IJESRT
INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

A REVIEW OF PERVAPORATION MEMBRANE SYSTEM FOR THE SEPARATION OF ETHANOL/WATER (AZEOTROPIC MIXTURE)

Nitin G. Kanse*, Dr. S. D. Dawande

* Research Scholar, Department of Chemical Engineering Laxminarayan Institute of Technology, Nagpur.

ABSTRACT
Membrane separation process has become one of the emerging technologies that undergo a rapid growth for the past few decades. Pervaporation is the one of the membrane separation processes that have gained increasing interest in the chemical and allied industries. Pervaporation has significant advantages in separation of azeotropic systems where traditional distillation can recover pure solvents with the use of entrainers, which then must be removed using an additional separation step. Pervaporation can be used to break the azeotrope, as its mechanism of separation is quite different to that of distillation. This review presents the separation of Azeotropic mixture such as ethanol-water by using Pervaporation. The fundamental aspects of Pervaporation over different types of membrane are revived and compared. The focus of this review is on separation of azeotropic mixture by using different membrane and effect of various parameters on Pervaporation.

KEYWORDS: Pervaporation, Azeotropic mixture, Membrane, selectivity.

INTRODUCTION
Pervaporation is a new membrane technique which is used to separate a liquid mixture by partly vaporizing it through a nonporous permselective membrane. The feed mixture is allowed to flow along one side of the membrane and a fraction of it (the 'permeate') is evolved in the vapor state from the opposite side, which is kept under vacuum by continuous pumping Membrane separation processes offer many advantages over existing separation processes such as higher selectivity, lower energy consumption, moderate cost to performance ratio and compact with modular design [12, 19].

In theory, Pervaporation can be used to separate any liquid mixtures but in practice, Pervaporation tends to be used to separate azeotropic mixtures, close boiling point mixtures, for the recovery of small quantities of impurities and for the enhancement of equilibrium reactions. When looking at membranes to enhance performance, there is often a trade-off between separation factor and flux, performing a modification that may increases separation factor with decrease in flux.

In literature Pervaporation membrane system can offer energy savings of 35% over conventional distillation. In addition the membrane is capable of dehydrating feed to ppm levels of water as well as being resistant to a wide range of aggressive organic solvents.

It had been demonstrated that large energy savings can be achieved by using Pervaporation systems as compared to azeotropic distillation of organic mixtures. Besides the energy consuming distillation step, the distillation process requires an entrainer, such as benzene, to break the azeotrope. The removal of this entrainer gives rise to a second distillation, thus increasing energy use and installation costs significantly. Because Pervaporation systems make use of more advanced technologies than conventional separation methods, investment costs are considered comparatively lower while operation cost are expected to be even lower than the conventional separation process. Simple pay back times of less than 1 year have been reported for Pervaporation installations.

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

PERVAPORATION PROCESS

2.1 Basic Principle of Pervaporation

Pervaporation is derived from combining permeation and evaporation, the two mechanisms involved in the process. In a Pervaporation process, components of a liquid feed permeate through a membrane and evaporate into the downstream at different rates. The fact that feed components undergo phase change makes PV unique among membrane processes. The driving force behind the process is the difference in chemical activity of components in the feed and the permeate. The separation occurs because of the different rates of sorption and diffusion of the feed components through the membrane.

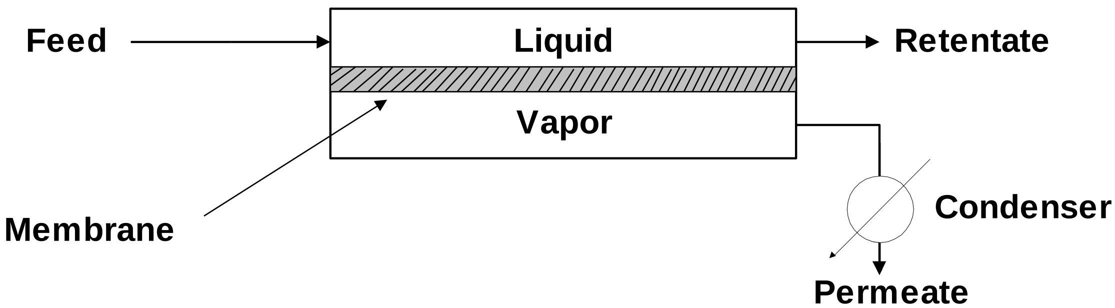

Figure 1: Schematic diagram of Pervaporation process

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

$$\alpha = \frac{y_a/y_b}{x_a/x_b}$$

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

$$\alpha = \alpha_S \times \alpha_D$$

Either or both of these selectivities contribute to the preferential permeation of feed component(s) through a given membrane. However, in most cases, selectivity of a membrane is mainly governed by the sorption component of the selectivity

