Journal of International Scientific Publication:
Materials, Methods & Technologies, Volume 4, Part 1

PERVAPORATION: NEW SEPARATION TECHNIQUE FOR BIOETHANOL RECOVERY AND DEHYDRATION

Madlena P. Lazarova

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

Abstract

Biofuels are combustible fuels produced from biomass. Among them bioethanol is considered the most promising one due to its high energy value and may be used to replace refined petroleum in the future. Distillation is largely used for the production of ethanol. The main commercial problem is the excessive amount of wastewater discharged from the distillation columns, as well as this process becomes energy-inefficient for azeotrope-breaking or separation/recovery of organic chemicals from relatively dilute aqueous solutions. Pervaporation separation technique shows to be a highly potential alternative for both recovery and dehydration of ethanol.

Key words: *pervaporation, bioethanol, recovery, dehydration*

1. INTRODUCTION

The climatic impact of carbon dioxide emissions from fossil fuel burning has become a major problem (Hilmioglu, 2009). The production of fuel-grade ethanol from renewable resources, such as biomass, is receiving much attention due to its economic and environmental benefits. Ethanol can be obtained from a variety of biomass materials such as cereal crops and sugarcane (Jain, 2005), as well as from lignocellulosic materials – vegetable and wood remnants (Lynd et al., 2001, Aroujalian et al., 2003). Depending on the biomass source, the ethanol concentration in the fermentation broth can range from 1 to 15 % w/w. Thus, in order to produce fuel-grade ethanol, the water content has to be reduced from 85-99 % w/w to less than 1.3 % w/w (Vane et al., 2008).

Membrane separation processes offer higher selectivity and lower energy consumption over the conventional separation technologies absorption, adsorption, extraction and distillation. Pervaporation is one such membrane separation process and it has been demonstrated to be an effective and economical technique for separation of liquid mixtures, especially for solvent dehydration and separation of organics from their solutions.

The focus of this paper is on the potential of pervaporation for recovery and for dehydration of ethanol, as well as on the membranes suitable for these applications.

2. BASIC PROCESS LAYOUTS OF PERVAPORATION

Pervaporation is a selective membrane technique in which a liquid mixture is separated by means of partial vaporization through a dense perm-selective membrane. The liquid stream (feed) is brought into contact with one side of the membrane. Vacuum (vacuum pervaporation) or, less commonly, gas purge (sweep gas pervaporation) is applied to the other side of the membrane creating the permeate vapor stream (Vane, 2008). The liquid components sorb into the membrane, diffuse through it and evaporate into the permeate phase. The selectivity of the process is not based on thermodynamical equilibrium, but utilizes the differences in both sorption and diffusion behaviour of the feed

components. Due to the different membrane affinity and different diffusion rates through the membrane, even a less volatile compound from a more volatile solvent can be enriched in the permeate. The mass transport through the membrane is described by the solution-diffusion theory and the driving force is the gradient of chemical potential across the membrane based on a partial pressure difference (Lipnizki, 2004).

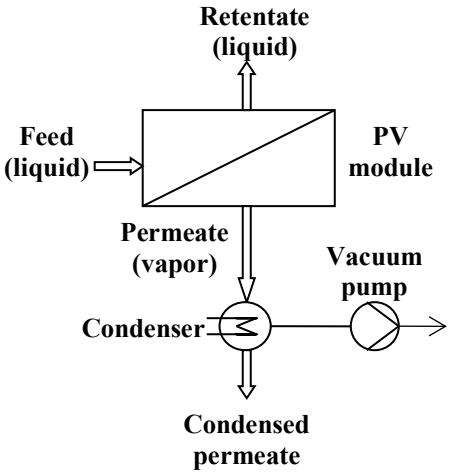

Fig.1. Schematic diagram of a pervaporation (PV) system

A simple pervaporation system consists of pervaporation (PV) module, condenser and vacuum pump as shown in Fig.1. The liquid feed containing two or more miscible components is lead into the PV module and is separated into two streams: the fraction that diffuses across the membrane is defined as permeate and the fraction that fails to pass through – as retentate. As a result, both the more permeable species in permeate and the less permeable ones in the feed can be concentrated. The permeate is then condensed to maintain the vapor concentration low, while the retentate is often recirculated to allow further separation.

