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Simulation of a hybrid pervaporation–distillation process

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Abstract

This study explores the possibility of simulating a hybrid pervaporation membrane process with the help of Aspen PlusTM (Aspen Tech) flowsheeting. Because Aspen Plus does not contain membrane modules in its Model Library, the pervaporation membrane is simulated within Excel Visual Basic for Applications (VBA). Excel VBA is then linked with Aspen Plus to perform the hybrid simulation. In this way, the user can control the simulation even during the calculations.

Case studies, in which industrially relevant hybrid distillation–pervaporation processes are simulated, are used to test the program. First, the dehydration and recycling of ethanol in an industrial plant is looked at, to explore whether an economic improvement can be established with a hybrid process. Secondly, the same is done for the purification of acetic acid in an industrial plant. The results presented here indicate the value of this software as a design tool.

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1. Introduction

Membrane systems, such as pervaporation, have become viable alternatives to traditional energy intensive separation methods such as distillation. They often offer lower capital and utility costs and can be used for a wide range of separations. Pervaporation is a promising alternative to conventional energy intensive technologies for being more economical, safe and ecofriendly and for having interesting energetic aspects (Smitha, Suhanya, Sridhar, & Ramakrishna, 2004; Van Hoof, Van den Abeele, Buekenhoudt, Dotremont, & Leysen, 2004). It can achieve separations that are otherwise technically difficult, due to e.g. the formation of azeotropes, and operates simpler than ‘conventional’ azeotropic distillation solutions such as pressure swing distillation or extractive distillation. As a process on its own pervaporation is probably not economically feasible, but in a hybrid or combined process, coupled with a

distillation unit or a reactor, it can improve the overall/global efficiency.

The economics of membrane separation processes depend on process design (Qi & Henson, 2000). The simulation of a process allows easy evaluation and optimisation of the operating variables and process configurations, thereby giving more insight in the influence of important parameters on process design. Most commercial process simulators or flowsheeting packages have built-in process models and optimisation toolboxes, thus offering a convenient and time saving means of examining an entire process. A wide variety of software directed at process engineering is presently available. However, membrane modules containing an internal membrane process model are hardly ever implemented in this software.

Weller and Steiner (1950) were the first to address the issue of mathematical modelling of membrane gas separators. Since then, various mathematical models and calculation methods have been reported in literature. To simulate the pervaporation process, Lipnizki, Olsson, and Trägårdh (2002) designed an algorithm for multi-component systems, in this way overcoming limitations of other approaches, whilst Aminabhavi,

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Nomenclature

A	membrane area (m^2)
c	concentration (mol m^{-3})
D	binary Fick diffusion coefficient ($\text{m}^2 \text{h}^{-1}$)
$\bar{D}$	Maxwell–Stefan diffusion coefficient ($\text{m}^2 \text{h}^{-1}$)
E_J	activation energy for flux (J mol^{-1})
f	fraction acetic acid permeating through the membrane
F	permeability coefficient ($\text{mol m}^{-1} \text{h}^{-1} \text{bar}^{-1}$ or $\text{kg m}^{-1} \text{h}^{-1} \text{bar}^{-1}$)
F'	permeability for constant membrane thickness ($\text{mol m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ or $\text{kg m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)
H	adsorption coefficient or solubility ($\text{mol m}^{-3} \text{bar}^{-1}$ or $\text{kg m}^{-3} \text{bar}^{-1}$)
ΔH^{vap}	heat of vaporization (kJ kg^{-1})
J	total invariant flux ($\text{mol m}^{-2} \text{h}^{-1}$ or $\text{kg m}^{-2} \text{h}^{-1}$)
L	membrane thickness (m)
n	number of sub-membranes
p	partial vapour pressure (bar)
Δp	trans-membrane partial pressure difference (bar)
P	pressure (bar)
ΔP	trans-membrane pressure difference (bar)
p^{vap}	saturated vapour pressure (bar)
Q	energy required for pervaporation (kJ h^{-1})
R	gas constant ($8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	temperature (K)
x	mole fraction; retentate molar fraction
$\bar{x}$	average molar fraction in Eq. (8)
∇x	molar fraction gradient (m^{-1})
y	permeate molar fraction
z	coordinate perpendicular to the membrane surface

Greek symbols

α	separation factor
γ	activity
φ	mass flow (kg/s)

Subscripts

0	reference temperature
i	component i
j	component j
k	sub-membrane k
m	membrane

Superscripts

feed	feed
perm	permeate
ret	retentate

for their modelling of the separation of binary mixtures through polymeric membranes.

Other software packages used and described for simulations of membrane modules are HYSYS (Davis, 2002) and gPROMS combined with the *Multiflash* software package (Marriott & Sørensen, 2003a, 2003b; Marriott, Sørensen, & Bogle, 2001). The same software can also be used to simulate hybrid processes. González and Ortiz (2002) used gPROMS to simulate a pervaporation–distillation hybrid process. Eliceche, Daviou, Hoch, and Ortiz Uribe (2002) combined gPROMS and HYSYS for the same purpose, but used Fortran language to make the combined implementation work.

Another software package, frequently used in industry and academe, is Aspen Plus™ (Aspen Technology, Cambridge, MA, USA). This is a steady-state sequential modular simulation package used as a tool to simulate and design chemical processes (Aspen Plus, 2001). It offers the possibility to simulate various combinations of unit operations such as reactors, distillation towers, heat exchangers and compressors using the built-in process models. Although a built-in stand-alone model for membrane separation processes is not available in the standard version of Aspen Plus, a detailed membrane model and a solution procedure can be implemented and used (Sommer & Melin, 2004; Van Veen & Pex, 2006) as a user-supplied subroutine. This can however be very complicated and time consuming. Furthermore, after starting and running the simulation, this USER model is implemented in the code of Aspen Plus as a subroutine, and as a consequence the user has no longer control over it once program execution starts. This makes the user completely dependent on the way Aspen Plus handles this model and makes it difficult to direct the simulation in response to the results.

More recent versions of Aspen Plus offer the possibility to use custom or proprietary models from Microsoft Excel spreadsheets. With the help of the programming language Visual Basic for Applications (VBA) in Excel, one can program a membrane model and a graphical user interface (GUI). Via the GUI the user has complete control over both the program and Aspen Plus, because Aspen Plus hands the control back to Excel VBA after calculating a certain step. By programming a membrane module in Excel VBA, and connecting it to a flowsheet in Aspen Plus, containing a different separation or reaction unit, a hybrid process can be simulated.

