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Rigorous modelling and optimization of hybrid separation processes based on pervaporation

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Abstract: Hybrid separation processes are becoming more and more important in the practice if membrane technologies are also involved. In this work, a systematic investigation is completed for three sequence alternatives of distillation and pervaporation. These are the following: pervaporation followed with distillation (PV+D), distillation followed with pervaporation (D+PV), two distillation columns and a pervaporation unit between them (D+PV+D). The hybrid separation process alternatives are evaluated with rigorous modelling tools, but first, a rigorous simulation algorithm is determined for the pervaporation. The three hybrid separation processes are rigorously modelled with CHEMCAD, and optimized with the dynamic programming optimization method for the case of the separation of ethanol-water mixture. The objective function is the total annual cost (TAC).The energy consumption is also investigated. The selection of the ethanol-water mixture has two motivations: (i) it is quite often studied and well known, and (ii) to make biofuel (ethanol) production more economical, membrane technologies might also be applied. The results are compared with each other and with the classical separation completed with heteroazeotropic distillation. The optimized TAC shows that the distillation column followed with pervaporation is the most economical hybrid separation process alternative. Its TAC is about 66% of that of the classical separation.

Keywords: hybrid separation processes, CHEMCAD

1 Introduction

Engineers are permanently forced to design or develop production processes that fulfil product and production requirements in both economic and environmentally-conscious

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ways. During these activities the efficient use of natural resources should be realized, on the one hand, with e.g. the recycling of materials and/or energy (off-site or on-site) [1]. On the other hand, nowadays clean technologies are going to be applied more and more to complete environmental expectations and also contribute to sustainable development and consumption.

A relatively new tool of clean technologies is the application of different kinds of membranes for separation purposes. Membrane separation technologies offer numerous advantages over other mass transfer processes, such as: high selectivity, low energy consumption, moderate cost to performance ratio, compact and modular design. Pervaporation is one of the newest and most rapidly developing membrane technologies and it has the advantage that it can be used for special separation tasks. The separation of liquid mixtures by pervaporation is namely not limited by the vapour-liquid equilibrium and azeotropic mixtures can be more simply separated with pervaporation than with classical distillation techniques such as azeotropic distillation. Depending on the type of membrane applied, the pervaporation can be also a successful separation alternative for the solution of different complicated separation processes; e.g., dehydration of organic solvents, the recovery of organic compounds, and the separation of organic mixtures. Currently, about one hundred pervaporation units are operating world wide; most of them dehydrate different solvents, such as ethanol, isopropanol, tetrahydrofurane, etc. [2–8]. Pervaporation systems are now commercially available for two major applications [9]. The first and most important one is the removal of water from concentrated alcohol solution. GFT, now owned by Sulzer, the leader in this field, installed the first pilot plant in 1982. The second commercial application of pervaporation is the removal of small amounts of volatile organic compounds (VOCs) from contaminated water [10, 11]. This technology was developed by Membrane Technology and Research [12–14]; the first commercial plant was sold in 1996.

In recent years, pervaporation has established itself as one of the most promising membrane technologies [3]. Generally, in many cases, the pervaporation alone can not supply products suitable for further processing or waste disposal [11]. That is why pervaporation is usually combined with other separation processes such as distillation, liquid-liquid extraction, adsorption, and stripping. The advantages of a pervaporation process can be even increased with special combinations. Such combined separation processes are the so called hybrid separation processes [2]. These hybrid separation processes are becoming more and more important in the practice and newer and newer processes are designed due to the more and more complex separation problems. The advantages of the application of hybrid separation processes are that the different kinds of unit operations can mutually strengthen their merits, and more effective separation processes can be constructed than only with using homogenous separation units [15].

The proper design of hybrid separation processes needs, however, comprehensive engineering knowledge and design tools. One important design tool is the rigorous modelling of the individual units of the designed hybrid separation process [16–18]. Such rigorous modelling can be completed with professional flowsheeting software packages such as ASPEN [19–21] or CHEMCAD. In order to commercially apply any new process, the influence of different parameters must be well understood. With the help of the professional flowsheeting software packages such an investigation can be completed. These professional software tools contain reliable physical property data banks and also rigorous models for several chemical engineering units. With the help of the flowsheeting software packages, the design parameters of the unit operations can be determined with exhaust and reliable modelling and optimization according to a defined objective function. Since the pervaporation is a relatively new separation method its rigorous model is not yet included in the flowsheeting packages.

There have been incentives to enable these software packages for such an investigation with the addition of a pervaporation module. A module in AspenPlus environment solves mass and energy balances for pervaporation by using an empirical model for heat and mass transfer. The empirical model is based on experimental results [10].

In our work three hybrid separation process alternatives (different combinations of distillation and pervaporation) are investigated with the professional flowsheeting tool CHEMCAD. The pervaporation mass transport is described with the "solution-diffusion" model. The different hybrid separation process alternatives are compared on an economic basis with each other and with a non-hybrid separation alternative considered as base case. To complete such a comprehensive investigation, first the "solution-diffusion" model of the pervaporation is transformed into the professional software environment.

2 Modelling of pervaporation

Pervaporation is a method for separation of two or more components in a liquid mixture. The separation can take place through a non-porous permselective membrane [22–25]. The liquid feed-mixture is circulated in contact with the membrane, and the permeate is collected in vapour phase on the opposite side of the membrane, that is under vacuum. The transport of the permeate through the permselective membrane film involves three successive steps:

- selective sorption
- selective diffusion
- desorption

Behaviour of the pervaporation membrane used to separate a binary A-B liquid mixture is characterized by two experimental parameters, the selectivity (α) and the permeate flux (J). The selectivity can be also defined as follows [26]:

$$\alpha = \frac{\frac{c_{AP}}{c_{BP}}}{\frac{c_{AF}}{c_{BF}}} = \frac{c_P \cdot (1 - c_F)}{c_F \cdot (1 - c_P)} \tag{1}$$

c_F and c_P are the concentrations of the permeating component (A) in the feed and in the permeate, respectively. The permeate flux can be expressed with the following equation:

$$J_i = \frac{1}{a} \frac{dv_i}{dt} \tag{2}$$

where a is the active membrane area, dv_i is the volume of permeate for component i during dt period of time.

Since the permeated material flow is usually not known, the flux should be also defined in a different way. The ideal sorption and diffusion behaviour shows Fick's law function:

$$J_i = -D_i \nabla c_i \tag{3}$$

where D_i is the diffusion coefficient and ∇c_i is the driving force.

The advantage of Fick's law is that it is extremely simple in mathematical form but it has, however, the disadvantage that the diffusion coefficient depends on the concentration in a very complicated form when dealing with non-ideal systems.

There have been several attempts to model the pervaporation with the proper application of diffusion coefficients - e.g., Nagy [27].

Baker [9] has investigated the effect of concentration polarization in liquid separation processes. He has found that the "concentration polarization modulus" in the case of pervaporation applied for dehydration is practically equal to 1. That means, that the concentration polarization has negligible effect in such cases.

To overcome this problem, Rautenbach [22] has recommended a model for pervaporation. The model is the so called "solution diffusion" model which corresponds to the physical occurrence of pervaporation. The model is capable of describing the behaviour of pervaporation if a so called "composite" membrane is applied. The composite membranes have two layers: a permselective active layer and a porous support layer. The model expresses the molecular transport practically with the gradient of chemical potential because in this case the transport coefficient, $\overline{D}_{i0}$ can be applied to describe the pervaporation. The transport coefficient depends on the concentration but in a negligible way [22].

$$J_i = -\frac{cD_{i0}}{f_{i0}} \frac{1}{\gamma_i} \nabla f_i \tag{4}$$

or, in one-dimensional case

$$J_i = -\frac{cD_{i0}}{f_{i0}} \frac{df_i}{dz} \tag{5}$$

where f is fugacity for component i.