Aptel et al. [8], Néel [9] and Binning et al. [13] suggested that the unswollen fraction of the skin layer in a Pervaporation membrane controls the permselectivity of the membrane. Therefore, the choice of proper membrane material is a crucial factor for a specific separation. On one hand, a polymer with great affinity towards one component of the feed is preferred because it leads to higher selectivity. On the other hand, if this affinity exceeds a certain level, the membrane gets swollen by the compound and loses its integrity and therefore its selectivity. Consequently, in the preparation of a proper membrane, it is important to suppress or control its degree of swelling. In addition to the specific characteristics of the feed components and the membrane, the operating parameters influence the overall performance of a Pervaporation process. These parameters include feed temperature, feed concentration, and downstream pressure. It is generally believed that feed pressure has insignificant effect on the permeability and selectivity of Pervaporation membranes.

2.2 Pervaporation Process Advantages and Benefit

1. More cost-effective and thorough separation of azeotropic miscible liquids (liquids composed of components with close boiling points)
2. No catalyst or entrainers required to affect separation of miscible mixtures

3. Significant capital cost and operating cost savings over conventional systems
4. Easy adaptability to hybrid processes.
5. Small and compact modular installations, easily incorporated into existing production lines
6. Low running costs
7. Simplicity of handling and operation
8. No addition of chemicals, no entrainment or absorption, no need for additional separations;
9. Environmentally friendly and inexpensive upgrading.
10. Multistage system can be used

2.3 Types of Pervaporation Membrane Separation Modules:

The application of membrane techniques on industrial purposes requires the development of high quality membrane modules. The earliest design were based on simple filtration technology and consisted of flat sheets of membrane held in a type of filter press. These are called plate-and-frame modules. Systerns containing a number of membrane tubes were developed at about the same time. Later, with the advent of spiral-wound and hollow-fiber modules, the application of membrane techniques was quickly extended to wider industrial areas. Spiral-wound and hollow-fiber modules have dominated commercial market for r quite long period. However, recently, new generation of plate-and-frame Pervaporation modules is developed for some special applications. Refined design and new manufacturing techniques make the plate-and-frame configuration more cornpetitive than it used to be. Following are the major Pervaporation module configurations,

a) Plate-and-Frame Modules
b) Hollow-Fiber Modules
c) Spiral- Wound Modules
d) Tubular Module

2.4 Possible modes of Pervaporation:

Maintaining a vapor pressure gradient across the membrane produces transport through Pervaporation membranes. The vapor pressure gradient used to produce a flow across a Pervaporation membrane can be generated in a number of ways. Figure 2-7 illustrates several configurations of the Pervaporation membrane separation processes. The first two are introduced below only for simplicity. Figure 2 shows a vacuum driven Pervaporation. Vapor permeate is sucked out by using a vacuum pump, maintaining a pressure gradient across the membrane. The use of a vacuum pump speeds up the permeate transportation. Figure 3 illustrates a temperature gradient driven Pervaporation without any vacuum pumping. The vapor permeate is driven out by condensation. This system is simple, but the permeate transport speed is limited by the condensation efficiency. In FCT, the standard configuration combined the vacuum driven and temperature gradient driven approaches which takes the advantages of both systems. The heater improves the membrane separation efficiency. The transportation of the vapor permeate is speeded up by vacuum pumping.

