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# Comparison of pervaporation models with simulation of hybrid separation processes

*Nóra* Valentínyi / *Péter* Mizsey

RESEARCH ARTICLE

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***Abstract***

*The industrial application of pervaporation as a membrane separation technology is increasing caused by the numerous advantages of this method. However, to complete engineering design, like in the cases of distillation, azeotropic distillation and absorption, reliable and adequate modelling of the process in flowsheeting environment is indispensable. A proper model is especially needed if the more complicated but more economical and environmentally sound hybrid separation methods are designed or investigated.*

*In this study two pervaporation models, the solution-diffusion model of Rautenbach [1] and its developed form [2], are compared and evaluated with computer simulation on the dehydration processes of isobutanol-water and ethanol-water mixtures. Simulations of a hybrid separation method containing pervaporation for the separation of these mixtures are performed, thus proving the importance of using a proper pervaporation model regarding the discrepancies caused by the application of a false model.*

***Keywords***

*Membrane · Pervaporation · Simulation · Mathematical modelling*

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**Nóra Valentínyi**
Department of Chemical and Environmental Process Engineering,
Budapest University of Technology and Economics,
Műegyetem rkp. 3., H-1111 Budapest, Hungary
e-mail: valentinyinora@gmail.com

**Péter Mizsey**
Department of Chemical and Environmental Process Engineering,
Budapest University of Technology and Economics,
Műegyetem rkp. 3., H-1111 Budapest, Hungary
Research Institute of Technical Chemical and Process Engineering,
University of Pannonia, Egyetem u. 2., H-8200 Veszprém, Hungary

## 1 Introduction

Pervaporation is a still underestimated but continually developing membrane technique suitable for the separation of special liquid mixtures [1,3-5]. Separation takes place by the following steps: the liquid feed mixture contacts one side of the membrane, a phase change takes place in the – most frequently composite – material of the membrane then vapour is removed on the other side of the membrane, that is called the permeate side. The process is not restricted by thermodynamic equilibrium but rather by the affinity to the membrane material.

Three main application areas of the process are:

- removal of water from organic solutions (dehydration), mostly applied for alcohol-water mixtures,
- removal of organics (for e.g. VOCs-volatile organic compounds) from water,
- separation of organic mixtures [6-10].

Pervaporation is most efficiently employed if liquid mixtures form an azeotrope; in case of separating close boiling components or if mixtures contain thermally unstable components [11].

Though the process was already mentioned in the early 20th century, first major research efforts were made by Binning et al. in the 1950s at the American Oil Company in Texas, mostly for the separation of organic mixtures in the petrochemical industry [12]. However, the first commercial-scale pervaporation plant was built for the dehydration of ethanol at a pulp and paper mill in Germany [13].

In the course of this work also the dehydration of certain alcohol solutions are studied in detail. The main advantages of dehydration by pervaporation are that the concentrated alcohol is free from entrainer traces thus producing a more valuable product. The process is flexible and adjustable to changing conditions like changes in the feed mixture composition regarding industrial application. According to Drioli and Giorno [14], purification and product recovery processes represent more than 40% of the energy need of chemical production industry. Pervaporation ensures high selectivity with simple operating procedures and scale-up possibilities in a quite compact and adjustable modular design and with low energy consumption resulting in reduced operational costs [4,13,15]. These properties make pervaporation an effective and environmental conscious alternative to conventional separation methods.