The integration of equation (5) results in:

$$J_i = \frac{cD_{i0}}{\delta \overline{\gamma}_i} \left(\frac{f_{i1-f_{i3}}}{f_{i0}} \right) = \frac{\overline{D}_{i0}}{\overline{\gamma}_i} \left(\frac{f_{iF} - f_{iP}}{f_{i0}} \right) \tag{6}$$

$\overline{\gamma}_i = \sqrt{\gamma_{iF} \cdot \gamma_{iP}}$ and $df_i = f_{iF} - f_{iP}$.

The temperature dependency of the thermodynamic diffusion coefficients - D_{i0} if the Fick's law is concerned, or the transport coefficient $\overline{D}_{i0}$- follows an Arrhenius type law:

$$\overline{D}_{i0} = \overline{D_{i0}}^{\bullet} \exp \left(\frac{E_{i0}}{R} \left(\frac{1}{T^{\bullet}} - \frac{1}{T} \right) \right) \tag{7}$$

The support layer of the composite membrane is a porous layer and it should be also described. The flux through the porous layer can be described with:

$$J = Q_0 \Delta p_{por} \tag{8}$$

where p_{por} is the pressure drop on the porous layer.

The description of the flux of the individual components through a composite membrane needs the combination of eq 6 and 8. Considering the low pressure, the fugacity values can be replaced with the pressure values. The combination results in the following equation that describes the flux through a composite membrane:

$$J_i = \frac{1}{1 + \frac{\overline{D}_{i0}}{Q_0 p_{i0} \overline{\gamma}_i}} \cdot \frac{\overline{D}_{i0}}{\overline{\gamma}_i} \cdot \left(\frac{p_{iF} - p_{iP}}{p_{i0}} \right) \tag{9}$$

The parameters of the model $(Q_0, \overline{D_{i0}}\,^{\bullet}, E_{i0})$ should be determined with pervaporation experiments made with liquid mixture on the membrane selected for application. If the coefficients are determined, the modelling of the pervaporation can be solved.

Since the aim of this work is to model the pervaporation in a professional software environment and those software tools are not prepared for such a situation, the problem should be solved in a different way. Instead of solving a differential equation system, a difference equation system can be applied supposing such an infinitesimally small piece of membrane area/section (a_{inf}) where constant feed composition and temperature can be supposed; that is, the volume of the membrane unit assigned to this small membrane area is considered as a perfectly mixed volume. The pervaporation can be modelled with the equation (9) for such a small membrane area [28]. The total membrane can be divided into "n" hypothetical pieces of small membrane section:

$$n = \frac{a}{a_{inf}} \tag{10}$$

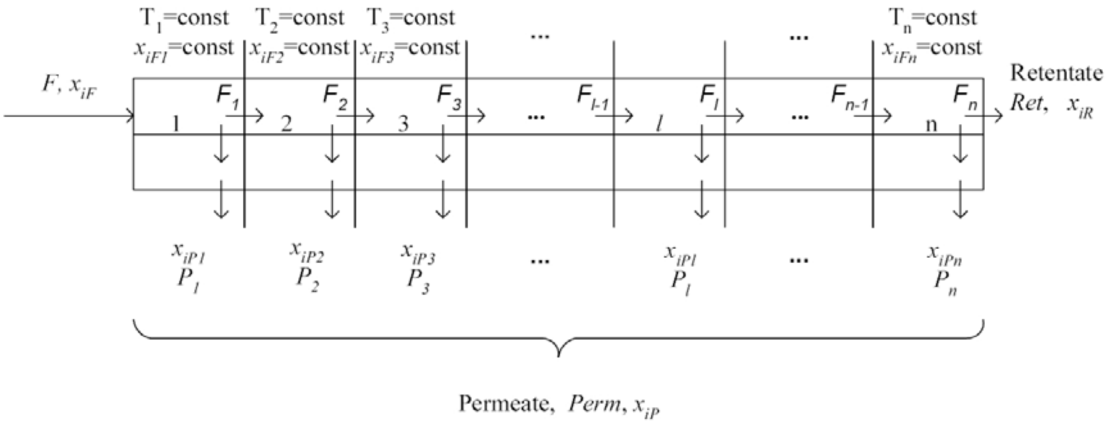

Fig. 1 Scheme for the modelling of pervaporation supposing sections.

The heat and material balances can be determined (see Figure 1). For the overall membrane it can be written that:

$$F = Ret + Perm \tag{11}$$

$$F \cdot x_{iF} = Ret \cot x_{iR} + Perm \cdot x_{iP} \tag{12}$$

For any selected small membrane section, it can be also written that:

$$F_{l-1} = F_l + P_l \qquad l = 1...n \tag{13}$$

$$F_0 = F \tag{14}$$

$$F_n = Ret \tag{15}$$

The permeate flow of any selected small membrane section is:

$$P_i = \left(\sum_{i=1}^{k} J_i \right) \cdot a_{inf} \qquad i = 1...k \tag{16}$$

where k is the number of pervaporating components

$$Perm = \sum_{l=1}^{n} P_l \tag{17}$$

The heat balance for any small membrane section can be also determined. Since the heat requirement of the pervaporation is covered by the sensible heat of the feed flow, if no external heating is applied, the temperature drop of the feed flow after every small membrane section can be determined

$$\Delta T_l = \frac{\left(\sum_{i=1}^{k} \lambda_i \cdot J_i \right) \cdot a_{inf}}{F_l \cdot c_{Pl}} \qquad l = 1...n \tag{18}$$

The temperature of the permeate flow is supposed to be equal to the temperature of the liquid flow leaving the hypothetical small membrane section ($T_1, T_2 \ldots$ etc). In the user added subroutine written in CHEMCAD, internal iterations are applied for each small membrane area section to obtain more accurate data, with convergence. Isothermal option of the pervaporation is also an option of the user-added CHEMCAD subroutine. In those cases the heating requirement is calculated with the help of the heat balance.

An important parameter of this calculation is the area of the small membrane section where constant composition and temperature can be still supposed. It can be determined in such a way that always smaller and smaller membrane sections are supposed, and the whole membrane is modelled with the small membrane sections supposed. If the calculated data with decreasing membrane section area is not changing, the section area can be accepted. A test calculation is made with changing membrane section area. The feed stream is 100°C, 100 kg/h, 94 wt% ethanol and the membrane area is 50 m^2. Figure 2 shows the retentate stream and its composition changes with growing number of membrane sections related to 1 m^2 membrane area. In this case the 20 hypothetical membrane section per m^2 gives acceptably good result.

This model based on Rautenbach's work [22] with our development is quite suitable for engineering calculations and design. The additional heat balance enables the calculation both in isothermal and adiabatic way [28]. According to this model, a special user added subroutine is written in the frame of the CHEMCAD software.

