

Joanna MARSZAŁEK¹ and Władysław KAMIŃSKI¹

CONCENTRATION OF BUTANOL-ETHANOL-ACETONE-WATER USING PERVAPORATION

ZATEŻANIE UKŁADU BUTANOL-ETANOL-ACETON-WODA ZA POMOCĄ PERWAPORACJI

Abstract: The purposes, objectives and technology pathways for alternative energy are biofuels. The main interest so far has been focused on bioethanol due to the availability of raw materials as well as developed methods for separation and purification. Butyl alcohol can also be regarded as a potential biofuel, and used for internal combustion engines. Butanol can be obtained by means of chemical reaction as well as by fermentation of biomass well known as acetone-butanol-ethanol (ABE) fermentation. Separation of butanol from fermentation broth is a very difficult technical problem. The distillation process traditionally used is economically unprofitable. Review of methods for product recovery from fermentation broth indicates that pervaporation is a modern membrane technology which allows for the separation and concentration of the product during a single process. This work presents results of research on biobutanol separation from the acetone-butanol-ethanol-water system by pervaporation. The concentration of biobutanol was changed in the 0.25÷3 wt. % range. The quaternary system was prepared similarly to that obtained from the ABE fermentation process. The process was carried out on a flat, hydrophobic, commercial membrane at steady state conditions. The pressure at the permeate side was 30 mbar, the temperature range was 50÷70°C and feed flow rate was 20, 40 and 60 dm³/h. The chemical constitution of permeate and retentate was analyzed by gas chromatography. Based on experiments, separation and enrichment factors of the organic phase for individual components were obtained. The mass fraction of individual components in the output flux was determined as well. Satisfactory performance of the analyzed system on the selected membrane was obtained.

Keywords: biobutanol, ABE fermentation, pervaporation

Biofuels are one of the alternative sources of energy. They have been used in the past since in the case the inception of the automotive industry, however low prices of crude oil lead to the reduction of use of biofuels. At present, the ever-increasing prices of crude oil and necessity of greenhouse emission reduction from fossil fuels shift the interest back to biologically produced biofuels. Biomass quality is not directly related to fuel calorific value but it affects the cost of manufacture. The main interest so far has been focused on bio-ethanol due to the availability of raw materials and well developed methods for separation and purification. Butyl alcohol can also be regarded as a potential biofuel, and used for internal combustion engines. As its properties are similar to petrol (see Table 1) butanol can be used as petrol additive. Relatively low heat of vaporization is one of its advantages as it facilitates engine start up at low temperatures. It is less susceptible to separate from petrol in the presence of water than ethanol [1]. Moreover, it contains less oxygen per mass unit and thus can be added to petrol at higher volumes. Typical blends of ethanol with petrol contain 5÷20% ethanol, while blends with butanol contain 8÷32% butanol.

Butanol can be obtained by means of chemical reaction as well as by fermentation of biomass well known as *Acetone-Butanol-Ethanol* (ABE) fermentation. Typical raw

¹ Faculty of Process and Environmental Engineering, Technical University of Lodz, ul. Wólczńska 213, 90-924 Łódź, email: marszalek@wipos.p.lodz.pl

materials include sugar cane, corn or wheat but other cellulose containing materials could also be used such as wood waste, which would greatly decrease the cost of biobutanol production. The product of ABE fermentation is the acetone:butanol:ethanol aqueous solution with the 3:6:1 mass ratio, as a result of which butanol of the concentration of up to 3 wt. % is obtained. Separation of butanol from fermentation broth is a very difficult technical problem [2]. The distillation process traditionally used is not economically viable. Review of methods for product recovery from fermentation broth indicates that pervaporation is a modern membrane technology which allows for the separation and concentration of the product during a single process.

Table 1

A comparison of the properties of engine fuels [3]

Fuel	Calorific value	Enthalpy of vaporization	Motor Octane Number
	[MJ/dm ³]	[MJ/kg]	[-]
Petrol	32	0.4	81÷89
Butanol	29	0.7	78

Pervaporation is a separation technique which involves phase change combined with mass transfer across non-porous composite membrane. This technique, used for the dehydration of ethanol, involves hydrophilic membrane and water transport across the membrane [4]. In the case of ABE post-fermentation product, the organic fraction, mainly biobutanol is the component transported across the hydrophobic membrane. Literature provides examples of studies into *n*-butanol separation and recovery from aqueous solutions by *pervaporation* (PV) [5-8].