Regarding its relatively high installation costs and short depreciation time of the membrane itself pervaporation alone cannot replace the classical separation methods on an industrial scale so far. However, membrane units coupled with other separation methods (distillation, liquid-liquid extraction, adsorption, etc.) form the so-called hybrid separation processes that are feasible and cost-effective solutions [16,17]. Distillation is still the most popular separation method for a wide range of industrial problems (e.g. crude oil processing, process wastewater treatment, etc.); however it has a great energy demand as a huge drawback in an environmental point of view [19-20]. In case of alcohol dehydration, pervaporation is more efficient in that range of feed concentration where distillation is very inefficient, while at higher feed water concentrations distillation is the more reasonable choice. Therefore in certain cases the combination of them in a hybrid process can be the most economical option [17,21]. For adequate design and operation, proper modelling of the pervaporation process is inevitable. Since the exact separation process is still not completely understood the models of mass transfer through the membranes are diverse, thus a universal flowsheeting module does not exist for them yet. These professional flowsheeting software packages, for e.g. ASPEN Plus or ChemCAD, however, provide the tool of user added subroutines or modules. By adding a pervaporation model in these software environments the design and optimization of the individual membrane module and a complex hybrid system is attainable.

In case of separating azeotropic mixtures with such hybrid systems pervaporation can either be applied as the initial step combined with other processes to reach the desired product concentration, or as the final polishing unit following a conventional separation method. As Koczka et al. revealed, regarding a combination with a distillation column the latter is a more cost-effective alternative [7,17,22].

With a model developed in a previous work of the authors [2], based on the semi-empirical solution-diffusion model of Rautenbach, dehydration procedure of alcohols was defined more precisely in a wider concentration range. The aim of this work is the verification of this model in ChemCAD software environment and the comparison of the developed model with the one of Rautenbach [1].

## 2 Models of pervaporation

The component transport through a membrane can be based on the mechanisms of solution-diffusion, adsorption-diffusion, or size-sieving filtration [11]. Among the numerous and diverse pervaporation models described in the literature, the most popular ones are the pore-flow [23-25], the resistance-in-series [26,27], Maxwell-Stefan theory-based [28], and the most widely used solution-diffusion model [29-34]. According to the latter, the mechanism of pervaporation is defined by the following steps:

- diffusion of the key component to the membrane surface from the feed mixture,
- sorption onto the membrane material,
- desorption at the permeate side of the membrane in vapour phase [3].

The driving force of the component transport is difficult to define since the mechanism of the pervaporation is quite complex. The chemical potential difference can be considered as basis of the derivation of the so called solution-diffusion model. Since in the most typical case of pervaporation, pressure difference by vacuum on the permeate side is applied, the derivation results in fugacity difference. In the case of low pressure values, partial pressure differences can be applied instead of fugacity differences [2,35,36].

The pervading membrane type for pervaporation is usually composite membrane beside the more expensive ceramic ones. Composite membranes in most cases consist of two polymer layers, a thin selective layer and a more robust porous supportive layer. The type of the polymer depends on the nature of the preferentially permeating component that is either water or the organic component. For alcohol dehydration with pervaporation a hydrophilic, usually PVA/PAN (Polyvinylalcohol/Polyacrylonitrile) membrane is applied widely, which favours the permeation of water. The proposed semi empirical solution-diffusion model is suitable for the description of transport through a composite membrane. In this model the pressure in the membrane material is considered constant with the pressure gradient of the porous layer assumed to be negligible [1].

In our previous papers we presented a developed pervaporation model [2,35] based on the following one of Rautenbach (Model I) [1]:

$$J_i = \frac{1}{1+\left(\dfrac{\overline{D_i}}{Q_0 p_{i0}\overline{\gamma_i}}\right)}\frac{\overline{Di}}{\overline{\gamma_i}}\left(\frac{p_{i1}-p_{i2}}{p_{i0}}\right) \qquad i=(1,\ldots\mathrm{k}) \tag{1}$$

where $\overline{D_i}$ stands for the transport coefficient of component *i*; $Q_0$ is the permeability coefficient, $p_{i0}$ is the vapour pressure of component *i* at the feed temperature; $p_{i1}$ and $p_{i2}$ are the partial pressure of component *i* in the feed and in the permeate respectively, $\overline{\gamma_i}$ is the average activity coefficient of component *i*.

