability to separate benzene/cyclohexane azeotropic mixture. Replacement of the polyester macrodiol with the polyether one (PU-PET-1) resulted in a membrane material with a much higher permeability accompanied still by a lower selectivity. The increase in the flux value is commonly accompanied by the loss of the membrane selectivity. For the separation of MTBE/MeOH model mixture containing 15 mass % of MeOH, the obtained membranes were preferentially permeable to MeOH over MTBE. Excellent separation capability (100% of MeOH in permeance) is shown by PU-PET membrane prepared from polyether-based polyurethane. The substitution of the polyether in a polyurethane soft segment by the polyester resulted in more permeable membrane with slightly less separation ability. For the removal of benzene and chloroform from water, PU-PD-1 polyurethanes exhibit excellent selectivity. Structural modifications concerning the application of the polyether rather than the polydiene macrodiol (PU-PET-1 versus PU-PD-2) led to some improvement of the membrane permeability, however, at the expense of its selectivity.

Guo et al. [72] found that the partial water flux increases rapidly with feed water concentration. The selective layer of the composite membrane is made of polyvinyl alcohol (PVA) with hydroxyl substituted groups. Thus, it has a high polarity and experiences a strong interaction with water

through hydrogen bonding. At higher feed water concentrations, there are greater numbers of water molecules in contact with the selective layer of the membrane. Therefore, more water molecules are sorbed into the membrane, which causes a greater degree of swelling in the top layer of the membrane. Consequently, more water molecules can pass through the water-swollen membrane and water permeation flux increases as the feed water content increases. The percentage of increment for water permeance with increasing feed water content is slightly lower than that of water flux. Presence exhibits more accurate permeant-specific transport properties with feed concentration because it has significantly decoupled the effect of fugacity difference as the driving force from the overall membrane transport. Butanol concentration in the permeance decreases with an increase in feed water concentration for the 2-butanol, isobutanol, and tert-butanol/water systems while the trend is opposite to the 1-butanol/water system. 1-Butanol presents the highest flux compared with other alcohols because of the strongest affinity between 1-butanol and membrane and the highest linearity of 1-butanol molecular structure.

Ma et al. [73] studied the effect of water content in the feed varying from 2 wt% to 15 wt% in the esterification studies on lactic acid ethanol system using Amberlyst 15 ion exchange resin. With the increase of water content in the feed, the total flux increased from 271 g/(m²h) to 352 g/(m²h), while the separation factor decreased from 1380 to 268. Degree of swelling value of the CS-TEOS membrane increased with increasing water content in the feed, leading to the reduction of mass transfer resistance and the acceleration of diffusion velocity for components in the membrane. Meanwhile, the size of voids in the membrane became larger and larger with increasing *DS* value; ethanol molecules won more chance to pass through these voids, which resulted in the decrease of separation factor.

In the hydrolysis reaction of ethyl acetate (ethyl acetate (EAc), water, ethanol (EOH), and acetic acid (AsAc)) using polydimethylsiloxane (PDMS) membrane, Hasanoglu et al. [64] found that, with the increase in the ethyl acetate concentration in the feed, the ethyl acetate fluxes increase. While the ethyl acetate concentrations increase from 1 to 3 wt%, total fluxes (summation of partial fluxes) change in the range of 79–307 g/m²h for the quaternary mixtures. This phenomenon was explained related to the plasticizing effect of the organic molecules. As the EAc concentration in the feed increases, membrane swells more, and the polymer chains become more flexible, thus decreasing the energy required for the diffusive transport through the membrane. Acetic acid and ethanol permeate through the PDMS membrane in very small quantities. For the mixtures, which have the same EAc concentrations, an increase in ethanol concentration in feed yields higher partial fluxes of ethanol while the acetic acid flux is not much affected by feed concentration of acetic acid. The reason for this is that the three different feed mixtures having 3% EAc concentrations have different partial fluxes of EAc indicating the effects of mutual interactions of each component on the fluxes. The total fluxes increase with increasing EAc/water ratio due to the hydrophobicity of

the membrane and the affinity of the membrane to the EAc molecules. An increase in EAc/organic ratio in feed yields a decrease in EAc/organic selectivity. This is due to the reason that increases of ethyl acetate amount in the feed mixture, in which PDMS is more permeable causes, the membrane to swell. Therefore, the amount of other soluble components dissolved in the membrane increases due to the presence of ethyl acetate.