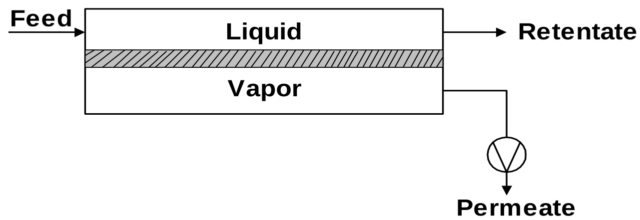

Figure 2 Vacuum Driven Pervaporation

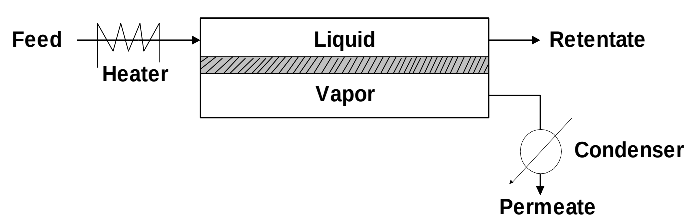

Figure 3 Temperature Gradient Driven Pervaporation

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

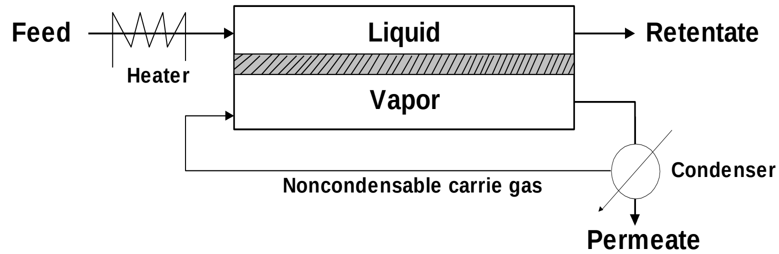

Figure 4 Carrier Gas Pervaporation

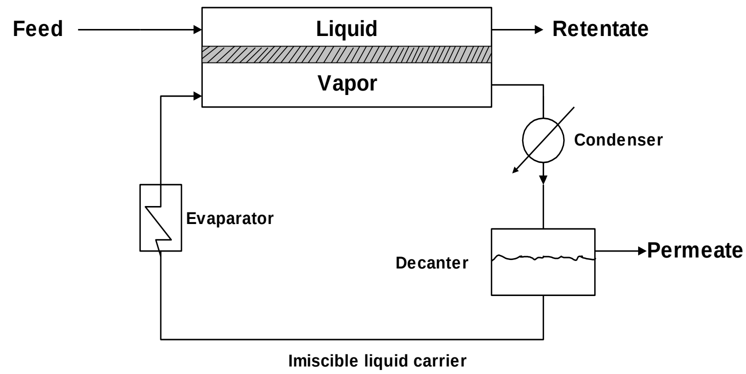

Figure 5 Pervaporation with a Condensable Carrier

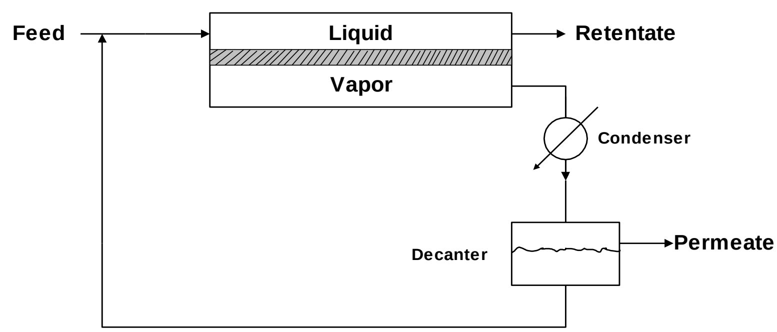

Figure 6 Pervaporation with a Two-phase Permeate and Partial Recycle

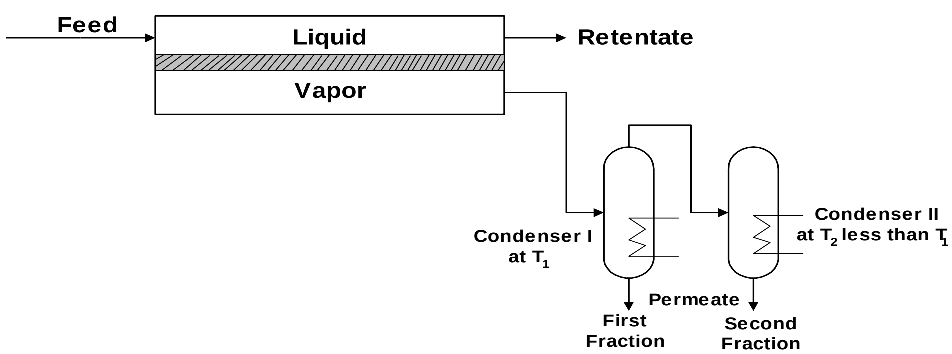

Figure 7 Pervaporation with Fractional Condensation of the Permeate

2.5. Application of Pervaporation:

Pervaporation is effective for diluting solutions containing trace or minor amounts of the component to be removed. Based on this, hydrophilic membranes are used for dehydration of alcohols containing small amounts of water and hydrophobic membranes are used for removal/recovery of trace amounts of organics from aqueous solutions.

Pervaporation is a very mild process and hence very effective for separation of those mixtures which cannot survive the harsh conditions of distillation.

- Solvent Dehydration: dehydrating the ethanol/water and isopropanol/water azeotropes
- Continuous ethanol removal from yeast fermentors.
- Continuous water removal from condensation reactions such as esterifications to enhance conversion and rate of the reaction.
- Membrane introduction mass spectrometry
- Removing organic solvents from industrial waste waters.
- Combination of distillation and Pervaporation/vapour permeation
- Concentration of hydrophobic flavor compounds in aqueous solutions (using hydrophobic membranes)

Recently, a number of organophilic Pervaporation membranes have been introduced to the market. Organophilic Pervaporation membranes can be used for the separation of organic-organic mixtures, e.g.:

- Reduction of the aromatics content in refinery streams
- Breaking of azeotropes
- Purification of extraction media
- Purification of product stream after extraction
- Purification of organic solvents