Transport coefficient has an Arrhenius-type temperature dependence:

$$\overline{D_i} = \overline{D_i^*}\exp\left[\frac{E_i}{R}\left(\frac{1}{T^*}-\frac{1}{T}\right)\right] \tag{2}$$

This model applies the transport coefficient ($\overline{D_i}$) instead of the diffusion coefficient because of its regarded negligible concentration dependence [1,18]. However, our experiments pointed out that in higher feed concentrations of the permeating compound, this model shows anomalies [37]. Therefore we improved the model by adding an exponential factor to the transport coefficient containing the concentration of the permeating component, representing that it cannot be considered as constant after all (Model II) [2]:

$$J_i = \frac{1}{1+\left\{\dfrac{\left[\overline{D}_i \cdot \exp\left(\mathrm{B}\cdot x_{i1}\right)\right]}{Q_0 \cdot p_{i0} \cdot \overline{\gamma}_i}\right\}} \cdot \frac{\left[\overline{D}_i \cdot \exp\left(\mathrm{B}\cdot x_{i1}\right)\right]}{\overline{\gamma}_i} \cdot \left(\frac{p_{i1}-p_{i2}}{p_{i0}}\right) \quad (3)$$

If the pressure drop in the porous support layer is negligible, the permeability coefficient can be regarded as infinitesimally high, $Q_0 \cong \infty$. In this case the value of its dimensionless group equals to 1 thus only the non-porous active layer has a resistance to the component transport [38].

The semi-empirical nature of these models means that laboratory experiments with the given membrane material and mixture cannot be omitted. With the help of the results of these experiments model parameters are fitted with a mathematical software, in our case the Statistica program environment. Our paper proved a better fitting of the improved model to the experimental data, of which an example can be seen in Fig. 1 for ethanol dehydration [2].

As mentioned before, simulation of the pervaporation process is sorely needed for design and optimization in the case of process design. Many authors have published numerous ways of simulating the component transport so far [39-41]. Our improved semi-empirical model reduces the modelling and computational effort compared to a detailed rigorous models, while still obtaining accurate results regarding the investigated systems for a wider concentration range, therefore for an extended operational window. During operational anomalies or the start-up and shutdown of the industrial system this wider operational range can be important. In our work a user added pervaporation subroutine is written and applied in ChemCAD process simulation software, with the help of which calculations can be made with both the original model of Rautenbach (Model I) and our improved solution-diffusion model (Model II).

## 3 Model verification

With the user added membrane module in ChemCAD software environment the verification of our developed exponential model becomes possible. A model verification step is carried out with the input of model parameters of Q, Di, Ei and B, previously fitted to experimental data, and given operating conditions (pressure, membrane area, section number). The model also distinguishes adiabatic and isothermal separation conditions. Results of laboratory experiments with isobutanol-water [42] and ethanol-water mixtures are implied to the software. According to the expectations, verification shows that the basic model of Rautenbach underestimates the experimental data in case of both mixtures at higher concentration ranges in contrast to our model, which reproduces the experimental results well (Fig. 2).