Thongsukmak and Sirkar [75] studied alcohol-water separation for feed alcohol concentrations of 5–10% in the presence of a small amount of n-butanol in the feed varying between 0.5 and 2.5 wt% over a feed temperature range of 30–54°C. In single organic solvent species in solution, three feed concentration levels, the values for 1.5, 5, and 10 wt% are taken. The selectivity of ethanol goes up to 38 at a feed temperature of 54°C and 10.0 wt% ethanol in feed. Higher feed ethanol concentration results in a higher selectivity and mass flux due to a higher driving force for the pervaporation of ethanol through the liquid membrane. In the studies on mixtures of n-butanol and ethanol, the selectivity and mass flux of ethanol got higher when the concentration of ethanol was higher in the feed. This is due to the higher concentration in the feed that provided a higher driving force via the increase in the ethanol effective partial pressure. The mass flux of ethanol obtained for 10 wt% ethanol in feed obtained was 16.2 g/(m²h), which is considerably higher than the flux for the experiment without n-butanol added to the feed (by 73%). The selectivity of ethanol went up to 66 for the mixture of 10 wt% ethanol with 1 wt% n-butanol in the feed at 54°C; this is much higher than the highest ethanol selectivity obtained with single species solution of ethanol at 54°C.

Pervaporation of esters with hydrophobic membrane was studied by Song et al. [76]. Permeation fluxes of esters were found to increase linearly as feed concentration increased while the permeation flux of the water was not affected by ester concentration in the feed. The fluxes can be expressed as follows:

$$J_i = K_i (C_i x_i^{\text{feed}} p_i^o (T^{\text{feed}}) - C_2). \quad (49)$$

At a given temperature, the permeation flux of ester is a function of k_i , saturation pressure of ester (p_i^o), and molar fraction of ester (x_i^{feed}). k_i increases with the feed concentration owing to the increasing solubility coefficient (S_i) and diffusion coefficient (D_i). As expected from the above equation, ester flux increased relatively linearly with increasing molar fraction in feed (x_i^{feed}). In the case of water flux, however, it might be inferred from the equation that water flux at a given temperature did not depend on ester concentration in the feed because the molar fraction of water in the feed (x_w^{feed}) remained virtually constant in the range of dilute ester concentration. That is why the permeation flux of water was not affected by ester concentration. The total flux increased with increasing ester concentration in the feed due to the high flux of ester.

As the feed ester concentration was increased from 0.15 to 0.60 wt%, the separation factor of EA at 40°C increased from 66.9 to 78.9. However, the separation factors of EP and EB were not much affected by feed concentration, which was

in the range of 106.5–97.3 and 120.5–122.8, respectively. The separation factors of PDMS membrane are higher than those of this study; separation factor of EA with PDMS GFT is 85.0–145.0; PDMS GFTz 254.0; PDMS DC 368.0. Those of EP and EB with PDMS are 79.0–171.2 and 96–196.3, respectively.

Ganapathi-Desai and Sikdar [56] in their studies on SBS polymer membrane, single VOC tests, and ceramic bilayer membrane for TCA and TCE transport reported that flux increased linearly with increasing feed concentration. Water flux stayed relatively constant over the range of concentration. K_{ov} increases with flow rate, proving the domination of boundary layer resistance in the overall transport of TCA across the membrane. Selectivity was found to increase with flow rate.

5. Intensification of the Esterification Reaction Using Pervaporation

Esterification is one of the most important chemical reactions in the chemical industry. Esters are derived from carboxylic acid by the replacement of hydrogen in the –COOH group of acid by the hydrocarbon group of alcohol. Esterification reaction is a slow reaction and is reversible in nature. The reaction is carried out in the presence of the catalyst. Homogeneous catalysts, such as H_2SO_4 , HCl [80], and p-toluenesulfonic acid [14], are frequently employed to esterification process. However, these catalysts have been found to attack membranes as well as the devices and are difficult to be separated from the products. As a result, there is an increasing effect on heterogeneous catalysts, such as ion-exchange resin [81], zeolite [82], and solid super acid [83]. Ion-exchange resin has displayed comprehensive superiority in many situations [84]. Amberlyst 15 ion-exchange resin possesses distinct advantages including being environmentally benign, being nontoxic, being long-term chemically and physically stable [85], and being easily recyclable [43, 84, 86] and has been successfully explored as a powerful catalyst for the esterification reaction.

Since the reaction is a reversible reaction and is equilibrium limited, the yield of ester is generally small. It is recommended that the ester be distilled off as soon as it is formed so that the reverse reaction does not happen. To improve the yield, it is customary to drive the position of the equilibrium to the ester side by either using excess of one of reactants (usually alcohol) or removal of the product of the reaction. However, there are challenges involved such that using excess of reactant would result in increased cost of the subsequent separation as the product stream is obtained in diluted form in the excess reactant. Subsequent removal of the product of the reaction via processes such as reactive distillation required that the difference in the volatility of product and reactants be sufficiently large. This is usually not the case in many processes and in addition formations of azeotropes were noted. The mismatching of the reaction and distillation temperature is an additional complication and in many cases the process performance and energy consumption in reactive distillation are the major cost factor in the manufacturing of esters.

