

EFFICIENCY OF ACETONE-BUTANOL-ETHANOL-WATER SYSTEM SEPARATION BY PERVAPORATION

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The article focuses on multicomponent system separation with the use of an innovative membrane-based technique i.e. pervaporation. Pervaporation is a membrane technique for separation of liquid mixtures on solid nonporous membranes. Pervaporation is used in this study to separate a quaternary system acetone-butanol-ethanol-water. Such a system may be derived from ABE fermentation process, and the resulting product, biobutanol, is a potential biofuel and may be used in internal combustion engines.

Experiments in the study involving concentration of butanol by pervaporation were performed using PERVAP 4060 flat-sheet commercial membrane. To describe the PV process a semi-empirical approach was used. As a result of experiments and calculations permeance coefficients were obtained. Separation and permeance factors were calculated to assess the efficiency of the system separation. Beforehand, activity coefficients were determined for all the components of the mixture with the NRTL equation. Separation coefficients for all the components differed depending on process parameters: concentration, feed flow rate and process temperature. The study confirmed the separation effect of the quaternary system. The most interesting results were obtained for the concentration of butanol. Pervaporation allows to concentrate butanol over 10 times. The permeance coefficient reached for butanol an average value of $7.06 \cdot 10^{-3}$ in comparison with the results for ethanol $3.24 \cdot 10^{-2}$ and acetone $1.83 \cdot 10^{-2}$ [$\text{kmol}(\text{m}^2\text{h})^{-1}$]. The temperature change from 50 to 70°C led to an increased permeance factor and there was no apparent effect on it in the feed flow rate. Due to the hydrophobicity of the membrane water fluxes in the quaternary system were negative.

Keywords: pervaporation, biobutanol, quaternary system

1. INTRODUCTION

Liquid multicomponent systems are often separated by distillation. However, as the process is energy intensive, and multi-phase, complex solutions are required to separate certain substances (azeotropes, close boiling liquids, chemically unstable substances etc.) new, better methods are constantly being elaborated. Membrane-based techniques are one of the options and, depending on a separation process, they may yield adequate quality and economic results. One of the examples is pervaporation, an innovative membrane-based separation technique used on an industrial scale.

Pervaporation process involves phase change combined with mass transfer across a nonporous composite membrane. Pervaporation has found viable applications in the following areas: dehydration of liquid organic mixtures, removal of organic compounds from water and separation of mixtures of two or more organic compounds. Following the solution-diffusion mechanism, transfer and separation of mass involves selective dissolution of a selected component of the solution on the membrane, and

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then its evaporation into the vapour phase through the membrane. Component pressure at the gas side is maintained below equilibrium by its condensation, using inert gas or applying low pressure at the permeate side. Pervaporation membranes have a solid structure, and components, as a result of dissolution and diffusion are transported across the membrane (Drioli and Giono, 2009; Kujawski, 1996; Narębska, 1997; Wijmans, 2004; Schaetzel et al., 2001; Schaetzel et al., 2004). The technique can be widely used in the industry e.g. in alcohols dehydration (Rapin, 1989). Hybrid systems, combining pervaporation and distillation allow for the production of e.g. absolute alcohols (ethanol, butanol), while a combination of pervaporation with a reactor for continuous fermentation results in a faster reaction and increased conversion, which improves efficiency and reduces the cost of biofuel production (Lipnizki et al., 1999).

After ethanol, there is now much interest in butanol due to the role it may play in the future. It is expected that biobutanol production may make automotive industry independent from crude oil and natural gas and reduce the emission of harmful gases into the atmosphere (Durre, 2008; Fortman et al., 2008). Research shows that the use of butanol as a fuel additive improving its quality is much more advantageous than the use of ethanol. Butanol is characterised by much higher combustion energy (29.2 MJ/dm³), relatively low heat of vaporisation and lower corrosiveness than ethanol (melting point -89.5°C; boiling point 117.2°C; flash point 36°C, auto ignition temperature 340°C) (Regulation 2008). Despite the fact that butanol is now only used as a petrol additive (typical butanol mixtures may contain from 8 to 32% of butanol, and ethanol mixtures from 5 to 20% of ethanol) much effort is devoted to designing engines that would operate using only this compound (Durre 2008; Wackett 2008).