Rautenbach, Knauf, Struck, and Vier (1996) integrated pervaporation as a user defined Fortran block into Aspen Plus. This simulation suffered from some disadvantages (Lipnizki et al., 2002), apart from the fact that the user has little or no control over the calculations after the simulation run has started. Han, Li, Chen, and Wickramasinghe (2002) showed that it is possible to simulate the pervaporation process using a stand-alone model in the Visual Basic programming language. This user-friendly design software provided a useful resource for designing new pervaporation processes, but was unfortunately not capable of simulating combined or hybrid processes.

In this study, a hybrid pervaporation–distillation process is simulated by using Excel VBA linked with Aspen Plus. In this way, a design and optimisation tool is provided, where the user

Naidu, Sridhar, and Rangarajan (2005) developed a C-language program to simulate the pervaporation separation of binary water–isopropanol mixtures. Hofmann, Fritz, and Paul (1998) used the InsightII/Discover software of molecular simulations

gives input to Aspen Plus via Excel VBA, with which Aspen Plus then calculates a result. Thereafter, control is handed back to Excel VBA, where the next step of the calculation can be determined, based on the results of the simulation in Aspen Plus. Thus, control is kept over the different parts of the simulation. The program is tested for two industrial cases.

2. Models

Transport of components through a membrane is a complex process. Over the years many different theories have been developed to describe the transport mechanism through the membrane. The program developed in this work contains the implementation of two theoretical models, as described by Bettens, Degreè, Van der Bruggen, and Vandecasteele (2007), based on the adsorption–diffusion theory for ceramic membranes.

In the adsorption–diffusion theory for ceramic membranes (Ten Elshof, Abadal, Sekulić, Chowdhury, & Blank, 2003; Verkerk, Van Male, Vorstman, & Keurentjes, 2001), the membrane is considered to be nonporous so that transport occurs only by diffusion and not by convection. A component from the feed solution then consecutively (1) sorbs onto the membrane, (2) diffuses through the membrane and (3) desorbs from the membrane (this last step is usually not considered explicitly since this process is in general very fast).

Based on this theory, a number of pervaporation models have been developed, expressing the performance of the membrane in terms of flux and separation factor. Two types of models are considered in the program: (1) models derived from Fick's binary diffusion equation (Bird, Stewart, & Lighthfoot, 2002; Taylor & Krishna, 1993) and (2) models derived from the Maxwell–Stefan theory (Ten Elshof et al., 2003; Verkerk et al., 2001).

2.1. Fick's binary diffusion equation

Fick's law of binary diffusion postulates a linear dependence of the diffusion flux of species i (J_i), defined with respect to the average mixture velocity, and its composition gradient. The diffusion flux J_i is usually related to the molar fraction gradient (∇x) by (Taylor & Krishna, 1993)

$$J_i = -cD_{ij}\nabla x_i \quad (1)$$

where D_{ij} is the Fick binary diffusivity, x_i the molar fraction of component i and c is the total mixture molar concentration.

Integrating over the membrane gives, for a constantly assumed diffusion coefficient D_{ij} :

$$J_i = \frac{D_{ij}}{L}(c_{mi}^{\text{feed}} - c_{mi}^{\text{perm}}) \quad (2)$$

with L the membrane thickness; c_{mi}^{feed} and c_{mi}^{perm} the concentrations of component i inside the membrane on the feed and the permeate side, respectively.

At low levels of sorption, by assuming that in pervaporation the components are transported as vapour species via surface diffusion, the vapour concentration in the membrane at

the membrane-feed stream interface may be obtained through Henry's law. This law makes use of the solubility parameter H , which is to be used in the expression (Ten Elshof et al., 2003)

$$c_{mi} = H_{mi}p_i \quad (3)$$

where p_i is the partial vapour pressure of component i in the phase adjoining the interface.

Combining the Fickian approach (2) with Henry's law (3), gives the following solution—diffusion equation (Ten Elshof et al., 2003; Verkerk et al., 2001):

$$J_i = H_{mi}D_{mi}\frac{p_i^{\text{feed}} - p_i^{\text{perm}}}{L} = F_{mi}\frac{\Delta p_i}{L} \quad (4)$$

In this equation, the partial pressure difference over the membrane is represented by $\Delta p = p_i^{\text{feed}} - p_i^{\text{perm}}$ and $F_{mi} = H_{mi}D_{mi}$ is termed the permeability coefficient. For constant membrane thickness, Eq. (4) becomes

$$J_i = F'_i\Delta p_i \quad (5)$$

The temperature dependence of the flux follows an Arrhenius (exponential) type of relation (Feng & Huang, 1996)

$$J_i = J_{i0}e^{-E_i/RT} \quad (6)$$

Apart from the flux, the separation performance of a membrane is expressed in terms of the separation factor, which is a combination of the membrane selectivity and the selectivity resulting from the vapour–liquid equilibrium at the membrane interface. The separation factor α , for use with components labelled i and j , is usually defined as (Ten Elshof et al., 2003)

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \quad (7)$$

where x and y are the molar fractions of components in the retentate and permeate, respectively and i and j are the fastest and slowest permeating component, respectively.

2.2. The Maxwell–Stefan theory

The binary diffusion equation (Fick) does not always work correctly if two (or more) components are present inside a membrane, since then the system is actually ternary (or multi-component), consisting of solute, solvent and membrane (M). In this situation, the Maxwell–Stefan equations are a better description for the transport of two components through membrane material. The transport equation for component i is based on the driving force for this component, and its friction with the membrane M and component j (Taylor & Krishna, 1993).

Assuming the components are transported as individual vapour species, this gives (Ten Elshof et al., 2003; Verkerk et al., 2001):

$$-\frac{1}{p_i}\frac{dp_i}{dz} = \frac{\bar{x}_j}{D_{ij}}\left(\frac{J_i}{c_i} - \frac{J_j}{c_j}\right) + \frac{1}{D'_{iM}}\frac{J_i}{c_i} \quad (8)$$

Here, z is the coordinate perpendicular to the membrane surface, D_{ij} the Maxwell–Stefan diffusivity for component pair i and j , D'_{iM} the Maxwell–Stefan diffusivity of component i in the

membrane, $\bar{x}_j$ the average molar fraction of component j in the adsorbed phase and J is the total invariant flux of component i or j .

