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ENERGY EFFICIENT HYBRID PROCESSES FOR ETHANOL DEHYDRATION: A COMPARISON OF BENCHMARK AND MEMBRANE ASSISTED CONFIGURATIONS

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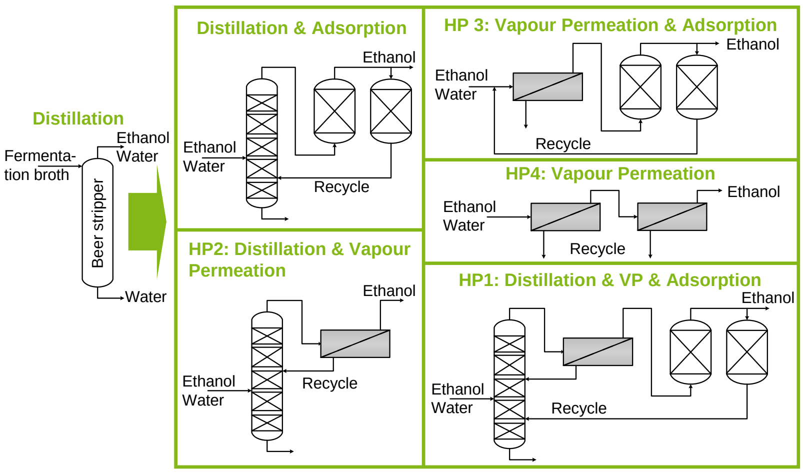
Abstract
One of the most promising processes for ethanol dewatering are hybrid separations consisting from different combinations of distillation with adsorption and/or vapour permeation. This paper presents a detailed process analysis showing the influence of decisive parameters on important target variables. The advanced mathematical models have been used for determination of optimal process configuration while using evolutionary algorithms.

Keywords: Hybrid separation process, vapour permeation, process analysis, optimization, dehydration of ethanol

1. Introduction

The development of new energy-efficient processes is a key issue for the chemical and petrochemical industry in order to remain competitive in the future. Especially for the separation of non-ideal multi-component mixtures into pure components, the smart combination of existing distillation processes with other separations can overcome existing limitations and bring about substantial synergies. The application of these so called hybrid separation processes can lead to an improvement in yield, production capacity and energy efficiency. Despite all advantages, hybrid separation processes consisting of distillation and membrane separation are not yet established in chemical and petrochemical industry mainly due to a short lifetime of the membranes, the lack of process know-how and no focus on energy efficiency in the past. The authors believe that hybrid separation processes become of more industrial relevance in the near future because of a continuing progress in the development of reliable membrane materials reported in literature in recent years[1,2] and increasing interest of industry in energy efficient processes. A very interesting example is the dehydration of ethanol. The benchmark process and four the most promising hybrid separation process configurations consisting of distillation, pressure swing adsorption and vapour permeation (VP) are presented in Figure 1.



- HP 1: Integration of VP into the benchmark process of distillation & adsorption [3]
- HP 2: Replacement of adsorption with vapour permeation Combination of distillation & vapour permeation
- HP 3: Replacement of distillation with vapour permeation: Combination of adsorption and vapour permeation
- HP 4: Replacement of distillation and adsorption. Vapour permeation as stand-alone process

Figure 1 Promising hybrid separation processes for dehydration of ethanol

In this paper the results of simulation and optimisation studies of these highly interlinked separation processes are presented. Each unit operation involved is simulated using the most reliable model i.e.

rate based approach for distillation, linear driving force approach for adsorption and a semi-empirical approach based on the solution-diffusion model for membrane separation. The parameters of the latter model have been determined experimentally in a lab scale vapour permeation setup. Detailed simulation studies of hybrid separation processes in industrial scale show the influence of decisive structural as well as operational parameters (e.g. recycle positions, transfer variables between the unit operations, reflux ratio) on ethanol yield, energy demand and operational costs. Finally process optimisations have been performed using an evolutionary algorithm. Two different types of dense polymeric membranes have been investigated.

2. Process modelling and experimental validation

In vapour permeation separation mechanism of mixtures consisting of components of different volatilities is similar to this for pervaporation (PV)[4]. It is based on different sorption and diffusion properties of the components in the membrane and interactions between the components themselves. Therefore the membrane separation is not limited by the thermodynamic vapour liquid equilibrium. PV and VP with hydrophilic membranes are mostly applied in industry for dewatering of organic solvents (e.g. isopropanol and ethanol) in combination with distillation[4-6]. But the application of organophillic membranes attracts more and more interest[8], e.g. for direct separation of ethanol from fermentation broth[9].