Butanol may be derived from solid fuels or as a result of ABE fermentation of typical raw materials such as crops including sugarcane, corn or wheat. As the raw materials are expensive, cellulose waste materials are used in the process i.e. straw or wood waste, and other sources of plant biomass are investigated that would be more cost efficient e.g. algae cultivation (Christi, 2008). These techniques are much more cost competitive and thus more attractive than ethanol production.

Concentration of biobutanol by distillation is not economically viable due to high energy consumption, especially with low butanol concentration (up to 3% weight). That is why other methods are now commonly used such as adsorption, pertraction, extraction, pervaporation, infiltration, reverse osmosis or “gas stripping” (Qureshi and Maddox, 1995). Pervaporation is potentially the best option because it allows for the separation and concentration of butanol on a hydrophobic membrane in a single process (Liu et al., 2005; Qureshi and Blaschek 1999). Literature provides several examples of n-butanol separation from aqueous solutions by PV on various membrane types (Fouad and Feng, 2008; Garcia et al., 2009a; Huang and Meagher, 2001; Khayet et al., 2008). Mathematical descriptions that model pervaporation process depending on membrane type are also available.

Modelling of mass transfer in membrane-based processes is based on two basic types of modelling, namely theoretical and experimental modelling (Rautenbach, 1996). Empirical models are applied for quick assessment of membrane operation and application (the choice of appropriate material and structure). In the pervaporation process, mathematical description of transfer phenomena is based on a solution-diffusion method, therefore apart from calculating sorption on a polymer, the rate of fluid flow through its area must also be determined. Multicomponent mass transfer theory allows for calculating the rate of fluid flow through polymer materials provided that interdiffusion and self-diffusion coefficients are known. They may be determined experimentally or calculated from molecular models based on other physical parameters of the system, e.g. free volume theory. A determination of the activity coefficient in a membrane-components system is then a difficult task so far.

Recently PV butanol recovery from aqueous solutions is one of the most interesting subjects in scientific research. There are many both experimental and modelling works. The research mainly focuses on binary and ternary systems. It is possible to model a process using: a purely theoretical approach, e.g. model Wenchang and Sikdar (El-Zanati et al., 2006), semi-empirical (Garcia et al.,

2009b) and empirical models (Cojocar et al., 2009). Due to the complex nature of the problem theoretical modelling of separation for the quaternary systems is extremely rare. The high complexity of mathematical models of PV separation of more than two components requires additional research. Therefore in the present work for a quaternary system it was decided to use semi-empirical modelling.

The aim of this study is a semi-empirical approach to modelling of quaternary system separation by pervaporation. This gives an opportunity to determine the permeance coefficient that decides about the efficiency of the membrane process, allows a comparison of obtained data and can be used to scaling up. The permeance factor will be determined on the basis of experimental data and activity difference on both sides of the membrane. The activity of the individual components will be calculated based on the NRTL equation.

2. THEORETICAL

In order to design an industrial installation, a mathematical description of the process is required in addition to laboratory scale experiments, which would allow for the prediction of transfer-separation effects. Transfer across nonporous pervaporation membranes is defined in qualitative terms by the solution-diffusion theory. According to the theory, mass transfer and separation in a pervaporation process consists of three consecutive stages: sorption of components on the membrane surface, diffusion across the membrane and desorption on the other side of the membrane (Boddeker, 1999; Doong et al., 1995; Neel, 1991; Trifunovic and Tragardh, 2002). Thermodynamic considerations related to the solution and diffusion model lead to the determination of a normalised permeance flux. Membrane characteristics for multicomponent mixtures expressed as normalised permeance flux may be described by the following Equation (1):

$$J_i = Kp_i \Delta a_i \quad (1)$$

where

$$J_i = \frac{J_{tot} w_i}{M_i} \quad (2)$$

The activity of a component is a function of state and it means that a change of activity does not depend on way of changes but only on the initial and final state of the matter. It is a very useful driving force for a complicated pervaporation process with a quaternary system. Coefficients Kp_i represent all resistance forces in mass transfer and they are similar to overall mass transfer coefficient when the driving force is presented in terms of activity. Similar approach is presented in the PhD Stachecka thesis (Stachecka, 2005). Coefficients Kp_i also reflect the ability of membrane to permeate giving component. A change in the activity of mixture components on both sides of the membrane is expressed by the following equation:

$$\Delta a_i = y_{iP} \gamma_{iP} - x_{iF} \gamma_{iF} \quad (3)$$

A practical application of Equation (1) consists in the experimental determination of permeate flux (J_i) and calculation of activity change (Δa_i) taking into consideration equations allowing for calculating activity coefficients and the composition of feed and permeate obtained in the experiments. With Kp_i (permeance) factor, scaling up may be performed.