Depending on the permeating component the process can be indentified as hydrophilic or organophilic pervaporation. An overview of these two main areas of pervaporation is given in Fig.2. To date, pervaporation has found viable applications in dehydration of organic solvents (Gimenes, 2007), removal of dilute organic compounds from aqueous streams (Thongsukmak and Sirkar, 2009) and organic-organic mixtures separation (Smitha et al., 2004). Further on in this paper the focus will be on the first two applications mentioned above, which are related to the production of bioethanol.

3. PERVAPORATION FOR ETHANOL DEHYDRATION. MEMBRANES.

Ethanol can be recovered from fermentation broths by means of distillation, but it is commonly known that ethanol forms azeotrope with water at 96 % w/w through which more anhydrous ethanol can not be produced (Boontawan et al., 2007). So, in order to apply distillation to break the azeotrope, entrainers, such as benzene or ethylene glycol (Hutahaean, 1995), have to be used or it has to be coupled with another process. In practice, the product stream from distillation is dried to fuel specifications by molecular sieve adsorption. Unfortunately, the cyclic nature of the sorption-regeneration process, the additional energy requirement and the capital cost make this combination not so appealing.

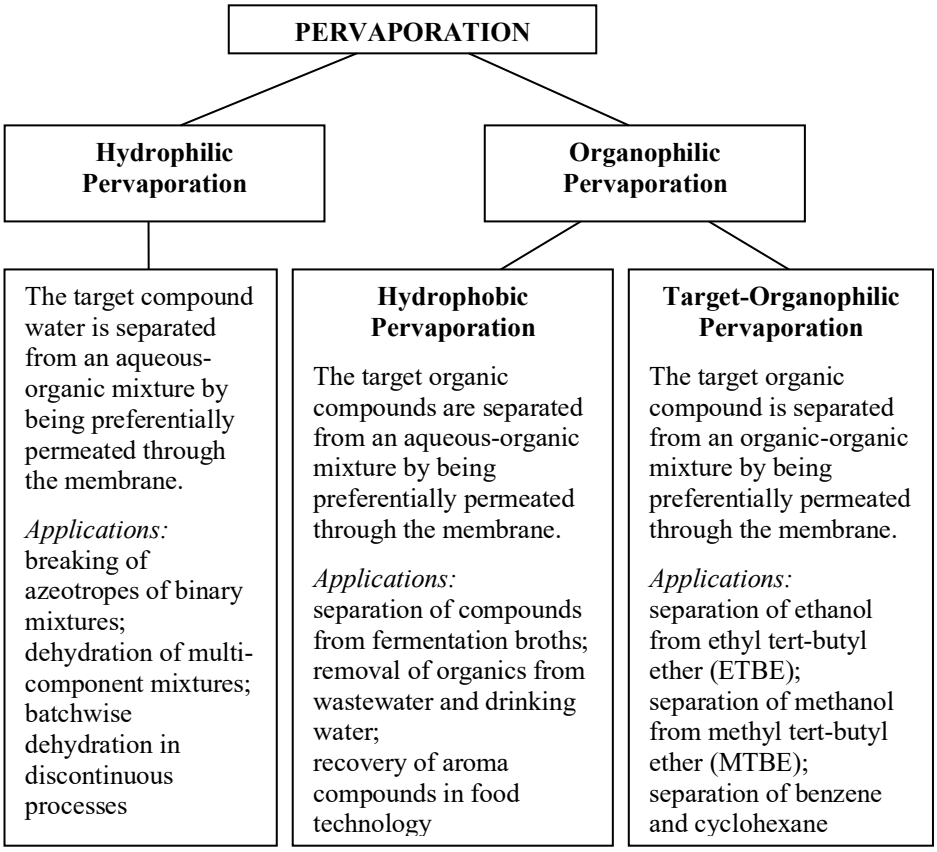

Fig.2. Areas of pervaporation (by Lipnizki et al., 1999)

Pervaporation can easily break azeotropes and is energy efficient for separation of low concentration components from liquid mixtures unlike distillation, and can be operated continuously unlike molecular sieves. In case of ethanol dehydration small amounts of water has to be removed. Thus, hydrophilic membranes are needed to preferentially allow water to permeate through, producing highly water-enriched permeate and dehydrated retentate.