6. Comparison of Esterification with and without Pervaporation

The integration of esterification reactor with a pervaporation pilot plant via hybrid reactor permits the selective permeation of the component (water) from the mixture. Hence the conversion of thermally limited esterification reaction is enhanced through controlled removal of one of the product species from the reaction mixture. Pervaporation is a rate controlled separation process and the separation efficiency is not limited by relative volatility. In pervaporation process, only water is permeated by membrane and accomplishes phase change. Hence, the energy required is comparatively lower. In addition to this, the temperature of operation of pervaporation setup matches with the temperature of reaction and hence could be advantageously used for enzymatic esterification due to temperature constraints normally imposed by enzyme stability. Different factors affect the pervaporation aided esterification reactor setup such as effect of initial molar ratios of the reactants, effect of catalyst concentration, effect of membrane area, and effect of temperature. Large membrane size could provide higher surface for the transfer of acid though the challenges of membrane rupture do surround the studies. An increase in temperature, catalyst concentration, and initial molar ratios of the reactants induces not only an acceleration of esterification but also acceleration in pervaporation.

The combination of pervaporation with the chemical reaction is very attractive system nowadays. The coupling of pervaporation separation process into conventional esterification processes with suitable membranes enhances the yield of the esters and conversion of acids [16, 44, 73]. Intensification of esterification of acetic acid and n-butyl alcohol using $Zr(SO_4)_2 \cdot 4H_2O$ using PVA/ceramic composite membrane was studied by Liu and Chen [87]. PV enhanced the conversion and it was higher for the PV-aided esterification than for the reaction without PV. Water content for the reaction without PV was higher than that for the PV-aided reaction due to water removal by PV. Table 3 and Figures 7 and 8 list comparative study of esterification reaction system without and with incorporated with pervaporation separation process. It summarizes the results of pervaporation esterification integrated system in terms of conversion, when compared to a nonintegrated system.

7. Effect of Operating Conditions on Esterification Coupled Pervaporation Process

Operating parameters were classified in three groups [88]:

- (1) Factors which influence directly the esterification kinetics: catalyst concentration and initial reactant molar ratio (alcohol/acid).
- (2) Factors that influence directly pervaporation kinetics: ratio of membrane area to initial reaction volume (A/V_0).

TABLE 3: Comparison of results of esterification reaction with and without pervaporation.

Esterification system	Catalyst/membrane	Without pervaporation	With pervaporation	Reference
Benzyl alcohol and acetic acid	p-Toluenesulfonic acid, GFT membrane (GFT PERVAP 1005)	Conversion of acetic acid = 0.45	Conversion of acetic acid = 0.6	[44]
Ethanol and acetic acid	HCl, hydrophilic membrane	Equilibrium conversion = 0.6	Equilibrium conversion = 0.82	[128]
Ethanol and lactic acid	Amberlyst 15, PERVAP 2201	Conversion of lactic acid = 0.21	Conversion of lactic acid = 0.88	[16]
Lactic acid and ethanol	Amberlyst 15 ion exchange resin, organic-inorganic hybrid membrane	Yield of ethyl lactate = 66% [wt]	Yield of ethyl lactate = 80% [wt]	[73]
Acetic acid and n-butyl alcohol	Zr[SO ₄] ₂ ·4H ₂ O, PVA/ceramic composite membrane	Conversion of n-butanol = 0.65	Conversion of n-butanol = 0.89	[87]
Acrylic acid and n-butanol	Amberlyst 131, PERVAP 2201	Conversion of acrylic acid = 0.68	Conversion of acrylic acid = 0.96	[129]
Oleic acid and ethanol	Amberlyst 15, hydrophilic poly[vinyl alcohol]	Yield of ethyl oleate = 23%	Yield of ethyl oleate = 50%	[130]
Acetic acid with isopropanol	Amberlyst 15, PVA membrane, PERVAP 2201	Mole fraction of isopropyl acetate = 0.3	Mole fraction of isopropyl acetate = 0.61	[38]
Lactic acid with ethanol	Amberlyst XN-1010, water selective membrane	Conversion of lactic acid = 0.5	Conversion of lactic acid = 0.82	[131]
Acetic acid and ethanol	Sulfuric acid, polymeric/ceramic composite membrane	Conversion of acetic acid = 0.72	Conversion of acetic acid = 0.81	[100]
Lactic acid with ethanol	Amberlyst XN-1010, GFT-1005	Conversion of lactic acid = 0.522	Conversion of lactic acid = 0.712	[19]
Lactic acid with isopropanol	Sulfuric acid, PVA-PES composite membrane	Conversion of lactic acid = 0.51	Conversion of lactic acid = 0.86	[132]
Lactic acid with n-butanol	Sulfuric acid, PVA-PES composite membrane	Conversion of lactic acid = 0.66	Conversion of lactic acid = 0.88	[133]
Acetic acid and ethanol	Dowex50, PVA-PVP incorporating PMA mixed matrix membrane	Conversion of acetic acid = 0.264	Conversion of acetic acid = 0.6065	[134]
Acetic acid with ethanol	Amberlyst 15, polydimethylsiloxane membrane	Conversion of acetic acid = 0.57	Conversion of acetic acid = 0.65	[42]
	Sulfuric acid, polydimethylsiloxane membrane	Conversion of acetic acid = 0.63	Conversion of acetic acid = 0.71	

