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A User-Defined Pervaporation Unit Operation in AspenPlus© on the Basis of Experimental Results from Three Different Organophilic Membranes

Antonia Rom*, Diana Esteve Gimeno, Anton Friedl

Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austriaantonia.rom@tuwien.ac.at

Simulation is an important tool to balance, compare and investigate processes. Due to new investigations and the variety of processes not every process step is available as unit operation in simulation software. Absence of unit operations is evaded with help of simplifications, assumptions and usage of similar process steps. At best unit operations should calculate in and outlet streams based on sophisticated models according to the theory in literature. Therefor the aim of this work was to generate a pervaporation unit operation on the basis of experimental results working on AspenPlus© platform.
Per-vaporation as a thermal membrane process step is gaining more and more interest from researchers in the last decades. The possibility to separate close boiling point, heat sensitive and azeotropic mixtures opens a big field for industrial application (Shao et al., 2007). Additionally energy savings are possible when effective process combinations are implemented (Vane, 2005). The membrane, as the heart of the pervaporation process, is currently the limiting factor. Despite high membrane costs, membrane fouling is also one big disadvantage. Therefore investigation of different membranes is also in focus of research works.
The potential energy savings offered when using pervaporation can be determined at its best, when the process step is investigated in simulation software. The aim of this work should enable this possibility to generate a pervaporation unit operation on the basis of experimental results. Therefore three different organophilic membranes were investigated on a laboratory setup. Influences like feed temperature, feed concentration, Reynolds number in the module and applied vacuum pressure were varied.
The gained results offer a data set to regress membrane and component specific permeances depending on the investigated parameters. The same experiments with all three membranes were carried out in the laboratory. A sequence from the trials is used to regress permeance models for each membrane and component. These regression models were implemented in the user defined unit operation. In the unit operation mass transport and simple heat balance including evaporation are considered.
As a result three unit operations with different membranes are available for simulation. Validation of the experimental results shows very good accordance with all three investigated membranes. The aim of a first estimation of the pervaporation step in the simulation software is reached. The results of this work enable the connection of the pervaporation unit operation in global process sheets and hybrid combinations.

1. Introduction

In pervaporation a liquid feed is in contact with a dense polymeric membrane or a porous zeolith membrane. By applying a vacuum on the permeate side liquid is diffusing in and transported through the membrane and evaporated on the permeate side. Depending on the use of the pervaporation step the membrane is either hydrophob or organophil for dehydration or volatile organic compounds removal respectively. In this work organophilic membranes were chosen, so the organic compound is enriched on the permeate side. The preferred transport from the feed to the permeate side of one component is the result of the selective membrane and the vapour liquid equilibrium of the components (Vane, 2005).

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In the work of Wijmans and Baker (1995) the solution-diffusion model is used to describe transport mechanism in pervaporation. The model describes the molar component flow N_i in [kmol/m²h] as the product of the permeance P_i, which is not mandatory constant, and the driving force as chemical potential gradient between feed and permeate side. Transformation to partial pressures leads to Eq.(1), where $p_{i,f}$ is the partial pressure of component i in the feed and $P_{i,p}$ in the permeate side.

$$N_i = P_i(p_{i,f} - p_{i,perm}) \quad (1)$$

The permeance as membrane specific coefficient in [kmol/m²h] includes membrane specifications as membrane thickness, diffusivity and sorption coefficient. Since these parameters are not always available for the investigated membranes, permeance is often the preferred used term.
Regarding simulation of PV a few modelling approaches for the transport mechanism in pervaporation are investigated in literature (Marriot et al., 2001). In the work of Schiffmann and Repke (2012) a stepwise development from a shortcut, over discrete to a rigorous model is presented. The developed model can be integrated in AspenPlus© and offers the opportunity to connect and balance the pervaporation step to other processes. In the work of Veroef et al. (2008) the pervaporation step is calculated in visual basic and connected with AspenPlus©. However the system cannot be fully described yet. The challenge to accept pervaporation in industry is connected to the process understanding and process modelling. Depending on the application different components as well as the membrane itself has to be investigated and therefore further investigation in modelling has to be done.