Membranes are the essential part for effective pervaporation performance. There are many available materials which can be considered for selective removal of water. The membrane can be polymeric, inorganic or a mixed matrix material. By modifying its properties in various ways, the separation performance of the membrane can be altered in order to find an appropriate membrane for a given process.

Polymeric membranes are widely used for alcohol dehydration. The material and structure of the membrane along with its support, if any, determine the performance of the membrane. The benchmark

hydrophilic polymer is poly(vinyl alcohol) because of its excellent water perm-selective properties (Guo, 2004). Ethanol dehydration of PVA-based membranes is shown in Table 1.

Table1. Polymer-based membranes for ethanol dehydration by pervaporation

EtOH/H_2O mass ratio	Membrane separation layer	Temperature (◦C)	Separation factor	Reference
90:10	PVA	60	115	[15]
90:10	Sericin/PVA	60	105	[15]
90:10	Sericin	60	90	[15]
94:6	PVA	75	110	[12]
95:5	PVA,PAA	50	50	[16]
95:5	PVA	50	185	[17]
Azeotrope	PVA	60	10	[18]
90:10	Chitosan	50	127	[19]
95:5	Chitosan	80	350	[20]
Azeotrope	Chitosan/PAA	30	1008	[21]
90:10	Alginate	50	300	[22]
95.4:4.6	Na-Alg/PVP	30	364	[23]
Azeotrope	Alginate	50	99	[24]
90:10	BAPP	25	22	[25]
95:5	PI-2080	60	900	[26]

Chitosan is also a good starting polymer material for water separation by pervaporation because of its easily modifiable structure. Other hydrophilic polymeric materials used are alginate- and polyimide-based membranes. Their pervaporation performance in ethanol dehydration is reviewed in Table 1.

Inorganic membranes offer higher thermal and chemical stability than most polymeric ones. They are inert, do not swell and give a more constant performance. Problems with brittleness may occur due to their harder and thicker structure compared to the thin structure of the polymeric membranes (Chapman et al., 2008). The most inorganic membranes for removal of water by pervaporation are based on silica and zeolites (Table 2).

When an inorganic material is dispersed into a polymeric basis, a mixed matrix membranes is obtained. The combination of polymeric-inorganic materials can strengthen the mechanical properties of the membrane and reduce the free volume through which molecules may diffuse, thus better separation can be achieved. Examples of mixed matrix membranes used for ethanol dehydration by pervaporation are given in Table 2.

As it can be seen from Tables 1 and 2, water-ethanol separation factors vary in a wide range (from 10 to 10 000) because of the variety of materials used for pervaporation dehydration membranes, as well as due to different process conditions (temperature, pressure, etc). A number of companies produce commercial polymeric membranes highly suitable for water removal. Inorganic membranes give more stable performance, but are expensive and economically less viable.

Table2. Inorganic membranes and mixed matrix membranes for ethanol dehydration by pervaporation

EtOH/H_2O mass ratio	Membrane separation layer	Tempeature (◦C)	Separation factor	Reference
89:11	Amorphous silica	70	160	[28]
90:10	PVA	50	56	[29]
91:9	Silica	70	50	[30]
98:2	Silica	70	160	[30]
90:10	Zeolite A	75	10 000	[31]
90:10	Zeolite X	75	360	[31]
95:5	NaA Zeolite	75	16 000	[32]
80:20	PVA+11 % w/w KA zeolite	50	15.5	[33]
90:10	Polyamide/ SDS-clay	25	12	[34]
91:9	PAN + 32 % w/w zeolite X	50	51.9	[35]
96.5:3.5	q-Chitosan/ 10 mol% TEOS	40	3098	[36]