One of the methods of activity coefficient calculation is the NRTL (Non-Random Two-Liquid) concept. In this paper, the activity coefficients in a liquid for acetone-butanol-ethanol-water quaternary system under atmospheric pressure were determined using the NRTL equation as follows (4).

$$\ln \gamma_i = \frac{\sum_{j=1}^n \tau_{ji} x_j G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \left[\tau_{ij} - \frac{\sum_{m=1}^n \tau_{mj} x_m G_{mj}}{\sum_{k=1}^n x_k G_{kj}} \right] \quad (4)$$

where

$$G_{ij} = \exp(-\sigma_{ij} \tau_{ij}) \quad (5)$$

$$\tau_{ij} = a_{ij} + b_{ij} / T + e_{ij} \ln T + f_{ij} T \quad (6)$$

$$\sigma_{ij} = c_{ij} + d_{ij} (T - 273.15) \quad (7)$$

$\tau_{ii} = 0$; $G_{ij} = 1$; a_{ij} , b_{ij} , e_{ij} , f_{ij} are unsymmetrical.

a , b , c , d , e factors in binary systems were provided by the University of Dortmund courtesy.

Equation (8) was used to calculate theseparation factor (α_i) for individual components, which along with permeance factor (Kp_i) allows for the selection and comparison of pervaporation processes carried out using various membranes.

$$\alpha_i = \frac{x_{iP}}{x_{iF}} \cdot \frac{1 - x_{iF}}{1 - x_{iP}} \quad (8)$$

3. EXPERIMENTAL RESULTS

The efficiency of each membrane-based process depends on the selection of a proper membrane. A membrane, as a selective barrier separating two phases of different component concentrations, should enable preferential transfer of the components.

A commercially available hydrophobic, nonporous membrane PERVAP 4060 provided by Sulzer Chemtech was used in the study. The membrane is used for the separation of organic solvents such as alcohols from water. The membrane of active surface of 0.0177 m² was placed in a flat module. The experiments were carried out with the use of Sulzer Chemtech laboratory apparatus (Fig. 1), under fixed pressure at the low-pressure side of the membrane (3 kPa) with the volume flow rate (20, 40, 60 dm³/h), temperature (50, 60, 70°C) and feed composition which varied throughout the tests.

The model feed consisted of an aqueous solution of three organic components with the following mass ratios: acetone:butanol:ethanol 3:6:1 prepared from pure reagents. Butanol concentrations in the solution ranged from 0.25 to 3% wt. The liquid fed to the module was thermostated. Due to the small surface of the membrane, any temperature changes in the module were neglected.

The feed, permeate and retentate compositions were analysed by gas chromatography using an internal standard. A Thermo Finnigan chromatograph was equipped with FID and 30 m Quadrex Corporation column, model BTR-CW-30V-1.0F 0.53 mm and 1.0 µm thick.

Activity coefficients (γ_i), permeance factors (Kp_i) and separation factors (α_i) for individual components were calculated using a specially prepared calculation procedure. The activity coefficients were calculated based on pairs of coefficients for binary systems. The results of calculations of the coefficients τ_{ij} and G_{ij} (for 323.15 K) using Equation (4) are presented in Tables 1 and 2.

