

Investigation of Process Alternatives for the Separation of Ethanol, N-Butanol and Water Ternary Mixture

Nora Valentinyi^{a,*}, Gaspar Marton^a, Andras J. Toth^a, Eniko Haaz^a, Anita Andre^a, Peter Mizsey^{a,b}

^aDepartment of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary

^bDepartment of Fine Chemicals and Environmental Technology, University of Miskolc, Miskolc, Hungary
 n.valentinyi@mail.bme.hu

Biofuel production is an ever current topic, as bioethanol and biobutanol have a great potential to partially or completely replace fossil fuels in the automotive industry due to their attractive characteristics. They are usually produced by fermentation resulting in a highly diluted mixture, which poses a challenge to the downstream processing and the production of pure alcohols.

In the course of this work, conventional separation systems of simple, extractive and heteroazeotropic distillation are compared with hybrid distillation-pervaporation systems for the separation of a ternary ethanol-n-butanol-water (EBW) mixture. Pervaporation (PV) is studied as an option for the final dehydration of the alcohol-water mixtures due to its great industrial potential in the separation of azeotropes. Simulations are carried out in ChemCAD® flowsheeting software, and the process alternatives are evaluated in an economic point of view, revealing the potentials and drawbacks of PV in a complex separation task.

1. Introduction

Biofuel production from renewable sources is in the focus of research for decades due to the growing environmental concerns and energy crisis (Wei et al., 2014). Bioethanol and biobutanol are renewable and clean fuel alternatives/additives in transportation with a potential of reducing global warming emissions. Additionally, biobutanol (BuOH) has the advantages of a non-hygroscopic nature and lower volatility than ethanol, with an unrestricted blending ratio with petrol, as opposed to ethanol (EtOH).

Both alcohols can be produced through a biotechnological route from renewable resources such as lignocellulosic biomass, which is a low-cost non-food feedstock. Although, fermentation results in a highly diluted broth containing only very low concentrations of the bioalcohols (Salemme et al., 2016). Traditional methods for separating this diluted mixture to obtain pure products is azeotropic distillation, extractive distillation, vacuum distillation, adsorption, gas-stripping, or extraction (Kujawska et al., 2015). In addition, the ternary EBW mixture is a complex, highly non-ideal system forming azeotropes (shown in Table 1), thus making the downstream separation costly and energy intensive.

Table 1: Boiling points and azeotrope compositions of the EBW mixture

	Boiling point [°C]	Composition [wt%]		
		EtOH	n-BuOH	Water
Ethanol	78.29			
n-Butanol	117.66			
Water	100			
Ethanol - Water	78.17	95.9		4.1
n-Butanol - Water	92.19		58.5	41.5

Pervaporation emerged as a promising alternative to reduce the high energy demand of conventional methods, such as distillation, in the production of pure alcohols. During pervaporation, liquid mixtures are separated by the partial evaporation of the preferentially permeating compound through a dense, non-porous membrane (Baker, 2004). The enthalpy of vaporisation is provided by the sensible heat of the feed mixture. PV has high selectivity under moderate operating conditions, and no added entrainers are needed for the process (Nagy et al., 2015). The most widespread application area of PV is solvent dehydration since hydrophilic membranes are much more selective than the organophilic ones. Intensive research is aimed at the improvement of the characteristics of both membrane types (Hieu and Duy, 2017). However, the high capital costs and generally low fluxes of the membranes hinder the individual application of pervaporation. The investment cost can be reduced if PV is coupled with common fluid separation techniques forming, so called, hybrid processes. The combination of pervaporation membranes and distillation columns has been widely investigated in the literature as a means of process intensification (Koczka et al., 2007; Rom et al., 2016; Valentinyi and Mizsey, 2012).