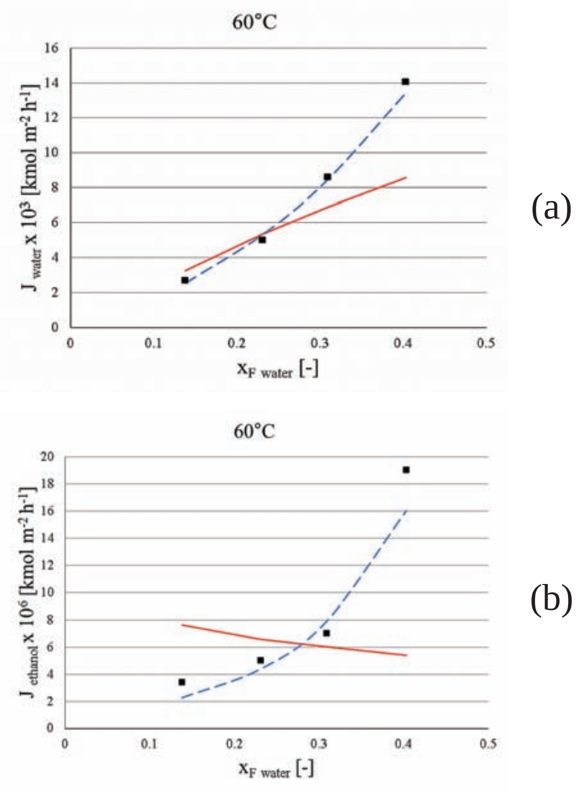

**Fig. 1.** Measured (■) partial fluxes of water (a) and ethanol (b) with PERVAP 2210 (lightly cross-linked PVA-PAN) membrane compared to fitted curves of the Rautenbach model (Model I) (-) and the improved exponential model (Model II) (--)

## 4 Simulation of a hybrid system

Due to programming the above mentioned user added subroutine module into ChemCAD software environment, simulation of industrial processes is viable. Hybrid separation systems for alcohol dewatering are simulated to discover the differences between the two pervaporation models. The system consists of a distillation column and several subsequent pervaporation units. The aim of the processes is to produce isobutanol and ethanol with a purity of min. 99.7 wt%.

With the application of hybrid systems azeotropic mixtures can be separated with fewer trays in the distillation column and without adding an extra entrainer component (which should be removed later), with lower overall energy demand [17]. A pervaporation unit can be inserted into such hybrid system in three ways:

- prior to the distillation column (PV+D),
- in between distillation columns (D+PV+D), or
- processing either the bottom or the top product of the column to reach the desired product purity (D+PV).

Koczka [38] pointed out that the optimal arrangement for alcohol dehydration purposes to obtain a 99.7 wt% alcohol concentration is the D+PV structure, a distillation column followed by a membrane unit. Therefore in our work we apply this coupling arrangement where the azeotropic mixture produced in the distillate of the column is further concentrated by several pervaporation units connected in series.

Since the heat requirement of evaporation is assured by the sensible heat of the feed liquid, it cools down during the pervaporation process. To ensure high flux and effective separation, operation temperatures should be as high as possible bound by the long term temperature durability of the membrane; thus only a limited temperature drop is allowed regarding a single membrane unit. Retentate stream is reheated after each pervaporation unit by heat exchangers [21]. The applied membrane area per unit should be limited to a size that ensures an acceptable temperature drop. If the temperature decreases below 50°C, the pervaporation process stops.

The hybrid system for isobutanol dehydration is depicted in Figure 3. Operating parameters of the distillation columns for both mixtures are shown in Table 1.

The first step of the simulation procedure was to optimize the distillation column and its operating parameters (number of theoretical plates, reflux ratio, etc.) to produce the azeotropic mixture at the top and a maximum of 0.05 wt% alcohol content of the bottom product. In the case of isobutanol, a phase separator is connected to the top of the column, as isobutanol forms a heteroazeotropic mixture with water. The distillate stream – in case of isobutanol dewatering, the organic rich phase - is reheated in a heat exchanger to 90°C prior to the first membrane unit. Retentate streams of each membrane unit are also the feed streams of the following one, except for the last module where the retentate is the product, the concentrated alcohol. Permeate streams leaving the pervaporation units are collected, mixed, condensed and recycled to the column to remove the alcohol thoroughly. The feed pressure of the membranes are adjusted to 4 bar, while permeate pressure is kept at 0.0027 bar, similarly to the laboratory experiments.