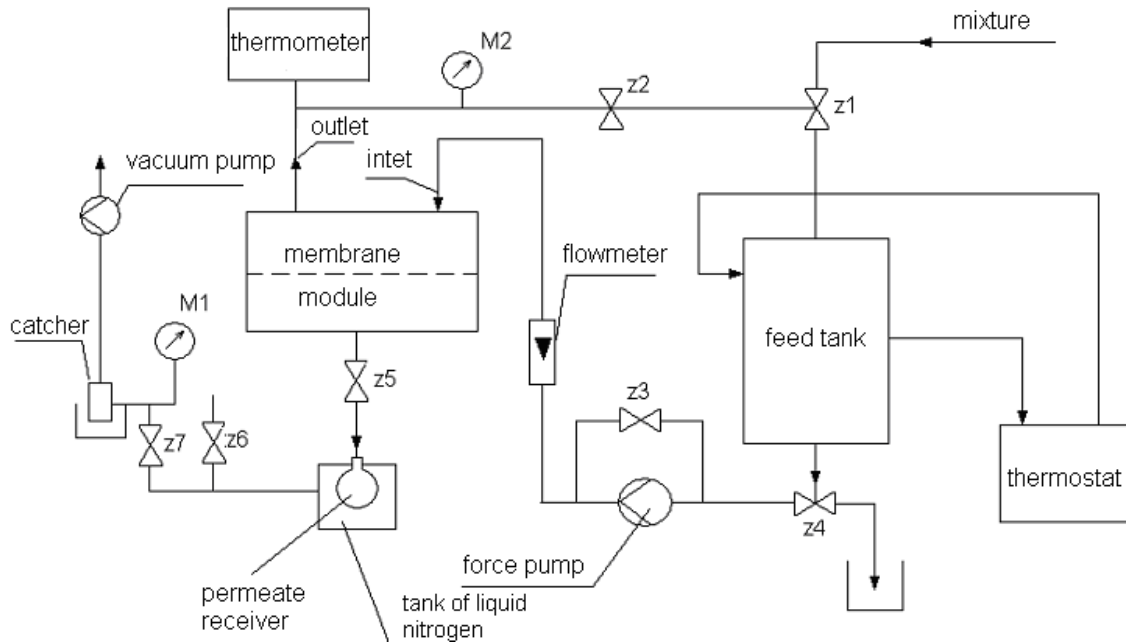


Fig. 1. Schematic diagram of the pervaporation equipment

 Table 1. The values of τ constant used to determine activity coefficients

	acetone	butanol	ethanol	water
acetone	0	0.635263	0.292223	0.800108
butanol	0.003801	0	0.397653	0.323322
ethanol	0.403738	-0.26371	0	-0.03909
water	1.354018	2.777681	1.64415	0

 Table 2. The values of G constant used to determine activity coefficients

	acetone	butanol	ethanol	water
acetone	1	0.82648	0.916066	0.786602
butanol	0.99886	1	0.887545	0.907559
ethanol	0.885926	1.082328	1	1.011795
water	0.666173	0.434611	0.610642	1

4. RESULTS AND DISCUSSION

Based on the experiments, the total flux of permeate (J_{tot}) and its composition in the form of mass fractions (w_i) were determined and then permeate fluxes were calculated for individual components (J_i), including water. Using Equation (1) and the activity coefficients (γ_i) permeance (Kp_i) was calculated for individual components for various conditions. Based on experimental data, separation factors (α_i) were also calculated. To determine effectiveness of the process of separation of acetone-butanol-ethanol system from water, the calculated values were added to the graph $Kp = f(\alpha)$ (Fig. 2 and 3).

Figures 2 and 3 present the results of calculations for separation of acetone-butanol-ethanol-water system on PERVAP 4060 membrane. Irrespective of the component, the points are located along a

certain area which can be described by $Kp_i = f(\alpha_i)$ space. The space is the operational space of the process. In the case of butanol, the separation factor is within the range 4.12–19.48 and permeance is in a narrow range (average $7.06 \cdot 10^{-3}$ with standard deviation $3.78 \cdot 10^{-3}$ [$\text{kmol}(\text{m}^2\text{h})^{-1}$]). It is possible to control the separation of butanol with permeate flux. For ethanol permeance coefficient changing from $1.05 \cdot 10^{-2}$ to $7.95 \cdot 10^{-2}$ [$\text{kmol}(\text{m}^2\text{h})^{-1}$] and separation factor is in a narrow range (average 5.75 with standard deviation sd 0.92). In this case, we can obtain high ethanol flux for similar effects of separation. For acetone there is no specific area of the separation factor and permeance coefficient. The effectiveness of acetone separation from a quaternary system (acetone-butanol-ethanol-water) is the worst. As the membrane is hydrophobic, water fluxes in the system are negative and the separation factors and permeance coefficient create a large area (Figure 3).