4. PERVAPORATION FOR ETHANOL RECOVERY. MEMBRANES.

Recently, there has been growing research interest in the application of pervaporation in the area of recovery of ethanol from fermentation broths obtained from lignocellulosic biomass. Such fermentation broths are very diluted and ethanol concentrations usually vary between 1-5 % w/w. In this case pervaporation is considered as an attractive alternative to conventional techniques, such as distillation, due to its higher separation efficiency and capital and energy savings (Khayet et al., 2008).

Since ethanol is to be separated from its solution, organophilic pervaporation has to be applied where alcohol-selective membranes give permeate enriched in ethanol. Here once again the choice of appropriate membrane is of greatest importance. Silicone rubbers have higher flux and ethanol-water selectivity than most other hydrophobic ethanol-permeable polymers. Poly(dimethyl siloxane) [PDMS] is the benchmark hydrophobic polymer for ethanol recovery by pervaporation. Nevertheless, separation factors values for ‘pure’ PDMS membranes do not exceed 10. Thus, much effort has been done over the past few years to obtain polymeric membranes with better separation performance. Examples are listed in Table 3.

Table3. Polymeric membranes for ethanol recovery by pervaporation

EtOH/H_2O mass ratio	Membrane separation layer	Tempeature (◦C)	Separation factor	Reference
6:94	PDMS	35	5	[38]
5:95	PDMS	22.5	7.6	[39]
4:96	PDMS	25	10	[40]
2:98	PDMS	35	8	[41]
1.5:98.5	PDMS	66	10.4	[42]
6:94	PTMSP	30	19.9	[43]
1.5:98.5	PTMSP	66	18.7	[42]
7:93	PTMSP/PDMS	30	28.3	[44]
4:96	Plasma polymerized silane	25	18	[45]
2.5:97.5	IPAA/FA-PDMS	24	19.7	[46]

Poly(trimethylsilyl propyne)[PTMSP] shows greater permeability than PDMS, but delivers unstable performance and selectivity declines with time (Vane, 2005).

Alike hydrophilic pervaporation, along with polymeric materials there are inorganic and mixed matrix materials which are used for preparation of membranes for recovery of ethanol by means of pervaporation. The inorganic membranes are based on hydrophobic zeolites and their main types are presented in Table 4. The pervaporation performance exceeds a few times that of PDMS, but the inorganic membranes are expensive and there are difficulties of producing defect-free commercial-scale membranes. Thus, researchers investigated recently the potential of mixed matrix membranes consisting of silicalite particles dispersed in PDMS. Information about them is also given in Table 4.

Table4. Inorganic membranes and mixed matrix membranes for ethanol recovery by pervaporation

EtOH/H_2O mass ratio	Membrane separation layer	Tempeature (◦C)	Separation factor	Reference
4:96	Silicalite zeolite	30	26	[48]
5:95	Silicalite zeolite	30	41	[49]
5:95	B-ZSM-5 zeolite	30	31	[50]
5:95	Ge-ZSM-5	30	47	[51]
1.5:98.5	Silicalite-PDMS	66	11.1	[42]
4.4:95.6	Silicalite-PDMS	50	29.3	[52]
5:95	Silicalite-PDMS	30	17	[53]

In comparison to PDMS, the higher ethanol-water separation factors of the mixed matrix membranes with little cost increase stimulate further investigation in this area.

5. CONCLUSIONS

Pervaporation is an emerging technology with significant potential for both efficient dehydration and recovery of ethanol from fermentation broths. It is extensively studied in the area of water removal where many suitable polymeric materials are available because most polymers are water perm-selective. That is why, in case of ethanol separation the choice of polymers is somewhat restricted and new polymer modifications, such as cross-linking, grafting, copolymerization are required. More recently, inorganic and mixed matrix membranes have increasingly become a focus of research. Although these are more difficult to produce on a large-scale and are often expensive, they offer a number of advantages over polymeric membranes such as solvent resistance and operation at higher temperatures. The utilization of new materials and further development of fabrication techniques in membrane production will ensure the successful application of pervaporation for the production of fuel-grade bioethanol.