Explicit expressions for J_i and J_j can be obtained from (8) in case $J_j/c_j \ll J_i/c_i$ and Henry's law (3) applies. This is, for example, the case in dehydration applications, where one component is water (i), and the other the solvent (j).

$$J_i = H_{mi} \left(\frac{\bar{D}_{ij} \bar{D}'_{iM}}{\bar{D}'_{iM} \bar{x}_j + \bar{D}_{ij}} \right) \frac{\Delta p_i}{L} \quad (9)$$

$$J_j = H_{mj} \bar{D}'_{jM} \frac{\Delta p_j}{L} + \frac{\bar{x}_j \bar{D}'_{jM}}{\bar{D}_{ij}} J_i \quad (10)$$

When determining parameters from measurements on a membrane with constant thickness, some parameters in Eqs. (9) and (10) can be combined, assuming they are concentration independent. This reduces the number of unknown parameters from six to four. The resulting equations then become

$$J_i = \frac{1}{A \bar{x}_j + B} \Delta p_i \quad (11)$$

$$J_j = C \Delta p_j + D \bar{x}_j J_i \quad (12)$$

with

$$A = \frac{L}{\bar{D}_{ij} H_{mi}} \quad (13)$$

$$B = \frac{L}{\bar{D}'_{iM} H_{mi}} \quad (14)$$

$$C = \frac{H_{mj} \bar{D}'_{jM}}{L} \quad (15)$$

$$D = \frac{\bar{D}'_{jM}}{\bar{D}_{ij}} \quad (16)$$

None of these four parameters should become negative, as they are calculated from positive values.

Adsorption–diffusion models based on Fick's diffusion equation can be used to describe some coupling effects, if they are modified to include concentration dependent diffusion and/or sorption coefficients. They are however incapable of describing a drag effect, in which the fastest permeating component increases the flux of the slower permeating component. This effect can be better modelled through models based on the Maxwell–Stefan theory. Here, information on the concentration dependence of diffusion and sorption is also needed (Bettens et al., 2007).

3. Software program

Based on the above models, a Windows-based, user-friendly design software was developed using Excel Visual Basic for Applications (VBA) to simulate a pervaporation unit. The software consists of two major parts. The first is a simulation program that is able to simulate a flowsheet containing a pervaporation unit. The user can specify which of the aforementioned models should be used for calculating the membrane process.

There is also an option that enables this part of the program to do several follow-up simulations (sensitivity analysis), thereby varying a specified variable in the way the user would like to.

The second part consists of a design program, capable of determining the number of membrane units or the total membrane area required to reach a specified separation criterion. With these two parts of the program, both the performance of a membrane with known properties and the requirements for a membrane unit for a known process performance can be calculated.

In order to use the possibilities of this software for the simulation of a hybrid process, a link with Aspen Plus had to be established. This was done according to the training manual for running Aspen Plus with Microsoft Excel/Visual Basic, provided by Aspen Technology (Aspen Technology Inc., 2002), that describes the establishment of data exchange between Aspen Plus and Excel VBA.

To simulate a hybrid process, first an Aspen Plus flowsheet has to be made for the entire process, with exception of the membrane module(s). The VBA program will connect to this flowsheet and incorporate the membrane modules. In order to do the calculations for the hybrid simulation, exchange of data between the two programs is required. However, if somewhere during the calculations an error occurs in Aspen Plus, the connection between both programs is broken, thereby losing all the data calculated so far. To overcome this problem, the flowsheet has to be prepared by the following rules:

- the feed for the membrane unit has to be shown on the flowsheet, unless the feed is coming from another membrane unit;
- if the source of a membrane feed is not connected to a block on the flowsheet, this leads to problems in Aspen Plus, resulting in a disconnection of the programs. Connecting the stream to a MIXER block that does not alter the stream can solve this;
- no blocks need to be placed to represent a membrane unit. The VBA program automatically places a SEP2 block on the flowsheet as the membrane unit, including the exiting product streams;
- the flowsheet should be able to work without the membrane blocks. This means all blocks, streams, components and connections must be completely defined and in most cases a liquid–vapour thermodynamic property model must be chosen;
- the VLE property set must be active for the program to be able to obtain vapour liquid equilibrium data.

These rules will be explained with help of an example flowsheet. Fig. 1 gives an example of a complex hybrid process. Fig. 2 shows the correct Aspen Plus flowsheet representation to simulate this process. For the membrane placed in the FEED2 stream, an input flow has to be defined in the Aspen Plus flowsheet. Placing a separate MIXER unit on the flowsheet, which has an equal input and output stream, defines the feed stream for the membrane. The retentate of the membrane is then selected as a feed for the distillation column. For the membranes in the product streams of the distillation column, the feed streams are given by this flowsheet or come from another membrane unit. In

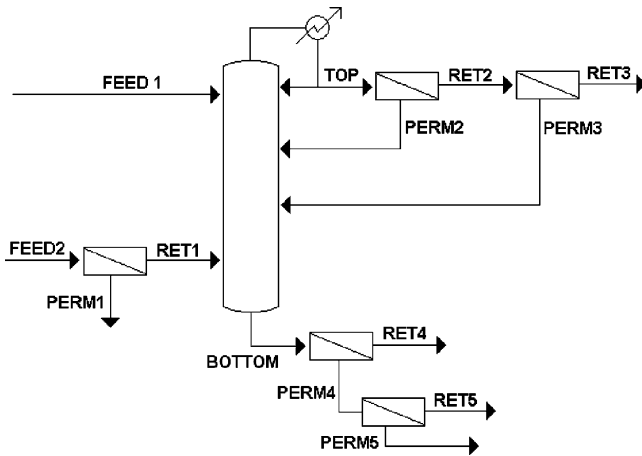


Fig. 1. Example of a hybrid process.

the VBA program, the destinations of the retentate and permeate streams can be selected.

As can be seen, at this moment no blocks are explicitly defined for the membrane units in Aspen Plus. The VBA program will place these automatically. Even without these membrane units, this flowsheet can be used for simulations. By using the VLE property set inside Aspen Plus, all vapour liquid equilibrium data can be accessed, so they can be used or tabulated elsewhere.

The VBA program places in the Aspen Plus flowsheet a SEP2 block to represent each of the membrane modules present in the process. A SEP2 block splits an incoming stream into two product streams according to user-specified component split ratios. This is a logical representation of a membrane module, where the feed is split into a permeate and a retentate. The chosen model in the VBA program, based on either Fick or Maxwell–Stefan diffusional transport, determines the distribution for the split after calculation of fluxes and compositions for both permeate and retentate.