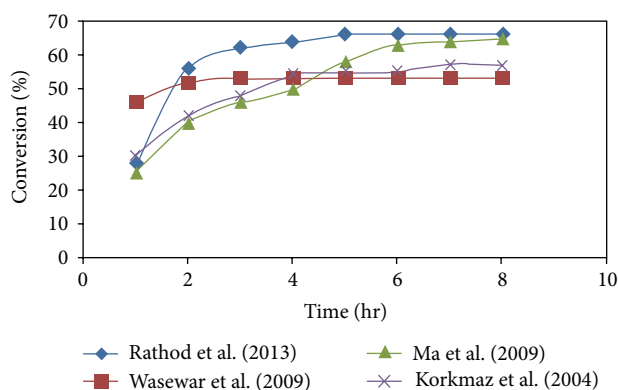


FIGURE 7: Different trends of conversion of acid with time for esterification without pervaporation system.

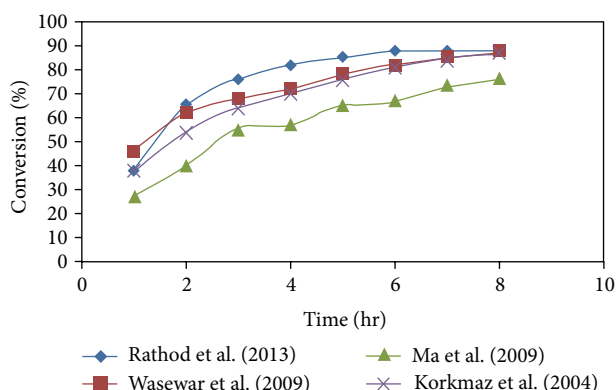


FIGURE 8: Different trends of conversion of acid with time for esterification with pervaporation system.

(3) Factors that influence simultaneously the esterification and pervaporation kinetics: temperature.

7.1. Effect of Initial Reactant Ratio. Delgado et al. [16] studied effect of ethanol:lactic acid initial feed molar ratio (R) over

a range of 1:1 to 3:1; catalyst (Amberlyst 15) loading, 2%; ratio membrane (PERVAP 2201) area to initial volume of reaction, $S/V_o = 23 \text{ m}^{-1}$; and reaction and pervaporation temperature, 348.15 K. It was found that at the beginning of the process the higher the initial reactant molar ratio, the higher the reaction rate. However, as the reaction proceeds, it was found that higher ester formation was obtained when working in stoichiometric proportion. This may be due to the dilution effect of ethanol. In simple esterification reactions, higher equilibrium conversions were obtained by increasing the initial reactant molar ratio, but the limited reactant will never react completely. In esterification-pervaporation reactors a complete conversion of one reactant is obtainable when the other reactant is in excess, no matter how small the excess is. Conversion in this kind of integrated process can go beyond the equilibrium conversion, which is the maximum conversion reached in a conventional reactor.

In pervaporation aided esterification of acetic acid and n-butyl alcohol using catalyst, p-toluenesulfonic acid and solid super acid, and membrane, phosphatic poly(vinyl alcohol)/poly acrylonitrile (PPVA/PAN) composite membrane, Xuehui and Lefu [90] found that higher ester formation occurs at higher R for fixed time (where R is ratio of initial molar quantity of alcohol to acid). Maxima in water concentration also obtained at lower times when higher R is used. Liu et al. [89] reported the result of esterification of acetic acid + n-butyl alcohol + $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ + PVA/ceramic composite membrane, in the form of dimensionless parameter, F , that stands for the interaction between water removal and water production during the coupling process. Conversion was increased and water production rate decreases with R_o increasing. Maximum in water content in the mixture had higher amplitude at a lower R_o .

Ma et al. [73] reported that the yield of ethyl lactate using Amberlyst 15 ion exchange resin did not remarkably increase with the initial molar ratio of ethanol to lactic acid from 2 to 4. R_o played a part in reaction rate but exerted no effect on kinetics of PV. Water production rate is decreased with the increase of R_o and caused the maximum amplitude in water content lower at a higher R_o .