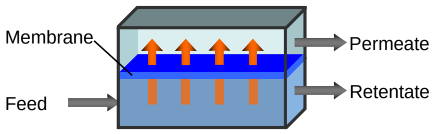


Figure 2 Principle of a vapour permeation membrane module

Figure 2 shows the working principle of a VP membrane module, which separates the vaporous feed into vaporous permeate and vaporous retentate. The separation mechanism can be described by the solution diffusion model[4], which assumes sorption on the membrane surface, diffusion through the membrane matrix and desorption into the permeate bulk phase. The transmembrane flux *J* of a component *i* is equal to the permeance Q_i multiplied by the driving force DF_i, which can be simplified seen as the difference of partial pressures or fugacities between feed and permeate:

$$J_i = Q_i \cdot DF_i \qquad (2)$$

The selectivity $\alpha_{i,j}$ for a binary mixture is defined as the ratio of permeances and shows the capability of a membrane to separate two components *i* and *j* [10].

$$\alpha_{i,j} = \frac{Q_i}{Q_j} \qquad (3)$$

Permeance and selectivity are the most important parameters characterizing a membrane[11]. Therefore they have been determined in a series of experiments for a commercial available polyimide membrane module provided by WHITEFOX TECHNOLOGIES LTD[12] and for a new type of membrane[13]. Both parameters have been than implemented into the model of the whole hybrid separation processes, consisting of combination of distillation with adsorption and/or vapour permeation. The model considers not only the unit operations but also peripheral devices like heat exchanger, pumps and compressors. The membrane model of Kreis[14] has been combined with the distillation column of Klöker et al.[15], which is based on the rate-based approach. For the simulation of the adsorption process a mathematical model based on the linear driving force approach (LDF)[16] has been implemented. Commercial available 3Å zeolites were applied and the equilibrium between solid and fluid phase is described with the Langmuir isotherm. Based on equations published in literature functions for calculating the costs were implemented in each model[17]. For the optimisation studies an evolutionary algorithm developed by Frerick et al.[18] was linked to the simulation tool.

3. Process analysis

A detailed process analysis and a process optimisation have been carried out for all hybrid separation process configurations presented in Figure 1. Exemplary results are presented in this paper only for the process configuration HP 4 consisting of a beer stripper and vapour permeation modules. Figure 3 shows a flow sheet with all relevant peripheral devices (heat exchanger, pumps, compressor, etc.).

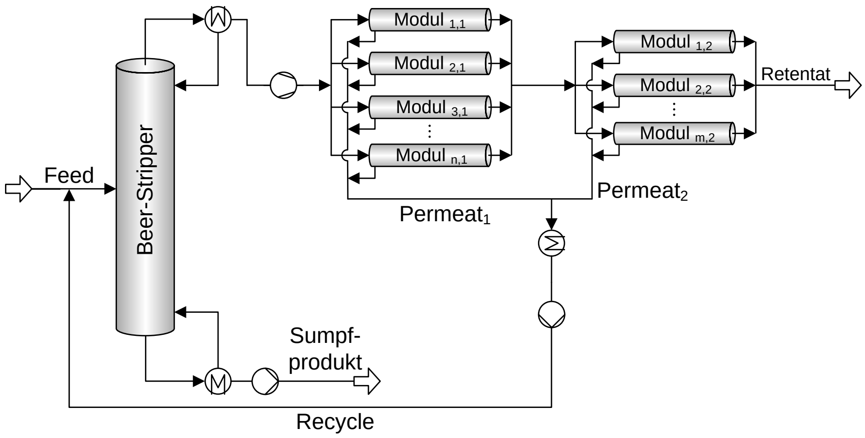


Figure 3 General flow sheet of hybrid separation process HP 4

The fermentation broth (ethanol mass fraction 10 wt-%) is separated by a distillation "beer stripper" up to specified ethanol mass fractions (45; 80; 92 wt-%). The separation occurs in batteries of parallel connected membrane modules, whereas the batteries can be connected in series. The desired ethanol purities are on the one hand 99.6 wt-% for the use as a car fuel and on the other hand 99.95 wt-% for the application in the chemical and pharmaceutical industry. Depending on the ethanol loss through the membrane, the permeate stream has to be recycled back to the distillation column. The distillate pressure of the beer stripper and the pressure of the membrane feed are important operating parameters of the process. Either the beer stripper can operate at the same pressure level as the membrane separation or a compressor between distillation column and membrane modules is necessary to increase the feed pressure of the membrane, which results into higher transmembrane fluxes and consequently smaller membrane area.