2. Material and Methods

With the help of a design of experiment the influence of feed temperature, feed concentration, flow rate and vacuum pressure were investigated. A trial of twenty experiments was defined. In Table 1 set process parameters are listed. The experiments were carried out on a lab scale pervaporation setup. Further detailed informations can be found in the earlier work of Rom et al. (2013).
Model solutions were prepared with 96 % Merck butanol and distilled water. Three different PDMS [Polydimethylsiloxan] membranes are investigated and with every membrane the defined trial of 20 experiments was carried out.
Transmembrane component flux J_i in [kg/m²h] was calculated and is described as the mass flow of component i as m_i passing the membrane divided by the membrane area A and the experimental time t according to Eq(2)

$$J_i = \frac{m_i}{At} \quad (2)$$

The selectivity of the process is described as the ratio of the separation facto of the single components, as ist is described in Eq(3)

$$\alpha_{ij} = \frac{w_{i,p} w_{j,f}}{w_{i,p} w_{i,f}} \quad (3)$$

Combining Eq(1) and Eq(2) and transferring the transmembrane flux to a molar basis with M_i as molar mass gives the equation for the permeance of one component according to Eq(4)

$$P_i = \frac{J_i / M_i}{(p_{i,f} - p_{i,perm})} \quad (4)$$

A set of 15 permeances, calculated from Eq(4) as a function of feed temperature T, feed concentration c, flow rate V and vacuum pressure p were regressed with multiple linear regression in the mathematical software programme R. The function used considers no interaction between investigated variables according to Eq.(5) using linear relations

$$P = A * c + B * p + C * T + D * \dot{V} + E \quad (5)$$

Table 1: process parameters during pervaporation experiments

experiment	temperature (°C)	pressure (mbar)	initial butanol concentration (w%)	flow rate (L/h)
1	55	4	0.5	200
2	35	7	1	150
3	25	10	0.5	200
4	55	10	0.5	200
5	25	4	1.5	200
6	25	10	1.5	200
7	25	4	1.5	100
8	35	7	1	150
9	25	4	0.5	200
10	55	4	1.5	200
11	55	10	1.5	200
12	25	10	1.5	100
13	55	10	1.5	100
14	35	7	1	150
15	55	10	0.5	100
16	55	4	0.5	100
17	35	7	1	150
18	55	4	1.5	100
19	25	4	0.5	100
20	25	10	0.5	100

with A, B, C, D and E as regressed coefficients for each component and each investigated membrane. Since calculated permeances show no interaction between influences in the investigated range a univariate approach is tested. If special process conditions require multivariate data regression a more complex model has to be applied (Drljo et al., 2012).

The regressed functions for the permeance of components i,j were implemented in the user-defined unit operation for pervaporation. The unit operation is based on simple mass transport and heat balances. Mass transport mechanism is calculated according to the solution diffusion model in Eq(1). The driving force as partial pressure difference is calculated on the basis of physical property models in AspenPlus©. Only the regressed function for the permeance describes the membrane and the diffusivity of the investigated components. As simplification heat transfer is calculated only considering heat of vaporization (Karlsson and Trägårdh, 1996). Since three different membranes were investigated three different unit-operations were implemented in the simulation software.

The importance of permeance, as intrinsic membrane coefficient, as well as molar based selectivities, is described in the work of Baker et al. (2010). Despite the fact that in this work the model is based on the membrane permeance, further investigations of the membranes are not discussed. Since in simulation flow sheets separation rate and stream properties are the focus, results will be discussed in terms of J_i and α_{ji} according to Eq(2) and Eq(3).

3. Results

First the validation of the regressed model is discussed. All six models show good significance. With this statement further simulation with all three membranes are performed.

3.1 Validation of the model

As it was described in section 1 and 2 the regressed model based on fifteen experiments should predict and calculate validation points. A common way to show the reliability of the regressed model is to compare experimental validation points with the calculated results of the model. To validate the significance of the model a test validation set of five additional experiments was used. Figure 1 compares the calculated permeances by the model (P_{MOD}) with the experimental investigated permeances (Pexp) butanol and

water for each membrane. As it can be seen the points lie close to the y=x line, which means zero deviation. Squared correlation coefficient for the butanol permeance models lie between R^2=0.743 and R^2=0.939.

The water permeance models show similar significance, with R^2 between 0.75 and 0.948.Validation of the models for PDMS membrane 1 with both R^2 over 0.9 shows the best significance, which yields in very good simulation results during latter calculation in AspenPlus©. The results show, that further improvement in the model and a wider value range should be aspired. However all six models show good significance based on a minimal amount of 15 experiments.