Materials and methods

The experimental part of the study presents results of research on biobutanol separation from the acetone-butanol-ethanol-water system by pervaporation. The model feed consisted of aqueous solution of three organic components, namely butanol, ethanol and acetone. The quaternary system was prepared similarly to that obtained from the ABE fermentation process (acetone:butanol:ethanol 3:6:1). The concentration of biobutanol was changed in the range of 0.25÷3 wt. %. The process was carried out on a flat, hydrophobic, commercial membrane PERVAP 4060 [9] using Sulzer Chemtech laboratory apparatus at steady state conditions (Fig. 1). The pressure at the permeate side was 3 kPa, the temperature range was 50÷70°C and the flow rate of feed was 20, 40 and 60 dm³/h [10].

The chemical constitution of permeate and retentate was analyzed by gas chromatography using ThermoFinnigan apparatus and BTR-CW column. In most cases, due to the low solubility of *n*-butanol in water of approximately 8 wt. %, the permeate obtained was separated into two phases: lower, aqueous phase and upper, organic phase. To measure the concentration, the sample was additionally diluted with 5% aqueous methanol solution that was at the same time used as the internal standard, to the final *n*-butanol content of max. 10 wt. %. The obtained one-phase solution was examined by chromatography.

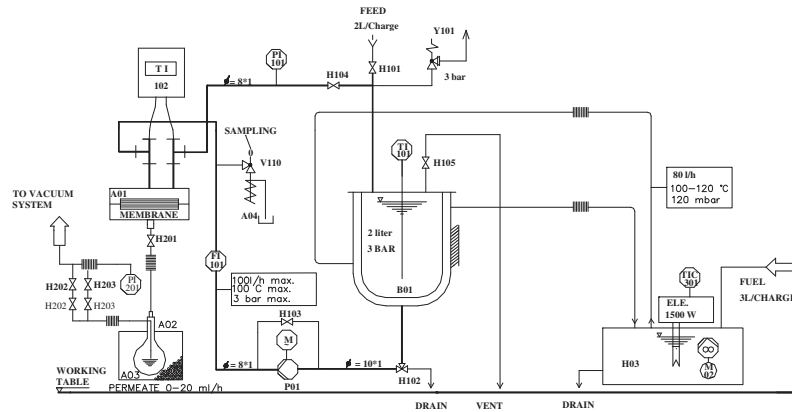


Fig. 1. Schematic diagram of the pervaporation equipment

Results

Based on the experiments, permeate weight and mass fractions of individual components in the permeate (w_{ip}) were obtained. The data was used to determine the total permeate flux (J_{tot}) and the mass fraction of individual components (J_i) in the output flux, according to the following formula:

$$J_i = J_{tot} w_{ip} \left[\frac{\text{kg}}{\text{m}^2 \text{h}} \right] \quad (1)$$

where: J_i - partial flux of component i [$\text{kg} (\text{m}^2 \text{h})^{-1}$], J_{tot} - total flux [$\text{kg} (\text{m}^2 \text{h})^{-1}$], w_i - mass fraction of component i in the permeate (p) or feed (F) [-].

The separation (α_i) and enrichment (β_i) factors define membrane selectivity and allow for the comparison of pervaporation results on various membranes. The separation and enrichment factors of the organic phase for individual components were calculated using the following formulas:

$$\alpha_i = \frac{x_{ip}}{x_{iF}} \cdot \frac{1 - x_{iF}}{1 - x_{ip}} \quad (2)$$

$$\beta_i = \frac{x_{ip}}{x_{iF}} \quad (3)$$

where x_i - mole fraction of component i in the permeate (p) or feed (F) [-].

During the experiments, due to the varying mass content of the organic phase in the feed (with acetone:butanol:ethanol 3:6:1 ratio maintained at all times), various concentrations of the permeate were obtained. Figure 2 presents an exemplary relationship between the mass content of a selected component of the organic phase in the feed and the mass content of the same component in the permeate. Higher concentrations may be observed for lower content of the organic phase in the feed. Additionally, it was found that

butanol tends to concentrate better (up to 25 wt. %) at lower temperatures and feed flow rates, as shown in Figure 3. The remaining components of the organic phase also diffused across the membrane. For acetone, the results were much more distributed for higher feed content of the component than for ethanol.