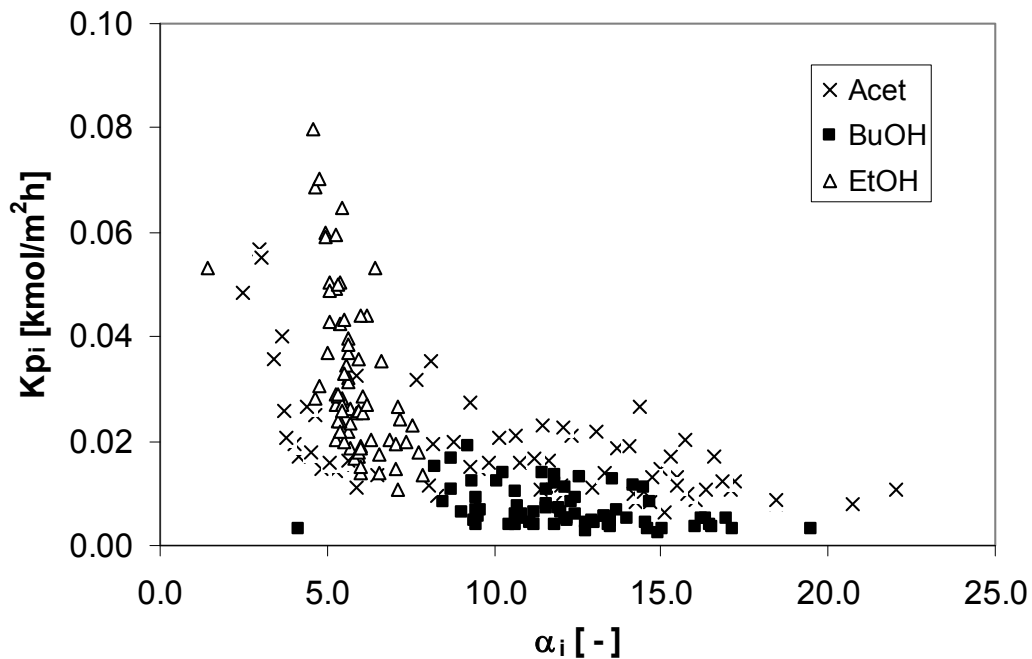


Fig. 2. Permeance coefficient (Kp) as a function of separation factor for acetone (Acet), butanol (BuOH) and ethanol (EtOH) in a quaternary system

Increased Kp factor and the resulting permeate flux increase, beneficial from the point of view of the process, result in lower effects of separation, unfavourable from the point of view of the process. Conversely, high separation results cause the permeate flux to decrease. An improvement of both of these opposite effects i.e. permeance and component separation result is possible if a different membrane is used. Nevertheless, the process of component separation by permeation is possible if the process driving force is maintained.

The separation efficiency of individual components in the acetone-butanol-ethanol-water system was also compared taking into consideration the feed volume flow rate and process temperature. Figures 4 and 5 present the relationship for butanol whose recovery is significant. The distribution of points demonstrates that the process temperature has a much bigger effect on the efficiency than the feed volume flow rate. A temperature increase (from 50 to 70°C) results in an increase of Kp factors, yet the separation factor value changes as well, and it is better at lower temperatures. Membranes that would operate at higher temperatures would improve the efficiency of pervaporation process.