7.2. Effect of Catalyst Concentration. In the esterification of benzyl alcohol and acetic acid using p-toluenesulfonic acid and employing commercial GFT membrane (GFT PERVAP 1005), Domingues et al. [44] found that increase in the amount of catalyst leads to an increase in the reaction rate; however beyond 4.1 mol/m^3 , there is no significant increase. Liu et al. [89] (system: acetic acid + n-butyl alcohol + $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ + PVA/ceramic composite membrane) found that water production rate was proportional to and increased with the increase of catalyst concentration. When the catalyst concentration was increased, the maximum in water content in the mixture was increased and shifted to shorter time and the final water content decreased. Ma et al. [73] varied Amberlyst 15 from 0.5 wt% to 3.0 wt% in esterification of lactic acid + ethanol in pervaporation studied in organic-inorganic hybrid membrane prepared by in site hydrolysis and condensation of tetraethoxysilane

with chitosan aqueous solution. Yield of ethyl lactate was improved with the increase of catalyst loading. The reason for this is increasing catalyst active sites and decreasing of reaction activation energy which could obviously accelerate reaction rate. The water contents in the reactor had higher maximum amplitude for a higher catalyst concentration during the reaction. Delgado et al. [16] studied effect of catalyst (Amberlyst 15) concentration (2, 3.5, and 5.5 wt% of total initial solution) in esterification of ethanol + lactic acid using PERVAP 2201. Increase in the amount of catalyst leads to an increase in the reaction rate. In the studies on dilute acid the effect is not higher due to the high initial amount of water in the reactor.

7.3. Effect of Membrane Area to Initial Reaction Volume Ratio.

Delgado et al. [16] varied the membrane area to initial reaction volume ratio for $12\text{--}46 \text{ m}^{-1}$ in the esterification of ethanol and lactic acid using Amberlyst 15 and PERVAP 2201. It was found that the higher the value of this ratio, the higher the ethyl lactate concentration in the reactor; therefore higher conversions are reached. This result is obvious since water concentration in the reactor will decrease faster when the membrane area per unit of reaction volume is larger. Domingues et al. [44] found that in the esterification studies on benzyl alcohol and acetic acid using p-toluenesulfonic acid as catalyst and GFT PERVAP 1005 membrane to obtain 60% conversion of AA increase in membrane surface area (S) leads to less operating time to reach the conversion level. In addition the 100 percent conversion of alcohol was achieved.

To measure the capacity of membrane unit, membrane parameter ω (characterizing membrane permeability) and operating parameters S and V_o are combined as a single variable, $\omega S/V$ (permeability * surface area/volume of reaction mixture) [60]. It was found that conversion of the membrane reactor can go beyond the equilibrium conversion. Gap between the two limits, that is, $\omega S/V$ varies from 0 to infinity, becomes larger as the reaction time increases, indicating that the reaction is increasingly facilitated by membrane pervaporation. The higher the value of $\omega S/V$, the higher the conversion. When membrane is used to enhance the reaction, water concentration (C_w/C_o { C_w is water concentration and C_o is the water concentration that would be obtained at complete conversion}) undergoes a maximum as reaction proceeds in time. The larger the value of $\omega S/V$, the shorter the time required for water to reach maximum concentration and the smaller the magnitude of the maximum water concentration. As reaction proceeds, reaction rate decreases. Such a decrease in reaction rate is, however, slowed down by the use of a membrane because selective removal of water further concentrates the reactants. Despite the fact that pervaporation can shift the equilibrium toward the ester side and go beyond equilibrium conversion, it cannot drive the reaction to completion, that is, $X = 1$, in a finite time scale, no matter how large the value of $\omega S/V$ is. When one of the reactant species is used in excess, a complete conversion of the other is achievable.

The result was explained in the way that the concentration of water in the reactor will be reduced more rapidly when the membrane is more permeable and/or when the membrane

area per unit reaction volume is larger, so higher is the conversion. During the early period of reaction, the rate of chemical reaction is high, whereas water concentration is low and so is the rate of water removal from the reactor. Consequently, water concentration gradually increases until it reaches maximum when its formation rate and removal rate become equal. Thereafter the water removal is faster than formation, resulting in depletion of water in the reactor.

Liu et al. [89] (system: acetic acid + n-butyl alcohol + $Zr(SO_4)_2 \cdot 4H_2O$ + PVA/ceramic composite membrane) stated that rate of water removal was reduced with the decrease of S/V . Further liquid had higher amplitude at a lower S/V . Ma et al. [73] (system: lactic acid + ethanol + Amberlyst 15 + organic-inorganic hybrid membrane) found that S/V exerted no influence on reactive kinetics but caused the variation of the water extraction rate. Water production rate is decreased with the increase of S/V .