The separation of binary azeotropes with azeotropic, extractive, and pressure-swing distillation has also been subject to great attention (Timoshenko et al., 2015; Toth et al., 2017; You et al., 2015). During extractive distillation an entrainer is added to the column to change the relative volatility of the mixture. Thus, the energy consumption might be lower, but the added extractive agent has to be separated in an additional step and recycled into the process (Zhao et al., 2017). In the case of heteroazeotropic distillation, the mixture forming a heteroazeotrope is distilled mostly to its azeotropic composition and then fed into a phase separator, where liquid phases are separated. The pure product is produced in a subsequent distillation column.

In the course of this work, separation alternatives of a diluted ethanol – n-butanol – water ternary mixture were proposed, modelled and evaluated based on economic aspects, namely the total annual cost (TAC) of each alternative.

2. Process alternatives and simulation results

1.1 Pervaporation model

The pervaporation model used in this work is based on the separation mechanism of the solution–diffusion model (Heintz and Stephan, 1994). The flux model was obtained with the help of laboratory experiments reported in a previous work of the authors (Valentinyi et al., 2013). The semi-empirical model of Eq(1) was implemented in ChemCAD® software environment enabling the design of the hybrid systems and their simulation. The flux model is the following:

$$J_i = \frac{1}{1 + \left(\frac{\bar{D}_{i0}}{\bar{Y}_i p_{i0} Q_0} \right)} \cdot \frac{\bar{D}_{i0} \exp(A_i x_{iF})}{\bar{Y}_i} \cdot \left(\frac{p_{iF} - p_{iP}}{p_{i0}} \right) \quad (1)$$

where J_i is the component flux [kmol/(m²h)], \bar{D}_{i0} is the transport coefficient of component i [kmol/(m²h)]; x_{iF} is the concentration of component i in the feed mixture [mol/mol]; Q_0 is the permeability coefficient [kmol/(m²hbar)]; p is the partial pressure [bar]; γ is the activity coefficient; and A is a fitted constant.

1.2 Process modelling

Structure alternatives were modelled and simulated in the ChemCAD® software with UNIQUAC property method, considering also the vapour-liquid-liquid equilibrium of the ternary system. The objective function of the optimisation of each process variation regarding the number of theoretical plates, concentration of the streams and products, required membrane area, etc. was the total annual cost.

1.3 Process alternatives and simulation results

The 800 kg/h ethanol (2 wt%) – n-butanol (2 wt%) – water (96 wt%) ternary mixture was preheated to 93°C and fed into the first column (C1), where the ternary mixture was separated to a binary ethanol-water (EW) mixture at the top of the column, and the dilute binary mixture of n-butanol-water (BW) at the bottom. This C1 column is the common first step of all alternatives. Two different options are investigated for the separation of the binary EW mixture leaving the top of the C1 column, and two additional options for the binary BW mixture leaving the bottom of the C1 distillation column. The EW mixture near to its azeotropic composition can be separated either through extractive distillation using ethylene glycol (Kiss and Ignat, 2013) as entrainer (C2 and C3) or by hydrophilic pervaporation (PV1) shown in Figures 1 and 2, respectively. The production of pure n-butanol from the bottom product of C1 was realized by heteroazeotropic distillation (C4 and C5) or by a distillation-pervaporation hybrid separation method (C4 and PV2) depicted in Figures 3 and 4. The aim was to produce ethanol and n-butanol with a purity of 99.7 wt%, while water should leave the system with a maximal

organic contamination of 10 ppm. All columns are operated at 1 atm. Mass stream values, number of theoretical stages, feed stages, reflux ratios, membrane area and component concentrations resulted from the optimization are indicated in the figures of each process alternative.

The objective function of finding the optimal alternative was the minimization of the total annual cost (TAC), the sum of the annual capital costs (calculated with a depreciation of 10 years) and the annual operating costs. The operating costs comprise the entrainer cost, and the annual steam, cooling water, and electrical energy expenses. Capital costs incorporate the costs of the columns with bubble cap trays, the reboilers and condensers, the heat exchangers for cooling or reheating purposes, the permeate cooling unit and the costs of the membrane modules.