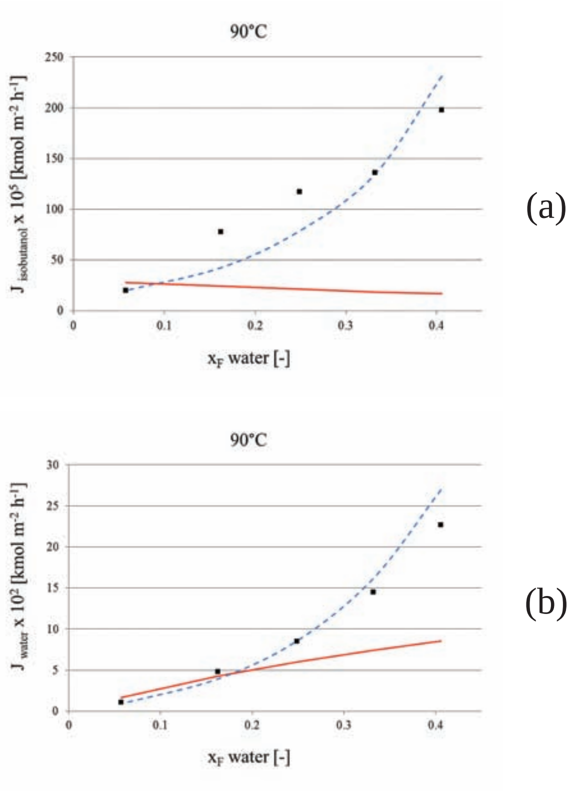

**Fig. 2.** Measured (■) partial fluxes of water (a) and isobutanol (b) with PERVAP 1510 membrane compared to ChemCAD verified models of the Rautenbach model (Model I) (-) and the improved exponential model (Model II) (--)