7.4. Effect of Temperature of Reaction and Pervaporation.

Delgado et al. [16] in the esterification of ethanol and lactic acid using Amberlyst 15 and PERVAP 2201 found that water content in the reaction medium decreased rapidly when membrane permeation flux increased as a consequence of an increase in pervaporation temperature (338.15, 348.15, and 358.15 K). As a result, the esterification rate increases. Xuehui and Lefu [90] (system: acetic acid + n-butyl alcohol + p-toluenesulfonic acid and solid super acid + PPVA/PAN composite membrane) reported that higher ester is formed at higher temperature for fixed time. Maxima in water concentration also obtained at lower times when higher temperature is used.

Liu et al. [89] (system: acetic acid + n-butyl alcohol + $Zr(SO_4)_2 \cdot 4H_2O$ + PVA/ceramic composite membrane) found that dimensionless parameter, F , that stands for the interaction between water removal and water increases with increasing temperature indicating that the acceleration of the rate of water extraction is faster than that of water production rate. This is due to the reason that both the water production rate and permeability coefficient are higher at a higher temperature. Maximum in water concentration was increased with temperature but shifted to a shorter time due to the higher water production rate. Before the water content went through its maximum value, the rate of water production was larger than that of water removal; after water content attained the maximum value, the rate of water production was less than that of water removal.

Ma et al. [73] studied the effect of temperature from 50°C to 80°C in the esterification of lactic acid + ethanol using Amberlyst 15 ion exchange resin and organic-inorganic hybrid membrane. Esterification of lactic acid and ethanol was an endothermic reaction (based on Arrhenius plot); accordingly, the yield of ethyl lactate increased with increasing reaction temperature in pervaporation assisted esterification. Liu and Chen [87] (system: acetic acid + n-butyl alcohol + $Zr(SO_4)_2 \cdot 4H_2O$ + PVA/ceramic composite membrane) found that reaction rate constants for the esterification are a function of process temperature and were increased with the increase of the temperature (70–90°C). The accelerating of the reaction rate constant with the increase of the temperature

for the forward reaction was faster than the backward process. So water production rate was higher in a higher temperature than in a lower temperature. Meanwhile, the permeation parameter for water is also varied with the temperature and was increased with the increase of the temperature. As a result, water permeation flux was increased with the increase of the process temperature. Water concentration had a higher maximum value for a higher process temperature. This may be explained by the fact that the acceleration for water production rate had a higher value at a higher temperature, so water content increased faster during the earlier reaction stage due to a slower backward reaction rate, while it decreased faster later due to a higher backward reaction rate.

Grob and Heintz [91] studied isotherms of aromatic compounds in organophilic polymer membranes (polyether-polyamide block-copolymer (PEBA)), used in pervaporation, and found that sorption of phenol, aniline, 2-chlorophenol, 4-nitrophenol, 2,4-dinitrophenol, 4,4'-isopropylidenediphenol (bisphenol A), and pyridine decreases with temperature. Sorption coefficients are obtained as slopes of the straight lines. The number of the free hydroxyl groups plays a certain role for the affinity of the aromatic compounds for the membrane material PEBA. The sorption process of transferring aromatics from aqueous solution to the membrane is exothermic. Values of calculated sorption enthalpies Δh_{∞} range between –25 and –12 kJ/mol. The sorption of both aniline and phenol in the membrane material was not affected by the presence of the second aromatic compound. The system phenol/bisphenol A shows a certain synergistic solubility effect. The solubility of phenol is enhanced by the presence of bisphenol A, but the phenol has no influence on the solubility of bisphenol A. Burshe et al. [71] studied dehydration of glycerine-water mixtures by pervaporation using membranes such as Nafion (NA), cellulose triacetate (CA), polyimide, carboxylated polyvinyl chloride (CPVC), and polyethersulfone (PES). Temperature was varied from 30 to 70°C. It was found that increased feed temperature decreased the sorption of water and heat of sorption (ΔH_s) is negative.

7.5. Other Factors

7.5.1. Effect of Downstream Pressure on Various Terms. Generally downstream pressure is less than 1 mm Hg. If downstream pressure increases, at membrane permeant interface, desorption slows down; thus downstream pressure becomes the rate controlling. Increase in pressure increases the activity of both permeances dissolved in the downstream layer of the working membrane. If pressure increases and exceeds the saturated vapor pressure of permeance, selectivity falls. At low downstream pressure, desorption is rapid; thus diffusion becomes the rate controlling. Beyond the transition pressure, desorption slows down and progressively governs the selectivity of pervaporation transport. In this regime, selectivity is determined by the relative volatilities of the feed components. If the more rapid permeating species is also the more volatile, selectivity increases as the downstream pressure is raised. In the opposite case a steep decrease in

selectivity is observed. For ideal gas mixtures with permeance containing no significant amount of noncondensable gas, the permeant composition (X'_A , mole fraction) depends on the downstream pressure (P):

$$X'_A = \frac{P_A P_B}{P_B^* - P_A^*} \frac{1}{P} - \frac{P_A}{P_B^* - P_A^*}, \quad (50)$$

where A and B are the fast and slow permeances.