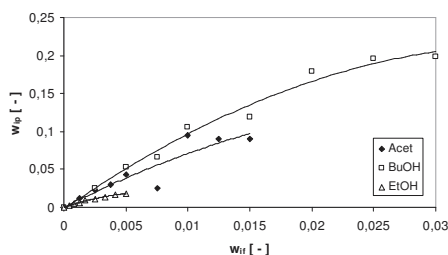


Fig. 2. Organic phase content in the permeate (w_p) depending on its feed content (w_{ff}) for processes carried out at $T = 70^\circ\text{C}$ and $u = 20 \text{ dm}^3/\text{h}$

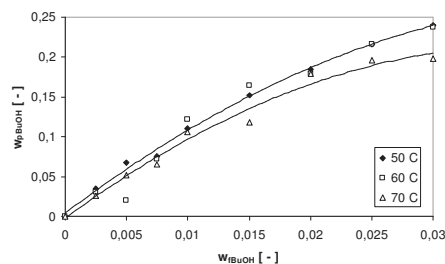


Fig. 3. Butanol content (BuOH) in the permeate ($w_{p\text{BuOH}}$) depending on its feed content ($w_{ff\text{BuOH}}$) at various temperatures and feed flow rate of $u = 20 \text{ dm}^3/\text{h}$

Total permeate flux increases with the increase of mass flow rate, feed temperature and feed content of butanol (Fig. 4). Figure 5 presents butanol fluxes in relation to the mass content of organic phase (butanol) in the feed averaged for several feed flow rates. Also here the fluxes are higher at higher operating temperatures and for the increased feed content of organic phase.

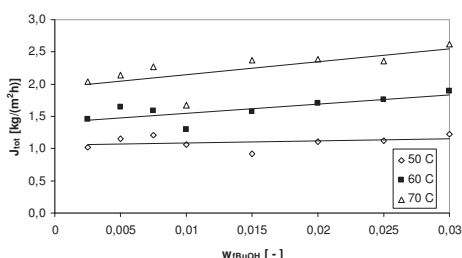


Fig. 4. Total mass flux of permeate (J_{tot}) depending on mass content of butanol in the feed for $u = 60 \text{ dm}^3/\text{h}$

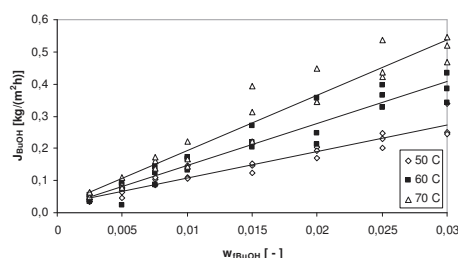


Fig. 5. Mass flux of butanol (J_{BuOH}) depending on mass content of butanol in the feed for various feed flow rates

Separation coefficient (α_i) for butanol calculated based on experimental data, and averaged for various feed flow rates ranges from $11 \div 15.5$ at operating temperature of 50°C , $10 \div 14$ at 60°C and $8.7 \div 12$ at 70°C . The values are lower for other components. The mean selectivity for acetone, initially high for low content of the component and similar to the selectivity for butanol, significantly decreases with the increase of its content in the feed. Separation factor for ethanol remains virtually constant over the entire range of concentrations. Figure 6 presents the average separation factor of the organic phase (α_i) for

various temperatures and flow rates depending on butanol mass content in the feed. The figure shows that the rate of permeation of individual components across the membrane was found to be in the order of butanol>acetone>ethanol. Butanol is thus the component which is preferentially diffused across the membrane.

The above results lead to the following conclusions concerning pervaporation process conditions: higher concentrations of organic components in the feed (butanol 2÷3 wt. %) ensure better separation of butanol from acetone. However, at the same time enrichment factor (β_i) is decreased with average values for butanol, acetone and ethanol of 10.5; 11.8 and 5.7, respectively. Feed flow rate had no decisive influence on result analysis.

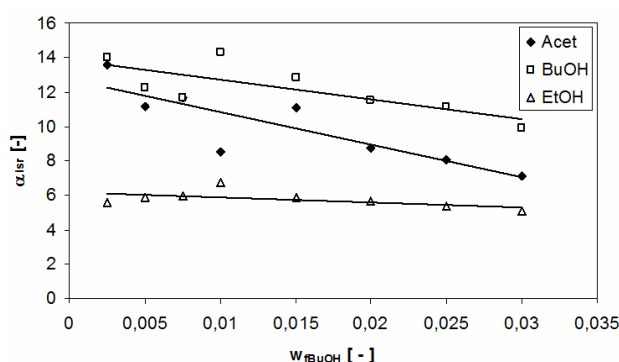


Fig. 6. Mean separation factor of the organic phase (α) for various temperatures and flow rates depending on butanol mass content in the feed

Conclusions

The experiments involving concentration of the model biobutanol system were aimed at analyzing pervaporation process to determine performance of the commercial membrane as regards the separation of aqueous and organic phases. The results analyzed within the range of butanol 0.25÷3 wt. % in the feed prepared at the same mass ratios of all of the components, namely acetone/butanol/ethanol/water confirm the dependence on flow rate and operating temperature. Transfer of organic phase, including butanol, across the membrane is higher for its lower content in the feed and lower temperatures despite higher fluxes. The studies into PERVAP 4060 membrane performance as regards pervaporative transfer and separation capabilities confirm its usability for the concentration of butanol following ABE fermentation.