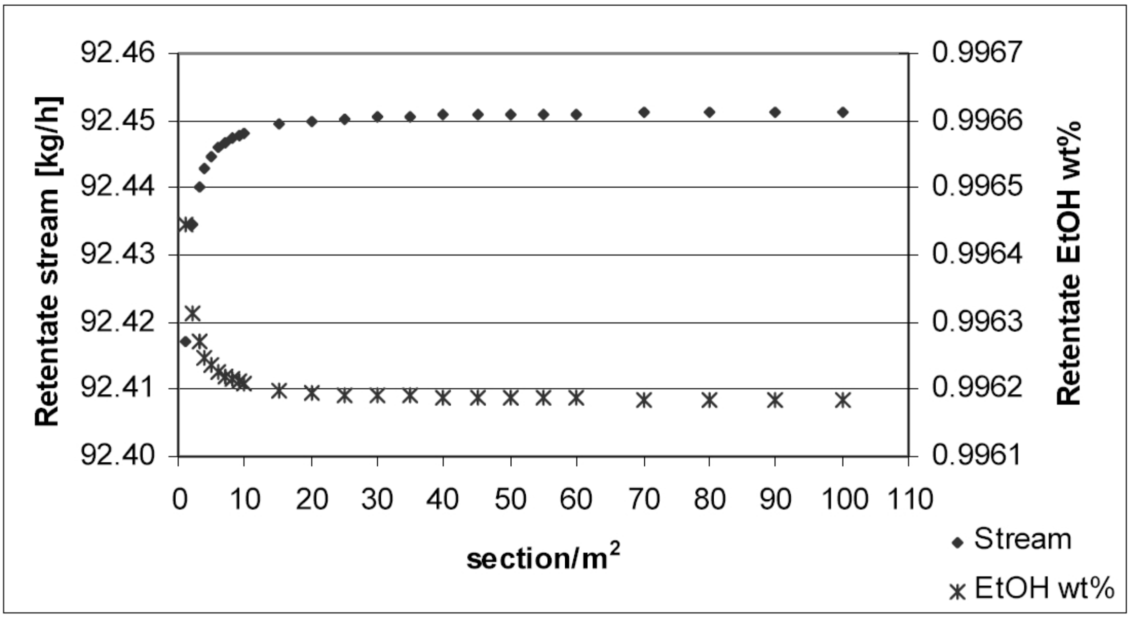

Fig. 2 Changes with number of membrane section.

3 Experiments

The user-added subroutine written according to equations 6–18 needs the parameters of pervaporation, that is, the transport coefficients for each component at fixed temperature ($\overline{D^{\bullet}_{i0}}$), the activation energy for each component (E_{i0}), and the permeability (Q_0). These parameters are determined with experiments. Ethanol-water system and composite membrane (PERVAP 2210 commercial PVA/PAN membrane) are selected since later the results of the rigorous design are compared with experiments.

The pervaporation experiments are carried out using a CM-CELFA MEMBRANTECHNIK AG P-28 pervaporation apparatus. The effective membrane area is 28 cm^2. The temperature of the system is controlled at a constant value (Figure 3). The permeate side is under vacuum of 8 mbar. The permeate solution is collected in a trap cooled with liquid nitrogen and analyzed by gas chromatograph (GC-14B standard model, Shimadzu Co). During the measurements, this analytical method is always applied. The fluxes of both components are determined. On the behalf of the measurements at different conditions, the parameters of the system needed for the model of the pervaporation are determined and applied for rigorous simulations.

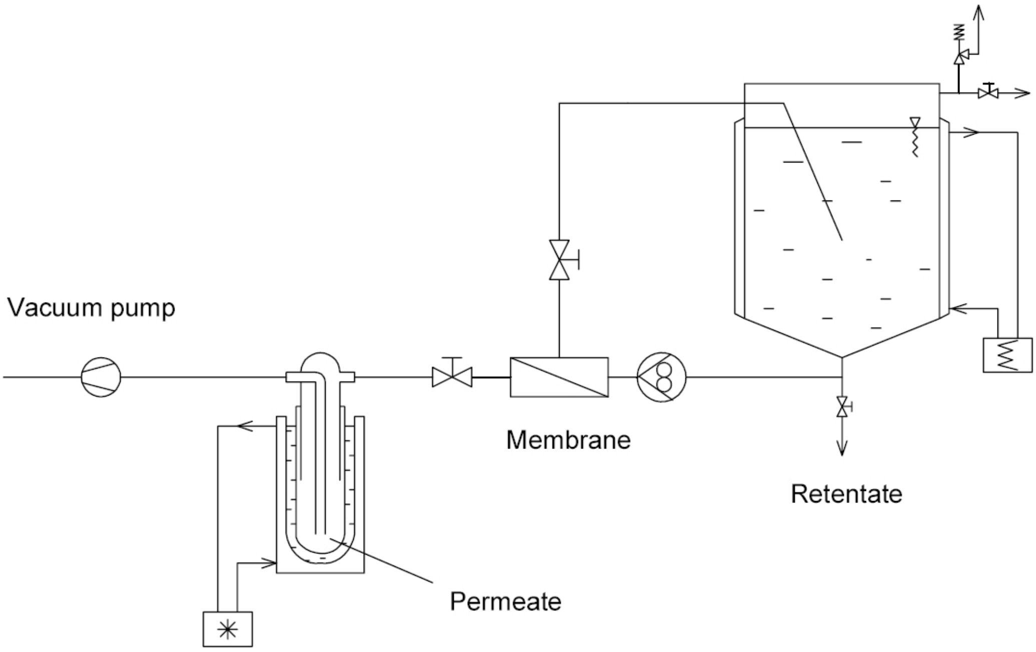

Fig. 3 Laboratory pervaporation system.

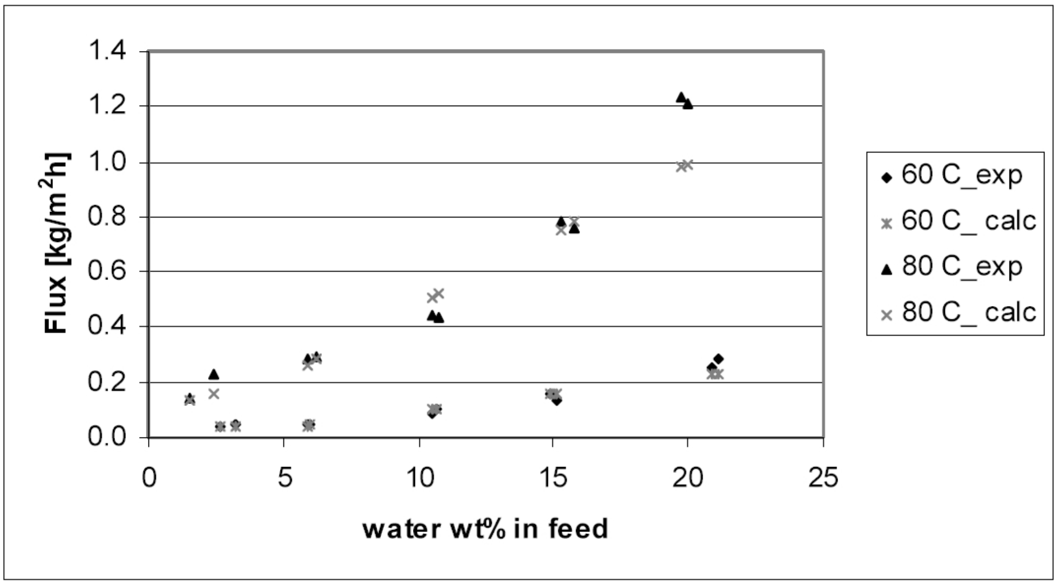

Fig. 4 Experimental and modelled Flux data by ethanol dehydration.

The measured and calculated flux and permeate composition data are compared. The comparisons are presented in Figures 4, 5 and they show good agreement.