Derivation gives

$$\frac{dX_A}{dP} = \frac{P_A P_B}{P_B^* - P_A^*} \times \frac{1}{P^2}. \quad (51)$$

If A is less volatile, $P_A^* - P_B^* < 0$, and selectivity decreases as P increases.

Burshe et al. [71] in the dehydration studies on glycerine-water mixture using various membranes found the effect of downstream pressure on the dehydration. Pressure was varied from 1 to 20 mm Hg. It was found that higher the downstream pressure lower in water flux. Selectivity is not affected by downstream pressure change. It is recommended that it is better to use 20 mm Hg downstream pressures as this reduces the load on the refrigeration unit supplying the cooling medium for condensing the water issuing from the equipment.

7.5.2. Effect of Molecule Size on the Permeability of Different Compounds. Song et al. [76] studied the permeation of different ester compounds (ethyl acetate, EA; ethyl propionate, EP; ethyl butyrate, EB) through surface-modified alumina membrane (Al_2O_3). Ester (EA, EP, and EB) concentrations in permeance increased almost linearly with increasing ester concentrations in the feed. The ester concentration in permeance increased in the order of EB > EP > EA as well as ester flux, even though molecular weight and molar volume of EB are greater than EP and EA. This may be attributed to the lowest solubility of EB in water, since the low solubility relates to the high hydrophobicity. Due to the lowest solubility, EB has highest affinity to the hydrophobic surface of the membrane. This is as would be expected, since organic species have a stronger affinity to the organophilic membrane than water-soluble solutes. Although the concentration of esters (EA, EP, and EB) was only 0.15–0.60 wt% in the feed, EA, EP, and EB in permeance were concentrated up to 9.13–32.26, 13.79–37.0, and 15.33–42.57 wt%, respectively. Phase separation occurred in permeant stream because the ester concentration in permeance was much above the saturation limit.

The difference in the flux and permeance of different component in a particular membrane is explained in terms of difference in affinity between the component and the membrane for the different components. A simple approach to describing the affinity between materials is the solubility parameter. Guo et al. [72] in the studies of dehydration of butanol mixtures found that the solubility parameters δ_{sp} (MPa^{1/2}) of PVA (the selective layer of membrane) and water are 39.1 and 47.9, respectively. The difference between solubility parameters for each pair of butanol/membrane is in the order

of 1-butanol/membrane (16) < isobutanol/membrane (16.4) < 2-butanol/membrane (17) < tert-butanol/membrane (17.4). The solubility parameter theory proposes that the materials will have strong interaction when their respective solubility parameters are close to each other. Therefore, based on this theory, the affinity between the butanol and the membrane is in the order of 1-butanol > isobutanol > 2-butanol > tert-butanol. Accordingly, the butanol fluxes present the same order, so do the butanol permeances.

Hasanoglu et al. [64] studied hydrolysis reaction of ethyl acetate (ethyl acetate (EAc), water, ethanol (EOH), and acetic acid (AsAc)) using polydimethylsiloxane (PDMS). PDMS membrane permeates EAc much more than the other components. This is not unexpected because the solubility parameter of PDMS is closer to ethyl acetate than the other components ($\delta_{PDMS} = 8.1 \text{ (cal/cm}^3)^{0.5}$) [92]. Thus, PDMS is more selective to ethyl acetate than other components. The solubility parameter is a measure of the affinity between polymer and penetrant and can give qualitative information about interaction between polymer and penetrant. As the affinity between permeant and polymer increases the amount of liquid inside the polymer increases, and consequently the flux through the membrane increases [93].

8. Conclusion

Membranes both hydrophilic and hydrophobic are widely used in industries for both product recovery and waste treatment. Nowadays it is widely used in industries for dehydrating solvents such as ethanol and isopropanol. As pervaporation is independent of vapor/liquid equilibria, it can preferentially remove water from a stream irrespective of the other components present. Therefore it can be considered as a substitute where distillation is difficult or costly. Moreover, pervaporation can be used progressively to improve reactor performance, by either purifying feeds or separating reaction products. Since pervaporation is a membrane process, these separations can be combined with the reaction step, resulting in substantial improvements in reaction efficiencies, yields, and process economics. In this regard lots of scope exists for separation of esterification product or the byproduct. Research is going on to develop new and better membranes, that is, with higher fluxes, better selectivity, and broader chemical resistance which will expand the areas where pervaporation-esterification hybrid is feasible.