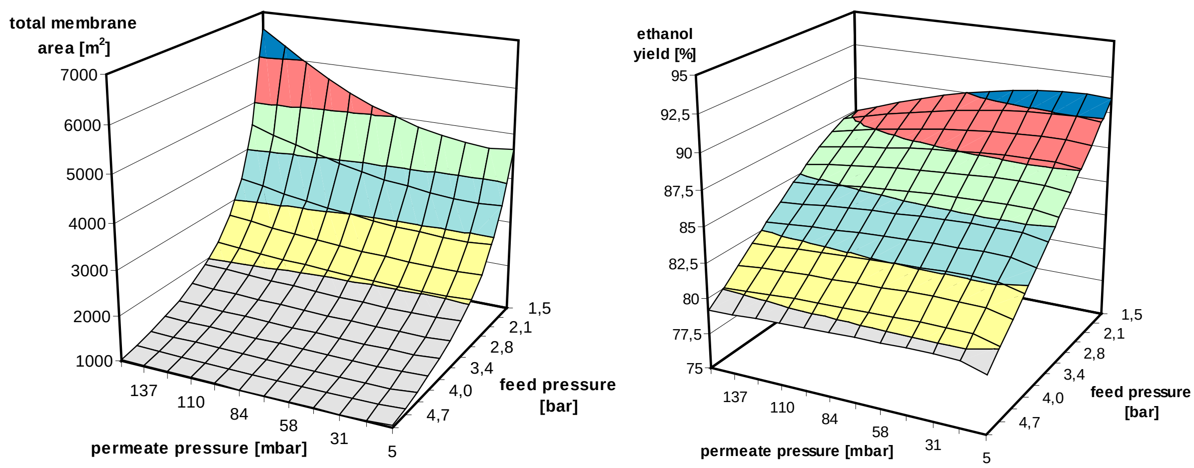


Figure 4 Influence of feed and permeate pressure on membrane area and ethanol yield; 45 wt.-% to 99.6 wt.-% ethanol; 25000 m³/a; Polyimide membrane (132 m²/module); single stage

Looking for the optimal process two main target variables should be considered: the total membrane area and the ethanol yield, which is defined as the ratio between ethanol mass flow in retentate and feed. The membrane area determines investment cost, whereas the ethanol yield is indirectly an indicator, how much ethanol has to be recycled to the beer stripper and thus affects the operating cost. In our study the influence of operating variables (temperature, feed and permeate pressure, permeances and selectivity) as well as structural parameters (module geometry, single battery or two batteries) has been investigated.

Figure 4 illustrates the strong influence of the feed pressure on total membrane area and ethanol yield. With increasing feed pressure the membrane area can be reduced significantly due to higher driving forces, while the ethanol yield decreases e.g. from 87% to 79% at a constant permeate pressure of 150 mbar. The minimum of costs results from the sum of investment and operating costs and thus can be reached at certain feed pressures. The pressure on the permeate side has no strong influence on area and yield for feed pressure higher than 2 bar since the driving force for water significantly decreases below that value. Thus the membrane area can be reduced and the ethanol yield increases. The permeate pressure decrease is limited through temperature of cooling water for the condensation of the permeate stream and is also taken into account for the cost optimisation.

The most common procedure to design and integrate a membrane separation into a whole process is to choose an available membrane type for a given separation and optimise the operating conditions. In this traditional approach “material”. i.e. membrane determines the “process” performance. Another way is the application of the innovative “materials by design” approach in which the separation process determines the optimal membrane characteristics, i.e. permeance and selectivity. It can be illustrated through the analysis of the influence of membrane selectivity at constant water permeances (100 and 250 mol/(hm²bar)) on total membrane area and ethanol yield for two separations (Figure 5 left: 45 to 99.6 wt.-% ethanol; right: 92 to 99.95 wt.-% ethanol).