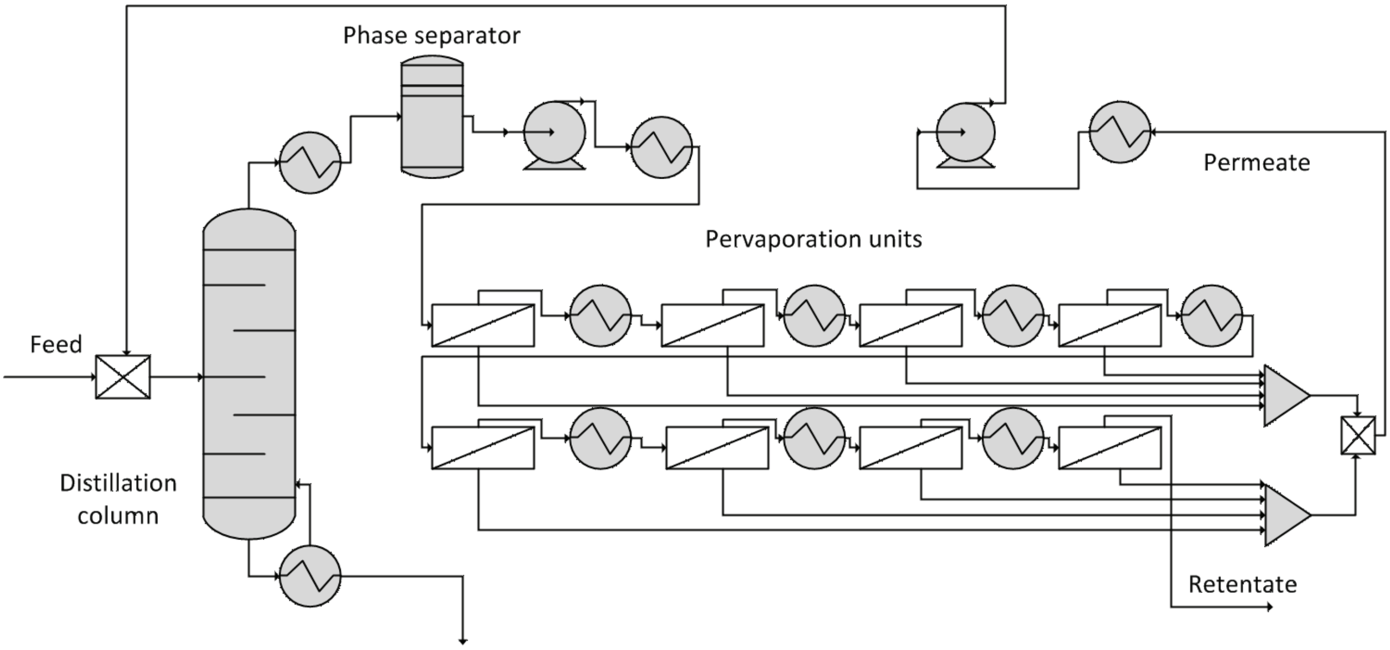

**Fig. 3.** Simulated hybrid separation system for isobutanol-water mixture

**Tab. 1.** Operating parameters of distillation columns

| | isobutanol-water dehydration | ethanol-water dehydration |
|---|---|---|
| Feed flow rate (kg/h) | 800 | 800 |
| Alcohol conc. in the feed (wt%) | 15 | 15 |
| Reflux ratio | 1 | 2 |
| Number of theoretical stages | 11 | 25 |
| Feed tray number | 5 | 20 |
| Alcohol conc. in the distillate (wt%) | 67.6 | 92.7 |
| Distillate temperature | 89.6 | 77.9 |

These hybrid processes clearly integrate green technology aspects, since the bottom product is almost pure water, where only heat contamination should be eliminated. The other product is the retentate which is concentrated alcohol, the desired product. Every other stream is recycled in the system. Steam demand could be further reduced with heat integration between heat exchangers. Thus with such a coupled system operational costs can be lower and environmental fines can be avoided [19].

## 5 Results and Discussion

### 5.1 Simulation Results

Results of the simulations with both models are listed in Tables 2 and 3, where F stands for feed flow rate of the distillation column; $F_{PV}$ is the feed flow rate to the first membrane module, R is the retentate flow rate leaving the last module; P is the recycled permeate flow rate, $Q_{reb}$ represents the heat requirement of the reboiler of the column, $Q_{PV}$ is the sum of the heat demand of the pervaporation units, $w_i$ is the isobutanol content of the retentate leaving the last module, $w_w$ is the water content of the recycled permeate flow in weight percent.

Markedly there are differences between the basic Rautenbach and our developed exponential model in the cases of both alcohol-water mixtures. An increased membrane area is required for generating the same product quality with the improved model. For e.g. ethanol dehydration can be achieved with a total membrane area of 116 m$^2$ (Model I) and 140 m$^2$ (Model II). The calculated stream flow rates and compositions also give slightly different results. It is already proven that in the case of dewatering isobutanol the basic Rautenbach model estimates a lower organic flux than the obtained experimental data [2]. This lower estimated organic flux in ChemCAD results in decreased organic loss of the retentate, therefore higher organic concentration is calculated in the product of the hybrid process. The decreased permeate stream requires less heat for evaporation in case of Model II. As more water permeates through the membrane at the exponential model, recycled permeate flow is also increased resulting in a slightly greater heat demand of the reboiler of the distillation column than in the case of Model I.

Ethanol-water mixture behaves a little different from isobutanol-water mixture. The Rautenbach model underestimates the experimental flux of the latter in the whole investigated feed concentration range, while for ethanol-water it overestimates real partial fluxes until around 0.28 mole fraction of water in the feed (Fig. 1). Over this value, this model underestimates the partial flux while the improved model fits to experimental data better in the whole range. Since ethanol concentration in the feed stream of the first membrane unit is 0.073 mole fraction in the hybrid system, the basic model produces a higher organic flux. In case of the subsequent membrane units this feed concentration decreases further. Therefore Model I requires a smaller overall membrane area than the exponential model to produce the same product quality.

### 5.2 Cost estimation

The conceptual phase of designing an industrial process takes a small part of the project costs, but offers a huge cost reduction opportunity for the whole project [43]. Hybrid systems for the

**Tab. 2.** Parameters of the isobutanol dewatering hybrid process [42]

| | F (kg/h) | $n_{PV}$ | $A_{PV}$ (m$^2$) | $F_{PV}$ (kg/h) | R (kg/h) | P (kg/h) | $Q_{reb}$ (MJ/h) | $Q_{PV}$ (MJ/h) | $w_i$ (wt%) | $w_w$ (wt%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Model I | 817.6 | 8 | 40 | 137.5 | 119.9 | 17.60 | 490.3 | 37.70 | 99.83 | 96.65 |
| Model II | 818.9 | 9 | 45 | 139.0 | 120.1 | 18.93 | 493.2 | 38.60 | 99.68 | 89.92 |
| Deviation (%) | +0.16 | +12.50 | +12.50 | +1.09 | +0.17 | +7.56 | +0.59 | +2.39 | -0.15 | -6.96 |