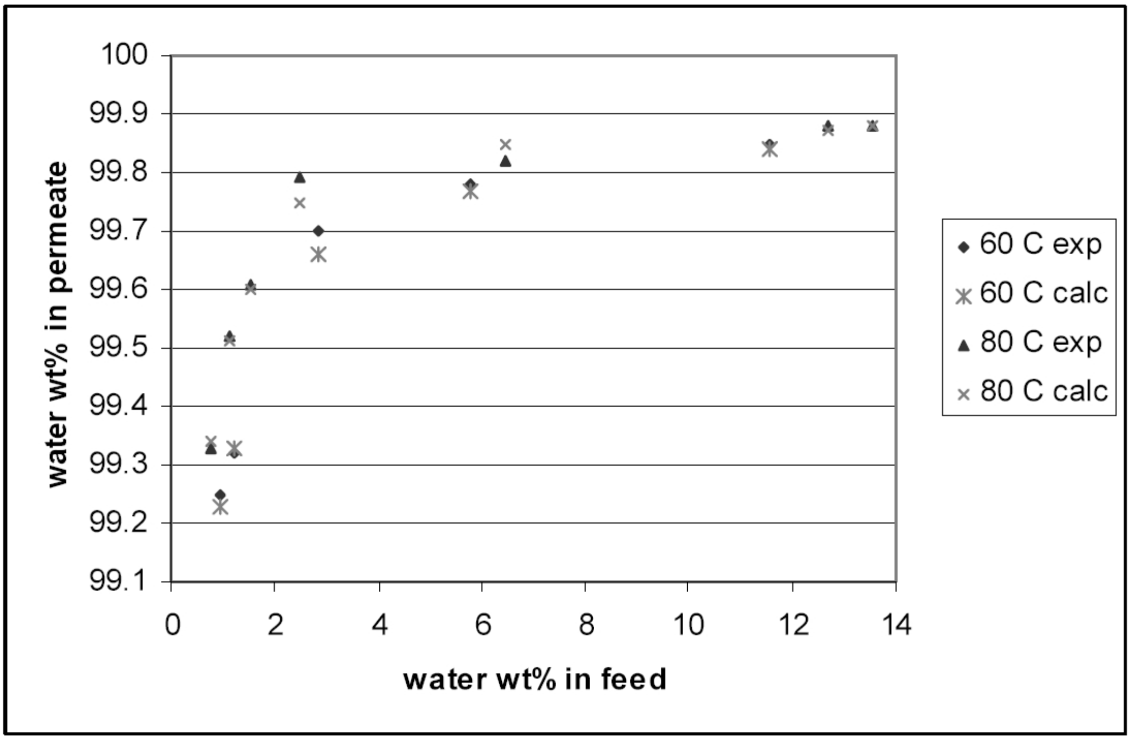

Fig. 5 Experimental and modelled permeate composition data by ethanol dehydration.

4 Results and discussion

4.1 Systematic investigation of hybrid separation processes

The hybrid separation processes which consist of distillation and pervaporation are very efficient for the separation of such organic compound and water mixtures, dehydration, where compounds form azeotrope since the pervaporation is not limited by the azeotrope. For the dehydration of such organic compound with distillation technique, e.g. azeotropic distillation is usually a complicated and expensive solution [29].

There can be several alternatives for the coupling of the distillation and pervaporation and a systematic investigation can be carried out.

The coupling of these two kinds of units can happen in different ways:

(1) Pervaporation followed with distillation of the permeate stream (PV+D);
(2) Distillation followed with pervaporation (D+PV);
(3) Distillation followed with pervaporation and another distillation (D+PV+D).

These three schemes of hybrid separation processes are designed with the help of rigorous modelling. The alternatives are optimized with dynamic programming. The objective function of the optimization is the total annual cost.

The results are compared with the classical azeotropic distillation, which is considered as base case. The mixture to be separated is an industrial problem (Table 1), that is the separation of ethanol and water. The product purity prescriptions are also taken from the industry. This mixture is deliberately selected since its behaviour is well studied and known, industrial data are available for its pervaporation, and the biofuel incentives all over the world makes its economics of separation actual again [30].

Table 1 Investigated separation problem.

Feed (F_{in}) [l/h]	800
Composition vol%	20 vol% water 80 vol% ethanol
Temperature [°C]	60
Pressure [bar]	1
Product purity requirement	99.7 wt% ethanol 99.9 wt% water

Both isothermal and adiabatic pervaporation cases are simulated to see its effects and obtain general conclusions. The optimisation steps are always completed according to the dynamic programming optimization method [31].

4.1.1 Pervaporation followed with distillation of the permeate stream (PV+D)

The hybrid separation process is shown in Figure 6. The basic data of the streams are shown for isothermal pervaporation in Table 2 and for adiabatic one in Table 3. The mixed feed stream (FF), the mixture of the feed (F_{in}) and the recycled distillate (D1), is fed into the membrane unit. At the retentate side, ethanol is obtained at the required purity. The permeate stream contains about $8-10$ wt% ethanol. The ethanol is recovered in a distillation column as distillate and recycled to the feed stream. The bottom product of the distillation column is pure water and it is assumed at the design step that the top product (distillate) has the same composition as the feed stream.

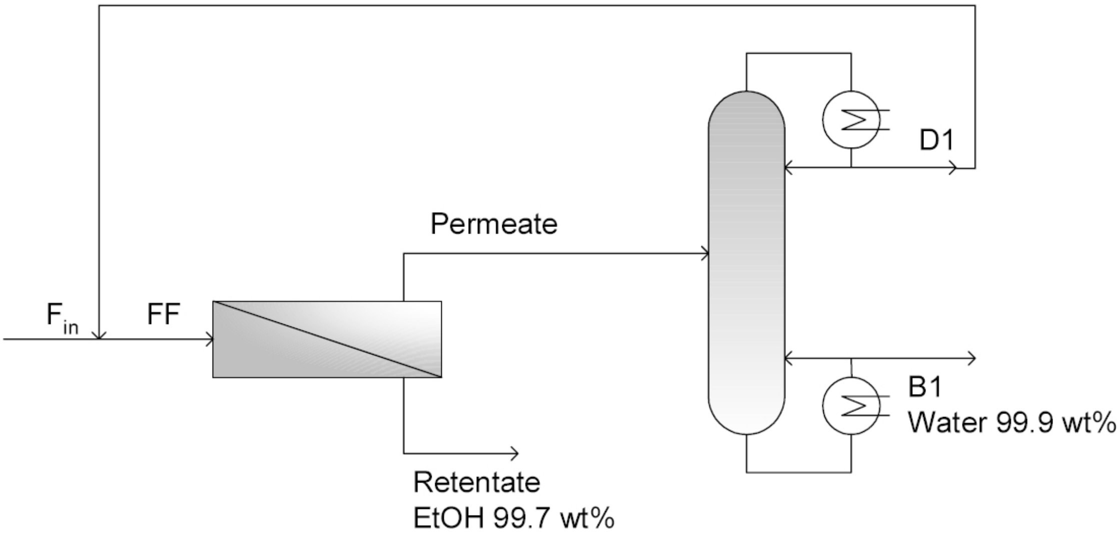

Fig. 6 Pervaporation followed with distillation (PV+D).

Table 2 Technological streams of isothermal pervaporation, PV+D.

PV+D	*FF*	*Permeate*	*Retentate*	*D1*	*B1*
Stream [kg/h]	690.60	179.69	510.91	21.1	158.59
EtOH wt%	80 vol%	9.2	99.7	80 vol%	0.1
Water wt%	20 vol%	90.8	0.3	20 vol%	99.9

Table 3 Technological streams of adiabatic pervaporation, PV+D.

PV+D	*FF*	*Permeate*	*Retentate*	*D1*	*B1*
Stream [kg/h]	688.92	177.86	511.06	19.39	158.47
EtOH wt%	80 vol%	8.3	99.7	80 vol%	0.1
Water wt%	20 vol%	91.7	0.3	20 vol%	99.9

During the rigorous simulation and optimization the objective function is the total annual cost. The manipulated variables are the necessary membrane area, the size of the distillation column(s) and their operating parameters, and the interconnecting streams between the units are to be determined.

4.1.2 Distillation followed with pervaporation (D+PV)

The opposite coupling of the two units is also investigated (Figure 7). The basic data of the streams are shown for isothermal pervaporation in Table 4 and for adiabatic one in Table 5. In this case the distillation is followed with the pervaporation. The mixed feed (FF), the mixture of the feed (F_{in}) and the permeate, is introduced into the distillation column. The bottom product is pure water. The distillate is fed into the pervaporation unit. This stream is concentrated there. The retentate stream contains 99.7 wt% ethanol. The permeate stream is about 8% of the feed (F_{in}). It is recycled and mixed to the feed. Control simulations show no significant change in system parameters if the permeate flow is recycled and fed individually into the distillation column.