Nomenclature

k_l :	Boundary layer mass transfer coefficient on the liquid side
$x_{i,j}$:	Organic concentration at the liquid-membrane interface
K_i :	Membrane mass transfer coefficient
t :	Membrane thickness
x_f, x_g :	Concentration of component in feed and permeance
J_i :	Flux of i across the membrane

$Q_{ov,i}$:	The overall mass transfer coefficient of i in terms of vapor pressure	w_i :	Weight fraction of the compound i in the feed (w_i^{feed}) and in the permeance (w_i^{permeate})
A :	Membrane area	p^p :	Permeant pressure
$P_{l,i}, P_{g,i}$:	Partial vapor pressures of i in the liquid side and in the permeance (or gas) side, respectively	β :	Ideal membrane selectivity
$K_{ov,i}$:	Overall mass transfer coefficient of i in terms of liquid concentration	C_{pwater}, C_{fwater} :	Water concentrations in the permeance and feed, respectively
$C_{l,i}$:	Concentration of i in the liquid	J_p :	Permeation flux ($\text{kg}/\text{m}^2\text{h}$)
$C_{g,i}^*$:	Concentration of i in the liquid	S_o :	Temperature-independent constant
$P_{l,i}$:	Partial vapor pressure of i in the liquid side	ΔH_s :	Heat of solution
$P_{g,i}$:	Partial vapor pressure of i in the gas side	D_o :	Temperature-independent constant in (33)
$C_{g,i}$:	Concentration in the gas side	E_d :	Activation energy for diffusion or it is a preexponential factor
γ_i :	Activity coefficient of i in the liquid side	P_w^o, γ_w :	The saturated vapor pressure and the activity coefficient of water, respectively
p_i^0 :	Saturation vapor pressure of pure i at the liquid temperature	x_w :	Mole fraction of water in an ethanol/water mixture
ρ_l :	Molar density of the liquid	ϕ :	Volume fraction of penetrant
P_T :	Total pressure in the gas side	γ :	Exponential constant (plasticizing constant, indicating the plasticizing action of the penetrant on segmental motion)
ρ_g :	Molar density of the gas	D_o :	Diffusion concentration at zero concentration in (41)
$K_{ov,i}$:	Apparent mass transfer coefficient	a_i :	Activity of penetrant inside the polymer
f_i :	Fugacity of component i	V_o :	Volume occupied by molecules at 0 K
P_i :	Permeability coefficient	D_T :	Thermodynamic diffusion coefficient
l :	Thickness of the active layer of the membrane	χ :	Interaction parameter is molar volume
S_i :	Solubility coefficient of the in the membrane	d :	Volume fraction of penetrant
D_i :	Diffusion coefficient of the in the membrane	$J_w(T^o, P^o)$:	Water flux measured at a feed side temperature of T^o and permeant side pressure of P^o .
$\gamma P^o / \rho_l$:	Conversion factor from a concentration driving force to a partial vapor pressure driving force		
Q_{ov} :	Overall mass transfer coefficient (in terms of vapor pressure driving force)		
K_{ov} :	Overall mass transfer coefficient (in terms of concentration driving force)		
Q_l :	Liquid phase mass transfer coefficient (in terms of vapor pressure driving force)		
K_l :	Liquid phase mass transfer coefficient (in terms of concentration driving force)		
Re:	Reynolds number = $\rho \bar{u} d_h / \mu$		
Sc:	Schmidt number = $\mu / \rho D$		
L :	Length of the system		
d_h :	Hydraulic diameter of the system		
$w_{i,PEBA}$ (i.e., membrane),	Weight fractions of component i in the PEBA material and the liquid feed solution in solubility equilibrium with the PEBA phase, respectively		
$w_{i,Feed}$:			
y, x :	Weight fractions of components in the permeance and feed, respectively		

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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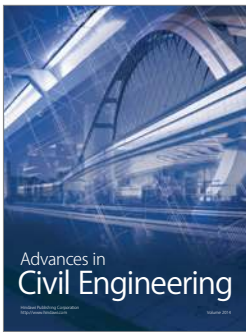
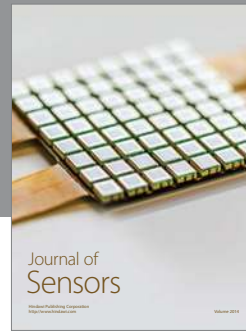
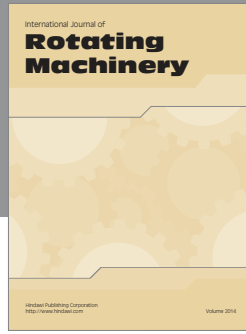
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