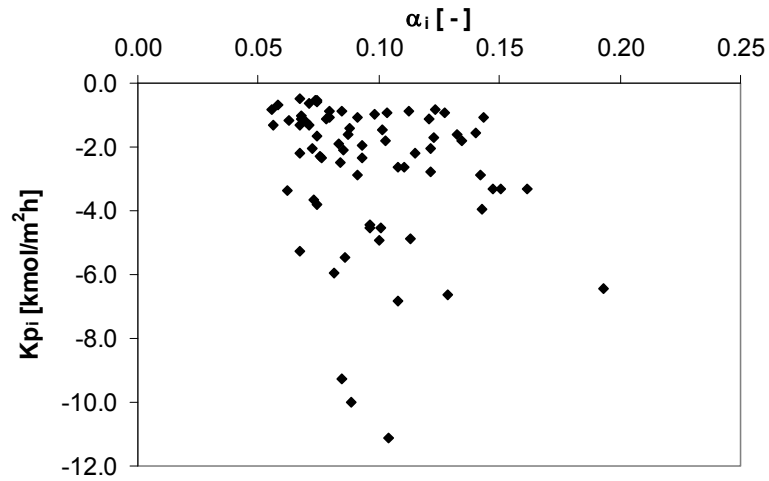


Fig. 3. Permeance coefficient (Kp) as a function of separation factor for water in a quaternary system acetone-butanol-ethanol-water

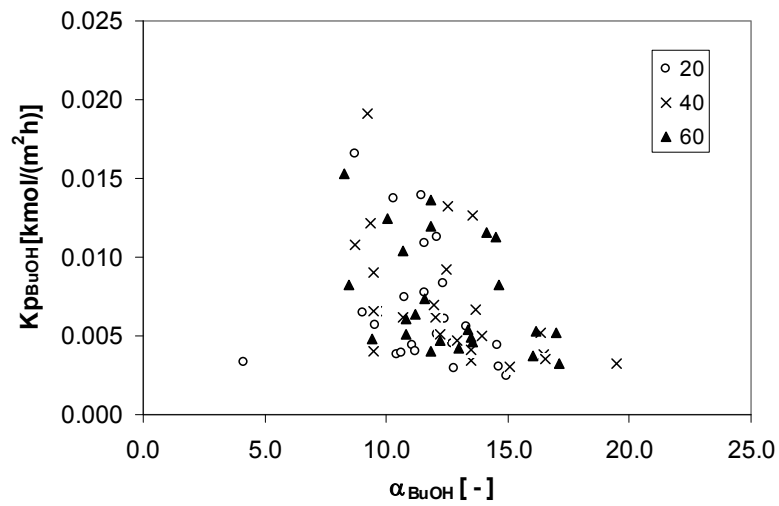


Fig. 4. Permeance coefficient (Kp) of butanol as a function of separation factor of butanol in acetone-butanol-ethanol-water system depending on a feed flow 20, 40 and 60 dm³/h

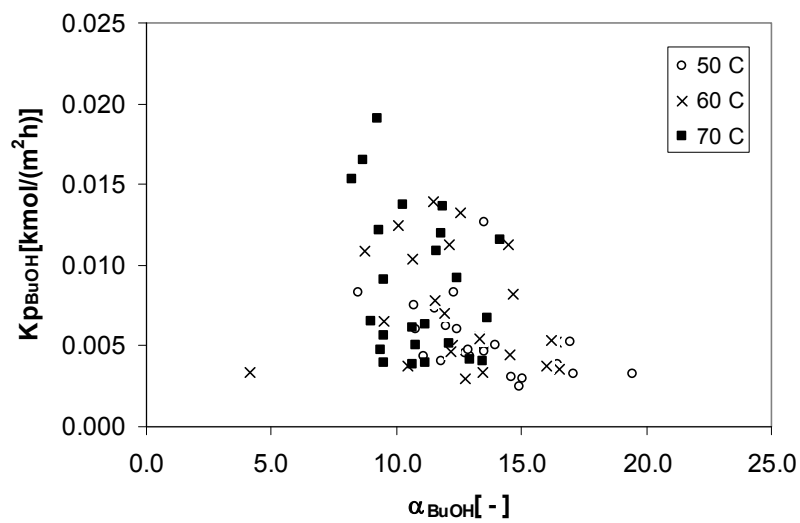


Fig. 5. Permeance coefficient (Kp) of butanol as a function of separation factor of butanol in acetone-butanol-ethanol-water system depending on a process temperature

5. CONCLUSIONS

The conditions under which membrane processes are carried out such as the composition and temperature of the feed or permeate pressure in pervaporation greatly affect the membrane separation performance. A combination of mathematical modelling with the results of experiments allows for a comparison of the process conditions as regards its efficiency. The study confirmed the separation effect of the quaternary system. The most interesting results were obtained for butanol concentration. Pervaporation allows to concentrate this component over 10 times. A higher concentration was observed for a lower share of butanol in the feed. Other components are concentrated to a lower degree.