Table 4 Technological streams of isothermal pervaporation, D+PV.

PV+D	*FF*	*Permeate*	*Retentate*	*D1*	*B1*
Stream [kg/h]	726.39	56.86	510.93	567.79	158.60
EtOH wt%	72.0	22.8	99.7	92.0	0.1
Water wt%	28.0	77.2	0.3	8.0	99.9

The composition of the distillate, the size of the distillation column, and the necessary membrane area are determined at the optimization step to achieve the minimal total annual cost.

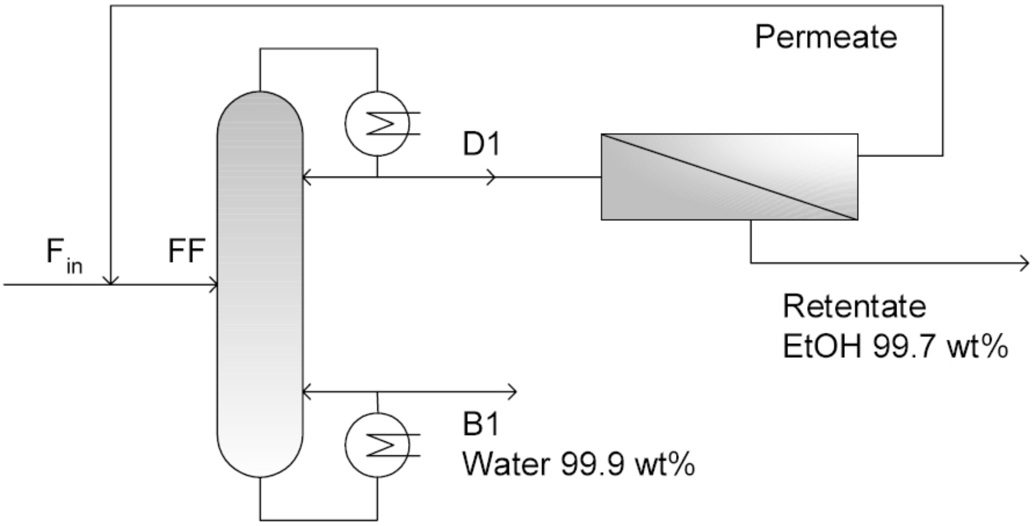

Fig. 7 Distillation followed with pervaporation (D+PV).

Table 5 Technological streams of adiabatic pervaporation, D+PV.

PV+D	*FF*	*Permeate*	*Retentate*	*D1*	*B1*
Stream [kg/h]	721.68	52.15	510.57	562.72	158.96
EtOH wt%	72.6	72.7	99.7	93.0	0.1
Water wt%	27.4	27.3	0.3	7.0	99.9

4.1.3 Distillation followed with pervaporation and another distillation (D+PV+D)

The third investigated hybrid separation system consists of the following units (Figure 8): a distillation column, a pervaporation unit, and another distillation column. In the first column the mixture of the feed stream and the recycled permeate (FF1) is concentrated close to the azeotropic composition. This is the distillate (D1) which is fed into the pervaporation unit only for breaking the azeotrope composition; that is, to increase the ethanol composition in the retentate above the azeotropic point. The retentate is fed into the second distillation column where pure ethanol (99.7 wt%) is produced as bottom product. The distillate of the second distillation column (D2) is fed back into the pervaporation unit. Therefore, the real feed of the pervaporation unit (FF2) is the mixture of D2 and D1. The compositions of the products of the distillation columns and the connecting flows are shown for isothermal case in Table 6 and for adiabatic case in Table 7. The size of the two distillation columns and the membrane area are determined with the optimization.

This hybrid separation system has the advantage over the other two systems in that this can produce ethanol at any desired purity, even close to 100% which is usually a typical requirement for gasoline replacement. Namely, at such product purity, the membrane separation can result in high recycle streams. However, membrane development might help to overcome this problem.

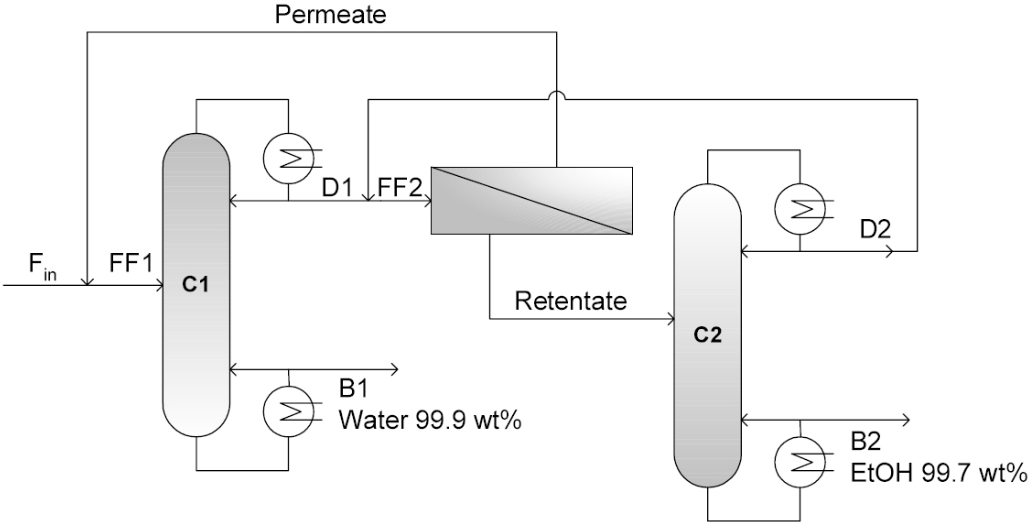

Fig. 8 Distillation followed with pervaporation and another distillation (D+PV+D).

Table 6 Technological streams of isothermal pervaporation, D+PV+D.

D+PV+D	*FF*1	*D*1	*B*1	*FF*2	*Perm*	*Ret*	*D*2	*B*2
Stream [kg/h]	723.49	564.90	158.59	634.59	53.97	580.62	69.69	510.93
EtOH wt%	71.9	92.0	0.1	92.7	19.1	99.5	98.0	99.7
Water wt%	28.1	8.0	99.9	7.3	80.9	0.5	2.0	0.3

Table 7 Technological streams of adiabatic pervaporation, D+PV+D.

D+PV+D	*FF*1	*D*1	*B*1	*FF*2	*Perm*	*Ret*	*D*2	*B*2
Stream [kg/h]	730.26	571.53	158.73	598.45	60.74	537.71	26.92	510.79
EtOH wtWater wt								

This advantage enables the D+PV+D system to be seriously considered for the production of ethanol as gasoline replacement.

4.1.4 Azeotropic distillation

The results of the hybrid separation processes are compared to the result of the classical separation method azeotropic distillation, or more specifically, heteroazeotropic distillation. This separation using cyclohexane as entrainer is also investigated (Figure 9). The basic flow streams are given in Table 8. The system consists of three distillation columns, phase separator, and several interconnecting streams. In the first column the bottom product is pure water (99.9 wt%) and the distillate is ethanol-water mixture of almost azeotropic composition (95.5 wt%). This mixture is the feed of the second distillation column where the entrainer is also added to get the ternary azeotrope in the distillate. The bottom product is the ethanol of 99.7 wt%. The top product is fed into the phase separator where the separation is facilitated with little water addition. The organic rich layer is recycled in the second distillation column. The water rich layer is processed in the third column and its bottom product is pure water.