**Tab. 3.** Parameters of the ethanol dewatering hybrid process

| | F (kg/h) | $n_{PV}$ | $A_{PV}$ (m$^2$) | $F_{PV}$ (kg/h) | R (kg/h) | P (kg/h) | $Q_{reb}$ (MJ/h) | $Q_{PV}$ (MJ/h) | $w_i$ (wt%) | $w_w$ (wt%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Model I | 810.1 | 4 | 116 | 129.8 | 119.7 | 10.8 | 618.1 | 20.81 | 99.95 | 89.1 |
| Model II | 809.7 | 7 | 140 | 129.4 | 119.7 | 9.7 | 633.6 | 21.26 | 99.7 | 96.7 |
| Deviation (%) | -0.05 | +75.00 | +20.69 | -0.31 | - | -10.19 | +2.51 | +2.16 | -0.25 | +8.53 |

dehydration of both alcohol-water mixtures and both models are compared also in an economic point of view. Capital costs of the distillation columns depend on many parameters, for e.g.: number of theoretical plates, the volume of the managed streams, and purity of the distillate. These costs are calculated after the optimization procedure of the column along with the cost of heat exchangers according to the cost correlations of Douglas [44] with current M&S index, while pump costs are estimated with the help of the ChemCAD software. Investment costs of membrane modules are calculated according to Koczka [38], who generated a membrane area-price function based on industrial data. Capital investment of the membrane modules depends on the membrane area required for the desired product purity; the heat exchangers for the reheating of the retentate streams, permeate cooling and the vacuum pump. Calculating the capital costs for permeate cooling, a COP=2 value is applied.

Operational costs are calculated based on industrial utility price data for 8000 operation hours per year. Membranes should be replaced in approximately every 2-5 years based on literature data; therefore 2.5 years are taken as membrane depreciation time in this work. These depreciation costs, as well as a 10 year depreciation time for the rest of the operational units, are also included in the economic evaluation.

Results of the cost evaluation are depicted in Fig. 4 and 5. Capital costs for Model II are higher in both cases. It can be seen that capital costs for isobutanol-water system are quite similar, due to the same column structure and the slight difference in the membrane unit areas. The increase of capital cost in the case of Model II is in a range of 0.32-7.7% regarding the different operational units. The greatest deviation is caused by the membrane are enlargement.

However in the case of ethanol dehydration a greater difference (0.53-88.9% cost increase) appears between the model of Rautenbach and the exponential models. The 88.9% increase is caused by a greater discrepancy in membrane areas and accordingly the reheating heat exchangers.

Operational costs of ethanol dehydration are higher than that of isobutanol dewatering; however the exponential model results in only a moderately higher value: 0.67-2.01% for isobutanol and 0.64-4.38% for ethanol dewatering.

## 6 Conclusions

Sustainability in industry means high product output with minimizing by-product and waste generation at low energy demand. Membrane pervaporation and hybrid separation processes including pervaporation can meet these requirements, in case of proper application. In the course of this work two pervaporation models are verified and compared with the simulation of hybrid separation processes for the dehydration of ethanol-water and isobutanol-water mixtures in ChemCAD software environment.