Non-porous dense membranes can also be applied in other separation processes such as gas separation. Furthermore, both gas separation and Pervaporation can be interpreted with the solution diffusion mechanism for mass transport in membranes. Membrane-based Pervaporation or vapor permeation is a promising alternative to distillation since it is an energy-saving one-step separation process. If the proper membrane material is selected, Pervaporation can separate azeotropic mixtures and close boiling mixtures that traditional distillation has difficulties in processing.

Table 1: Overview of available membrane separation processes

Membrane Process	**Feed phase / Permeate phase**	**Driving Force**	**Membrane**	**Main application**
Pervaporation	Liquid / vapor	Chemical potential gradient	dense,liophilic	Separation of liquid mixture
Vapor permeation	Vapor / vapor	Chemical potential gradient	dense,liophilic	Separation of liquid mixtures or vapors from gases
Gas separation	Gas/gas	Hydrostatic pressure gradient	Porous or dense	Separation of gaseous mixture
Membrane Distillation	Liquid/vapor	Vapor pressure gradient	Porous,liophilic	Ultrapure water, concentration of solutions

FACTORS AFFECTING PERVAPORATION

Feed composition and concentration

A change in the feed composition directly affects the sorption phenomena (degree of swelling) at the liquid membrane interface. This can be proved by the solution diffusion principle, and as the diffusion of the components in the membrane is dependent on the concentration of the components, the Pervaporation characteristic are, hence, dependent on the feed concentration as well.

Feed and permeate pressure

Driving force in the Pervaporation is the partial pressure difference of the components which in turn is dependent on the activity gradient of the components. The permeate pressure is directly related to the activity of the component at the downstream side of the membrane and strongly influence the Pervaporation characteristics. The maximum gradient can be obtained for zero permeate pressure and thus for higher permeate pressure, the feed pressure influence the Pervaporation characteristics.

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

Temperature
As the temperature of feed increases, the permeation rate generally follows an Arrhenius type equation. The selectivity is strongly dependent on temperature, in most cases a small decrease in selectivity is observed with increasing temperature.