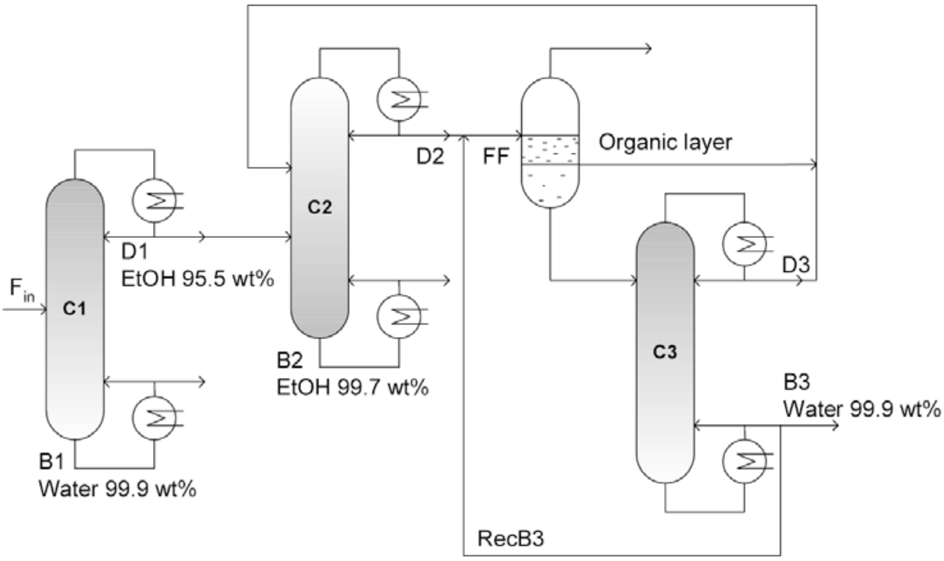

Fig. 9 Azeotropic distillation with cyclohexane as entrainer.

Table 8 Technological streams of adiabatic pervaporation, D+PV+D.

Azeotropic d.	*D*1	*B*1	*D*2	*B*2	*FF*	*Org.L.*	*D*3	*B*3
Stream [kg/h]	533.42	136.1	1234.85	510.92	1239.85	810.22	402.13	27.50
EtOH wt%	95.5	0.1	25.5	99.7	25.4	5.5	67.3	0.1
Water wt%	4.5	99.9	3.8	0.3	4.2	0.5	5.1	99.9
C6H12 wt%	-	-	70.7	-	70.4	94.0	27.6	-

This structure and the minimal cyclohexane needed are also optimized to obtain the minimal total annual cost.

5 Results of the rigorous modelling and optimization

During the design of the hybrid process alternatives, their basic parameters are determined with exhaustive rigorous simulation completed with professional software tool supplemented with the user added subroutine written for the modelling of pervaporation. The parameters of the pervaporation subroutine are determined with experiments.

Since the objective function of the hybrid separation process design is the total annual cost, the capital cost is estimated according to Douglas work and industrial data [32, 33]; the utility costs are also calculated. Table 9 shows the cost data used for the calculations. Continuous operation is assumed, the project life is 10 years, and one year consists of 8000 operating hours. Capital cost of replacing the membrane is also included in the objective function considering that they must be replaced every 2.5 years. Since the pervaporation unit production industry usually delivers the membrane units with the necessary heat exchangers, the price of a pervaporation unit (pervaporator) includes also the heat exchangers needed at pervaporation [33].

Table 9 Technological streams of adiabatic pervaporation, D+PV+D.

M&S (Marshall Swift)	1117
Low-pressure steam	18.1 USD/t
Cooling water	0.042 USD/t
Electric power	43 USD/MWh
Cyclohexane	11.4 USD/t
Membrane replacement cost	500 USD/m^2

With the application of the principles of the dynamic programming optimization method, the design parameters of the different hybrid separation process alternatives are determined so that the total annual cost should be minimal. These design parameters are the membrane surface, distillation column parameters (number of trays, feed tray location, reflux ratio, product purity) and operating conditions of the equipment items, flow rates, compositions of the flows, and energy requirement.

The step of optimization is presented for the D+PV scheme. An important design parameter is the composition of the distillate. If the distillate has low ethanol composition, a higher pervaporation unit is needed and vice versa. For that reason, an optimal distillate composition exists. The operation at the optimal distillate composition means also that the necessary parameters of the system are the optimal ones.

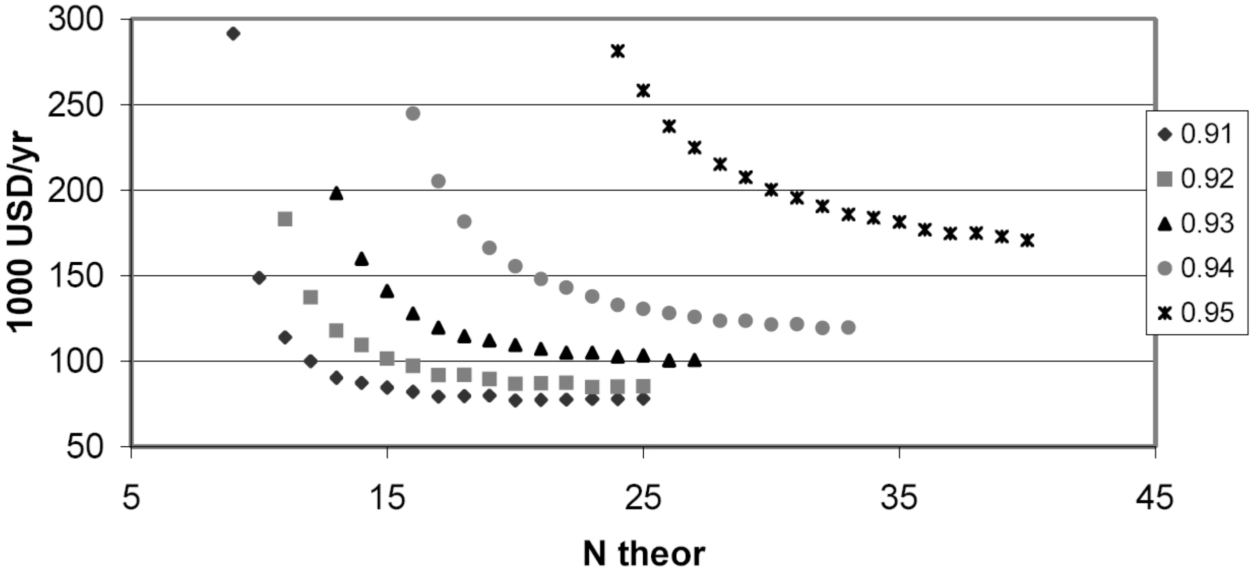

Fig. 10 Cost of distillation column.

Figure 10 shows the change of the cost of the distillation column of the D+PV hybrid separation system at different product purities (0.91 – 0.95 wt% ethanol) and different number of theoretical plates. The data represent the optimal parameters of the distillation column, that is, the optimal feed tray is located and the necessary reflux ratio is also determined.

It clearly shows that lower ethanol concentration in the distillate requires a smaller and cheaper distillation unit. This result is in agreement with the expectations. According to the dynamic programming, the pervaporation unit is involved in the subsequent step. The cost of the pervaporation unit consists of the capital cost and the operation costs considering heating and cooling, pumping, and vacuum cost [34]. The cost of the pervaporation related to annual basis should be summed up with the cost of distillation shown in Figure 10 but there can be two basic alternatives for consideration of the pervaporation: isothermal and adiabatic ones.

According to the experiences described also in the model applied, in the case of pervaporation the flux through the membrane is higher if the temperature is higher. Since during pervaporation the permeate is vaporized and the heat of evaporation is taken from the sensible heat of the feed, the temperature drops down if no extra heat is added to the system. If the temperature drops, the flux becomes lower and a pervaporator of higher membrane area is needed for the same performance. Since the price of the pervaporator is increasing with the area of the membrane, the heating has a paramount importance in the pervaporator. The pervaporator usually consists of several units of certain area and between these units the feed flow is reheated.