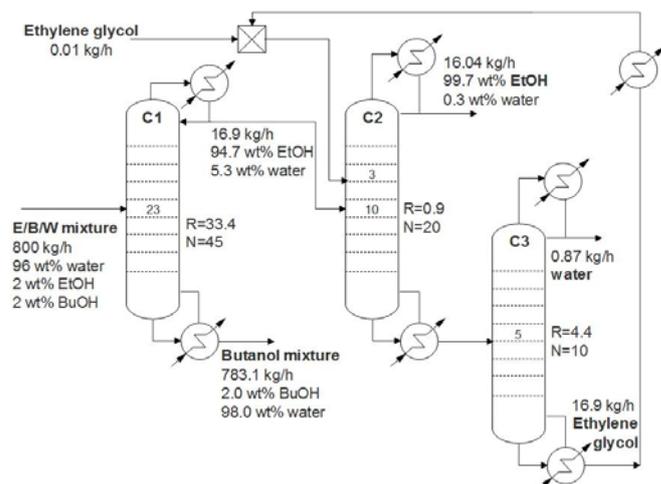


Figure 1: Extractive distillation structure for ethanol production

Figure 1 depicts the extractive distillation option. The top product of C1 is the binary EW mixture with 16 kg/h flow rate and an ethanol concentration of 94.7 wt%. This near azeotropic mixture is led to the 10th stage of C2, while the extractive agent of ethylene glycol is fed to the 3rd stage of the column. The 99.7 wt% ethanol product leaves the top of C2. Ethylene glycol is regenerated in C3 from the bottom of which it is recycled to the system. Only a negligible amount of the entrainer must be added due to small inevitable ethylene glycol loss.

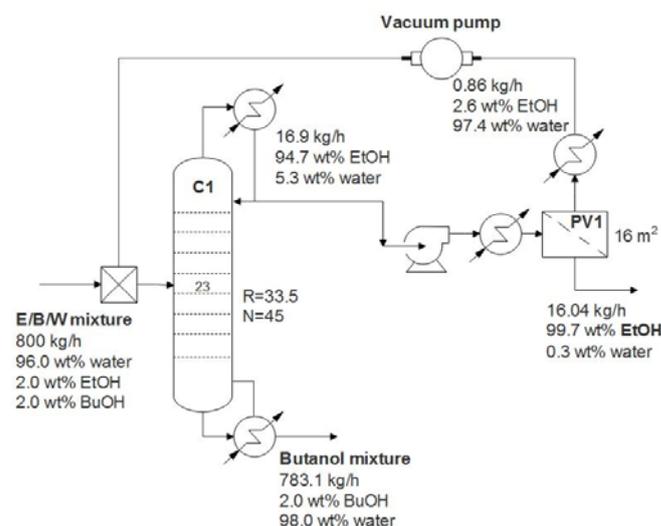


Figure 2: Production of ethanol with hydrophilic pervaporation

The pervaporation alternative is shown in Figure 2. The top product of C1, with the same composition as discussed above is, separated with multiple hydrophilic pervaporation modules connected in series (only one module is depicted in the figure). As the retentate stream cools down due to the heat demand of water

evaporation in the membrane, it has to be reheated prior to entering the next module. PV has higher driving force at elevated temperatures; therefore the retentate stream leaving a module is always heated to 90°C before it is fed to next one. Feed and permeate pressures of the membrane units were adjusted according to the experimental conditions to 4 bar and 0.0027 bar, respectively. Permeate streams are collected and condensed with a cooler. The stream contains 2.6 wt% EtOH, therefore it is recycled to the C1 column. A membrane area of 16 m² was sufficient to concentrate the retentate ethanol product to 99.7 wt%.