BEST PERFORMING MEMBRANES

Table 2: Highest fluxes and separation factor for PV dehydration of aqueous ethanol

Membrane polymer	Feed wt% water	Temp ^{0}C	Flux g/m^{2}h	Separation factor	Reference
Highest Fluxes					
Nafion-H+	4	70	5000	2.5	**[17]**
Teflon-g-polyvinylpyrrolidone	4	25	2200	2.9	**[8]**
Regenerated cellulose	50	45	2060	5	**[4,15]**
Alginic acid	5	60	2800	13	**[1]**
PVA/PAA	50	75	2800	60	**[5]**
K+ acrylate graft on PVF	20	70	4700	156	**[14]**
PVA /Fumaric acid	20	100	1511	211	**[24]**
Perfluorinated polymer on PAN support	1.3	50	1650	387	**[18]**
K+ acrylate graft on PAN	20	70	3000	500	**[14]**
PEI/PAA on RO membrane	10	70	4050	1075	**[10]**
Highest Separation Factors					
PVA/ γ-aminopropyl-triethoxysilane	5	50	36	537	**[11]**
PVA crosslinked with Fumaric acid	20	60	217	779	**[24]**
Poly(acrylic acid-co-acrylonitrile)	18	15	13	877	**[6]**
PVA/25% TEOS, annealed at 130 ◦C	15	40	4	893	**[15]**
PVA/inorganic Hybrid membrane crosslinked withTEOS (130 ◦C)	15	40	40	893	**[15]**
Chitosan / Sulphonated & GA	10	70	52	1560	**[20, 21]**
PVA crosslinked with GA	10-50	40	-	>2000	**[13]**
Chitosan GA crosslinked	4	40	4	2208	**[16]**
Chitosan acetate	4	40	2	2556	**[16]**
Chitosan/50% blend with hydroxyethylcellulose	10	60	112	10491	**[2]**

FUTURE SCOPE

- **Pervaporation of Apple Juice**

Pervaporation is used to recover any lost juice solution during evaporation. The vapor from the evaporation process is further processed using Pervaporation. The recovered, concentrated apple juice can be combined with the product solution to help the apple juice retain its aromatic and taste qualities.

- **Pervaporation in the Production of Fuel Ethanol**

To establish a continuous fermentation process, the ethanol concentration within the fermentation vessel must be kept at 5% by weight or lower. Pervaporation has been used to maintain the necessary ethanol concentration in the broth. The advantages of using Pervaporation in such a system include the ease of processing the clean, nearly pure ethanol extracted from the fermentation vessel and a significantly higher fermentation capacity or the reduction in fermentor size and costs.

CONCLUSIONS

Separation of Azeotropic Mixture by means of Pervaporation is now on the threshold of becoming an industrially applicable process. Its advantages with respect to investment and operation costs and the simplicity of its operation compared to distillation and adsorption processes are very attractive. At present, development of new membranes and our understanding of the basic principles on mass transport across non-porous membranes are improving rapidly.

Therefore, in the near future membranes will be available not only for the Separation of Azeotropic Mixture but also for a wide variety of separation problems in the chemical industry.