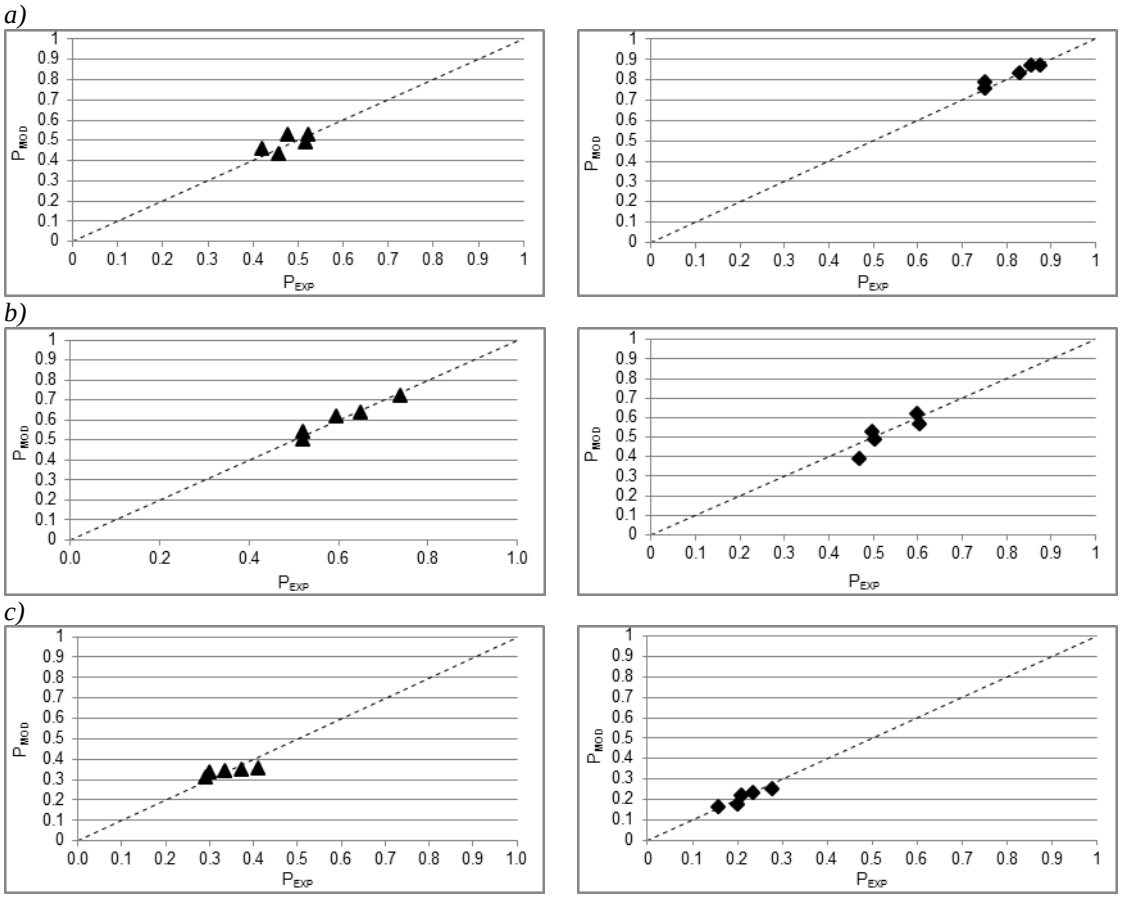

Figure 2: Predicted permeances by the regression model P_{MOD}, versus permeance calculated from experiments P_{EXP}: a) PDMS 1, b) PDMS 2, c) PDMS 3; butanol (triangle) and water (rhombus)

3.2 Flux and selectivity

Implementation of the user-defined unit operation in the simulation software offers the opportunity to compare membrane process parameters like transmembrane component flux and selectivity. In Figure 2 comparison of the experimental calculated values as well as the simulated values are plotted. As it can be seen all three unit operations simulate the membrane separation step with good significance, keeping in mind the aim as a first estimation in simulation.

Special distribution of the validation set can be recognized in Figure 2. Since the DoE allows only a variation of special parameters, for the validation set experiments with corner points like high/ low concentration or high/low pressure were chosen. In the simulation run these corner points can be simulated and compared with the results in the experiments.

According to the significance of the model membrane 3 with the lowest R^2 values shows highest deviations at high concentration and high temperature. All three membranes show higher deviations as the transmembrane butanol flux increases. This can be the reason due to measurement problems at higher transmembrane fluxes in the laboratory. A bigger modelling and validation set raises the significance of the regressed models. Additionally the regression model with only linear considerations might not fit perfectly. Nonlinear interactions at high temperature and high concentration could be considered in multivariate data

analysis. Another reason might be based in the developed unit-operation itself. Since the used unit operation is based on a discrete cross-flow model, further development to a rigorous state might be preferable. All three membranes show the same influence on transmembrane butanol flux as it increases with higher butanol concentration in feed as well as higher temperature. Highest selectivity was observed using PDMS 3 with the lowest transmembrane flux.