REFERENCES

1. Hilmioglu N. Bioethanol recovery using the pervaporation separation technique. Management of Environmental Quality: An International Journal 2009; 20: 165-174.
2. Jain A. Development of membranes for liquid phase ethanol-water separation. MSc-thesis, Division of Research and Advanced Studies University of Cincinnati 2005; p. 2.
3. Lynd L, Lyford K, South C, Walsum van P, Levenson K. Evaluation of paper sludges for amenability to enzymatic hydrolysis and conversion to ethanol, Tappi J February, 2001 1–19.
4. Aroujalian A, Belkacemi K, Davids S, Turcotte G, Pouliot Y. Effect of protein on flux and selectivity in pervaporation of ethanol from a dilute solution. Sep Sci Technol 2003; 38: 3239– 3247.
5. Vane L, Namboodiri V, Bowen T. Hydrophobic zeolite–silicone rubber mixed matrix membranes for ethanol–water separation: Effect of zeolite and silicone component selection on pervaporation performance. J Membr Sci 2008; 308: 230–241.
6. Vane L. Separation technologies for the recovery and dehydration of alcohols from fermentation broths. Biofuels Bioprod Bioref 2008; 2: 553–588.
7. Lipnizki F, Hausmanns S, Ten P, Field R, Laufenberg G. Organophilic pervaporation: prospects and performance. Chem Eng J 1999; 73: 113-129.
8. Lipnizki F, Hausmanns S, Field R. Influence of impermeable components on the permeation of aqueous 1-propanol mixtures in hydrophobic pervaporation. J Membr Sci 2004; 228: 129–138.
9. Gimenes M, Liu L, Feng X. Sericin/poly(vinyl alcohol) blend membranes for pervaporation separation of ethanol/water mixtures. J Membr Sci 2007; 295: 71–79.
10. Thongsukmak A, Sirkar K. Extractive pervaporation to separate ethanol from its dilute aqueous solutions characteristic of ethanol-producing fermentation processes. J Membr Sci 2009; 329: 119–129.