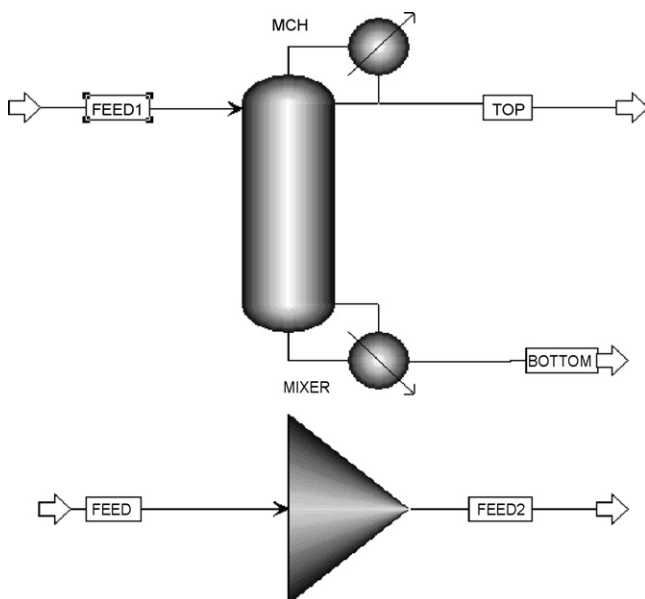


Fig. 2. Aspen Plus flowsheet for correct simulation of the hybrid process in Fig. 1.

From mass balances, the initial flows and compositions of all membrane streams can be derived. The mass fractions of retentate and permeate are used to determine the driving force for the membrane separation according to Eq. (17), which is based on the assumption of a perfectly mixed fluid being present at the retentate side.

$$\Delta p_i = x_i^{\text{ret}} \gamma_i^{\text{ret}} P_i^{\text{vap,ret}} - x_i^{\text{perm}} \gamma_i^{\text{perm}} P_i^{\text{vap,perm}} \quad (17)$$

In this equation, Δp_i is the driving force, x_i the molar fraction, γ_i the activity coefficient (obtained from Aspen Plus) and P_i^{vap} the vapour pressure (also calculated by Aspen Plus) of component i . In combination with information on the permeance, the flux of i through the membrane can be calculated. For the Fick model, the permeability coefficient for every component is required as input. For the Maxwell–Stefan model, parameters A – D are required. These parameters can be calculated from Eqs. (13) to (16), but are usually obtained a priori by fitting the model to a priori collected experimental data. With this user input, the trans-membrane fluxes of components i and j can be calculated according to Eqs. (5) and (11) or (12), so that a new composition for every stream can be derived.

In order to improve the accuracy of the flux calculations, the membrane is divided into sub-membranes with equal membrane area. The total membrane area of these sub-membranes is equal to the original membrane area. For every sub-membrane, flux and compositions are calculated as explained above. However, because the outgoing permeate and retentate concentrations are not a priori known for every sub-membrane, the fluxes (which depend on the composition gradients) need to be calculated iteratively. The total permeate and retentate flows after every sub-membrane are determined with help of the flux after the preceding sub-membrane and the product of the sub-membrane area and the trans-membrane flux, according to Eqs. (18) and (19).

$$\varphi_{i,k}^{\text{ret}} = \varphi_{i,k-1}^{\text{ret}} - A_k J_{i,k} \quad (18)$$

$$\varphi_{i,k}^{\text{perm}} = \varphi_{i,k-1}^{\text{perm}} + A_k J_{i,k} \quad (19)$$

For the simulation program, the total membrane area and number of sub-membranes to be used in the calculation are given as input. For the design program, not the number of sub-membranes and area are given as input, but the desired purity of permeate or retentate can be specified. With this information, the necessary membrane area to reach this purity is then calculated by the design program. For both programs, the output results consist of the pressure, temperature, mass flows (φ) and composition for every membrane stream. An overview of input and output parameters for both versions of the program is given in Table 1.

4. Case studies

With this software, two case studies are simulated from a retrofitting point of view to investigate whether the program is capable of performing these kinds of calculations. To this end, an industrial distillation process is compared to a hybrid process, assuming the membrane unit is added to the existing installation.

Table 1
Input and output parameters for simulation and design versions of the program

Simulation program			Design program		
Program user input	Aspen Plus data exchanged	Stream output	Program user input	Aspen Plus data exchanged	Stream output
A	γ	P	x_i or x_j	γ	P
n	p^{vap}	T	F (Fi)	p^{vap}	T
p^{perm}	Feed data	φ	A (MS)	Feed data	φ
F (Fi)		x_i	B (MS)		x_i
A (MS)		x_j	C (MS)		x_j
B (MS)			D (MS)		A
C (MS)					n
D (MS)					

(Fi)=Fick model; (MS)=Maxwell–Stefan model.

Also, some rough economic calculations have been performed without going into detail. The aim of these calculations is to show that the results from the developed process calculation tool can be used for economic comparisons. However, they only give an indication of the possibilities for the simulated process. Definitely more extensive calculations are necessary and will be done in the future for a detailed process, with economic comparison to be made between standalone distillation and hybrid (membrane and distillation) processes.

Fig. 3 shows a typical user interface of the software. At present, only a Dutch version is available, though an English translation will be made.

4.1. Case 1: purification of ethanol

In industry, a common separation process is the purification of ethanol. However, water and ethanol form an azeotrope at an

ethanol concentration of 95.6 wt%, causing a very small difference in volatility of the components for ethanol concentrations near this value. Therefore, this purification is difficult to obtain with conventional processes. Nowadays, the separation is performed by a distillation column consisting of 40 trays, with steam injection at the bottom and a reflux ratio of 12. The operating pressure values for the column are 0.04 barg pressure at the top, and 0.28 barg at the bottom.

In the investigated process, two streams of respectively 85 and 91 wt% ethanol must be obtained. A huge consumption of steam is required to reach this purity, since the purities of the product streams lie near the azeotrope concentration. Reducing the energy use of this column would be a major improvement. Adding a pervaporation unit to the existing system might thereby help minimising these important process costs.