On the other hand, the pervaporator producers are motivated for better heat transfer in the pervaporator. Ad absurdum two extremes can be imagined: isothermal pervaporation and adiabatic pervaporation.

At the modelling of the pervaporation these two alternatives are considered in the user added subroutine developed in the frame of this work: (a) isothermal pervaporation, (b) adiabatic pervaporation. If the isothermal pervaporation is selected it results in the minimum membrane area. This alternative calculates also the heat requirement needed to guarantee the isothermal operation.

If adiabatic pervaporation is selected that gives a higher membrane area, the area of the individual units in the pervaporator should be also determined and the reheating between them should be also designed.

5.1 Isothermal pervaporation

In this first alternative isothermal operation of the pervaporator is assumed. The parameters of the pervaporator are determined and also its cost values.

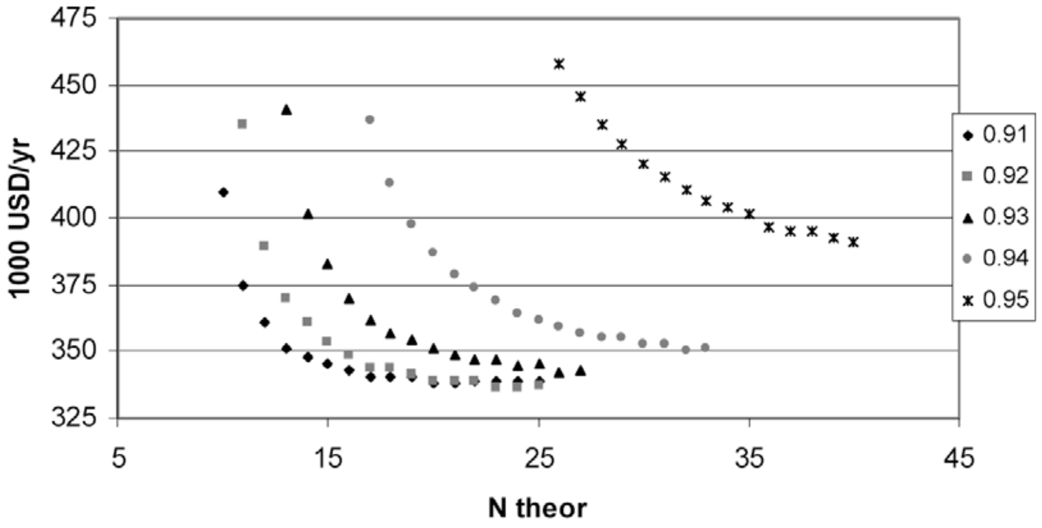

Fig. 11 Total annual cost of D+PV system.

Figure 11 shows the final result of the dynamic programming. On the contrary, to the individual column costs (Figure 10) the shape of the curves showing the total annual cost (TAC) change and they have different tendency. Curves cross each other and it is possible to find a minimal TAC at the distillate composition of 92 wt% ethanol as an optimum.

Table 10 Technological streams of adiabatic pervaporation, D+PV+D.

	PV+D	D+PV	D+PV+D		Azeotropic distillation		
Column			C1	C2	C1	C2	C3
N	11	23	23	65	50	18	18
N_F	4	20	20	44	46	3; 6	1
R	0.57	1.5	1.5	29.1	6.3	3.2	12.9
Diameter	0.152	0.457	0.457	0.610	0.762	0.762	0.762
$x_{D\ EtOH}$	20 vol%	92 wt%	92 wt%	98 wt%	95.5 wt%		
$x_{B\ EtOH}$	0.1 wt%	0.1 wt%	0.1 wt%	99.7 wt%	0.1 wt%	99.7 wt%	0.1 wt%
PV							
m^2	516	339	297		-		
$x_{Ret\ EtOH}$ wt%	99.7	99.7	99.5		-		
Cyclohexane						702 kg/h	

Similar optimization is made for the other schemes (PV+D; D+PV+D) and also for the base case of azeotropic distillation. The results of the data obtained with the optimization of dynamic programming are summarized in Table 10.

The total annual cost data of the investigated schemes are shown in Figure 12. It can be seen that the significant part of TAC is the investment cost of the pervaporator. In these cases, the biggest part of the operational costs is the heat-energy which is needed for the operation of the hybrid process.

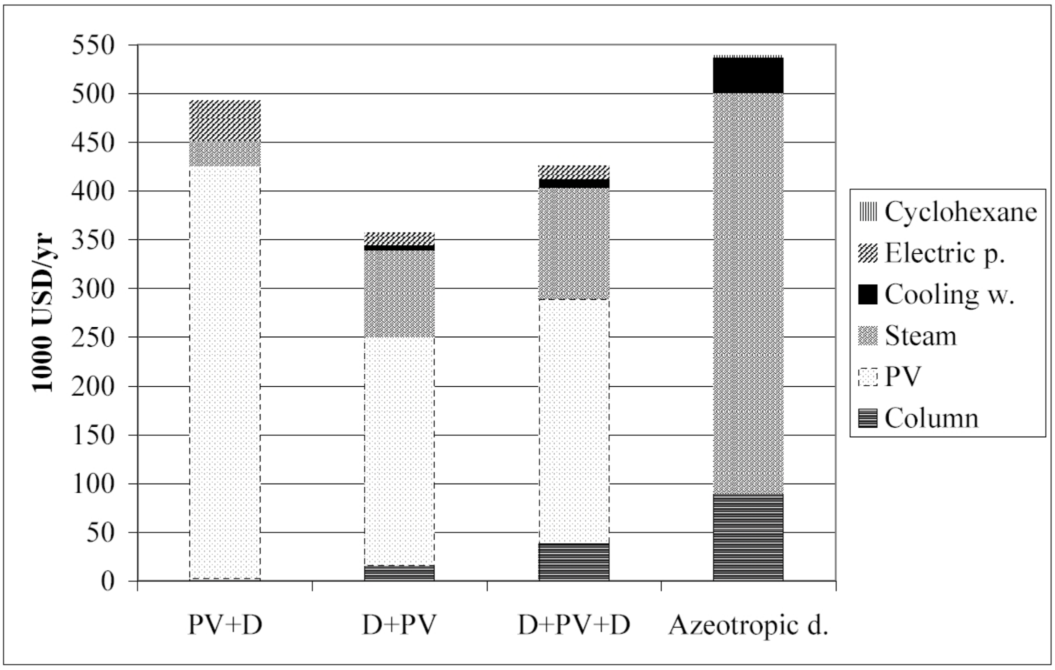

Fig. 12 Total annual cost with isothermal pervaporation.

In traditional azeotropic distillation, the steam demand is the biggest part of the cost items. It can be also seen that all of the three pervaporation based hybrid separation processes are more economical than the base case, the azeotropic distillation.

The most economical one is the distillation followed with pervaporation (D+PV) where the least material flow goes to the pervaporator.

5.1.1 Adiabatic pervaporation

The adiabatic operation represents such conditions where the heat transfer in the pervaporator takes place between its membrane units. According to real industrial examples and industrial case studies standard 27 m^2 membrane units are supposed and accepted.

The similar optimization procedures of dynamic programming are carried out also for these cases. Table 11 shows the optimal design parameters of the investigated schemes. In this case the optimal parameters change. It is important to remark that the necessary membrane areas are higher than in the corresponding isothermal case. This phenomenon results that in the case of D+PV in which the optimal distillate composition should be higher (93 wt%) than that of the isothermal one so that a pervaporator of smaller area than the isothermal one should be satisfactory for the requirement of the prescribed product composition.