11. Smitha B, Suhanya D, Sridhar S, Ramakrishna M. Separation of organic–organic mixtures by pervaporation—a review. J Membr Sci 2004; 241: 1–21.
12. Boontawan A, Schausberger P, Bösch P, Brinkmann T, Friedl A. Dehydration of Ethanol/Water Mixture using Pervaporation and Vapor Permeation Technique. J Appl Membr Sci Technol, 2007; 5: 1–7.
13. Hutahaean L, Shen W, van Brunt V. Heat integrated ethanol dehydration flowsheets. Sep Sci Technol 1995; 30: 1867–1882.
14. Guo W, Chung T-S, Matsuura T. Pervaporation study on the dehydration of aqueous butanol solutions: a comparison of flux vs. permeance, separation factor vs. selectivity. J Membr Sci 2004; 245: 199–210.
15. Gimenes M, Liu L, Feng X. Sericin/poly(vinyl alcohol) blend membrane for pervaporation separation of ethanol/water mixtures, J Membr Sci 2007; 295: 71.
16. Ruckenstein E, Liang L. Poly(acrylic acid)-poly(vinyl alcohol) semi- and interpenetrating polymer network pervaporation membranes, J Appl Polym Sci 1996; 62: 973.
17. Wei Y-M, Xu Z-L, Qusay F, Wu K. Polyvinyl Alcohol/Polysulfone (PVA/ PS) Hollow Fiber Composite Membranes for Pervaporation Separation of Ethanol/ Water Solution. J Appl Polym Sci 2005; 98: 247-254.
18. M, Mas A, Guimon M-F, Guimon C, Elharfi A, Schule´ F. Plasmamodified poly(vinyl alcohol) membranes for the dehydration of ethanol. Polym Int 2003; 52: 1222.
19. Zhang W, Li G, Fang Y, Wang X. Maleic anhydride surface-modification of crosslinked chitosan membrane and its pervaporation performance, J Membr Sci 2007; 295: 130.
20. Lee Y, Nam S, Woo D. Pervaporation of ionically surface crosslinked chitosan composite membranes for water–alcohol mixtures, J Membr Sci 1997; 133: 103.
21. Shieh J-J, Huang R. Pervaporation with chitosan membranes. 2. Blend membranes of chitosan and polyacrylic acid and comparison of homogeneous and composite membrane based on olyelectrolyte complexes of chitosan and polyacrylic acid for the separation of ethanol–water mixtures. J Membr Sci 1997; 127: 185.
22. Huang R, Pal R, Moon G. Characteristics of sodium alginate membranes for the pervaporation dehydration of ethanol–water and isopropanol–water mixtures. J Membr Sci 1999; 160: 101.
23. Kalyani S, Smitha B, Sridhar S, Krishnaiah A. Separation of ethanol–water mixtures by pervaporation using sodium alginate/poly(vinyl pyrrolidone) blend membrane crosslinked with phosphoric acid. Ind Eng Chem Res 2006; 45: 9088.
24. Huang R, Pal R, Moon G. Pervaporation dehydration of aqueous ethanol and isopropanol mixtures through alginate/chitosan two plycompositemembranes supported by poly(vinylidene fluoride) porous membrane. J Membr Sci 2000; 167: 275.
25. Wang Y, Tsai Y, Lee K, Lai J. Preparation and pervaporation performance of 3,3-bis 4-(4-aminophenoxy)phenyl phthalide based polyimide membranes, J Appl Polym Sci 2005; 96: 2046.
26. Yanagishita H, Maejima C, Kitamoto D, Nakane T. Preparation of asymmetric polyimide membrane for water/ethanol separation in pervaporation by the phase inversion process. J Membr Sci 1994; 86: 231.

27. Chapman P, Oliveira T, Livingston A, Li K. Membranes for the dehydration of solvents by pervaporation. J Membr Sci 2008; 318: 5–37.
28. Sommer S, Melin T. Performance evaluation of microporous inorganic membranes in the dehydration of industrial solvents. Chem Eng Process 2005; 44: 1138.
29. Peters T, Benes N, Buijs H, Vercauteren F, Keurentjes J. Thin high flux ceramic-supported PVA membranes, Desalination 2006; 200: 37.
30. van Gemert R, Cuperus F. Newly developed ceramic membranes for dehydration and separation of organic mixtures by pervaporation. J Membr Sci 1995; 105: 287.
31. Tanaka K, Yoshikawa R, Ying C, Kita H, Okamoto K-i. Application of zeolite membranes to esterification reactions. Catal Today 2001; 67: 121.
32. Okamoto K-i, Kita H, Horii K, Tanaka K. Zeolite NaA membrane: preparation, single-gas permeation, and pervaporation and vapor permeation of water/organic liquid mixtures, Ind Eng Chem Res 2001; 40: 163.
33. Gao Z, Yue Y, Li W. Application of zeolite-filled pervaporation membrane. Zeolites 1996; 16: 70.
34. Wang Y-C, Fan S-C, Lee K-R, Li C-L, Huang S-H, Tsai H-A, Lai J-Y. Polyamide/SDS-clay hybrid nanocomposite membrane application to water–ethanol mixture pervaporation separation, J Membr Sci 2004; 239: 219.
35. Okumus E, Gurkan T, Yilmaz L. Effect of fabrication and process paprameters on the morphology and performance of a PAN-based zeolite-filled pervaporation membrane. J Membr Sci 2003; 223: 23.
36. Uragami T, Katayama T, Miyata T, Tamura H, Shiraiwa T, Higuchi A. Dehydration of an ethanol/water azeotrope by novel organic–inorganic hybrid membranes based on quaternized chitosan and tetraethoxysilane. Biomacromolecules 2004; 59: 1567.
37. Khayet M, Cojocaru C, Zakrzewska-Trznadel G. Studies on pervaporation separation of acetone, acetonitrile and ethanol from aqueous solutions, Sep Purif Technol 2008; 63: 303–310.
38. Vankelecom I, Depre D, De Beukelaer S, Uytterhoeven J. Influence of zeolites in PDMS membranes: pervaporation of water/alcohol mixtures. J Phys Chem 1995; 99: 13 193–13 197.
39. te Hennepe H, Bargeman D, Mulder M, Smolders C. Zeolite-filled silicone rubber membranes. Part I. Membrane preparation and pervaporation results. J Membr Sci 1987; 35: 39-55.
40. O'Brien D, Senske G, Kurantz M Craig J, Jr. Ethanol recovery from corn fiber hydrolysate fermentations by pervaporation. Bioresource Technol 2004; 92: 15–19.
41. Kashiwagi T, Okabe K, Okita K. Separation of ethanol from ethanol/water mixtures by plasma-polymerized membranes from silicone compounds. J Membr Sci 1988; 36: 353–362.
42. Mori Y, Inaba T, Ethanol production from starch in a pervaporation membrane bioreactor using Clostridium thermohydrosulfuricum. Biotech Bioeng 1990; 36: 849–853.
43. Fadeev A, Kelley S, McMillan J, Selinskaya Y, Khotimsky V, Volkov V, Effect of yeast fermentation by-products on poly(1-trimethylsilyl-1-propyne) pervaporative performance. J Membr Sci 2003 214:229–238.