Fig. 4 shows a flowsheet of the current process. ETOH-91 and ETOH-85 are the two streams with purified ethanol of 91

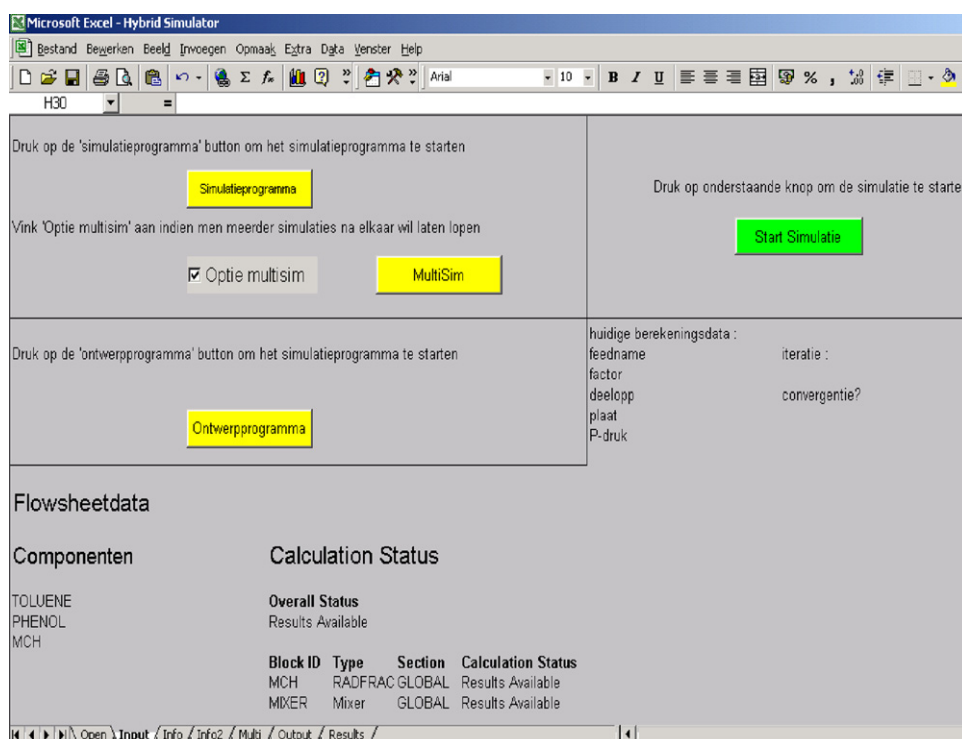


Fig. 3. Typical user interface of the software.

Table 2
Comparison of the results of the Aspen Plus simulation and the real process

	Relative flux	Ethanol (wt%)	Ethylacetate (impurity) (wt%)	Acetic acid (wt%)	Water (wt%)
F1	0.214	29.7	0.21	0.10	70.0
F2	1	12.5	0	0.17	87.33
Steam	0.203	–	–	–	100
ETOH-91					
Goal	0.0304	91	1.2	0	7.8
Calculated	0.0339	90.5	1.1	0.0000137	8.4
ETOH-85					
Goal	0.189	85	0.05	0	14.95
Calculated	0.189	83.4	0.0406	0.0009	16.6
Bottom					
Goal	1.19	0.01	0	0.16	99.83
Calculated	1.19	0.0102	0	0.2	99.8

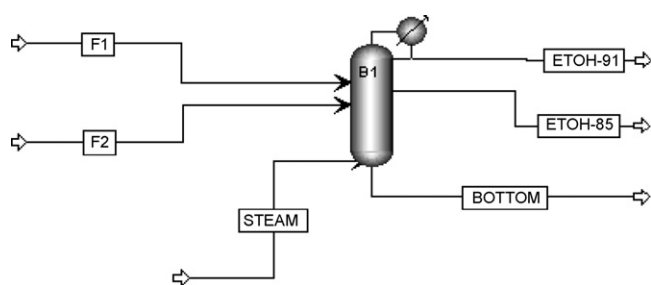


Fig. 4. Flowsheet of the ethanol purification process without the membrane unit.

and 85 wt% ethanol, respectively. The BOTTOM stream goes to the wastewater treatment unit and should therefore contain not too much ethanol.

For each stream, consisting of saturated liquid, the concentrations and flows are known, as are the temperature and pressure profiles in the column and the positions of the different feed and product trays. The column was simulated with Aspen Plus for the stand-alone distillation case to be able to correctly compare the results to the measured, real-life values. It was found that this column performance could only be reached if the bottom section of the column was assigned a plate efficiency of 0.5 and the top section a plate efficiency of 0.64.

The found energy consumption of the steam injection corresponds to a relative usage of 0.203 kg steam/kg F2. Table 2 displays the given information and the results of this calculation. The major deviation is the concentration of

the ETOH-85 stream, being 83.4 wt% (calculated) instead of 85 wt% (measured). However, these results agree well enough with the given performance of the column, to simulate a hybrid pervaporation–distillation process and to compare the performance and economics of both the conventional and the hybrid process.

For a hybrid process, there are different possibilities for placing the membrane unit in the process. In order to determine the energy gain of this situation, no alterations are made to the dimensional properties of the distillation column.

First, the purity of the top stream can be downgraded to 85 wt% ethanol. After removing the correct amount of 85 wt% ethanol from this stream, a pervaporation unit can purify the remainder to 91 wt%. This means that the two product streams of the column are reduced to one. In this case the retentate of the membrane is the ETOH-91 stream, and the permeate should go, just as the bottom stream, to the water purification unit. This requires permeation of (mainly) water through the pervaporation membrane, which can be achieved by using a hydrophilic membrane. Fig. 5 shows the new Aspen Plus flowsheet for this process. In this flowsheet the membrane unit is not shown explicitly, but it is placed after the ETOH2 stream by the VBA program.

To correctly compare the results of the conventional and hybrid process simulations with each other, the same specifications have to be set for the hybrid simulation as for the basic case. This means the specifications for the different product streams purities are set to 83.4 and 90.5 wt% ethanol (see Table 2). The

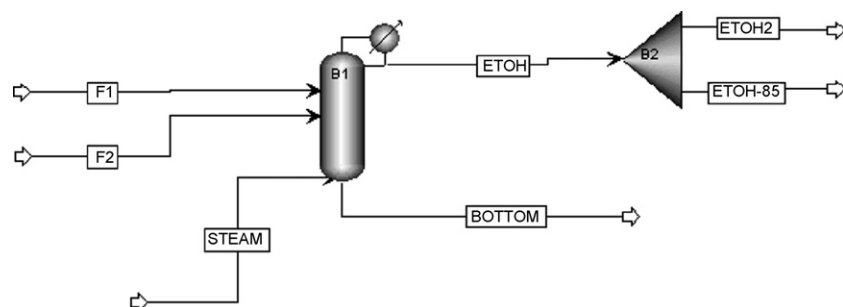


Fig. 5. Modified Aspen Plus flowsheet for the ethanol purification.

reduced steam consumption calculated in this way is a good indication for the reduction possible in an industrial process if a hybrid process is used instead of a pure distillation process.