Figure 13 shows the total annual costs of the investigated schemes in adiabatic mode compared with the base case, the azeotropic distillation. Since membrane areas of the pervaporators are higher than that of the isothermal ones, their investment costs are also higher. Due to this phenomenon the most expensive system is the pervaporation followed with distillation but the most economical one is the D+PV again.

Table 11 Optimal parameters of adiabatic pervaporation.

	PV+D	D+PV	D+PV+D		Azeotropic distillation		
Column			C1	C2	C1	C2	C3
N	11	26	20	66	50	18	18
N_F	4	23	16	54	46	3; 6	1
R	0.57	2	1.2	47.8	6.3	3.2	12.9
Diameter	0.152	0.610	0.457	0.457	0.762	0.762	0.762
$x_{D\ EtOH}$	20 vol%	93 wt%	91 wt%	97.5 wt%	95.5 wt%		
$x_{B\ EtOH}$	0.1 wt%	0.1 wt%	0.1 wt%	99.7 wt%	0.1 wt%	99.7 wt%	0.1 wt%
PV							
m^2	648	405	378		-		
$x_{Ret\ EtOH}$ wt%	99.7	99.7	99.5		-		
Cyclohexane						702 kg/h	

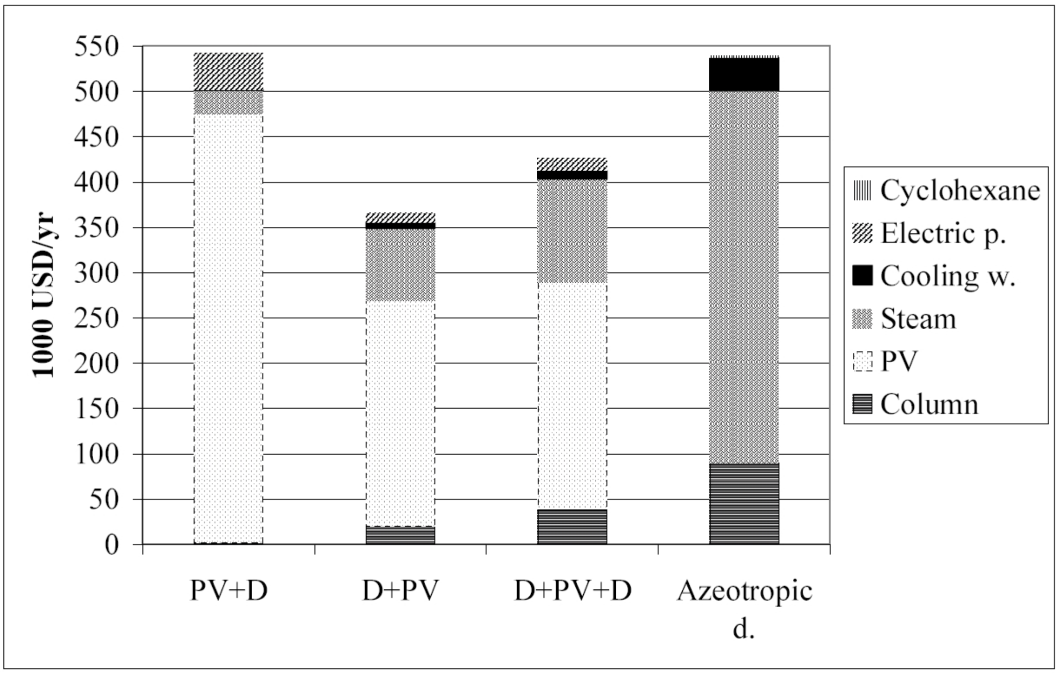

Fig. 13 Total annual cost with adiabatic pervaporation.

6 Comparison of energy consumptions

It is interesting to compare the energy requirement of the three hybrid separation processes and the base case, that is the azeotropic distillation. The energy consumption does not depend on the fact if adiabatic or isothermal pervaporations are considered, it is the same if the separation problem is the same.

Figures 12 and 13 show the results of the comparison where the energy costs are indicated, which are practically proportional with the energy consumption. The following conclusions can be determined:

- the azeotropic distillation has the highest energy cost and consumption by far,

- the D+PV+D alternative is more attractive than the azeotropic distillation if almost 100% pure ethanol should be produced e.g. as biofuel replacement. Its energy consumption is 33% of that of the classical separation solution,
- the PV+D alternative has the smallest energy cost and consumption It is 16
- the electric energy consumption becomes significant only in the case of the PV+D alternative.

The energetic investigation gives important information about the hybrid separation alternatives. The D+PV+D alternative helps to reduce both the costs and the energy consumption of biofuel production. It is worth mentioning that with membrane improvements it might become possible to produce practically 100% pure ethanol with reasonable recycle flow. Although the PV+D alternative is not the cheapest alternative, it has the smallest energy consumption.

7 Conclusions

The developed user added subroutine for rigorous modelling of pervaporation in professional software environment proves to be a useful and powerful tool for the design of hybrid separation processes also containing pervaporation. The systematic investigation of such hybrid separation processes that consist of distillation and pervaporation units is carried out and the optimal scheme of lowest total annual cost or energy consumption is determined with dynamic programming optimization method. The results show that a more efficient heat transfer in the pervaporation unit can decrease its area requirement and as a consequence its cost. According to the simulation of both isothermal and adiabatic pervaporation, it is found that the membrane area difference is about 10% between the two options. This cost reduction alternative is an important one since the capital cost of the pervaporation unit is the highest part of the total annual cost by far. It is also proved that the more economical scheme is that one if the distillation is followed with the pervaporation (D+PV) that is the possible least material flow is processed in the membrane unit. In the case of this scheme it is not a proper policy to design a distillation column producing a distillate of almost azeotropic composition since there is an optimum value for the distillate composition that is smaller with several percents than the azeotropic composition and depends on the cost of the pervaporation.

The D+PV+D scheme offers a more economical and also more energy efficient alternative for biofuel production compared to conventional azeotropic distillation, since this separation alternative is able to produce high purity ethanol without huge recycle streams. If only the energy consumption is considered, the PV+D scheme has the least energy requirement.

Acknowledgement

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Nomenclature

a	active membrane area, m^2
a_{inf}	area of infinitesimally small membrane section, m^2
A	component
B	component
c	concentration
c_P	coefficient of molar specific heat,$\frac{J}{mol\cdot K}$
D	diffusion coefficient, $\frac{mol}{m^2 s}$
$\overline{D}$	average transport coefficient, $\frac{mol}{m^2 s}$
$\overline{D^\bullet}$	average transport coefficient at fixed temperature, $\frac{mol}{m^2 s}$
E	activation energy, $\frac{J}{mol}$
f	fugacity, bar
F	feed flow, $\frac{mol}{s}$
F_{in}	industrial initial feed flow, $\frac{mol}{s}$
FF	mixed feed flow, $\frac{mol}{s}$
J	flux, $\frac{mol}{m^2 s}$
k	number of pervaporating components
p	pressure, bar
Δp_{por}	pressure drop on porous layer, bar
$Perm$	permeate flow, $\frac{mol}{s}$
Q_0	permeability coefficient of porous support, $\frac{mol}{m^2 s\cdot bar}$
R	ideal gas constant, $\frac{J}{mol\cdot K}$
Ret	retentate flow, $\frac{mol}{s}$
t	time, s
T	temperature, K
$T^\bullet$	fixed temperature, K
ΔT	temperature drop on feed side, K
v	volume of permeate, mol
x	mole fraction
z	dimension

Greek letters

α	selectivity factor
δ	thickness of the active layer, m
λ	heat evaporation, $\frac{J}{mol}$
γ	activity coefficient
$\overline{\gamma}$	average activity coefficient

Subscripts

i	general component index
F	feed side
l	index of the infinitesimally small membrane section
n	number of the infinitesimally small membrane section
P	permeate side
R	retentate side
0	pure component

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