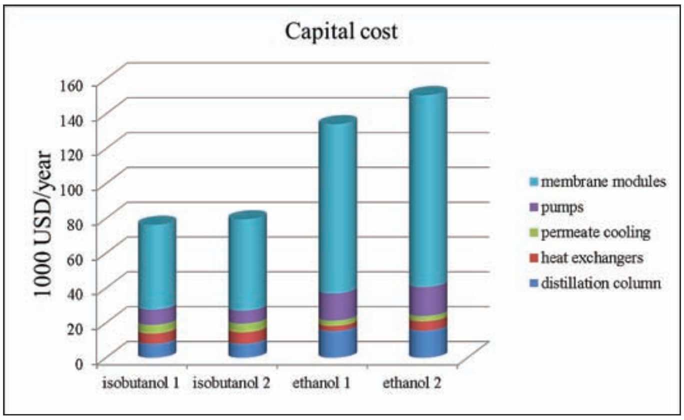

**Fig. 4.** Comparison of the capital costs of the hybrid dehydration systems for isobutanol-water and ethanol-water mixtures (1: Model I, 2: Model II)

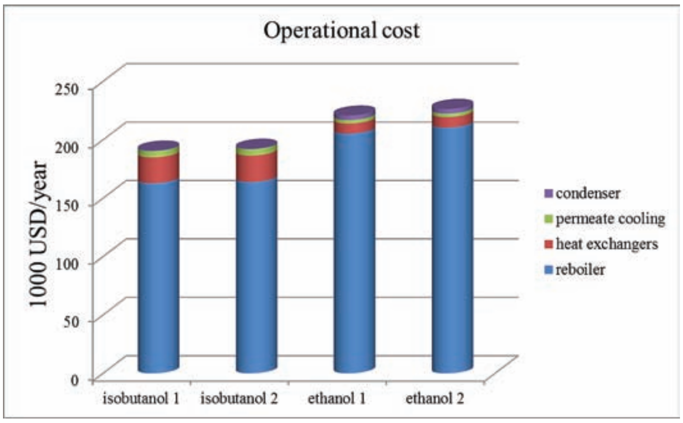

**Fig. 5.** Comparison of the operational costs of the hybrid dehydration systems for isobutanol-water and ethanol-water mixtures (1: Model I, 2: Model II)

Our improved model provides more accurate approximation of experimental results for the investigated separation problem. Results show that the statement made by Rautenbach about the concentration independent nature of the transport coefficient in the model should be argued and revised, since we found an exponential relation between the flux and the feed concentration of water. This proves the concentration dependence of the transport coefficient on the feed component concentration.

The higher costs estimated by the improved model are compensated by the resulted better and reliable product quality. Simulation results of the hybrid separation process show that Model II gives greater pervaporation membrane area in both cases. This means that using an inadequate pervaporation model can lead to false results for the design and optimization of complex separation processes that can cause an unpleasant surprise during the completion, resulting in poorer product quality during operation.

These results stress the necessity and the importance of adequate process models to obtain reliable design data.

## Nomenclature

| | |
|---|---|
| B | :constant in the developed model |
| COP | :coefficient of performance |
| D | :distillation |
| $\overline{D}_i$ | :transport coefficient of component *i* [kmol/(m$^2$h)] |
| $\overline{D}_i^*$ | :relative transport coefficient of component *i* [kmol/(m$^2$h)] |
| $E_i$ | :activation energy of component *i* in the equation for the temperature dependence of the transport coefficient (kJ/mol) |
| $J_i$ | :partial flux [mol/(m$^2$h)] |
| M&S | :Marshall and Swift cost index (1536.5 in April 2012) |
| $P_{i0}$ | :pure *i* component vapour pressure (bar, kPa) |
| $P_{i1}$ | :partial pressure of component *i* on the liquid phase membrane side (bar, kPa) |
| $P_{i2}$ | :partial pressure of component *i* between the active and the porous support layer of the membrane (bar, kPa) |
| PAN | :polyacrylonitrile |
| PV | :pervaporation |
| PVA | :polyvinylalcohol |
| $Q_0$ | :permeability coefficient of the porous support layer of the membrane [kmol/(m$^2$hbar)] |
| R | :gas constant [kJ/(kmolK)] |
| $T$ | :temperature (K) temperature on diagrams (°C) |
| $T^*$ | :reference temperature: 293 K |
| USD | :United States dollar |
| VOC | :volatile organic compound |
| PAN | :polyacrylonitrile |
| $\overline{\gamma}_i$ | :average activity coefficient of component *i* |

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