To calculate the hybrid process, information about a membrane appropriate for this separation is needed. This information is obtained from performed experiments for the ethanol dehydration at 60 °C (private communication) with a silica-based membrane (ECN, The Netherlands, Van Veen, Van Delft, Engelen, & Pex, 2001). With these data, parameters for Fick's binary diffusion equation and the Maxwell–Stefan model (see Sections 2.1 and 2.2) were determined by fitting the measurement data.

The parameters A – D in the Maxwell–Stefan model (Eqs. (13)–(16)) should not be negative. After fitting the model to the experimental results however, a negative value for A is found. This indicates a possible inaccuracy in the experimental results. To be able to proceed with the simulation, parameter A is set to zero and new values for B , C and D are fitted (this approach is called the limited determination). These newly found values were then used for further calculations. Table 3 lists for both models the fitting results for the different parameters. From the fits to the measurement data (not shown) it is found that the Maxwell–Stefan model describes the fluxes in a better way than Fick's binary equation, especially at ethanol weight fractions up to 91 wt%, in the range of importance for this separation. Therefore, the Maxwell–Stefan model is used for further calculations. With this parameter information the membrane is fully characterised and now the design program can determine the membrane area required to reach the purity specified for the product stream.

The removal of a product stream in the distillation column has a major influence on the calculations. First, new flow values of the product streams have to be calculated. This alters the flow profile inside the column, thereby changing the optimal locations of the feed trays, so that these have to be redetermined as well. After these changes and with the implementation of a hybrid separation, a reduction in steam consumption of 4.33% is found. To realise this reduction, a membrane surface of 14 m² is required, as calculated by the Maxwell–Stefan model.

When a membrane unit is added to an existing process installation, the profit of the hybrid process can be quantified, since the cost of the membrane has to be balanced by the economic gain of the steam reduction. With the costs of membrane and

steam known, the return on investment of the membrane can be determined by calculating the time it would take with the simulated steam reduction to pay for the cost of the membrane. This can be compared to the life expectancy of the membrane, to determine the economical savings of using a hybrid process.

In this case study, with a calculated steam reduction of 4.33% and a membrane area of 14 m² and estimated costs for steam and membrane (private communication), the payback time of the membrane implementation was calculated to be approximately five years (Huybrechs, 2006). However, it is likely that the membrane has to be replaced *within* 5 years because of the process conditions. This means this type of hybrid process, with the use of this particular membrane, shows no advantage over a distillation process. Depending on the choice of membrane however, a suitable option perhaps can be found in the future, when cost, lifetime and/or performance of membranes change.

A second possibility for the ethanol process is to use a membrane process to purify one of the feeds to the distillation column. Again, the changes in the flowsheet have consequences on the flows and optimal locations of column feed trays. However, it was found that no reduction in steam was possible in this process. This is due to the fact that the feed streams to the column are reduced in flow, but the product streams have to remain constant. Therefore, the column has to purify better than before, implying the use of more steam to reach the specifications.

4.2. Case 2: purification of acetic acid

Acetic acid is one of the most important base chemicals for an entire range of applications (Ullmann, 2000). The main purpose is as a solvent in the production of different resins and plastics. When used as a solvent, it is recycled by means of distillation. This is a difficult separation in the presence of water, since the boiling points of water (100 °C) and acetic acid (115 °C) are close to each other. In a huge distillation column consisting of 90 trays, the top stream will consist mainly of water, and the bottom stream of acetic acid.

Fig. 6 shows the flowsheet for the process that was simulated. There are four different feed streams, for which the flow, temperature, components and feed trays are known. In addition, the pressure drop over the column (0.04 barg at the top to 0.75 barg

Table 3
Calculated parameters for Fick's binary diffusion equation and the Maxwell–Stefan model

Permeability (F') (kg m ⁻² h ⁻¹ bar ⁻¹)				
Fick				
Ethanol			0.697	
Water			11.075	
	A (m ² h bar kg ⁻¹)	B (m ² h bar kg ⁻¹)	C (kg m ⁻² h ⁻¹ bar ⁻¹)	D
Maxwell–Stefan				
Unlimited	−0.0897	0.1594	0.6081	0.1054
Limited	0	0.0822	0.6081	0.1054

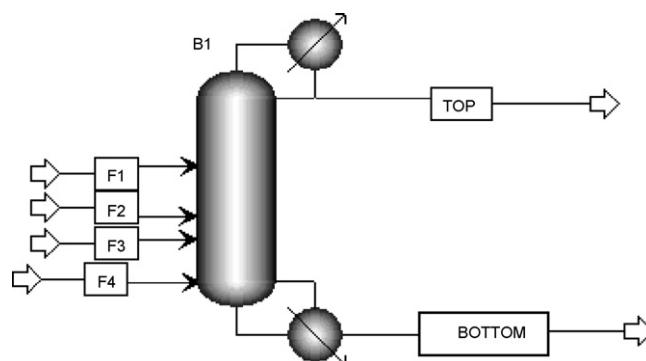


Fig. 6. Flowsheet of the acetic acid purification process without the membrane unit.

Table 4
Comparison of the results of the Aspen Plus simulation and reality

	Relative flow (–)	Acetic acid (wt%)	Water (wt%)
F1	0.150	51.16	48.84
F2	1	60.98	39.02
F3	0.436	88.00	12.00
F4	0.321	81.52	18.48
Top			
Goal	0.446	0.6	99.4
Calculated	0.446	0.6	99.4
Bottom			
Goal	1.460	91.0	9.0
Calculated	1.460	91.0	9.0

at the bottom) and the reflux ratio (3.1) are known, as is the weight fraction of acetic acid in the product streams. By making a mass balance, the flows of the product streams can be calculated. With these data, the column can be simulated in Aspen Plus.

The same approach as for the calculation of ethanol purification is followed. Table 4 summarises the given information and the simulation results of the distillation column and shows all specifications are perfectly realised. This result is obtained with a tray efficiency of 0.25 over the entire column. Again, all streams consist of saturated liquid.