References

- [1] BP DuPont Fact Sheet Biobutanol, http://www2.dupont.com/Production_Agriculture/en_US/assets/downloads/pdfs/BP_DuPont_Fact_Sheet_Biobutanol.pdf.
- [2] Kamiński W, Tomczak E, Górac A. Biobutanol - production and purification methods. *Ecol Chem Eng*. 2011;18:31-37.
- [3] Rozporządzenie Ministra Gospodarki z 27.12.2007 w sprawie wartości opałowej poszczególnych biokomponentów i paliw ciekłych. *DzU* z dnia 9 stycznia 2008 r.
- [4] Kaminski W, Marszałek J, Ciołkowska A. Renewable energy source - dehydrated ethanol. *Chem Eng J*. 2008;135:95-102. DOI: 10.1016/j.cej.2007.03.017.

- [5] Huang J, Meagher MM. Pervaporative recovery of *n*-butanol from aqueous solutions and ABE fermentation broth using thin-film silicalite-filled silicone composite membranes. *J Membrane Sci.* 2001;192:231-242. PII: S0376-7388(01)00507-5.
- [6] Garcia V, Pongracz E, Muurinen E, Keiski RL. Recovery of *n*-butanol from salt containing solutions by pervaporation. *Desalination.* 2009;41:201-211.
- [7] Fouad EA, Feng X. Use of pervaporation to separate butanol from dilute aqueous solutions: Effects of operating conditions and concentration polarization. *J Membrane Sci.* 2008;323:428-435. DOI: 10.1016/j.memsci.2008.06.054.
- [8] El-Zanati E, Abdel-Hakim E, El-Ardi O, Fahmy M. Modeling and simulation of butanol separation from aqueous solutions using pervaporation. *J Membrane Sci.* 2006;280:278-283. DOI: 10.1016/j.memsci.2006.01.029.
- [9] Khayet M, Cojocar C, Zakrzewska-Trznadel G. Studies on pervaporation separation of acetone, acetonitrile and ethanol from aqueous solutions. *Sep Pur Techn.* 2008;63:303-310. DOI: 10.1016/j.seppur.2008.05.016.
- [10] Marszałek J, Kamiński W. Perwaporacyjne zatężanie biobutanolu. Materiały konferencyjne *Membrany i Procesy Membranowe w Ochronie Środowiska. Monografie Komitetu Inżynierii Środowiska PAN.* Gliwice. 2010;66(2):35-40.

ZATĘŻANIE UKŁADU BUTANOL-ETANOL-ACETON-WODA ZA POMOCĄ PERWAPORACJI

Wydział Inżynierii Procesowej i Ochrony Środowiska, Politechnika Łódzka

Abstrakt: Jednym z rodzajów alternatywnych źródeł energii są biopaliwa. Główna uwaga do tej pory skupiana była na bioetanolu ze względu na dostępność surowców i dobrze opracowane metody wydzielania i oczyszczania. Alkohol butylowy może być również traktowany jako potencjalne biopaliwo i wykorzystany do silników wewnętrznego spalania. Butanol można otrzymać zarówno z paliw stałych, jak również przez fermentację biomasy. Produktami fermentacji ABE jest wodny roztwór acetonu, butanolu i etanolu. Wydzielanie butanolu z brzezki fermentacyjnej jest bardzo trudnym problemem technicznym. Tradycyjnie stosowana destylacja jest procesem energetycznie i ekonomicznie nieopłacalnym. Poszukiwane metody odzysku produktu z brzezki fermentacyjnej wskazują na nowoczesną technikę membranową, jaką jest perwaporacja, która umożliwia separację i koncentrację produktu w trakcie pojedynczego procesu. Niniejsza praca pokazuje badania perwaporacyjnego zatężania biobutanolu z modelowego czteroskładnikowego układu aceton-butanol-etanol-woda, przygotowanego zgodnie z informacjami o produkcie po procesie fermentacji ABE w zakresie stężeń 0,25÷3% mas. butanolu. Proces prowadzony był na płaskiej, hydrofobowej membranie komercyjnej w sposób ciągły, w warunkach ustalonych, z ciśnieniem po stronie permeatu wynoszącym 30 mbar, w zakresie temperatur 50÷70°C i z natężeniem przepływu nadawy 20, 40 i 60 dm³/h. Skład permeatu i retentatu był analizowany za pomocą chromatografii gazowej.

Słowa kluczowe: biobutanol, fermentacja ABE, perwaporacja