The permeance coefficient and separation factors define the process of component separation by pervaporation. The permeance coefficient reached for butanol an average value of $7.06 \cdot 10^{-3}$ in comparison with the results for ethanol $3.24 \cdot 10^{-2}$ and acetone $1.83 \cdot 10^{-2}$ [$\text{kmol}(\text{m}^2\text{h})^{-1}$]. A temperature change from 50 to 70°C led to an increased permeance factor. There were no apparent effects of the feed flow rate on the efficiency in this process. Due to the hydrophobicity of the membrane water fluxes in the quaternary system were negative. Membranes that would operate at higher temperatures would improve the efficiency of separation of the acetone-ethanol-butanol-water system.

SYMBOLS

K_p	permeance, $\text{kmol}/(\text{m}^2 \text{ h})$
J	flux, $\text{kg}/(\text{m}^2 \text{ h})$
M	molecular weight, kg/kmol
w	mass fraction, -
Δa	activity change, -
x, y	mole fraction, -
t	temperature, °C
T	temperature, K
G	variable in the NRTL equation, -
a	constant in the NRTL equation, -
b	constant in the NRTL equation, -
e	constant in the NRTL equation, -
f	constant in the NRTL equation, -

Greek symbols

α	separation factor, -
γ	activity coefficient, -
σ	variable in the NRTL equation, -
τ	variable in the NRTL equation, -

Subscripts

i, j, k, m	number of the component
P	permeate
F	feed
tot	total

REFERENCES

- Böddeker W.K., 1990. Terminology in pervaporation. *J. Membr. Sci.*, 51, 259-272. DOI: 10.1016/S0376-7388(00)80350-6.