The separation of the bottom product of C1 is more energy and cost intensive, due to its high, ~784 kg/h mass flow rate and the 2 wt% BuOH content. The first alternative to produce pure n-butanol from this stream is heteroazeotropic distillation shown in Figure 3. The dilute butanol mixture is introduced to the C4 column with 15 theoretical stages. The top product with 30 wt% BuOH content enters a decanter, where the stream splits into a butanol rich top phase, and an aqueous bottom phase. The organic phase enters the C5 column, where the bottom product is the 16.04 kg/h n-butanol stream with a purity of 99.7 wt%. The top product of C5 with an azeotropic composition is recycled to a mixer prior to the phase separator. C5 has 6 theoretical stages and its feed stream enters to the 3rd stage.

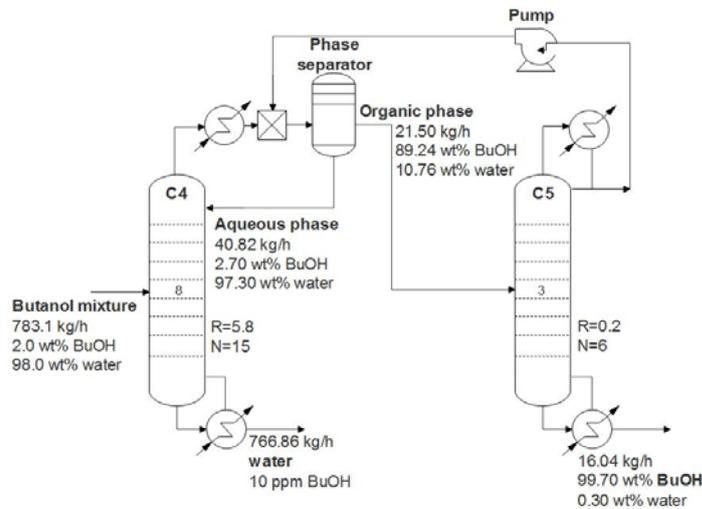


Figure 3: N-butanol production with heteroazeotropic distillation

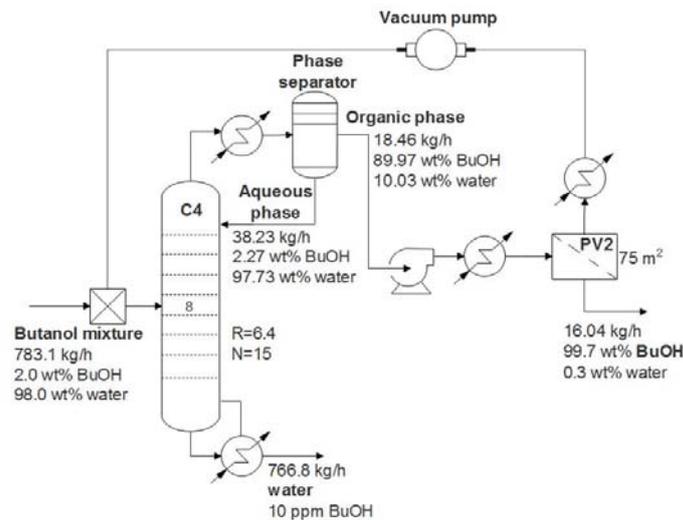


Figure 4: N-butanol production with hybrid distillation-PV system

Figure 4 illustrates the hybrid option coupling the C4 column with a hydrophilic PV unit. Here, the organic phase leaving the phase separator is introduced to the PV unit following a preheating to 90°C. The total membrane area is 75 m², where the area of a single unit is limited by the temperature drop. The area of one

unit was optimized, so that the temperature of retentate stream leaving a unit exceeds 55°C. The retentate of the last membrane module is the n-butanol product. Permeate streams are collected, condensed, and recycled the same way as described above. Feed and permeate pressures were also adjusted to 4 bar and 0.0027 bar, respectively. Purified water leaves at the bottom of C4.