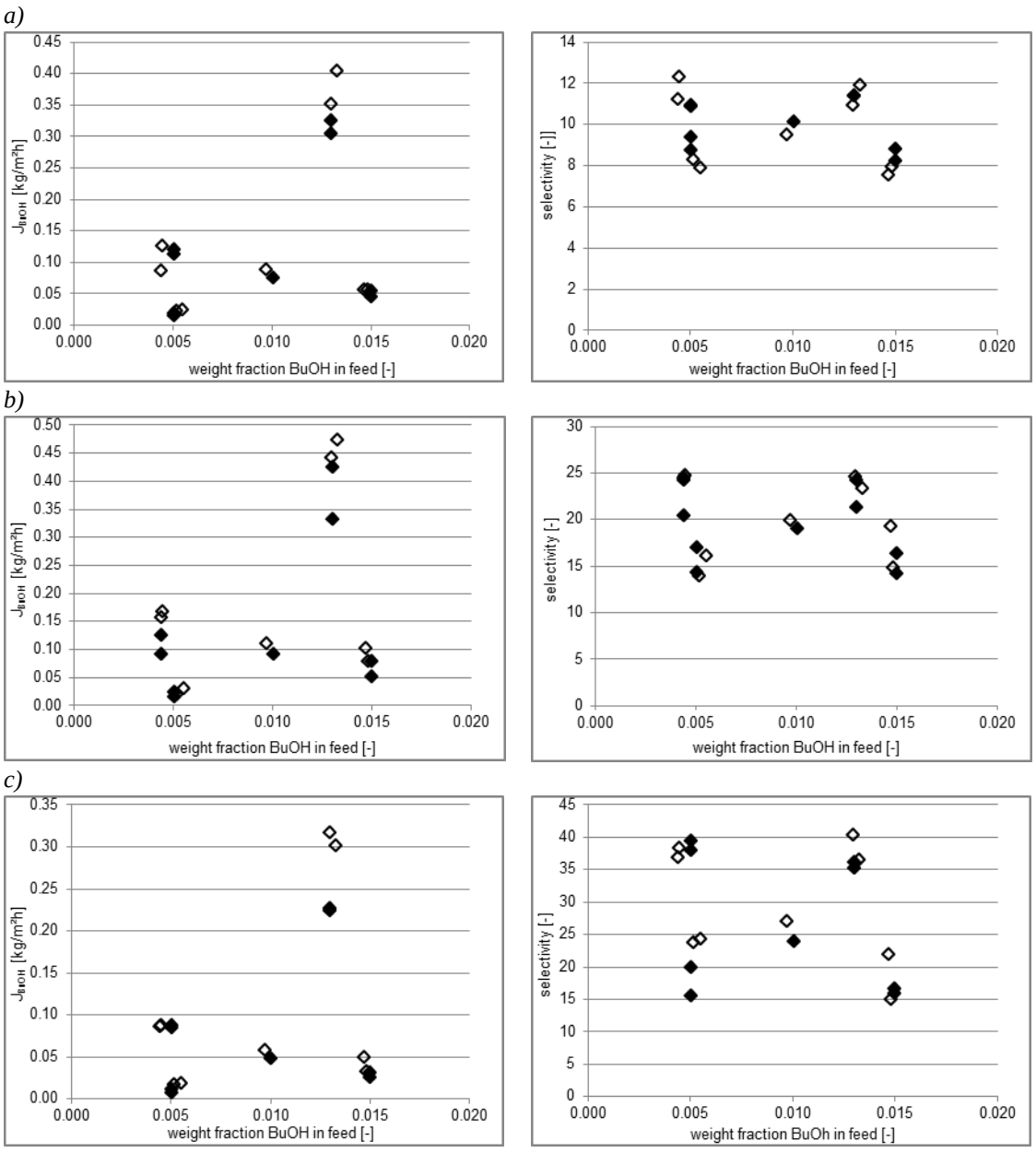

Figure 2: Transmembrane butanol flux on the right and selectivity on the left a) PDMS 1, b) PDMS 2, c) PDMS 3; full rhombus: simulated data with process settings of the validation set, white rhombus: calculated data from experiments of the validation set

4. Conclusion

A user-defined unit operation on AspenPlus© platform was investigated based on experimental results. Hybrid design of pervaporation and distillation offer great potential in energy savings and therefore simulation of this separation step is desirable.

With the help of design of experiment minimal amount of process parameters bring great output. By calculating the permeance at experimental conditions, a model for each component and each membrane was regressed. The applied user-defined unit operation is based on the sophisticated solution diffusion model for pervaporation processes from the work of Wijmans and Baker (1995). Validation of the regressed models shows good reliance and significance of the models is verified. Implementation of the user-defined unit operation in the simulation software and calculating membrane parameters like transmembrane flux and selectivity offer the opportunity to vary streams and connect the pervaporation step to other processes like distillation. Using simple mass and energy balances resulted in unit-operations generating acceptable data for the first approach. With a simple multiple linear regression different membranes can be simulated in the pervaporation step with good significance. In the next steps the discrete simulation model needs further development to a rigorous model. Also greater experimental data sets can offer better simulation results.

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