- Cojocar C., Khayet M., Zakrzewska-Trznadel G., Jaworska A., 2009. Modelling and multi-response optimization of pervaporation of organic aqueous solutions using desirability function approach. *J. Hazardous Mat.*, 167, 52-63. DOI:10.1016/j.jhazmat.2008.12.078.
- Christi Y., 2008. Biodiesel from microalgae beats bioethanol. *Trends Biotechnol.*, 26, 3, 126-131 doi:10.1016/j.tibtech.2007.12.002.
- Doong S.J., Ho W.S., Mastondrea R.P., 1995. Prediction of flux and selectivity in pervaporation through a membrane. *J. Membr. Sci.*, 107, 129 – 146. DOI: 10.1016/0376-7388(95)00109-P.
- Drioli E., Giorno L., 2009. *Membrane Operations: Innovative separations and transformations*, Wiley-VCH. DOI: 10.1002/9783527626779.
- Dürre P., 2008. Fermentative butanol production. *Annals New York Acad. Sci.*, 1125, 353–362. DOI: 10.1196/annals.1419.009.
- El-Zanati E., Abdel-Hakim E., El-Ardi O., Fahmy M., 2006. Modeling and simulation of butanol separation from aqueous solutions using pervaporation. *J. Membr. Sci.*, 280, 278-283. DOI: 10.1016/j.memsci.2006.01.029.
- Fortman J.L., Chhabra S., Mukhopadhyay A., Chou H., Lee T.S., Steen E., Keasling J.D., 2008. Biofuel alternatives to ethanol: pumping the microbial well. *Trends Biotechnol.*, 26, 7, 375-381. DOI: 10.1016/j.tibtech.2008.03.008.
- Fouad E. A., Feng X., 2008. Use of pervaporation to separate butanol from dilute aqueous solutions: Effects of operating conditions and concentration polarization. *J. Membr. Sci.* 323, 428-435. DOI: 10.1016/j.memsci.2008.06.054.
- Garcia V., Pongracz E., Muurinen E., Keiski R. L., 2009a. Recovery of n-butanol from salt containing solutions by pervaporation. *Desalination*, 241, 201-211. DOI: 10.1016/j.desal.2007.12.051.
- Garcia V., Landaburu-Aguirre J., Pongracz E., Peramaki P., Keiski R. L., 2009b. Dehydration of water/dichloromethane/n-butanol mixtures by pervaporation; optimisation and modeling by response surface methodology. *J. Membr. Sci.*, 338, 111-118. DOI: 10.1016/j.memsci.2009.04.040.
- Huang J., Meagher M. M., 2001. Pervaporative recovery of n-butanol from aqueous solutions and ABE fermentation broth using thin-film silicalite-filled silicone composite membranes. *J. Membr. Sci.*, 192, 231-242. DOI: 10.1016/S0376-7388(01)00507-5.
- Khayet M., Cojocar C., Zakrzewska-Trznadel G., 2008. Studies on pervaporation separation of acetone, acetonitrile and ethanol from aqueous solutions. *Sep. Purif. Technol.*, 63, 303-310. DOI: 10.1016/j.seppur.2008.05.016.
- Kujawski W., 1996. Membrane selectivity in pervaporation. *Sep. Sci. Technol.*, 31, 1555-1571. DOI: 10.1080/01496399608001413.
- Lipnizki F., Field W.R., Ten P.K., 1999. Pervaporation-based hybrid process: A review of process design, applications and economics. *J. Membr. Sci.*, 153, 183 –210. DOI: 10.1016/S0376-7388(98)00253-1.
- Liu F., Liu L., Feng X., 2005. Separation of acetone-butanol-ethanol (ABE) from dilute aqueous solution by pervaporation. *Sep. Pur. Technol.*, 42, 273-282. DOI:10.1016/j.seppur.2004.08.005.
- Narębska A., 1997. *Membrany i membranowe techniki rozdzielania*. Wydawnictwo UMK, Toruń.
- Neel J., 1991. Introduction to pervaporation, In: Huang R.Y.M. (Ed.), *Pervaporation Separation Processes*. Elsevier, Amsterdam, 1-109.
- Qureshi N., Maddox I., 1995. Continuous production of acetone-butanol-ethanol using immobilized cell of *Clostridium acetobutylicum* and integration with product removal by liquid-liquid extraction. *J. Ferment. Bioeng.* 80, 185-189. DOI: 10.1016/0922-338X(95)93217-8.
- Qureshi N., Blaschek H.P., 1999. Butanol recovery from model solution/fermentation broth by pervaporation: evaluation of membrane performance. *Biomass Bioenergy*, 17, 175-184. DOI: 10.1016/S0961-9534(99)00030-6.
- Rapin J. L., 1989. The Betheniville Pervaporation Unit – the first large – scale production plant for the dehydration of ethanol, in: Bakish R. (Ed.), *Proc. 3rd Int. Conf. on Pervaporation Processes in Chemical Industry*, Bakish Materials Corp., Englewood, 364 – 378.
- Regulation of the Minister of Economy, 27.12.2007 on the calorific value of various bio-components and liquid fuels. *Dziennik Ustaw* 2008 nr 3 poz. 12 (in Polish).
- Rautenbach R., 1996. *Membrane processes*, Scientific and Technical Publishing, Warszawa.
- Schaetzel P., Vauclair C., Luo G., Nguyen Q.T., 2001. The solution-diffusion model: Order of magnitude calculation of coupling between the fluxes in pervaporation. *J. Membr. Sci.*, 191, 103–108. DOI: 10.1016/S0376-7388(01)00457-4.

- Schaetzel P., Catherine Vaclair C., Nguyen Q.T., Bouzerar R., 2004. A simplified solution–diffusion theory in pervaporation: the total solvent volume fraction model. *J. Membr. Sci.*, 244, 117–127. DOI: 10.1016/j.memsci.2004.06.060.
- Stachecka A., 2005. Empirical and the semi-empirical models of alcohols dehydration by pervaporation, PhD thesis, Technical University of Lodz, Poland.
- Trifunovic O., Trägårdh G., 2002. Transport of diluted volatile organic compounds through pervaporation membranes. *Desalination*, 149, 1-2. DOI: 10.1016/S0011-9164(02)00682-3.
- Wackett L.P., 2008. Biomass to fuels via microbial transformations. *Current Opinion Chem. Biology* 12, 187-193. DOI: 10.1016/j.cbpa.2008.01.025.
- Wijmans J.G., 2004. The role of permeant molar volume in the solution-diffusion model transport equations. *J. Membr. Sci.*, 237, 39–50. DOI: 10.1016/j.memsci.2004.02.028.

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