REFERENCES

[1] Mochizuki, S. Amiya, Y. Sato, H. Ogawara, S. Yamashita, Pervaporation separation of water/ethanol mixtures through polysaccharide membranes. IV. The relationship between the permselectivity of alginic acid membrane and its solid state structure, Journal of Applied Polymer Science 40 (1990) 385–400
[2] A. Chanachai, R. Jiraratananon, D. Uttapap, G.Y. Moon, W.A. Anderson, R.Y.M. Huang, Pervaporation with chitosan/hydroxyethylcellulose blended membranes, Journal of Membrane Science 166 (2000) 271–280
[3] J. Néel, in: R.Y.M. Huang (Ed.), Pervaporation Membrane Separation Process, 1991, Chap. 1, p. 1.
[4] J.-J. Shieh, R.Y.M. Huang, Pervaporation with chitosan membranes II. Blend membranes of chitosan and poly (acrylic acid) and comparison of homogeneous and composite membrane based on polyelectrolyte complexes of chitosan and poly(acrylic acid) for the separation of ethanol-water mixtures, Journal of Membrane Science 127 (1997) 185–202.
[5] K.-H. Lee, H.-K. Kim, J.-W. Rhim, Pervaporation separation of binary organic aqueous liquid mixtures using crosslinked PVA membranes. III. Ethanol-water mixtures, Journal of Applied Polymer Science 58 (2003) 1707–1712.
[6] M. Yoshikawa, T. Yukoshi, K. Sanui, N. Ogata, Separation of water and ethanol by pervaporation through poly(acrylic acid-co-acrylonitrile) membrane, Journal of Polymer Science: Polymer Letters Edition 22 (1984) 473–475.
[7] P.D. Chapman, T. Oliveira, A.G. Livingston, K. Li, Membranes for the dehydration of solvents by Pervaporation, J. Membr. Sci. 318 (2008) 5–37.P. Shao, R.Y.M. Huang, Polymeric membrane Pervaporation, J. Membr. Sci. 287 (2007) 162–179
[8] P. Aptel, N. Challard, J. Cuny and J. N~I, Application of the Pervaporation process to the separation of azeotropic mixtures, J. Membr. Sc,1 (1976) 271-287.
[9] P. Aptel, J. Cuny, J. Jozefonvicz, G. Morel, J. Neel, Liquid transport through membranes prepared by grafting of polar monomers onto poly(tetrafluoroethylene) films III. Steady-state distribution in membrane during pervaporation, J. Appl. Polym. Sci. 18 (1974) 365.
[10] Q.G. Zhang, J. Qian, Y. Yang, Q. An, X. Liu, Z. Gui, Polyelectrolyte layer-bylayer self-assembly enhanced by electric field and their multilayer membranes for separating isopropanol-water mixtures, Journal of Membrane Science 320 (2008) 73–77.
[11] Q.G. Zhang, Q.L. Liu, Z.Y. Jiang, Y. Chen, Anti-trade-off in dehydration of ethanol by novel PVA/APTEOS hybrid membranes, Journal of Membrane Science 287 (2007) 237–245.
[12] R.W. Baker, Pervaporation Membrane Technology and Applications, second ed.,Wiley, New York, 2004, pp. 355–392.
[13] R.C. Binning, R.J. Lee, J.F. Jennings, E.C. Martin, Separation of liquid mixtures by permeation. Liquid phase permeation through thin plastic films has commercial potential for separating azeotropes and other organic mixtures, Ind. Eng. Chem. 53 (1961) 47.
[14] S.I. Semenova, H. Ohya, K. Soontarapa, Hydrophilic membranes for pervaporation: an analytical review, Desalination 110 (1997) 251–286.
[15] T. Uragami, K. Okazaki, H. Matsugi, T. Miyata, Structure and permeation characteristics of an aqueous ethanol solution of organic-inorganic hybrid membranes composed of poly(vinyl alcohol) and tetraethoxysilane, Macromolecules 35 (2002) 9156–9163.
[16] T. Uragami, K. Takigawa, Permeation and separation characteristics of ethanolwater mixtures through chitosan derivative membranes by pervaporation and evapomeation, Polymer 31 (1990) 668–672.
[17] T. Ishikawa, Membranes for dehydrating aqueous ethanol by pervaporation, Kemikaru Enjiniyaringu 29 (1984) 19–25.
[18] V. Smuleac, J. Wu, S. Nemser, S. Majumdar, D. Bhattacharyya, Novel perfluorinated polymer-based pervaporation membranes for the separation of solvent/water mixtures, Journal of Membrane Science 352 (2010) 41–49
[19] X. Feng, R.Y.M. Huang, Liquid separation by membrane Pervaporation: a review, Ind. Eng. Chem. Res. 36 (1997) 1048–1066.
[20] Y.M. Lee, Modified chitosan membranes for pervaporation, Desalination 90 (1993) 277–290
[21] Y.M. Lee, E.M. Shin, Pervaporation separation of water-ethanol through modified chitosan membranes. IV. Phosphorylated chitosan membranes, Journal of Membrane Science 64 (1991) 145–152.
[22] Y.M. Lee, Modified chitosan membranes for pervaporation, Desalination 90 (1993) 277–290.

ISSN: 2277-9655
(I2OR), Publication Impact Factor: 3.785

[23] Y. Maeda, M. Kai, Recent progress in pervaporation membranes for water/ethanol separation, in: R.Y.M. Huang (Ed.), Pervaporation Membrane Separation Processes, Elsevier, Amsterdam, 1991, Chapter 9

[24] Z. Huang, H.-M. Guan, W.-L. Tan, X.-Y. Qiao, S. Kulprathipanja, Pervaporation study of aqueous ethanol solution through zeolite-incorporated multilayer poly(vinyl alcohol) membranes: effect of zeolites, Journal of Membrane Science 276 (2006) 260–271