2. Cost estimation results

Investment costs of the columns and their internals (bubble cap tray), heat exchangers and pumps were calculated according to the cost correlations of Douglas (1988), applying 1604,6 as the Marshall & Swift Cost Index of April 2017. Investment costs per unit of membrane area for the PV modules was 1000 \$/m², based on personal communication with the manufacturer. The depreciation of the membranes was taken into account with their replacement every 2.5 years. For the rest of the operational units a 10 year depreciation time was included in the cost calculations.

Operating costs were estimated based on 8000 operation hours per year. Energy requirements of the columns and the heat exchangers are shown in Table 2. TAC results of the cost calculations are depicted in Figure 5.

Table 2: Energy demands of the distillation columns and the PV heat exchangers

	C1	C2	C3	C4	C5	PV1	PV2
Reboiler duty (MJ/h)	538.2	14.3	12.5	125.1	12.9		
Condenser duty (MJ/h)	534.7	25.7	10.5	102.1	8.3		
Heat duty of membrane heat exchangers (MJ/h)						2.2	6.2
Heat duty of permeate cooler (MJ/h)						2.3	5.4

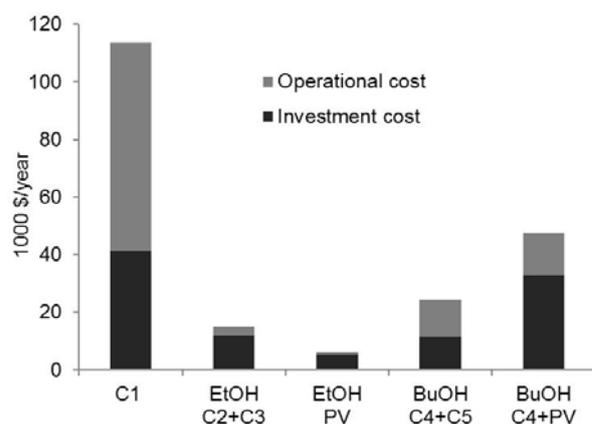


Figure 5: Total annual costs of the process alternatives

It can be seen in Figure 5, that the TAC of the C1 column is the highest of the whole process with 113,691 \$/y. In the case of ethanol production the hybrid system has lower operational and investment costs than the extractive distillation alternative, due to the fact that the latter includes two distillation columns while the PV system requires only a relatively small membrane area. The TAC of the hybrid system is 41.5 % lower than that of the extractive option, with 72.8 % lower operational cost. However, for the n-butanol production options the TAC of the hybrid structure is almost twice as much as the TAC of the heteroazeotropic distillation caused by the combined costs of the membrane modules and the heat exchangers between the modules. The operational costs of the two alternatives are comparable but the annual investment cost of the C4+C5 system is 30 % of that of the hybrid system, due to the large membrane area required to n-butanol production in the 99.7 wt% purity. The reason for the large membrane area in the case of n-butanol separation can be found in the membrane characteristics. The membrane exhibits rather low water fluxes at low feed water concentrations as the driving force of its permeation decreases (Valentinyi et al., 2013). It means, that reaching a product purity of 99.7 wt% n-butanol demands an increased membrane area.

3. Conclusions

In the present study, process alternatives for the separation of a diluted ethanol – n-butanol – water mixture are proposed and simulated in ChemCAD® flowsheeting software. The different structures are optimized and evaluated based on their total annual cost. Configurations of extractive, heteroazeotropic distillation and hybrid

distillation-pervaporation systems for ethanol and n-butanol production were optimized according to the economical evaluation based on the total annual costs. It can be concluded that the hybrid system should be applied for ethanol production, while n-butanol can be produced more economically with heteroazeotropic distillation in the case of such a highly diluted feed stream of bioalcohols. It should be noted, that further simulations and optimizations are required to investigate the effects of heat integration with a potential for cost reduction.