To be absolutely sure the simulation is correct, the reboiler duty from the simulation is compared to the real value. The calculated reboiler duty is found to be 96.4% of the real-life duty, which is 560 W per kg/h of feed flow. This means that the use of steam is slightly underestimated in the simulation. Therefore, the calculated value cannot be considered exact, but it gives a reasonable idea of the real value. The separation in this process was then further looked at by combining the column with a membrane unit.

Again, different possibilities exist to use a membrane in the hybrid process. The first possibility is to place the membrane in the top stream of the distillation column. If the reboiler duty of the distillation column is lowered, the top stream of the column contains more acetic acid (though the major compound still is water). This means the membrane must be hydrophobic and acetic acid should permeate. This permeated acetic acid is then sent to the bottom stream, to reach a higher concentration of acetic acid in that stream.

The temperature of the top stream is a little over 100 °C. Since no exact experimental data are known for the separation of acetic acid and water under these conditions, the feasibility of this method must be checked otherwise. Therefore, it was calculated what the permeability of the membrane must be to obtain a similar separation as in the former situation with a lower energy use of the column.

This is done by lowering the reboiler duty in the simulation and observing the effect on composition and flow of the top stream. A new top stream flow is calculated, making sure that the size of the permeate stream is taken into account, to maintain the reference value for the top flow after the membrane. The acetic acid rich permeate stream is sent to the bottom stream, in this

way making sure the reference flow and stream composition are also obtained here (mass conservation).

Now, the maximum membrane size needed can be calculated, if a membrane payback time of one year is assumed and if membrane and steam prices are known. Since the reboiler duty is provided by the condensation of steam, the steam flow needed for the reboiler can be calculated. Just as in the former case study, the savings made in steam consumption must pay for the cost of the membrane. Since the membrane area primarily determines the cost of the membrane, a maximum membrane surface can be determined. With this known, the minimum membrane flux and permeability can be calculated. The minimum flux is calculated by dividing the calculated permeate flux through the calculated membrane area. The minimum membrane permeability can be determined by dividing this flux through the driving force (Eq. (17)).

In this derivation for the permeability many assumptions are made. Therefore, the hybrid simulation program is used to calculate the process performance for a membrane with these specifications. With help of the Fick model it is checked whether all assumptions made give the correct result. By varying the reflux ratio and the reboiler duty, Aspen Plus, together with the hybrid simulator is used to obtain the initial process specifications in a hybrid process. In this way, the energy savings can be determined.

Performing this calculation for different energy savings gives an indication of the possible profit advantage for this hybrid process. Fig. 7 shows the result of these calculations. In this graph the permeability for acetic acid needed for reaching a certain percentage of the energy used in the distillation process is given (since acetic acid is the permeating component). Remarkable is the difference in permeability between values below and above 14% energy use of the original use for the distillation process. For values below 14%, the minimum permeability of the membrane increases strongly, while a low permeability change is calculated for values above 14% use. This indicates that a membrane with an acetic acid permeability of around $0.5 \text{ kg m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ can drastically decrease the reboiler duty.

Probably the permeability of the membrane must be slightly higher to reach these savings, since the calculated energy for the distillation column is lower than in the real process (see above),

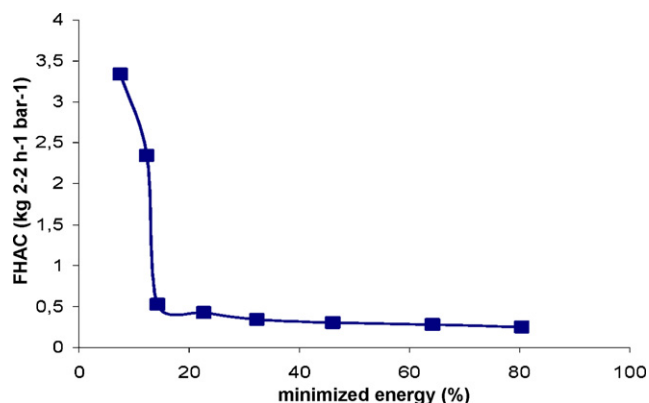


Fig. 7. Calculated minimal acetic acid permeability to reach a certain percentage of the original distillation reboiler duty.

and several assumptions have been made during the calculations. The permeability value required for the hybrid process to be economical is not unrealistic, so that from this point of view a suitable membrane could probably be found.

The main obstacle might be process conditions. The temperature in the bottom stream of the distillation column is calculated to be 129.9 °C. Ceramic membranes could be a possible solution when adapted to resist acetic acid, however these are more expensive, so a good separation or a high permeability must be obtained. At this moment no membrane is known that is able to separate acetic acid and water under these process conditions. However, with the help of this simulation program, the demands to a membrane can be calculated to see whether there is an economical gain in developing such a membrane.

A second possibility for the acetic acid separation process is to place the membrane in the path of the bottom stream coming from the distillation column. In this case, a hydrophilic membrane is needed to separate water from acetic acid since, although the stream contains more water when the reboiler duty is lowered, it still primarily contains acetic acid. By dehydrating this stream with the use of a membrane, the purity specifications can be reached.

For these calculations, different membrane areas are used to compare the performance of a hybrid and a stand-alone distillation process. The minimal reduction of steam to be achieved with a certain membrane area, to have a financial break-even situation, can be calculated for known prices of membrane and steam, and the assumption that the payback time of the membrane investment should be 1 year. In Aspen Plus a column was simulated with given top product flow and reboiler duty. From this simulation the mass fraction composition of the bottom stream, the partial vapour pressures and the activity coefficients of the compounds were obtained, ready to be used in the membrane module calculations.

Since it is not realistic to assume permeation of only water through the membrane, a fraction f is introduced, representing the fraction of acetic acid permeating through the membrane. This fraction is included in the mass balances over the membrane when calculating the composition of the different streams. With this information available, the driving force is calculated (Eq. (17)), and with this the minimum required value for the permeability. Again, the hybrid simulator with the Fick model is then used to test the performance of a membrane with these specifications and determine a new value for the reboiler duty of the distillation column. Table 5 shows the results of calculations for different membrane areas and acetic acid fractions present in the permeate. Both the permeabilities for water and acetic acid are given.