44. Nagase Y, Ishihara K, Matsui K. Chemical modification of poly(substituted-acetylene): II. Pervaporation of ethanol/water mixture through poly(1-trimethylsilyl-1-propyne)/poly(dimethylsiloxane) graft copolymer membrane. J Poly Sci Part B 1990; 28: 377–386.
45. Kashiwagi T, Okabe K and Okita K, Separation of ethanol from ethanol/water mixtures by plasma-polymerized membranes from silicone compounds. J Membr Sci 1988; 36: 353–362.
46. Aoki T, Yamagiwa K, Yoshino E, Oikawa E. Temperaturesensitive ethanol permselectivity of poly(dimethylsiloxane) membrane by the modification of its surface with copoly(Nisopropylacrylamide/ 1H,1H,2H,2H-perfluorododecyl acrylate). Polymer 1993; 34: 1538–1540.
47. Vane L. A review of pervaporation for product recovery from biomass fermentation processes. J Chem Technol Biotechnol 2005; 80: 603–629.
48. Ikegami T, Yanagishita H, Kitamoto D, Haraya K, Nakane T, Matsuda H, Koura N, Sano T. Highly concentrated aqueous ethanol solutions by pervaporation using silicalite membrane—improvement of ethanol selectivity by addition of sugars to ethanol solution. Biotechnol Lett 1999; 21: 1037–1041.
49. Nomura M, Bin T and Nakao S-I, Selective ethanol extraction from fermentation broth using a silicalite membrane. Sep Purif Technol 2002; 27: 59–66.
50. Bowen T, Kalipcilar H, Falconer J, Noble R. Pervaporation of organic/water mixtures through B-ZSM-5 zeolite membranes onmonolith supports.J Membr Sci 2003; 215: 235–247.
51. Li S, Tuan V, Falconer J, Noble R. Properties and separation performance of Ge- ZSM-5 membranes. Micropor Mesopor Mater 2003; 58: 137–154.
52. Chen X, Ping ZH and Long YC, Separation properties of alcohol-water mixture through silicalite-I-filled silicone rubber membranes by pervaporation. J Appl Polym Sci 1998; 67: 629–636.
53. Adnadjevic B, Jovanovic J, Gajinov S. Effect of different physicochemical properties of hydrophobic zeolites on the pervaporation properties of PDMS-membranes. J Membr Sci 1997; 136: 173–179.