Acknowledgments

The authors are grateful for the financial support to the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4- 15-2016- 00004 project, aimed to promote the cooperation between higher education and industry. This research was also supported by OTKA 112699, and the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

References

- Baker, R.W., 2004. Pervaporation, in: *Membrane Technology and Applications*. John Wiley & Sons, Ltd, pp. 355–392.
- Douglas, J., 1988. *Conceptual Design of Chemical Processes*, McGraw-Hill Chemical Engineering Series. McGraw-Hill Science: New York.
- Heintz, A., Stephan, W., 1994. A generalized solution—diffusion model of the pervaporation process through composite membranes Part I. Prediction of mixture solubilities in the dense active layer using the UNIQUAC model. *Journal of Membrane Science* 89, 143–151.
- Hieu, N.H., Duy, N.N.P., 2017. Fabrication, characterization, and pervaporation performance of graphene/poly(vinyl alcohol) nanocomposite membranes for ethanol dehydration. *Chemical Engineering Transactions* 56, 1693–1698.
- Kiss, A.A., Ignat, R.M., 2013. Optimal Economic Design of an Extractive Distillation Process for Bioethanol Dehydration. *Energy Technology* 1, 166–170.
- Koczka, K., Manczinger, J., Mizsey, P., Fonyo, Z., 2007. Novel hybrid separation processes based on pervaporation for THF recovery. *Chemical Engineering and Processing: Process Intensification* 46, 239–246.
- Kujawska, A., Kujawski, J., Bryjak, M., Kujawski, W., 2015. ABE fermentation products recovery methods—A review. *Renewable and Sustainable Energy Reviews* 48, 648–661.
- Nagy, E., Mizsey, P., Hancsók, J., Boldryev, S., Varbanov, P., 2015. Analysis of energy saving by combination of distillation and pervaporation for biofuel production. *Chem. Eng. Process. Process Intensif.* 98, 86–94.
- Ndaba, B., Chiyanzu, I., Marx, S., 2015. n-Butanol derived from biochemical and chemical routes: A review. *Biotechnology Reports* 8, 1–9.
- Rom, A., Miltner, A., Wukovits, W., Friedl, A., 2016. Energy saving potential of hybrid membrane and distillation process in butanol purification: Experiments, modelling and simulation. *Chemical Engineering and Processing: Process Intensification* 104, 201–211.
- Salemme, L., Olivieri, G., Raganati, F., Salatino, P., Marzocchella, A., 2016. Analysis of the energy efficiency of some butanol recovery processes. *Chemical Engineering Transactions* 49, 109–114.
- Timoshenko A.V., Anokhina E.A., Morgunov A.V., Rudakov D.G., 2015, Application of the partially thermally coupled distillation flowsheets for the extractive distillation of ternary azeotropic mixtures, *Chemical Engineering Research & Design*, 104, 139-155.
- Toth, A.J., Haaz, E., Nagy, T., Tari, R., Tarjani, A.J., Fozer, D., Szanyi, A., Koczka, K.-A., Racz, L., Ugro, G., Mizsey, P., 2017. Evaluation of the accuracy of modelling the separation of highly non-ideal mixtures: extractive heterogeneous-azeotropic distillation, in: *Computer Aided Chemical Engineering*. Elsevier, pp. 241–246.
- Valentinyi, N., Mizsey, P., 2012. Comparison of Pervaporation Models in Flowsheeting Environment. *Procedia Engineering* 44, 2098–2101.
- Valentinyi, N., Cséfalvay, E., Mizsey, P., 2013. Modelling of pervaporation: Parameter estimation and model development. *Chemical Engineering Research and Design* 91, 174–183.
- Wei, P., Cheng, L.-H., Zhang, L., Xu, X.-H., Chen, H., Gao, C., 2014. A review of membrane technology for bioethanol production. *Renewable and Sustainable Energy Reviews* 30, 388–400.
- You, X., Rodriguez-Donis, I., Gerbaud, V., 2015. Improved Design and Efficiency of the Extractive Distillation Process for Acetone–Methanol with Water. *Industrial & Engineering Chemistry Research* 54, 491–501.