For this Table 5 a remark has to be made. The results are not given in absolute terms, but more as an indication of possible membrane configurations. In membrane processes, the membrane area and permeability are directly linked to each other. If the area is changed, the permeability can also be changed and the same return on investment can be achieved. For example, if the permeability for a membrane would be a factor of three larger than indicated in this table, the membrane surface can be about a factor of three smaller, and the same separa-

Table 5
Indicative results for the simulations with the membrane in the bottom stream

Reboiler duty (% of original)	A (m ²)	$f=0.01$			$f=0.2$			$f=0.4$		
		$F' \text{ H}_2\text{O}$ (kg m ⁻² h ⁻¹ bar ⁻¹)	$F' \text{ HAC}$ (kg m ⁻² h ⁻¹ bar ⁻¹)	$F' \text{ H}_2\text{O}$ (kg m ⁻² h ⁻¹ bar ⁻¹)	$F' \text{ HAC}$ (kg m ⁻² h ⁻¹ bar ⁻¹)	$F' \text{ H}_2\text{O}$ (kg m ⁻² h ⁻¹ bar ⁻¹)	$F' \text{ HAC}$ (kg m ⁻² h ⁻¹ bar ⁻¹)	$F' \text{ H}_2\text{O}$ (kg m ⁻² h ⁻¹ bar ⁻¹)	$F' \text{ HAC}$ (kg m ⁻² h ⁻¹ bar ⁻¹)	$F' \text{ HAC}$ (kg m ⁻² h ⁻¹ bar ⁻¹)
95.6	18	10.624	0.0197	10.879	0.498	11.353	1.387	11.353	1.387	1.387
93.6	1,063	0.358	0.000667	0.367	0.017	0.382	0.047	0.382	0.047	0.047
87.5	4,545	0.125	0.000234	0.128	0.006	0.134	0.017	0.134	0.017	0.017
75.3	11,509	0.144	0.000280	0.148	0.007	0.154	0.020	0.154	0.020	0.020
63.1	18,473	0.128	0.000270	0.131	0.007	0.137	0.019	0.137	0.019	0.019
38.3	32,400	0.344	0.000932	0.353	0.024	0.368	0.066	0.368	0.066	0.066
26.1	39,364	0.362	0.00134	0.371	0.034	0.387	0.095	0.387	0.095	0.095
0.0	54,029	0.774	0.00267	0.792	0.068	0.827	0.188	0.827	0.188	0.188

The final row shows the results for a separation process consisting only of a pervaporation unit.

Table 6

Indicative energy calculations for the membrane process with a fraction $f=0.2$ for the permeating acetic acid

A (m ²)	Reboiler duty (%)	F' H ₂ O (kg m ⁻² h ⁻¹ bar ⁻¹)	F' HAC (kg m ⁻² h ⁻¹ bar ⁻¹)	Q (%)	Process energy (%)
18	95.6	10.879	0.498	0.2	95.8
1,063	93.6	0.367	0.017	0.3	93.9
4,545	87.5	0.128	0.006	0.5	87.9
11,509	75.3	0.148	0.007	1.4	76.7
18,473	63.1	0.131	0.007	2.1	65.1
32,400	38.3	0.353	0.024	10.3	48.6
39,364	26.1	0.371	0.034	14.5	40.6
54,029	0.0	0.792	0.068	41.5	41.5

All values for the energy are given in the percentage of the original/real value.

tion and return on investment will be achieved. This can be explained by the fact that larger membrane areas require a smaller flux to reach the same separation. This tendency can be seen in table, since the permeability necessary for the separation process initially decreases steeply if a larger membrane area is used. The drag factor f shows to have a minor influence on the permeabilities for an energetically better hybrid process.

Something else to take into account when comparing economics for the distillation and hybrid situation is the energy use of the pervaporation process. The reboiler duty is not the only energy used in the process, since an isothermal process requires energy to evaporate the permeating components in the membrane. This energy can be calculated from the sum over every permeating component of the multiplication of permeability (F') and pressure drop over the membrane (ΔP), membrane area (A) and heat of vaporization of the component (ΔH_i^{vap}), as given in Eq. (20).

$$Q = \sum_i F'_i \Delta P A \Delta H_i^{\text{vap}} \quad (20)$$

As an example, this calculation is performed for the case with the fraction f being 0.2. Table 6 shows the results for this calculation. As can be seen, the energy use for the membrane unit in a hybrid process is less than the energy use of the distillation column, and the total energy use of the hybrid process is lower than for the stand-alone distillation process.

When using only a membrane unit (the final row of table), the energy use is 41.5% of the energy use for a stand-alone distillation process. Although the membrane unit requires less energy, this is not a good solution for the separation process. The trend that can be seen from this table is that the membrane area increases strongly when the reboiler duty for the distillation becomes very low. However, the permeabilities increase too, suggesting the performance of the process decreases. This can also be concluded from the fact that the energy use of the membrane unit increases strongly.

When looking at the values for the membrane area and the permeabilities, indicative values for the optimal membrane area and reboiler duty for the process lie around 18,473 m² membrane area with a water permeability of around 0.131 kg m⁻² h⁻¹ bar⁻¹ (for the case when water permeates preferably, but a fraction of 20% acetic acid permeates too). As described earlier, these values are coupled, meaning that an increasing membrane area results in decreasing permeabilities.

This is the case for membrane areas up to 18,473 m². However, for larger membrane areas the permeabilities increase, indicating the separation process is less effective and uses more energy.

In practice, the values for membrane area and permeabilities will probably be higher, but the found values are not unrealistic, so a membrane meeting these performances could be found for this separation. A pervaporation membrane in the bottom stream appears to be even more profitable than placing the membrane unit in the top stream.

5. Conclusions

Since there is a great lack of a design and optimisation program for membrane processes, a combination of Excel Visual Basic for Applications and Aspen Plus is used to develop simulation and design software for hybrid pervaporation processes. By using this combination of programs, the user is able to maintain control over and during the entire simulation.

The program developed is tested for two cases. For both cases elementary and simple economic calculations have been performed to acquire an indication of the economical advantage of a hybrid process. First, the purification of ethanol by hybrid pervaporation–distillation is simulated. A hybrid process was found to gain no economic profit. Secondly, the purification of acetic acid by means of a hybrid pervaporation–distillation process was investigated. A hybrid process appears to be very interesting, if a suitable membrane, having a stable performance under the process conditions, can be found for this separation.

This software provides a useful tool for designing and optimising hybrid pervaporation processes. Since it is a visual, windows-based and user-friendly software, it has great potential to be frequently used.

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