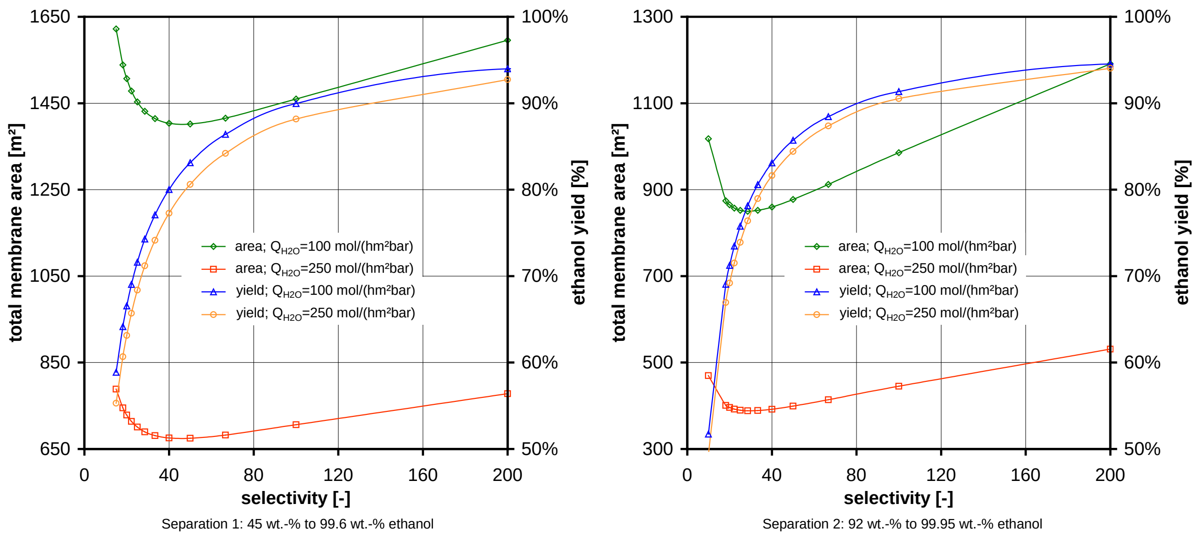


Figure 5 Influence of selectivity on membrane area and ethanol yield for two separations; 25000 m³/a; single stage; p_{Feed}: 5 bar; $p_{Permeate}$: 100 mbar

With increasing water permeance the transmembrane water flux increases and leads to a significant decrease of membrane area. A minimum of total membrane area can be observed for selectivities with values of 50 (left) and 29 (right) respectively. Very high selectivities result into high water concentrations on the permeate side and decreasing driving force for water is. Thus the water flux declines and membrane area increases. The ethanol yield decreases for very low selectivities, which leads to a significant increase in membrane area. The minimum of the total costs is not equal to the investment cost minimum, which is reached at a minimal membrane area, since at that point operating cost are high because of rather low ethanol yields around 80%. Therefore an optimisation of total costs with respect to the membrane selectivity is necessary. With this materials by design approach the costs can be significantly reduced, which leads to a competitive and energy efficient process.

4. Process optimisation

Basing on the process analysis the operating conditions (feed and permeate pressure) and the selectivity have been optimised to consider the impact of membrane area and ethanol yield on costs. The optimisation results of the feed and permeate pressure are exemplary presented in Table 1 for the separation from 45 wt.-% to 99.6 wt.-% ethanol and a production capacity of 25000 m³/a. The benchmark polyimide membrane has been applied in this study.

Table 1 Optimisation of feed and permeate pressure for HP 4

Pressure distillation	[bar]	2.3
Feed pressure VP	[bar]	4.1
Feed temperature VP	[°C]	141
Permeate pressure	[mbar]	213
Number of modules	[-]	11
Total membrane area	[m²]	1452
VP costs	[€cent/l]	8.4
Ethanol yield	[%]	80

Figure 6 shows a summary of several optimisations results, in which additionally to the operating conditions the selectivity and module geometry (fibre diameter, number and length) have been optimised. The table on the left side illustrates the costs of the VP with optimised operating conditions (temperature, feed and permeate pressure) for the separations from the specified ethanol mass fractions (45; 80; 92 wt-%) to the two product purities (99.6 wt.-% and 99.95 wt.-%). Generally the cost increase with higher product purity and lower ethanol concentrations in the feed, due to higher membrane areas. The bar diagram on the right side compares different optimisations for the separation from 80 wt.-% to 99.6 wt.-% ethanol related to the costs of the process with optimised feed and permeate pressure (4.6 €cent/l). It can be seen that with the capacity increase by factor of 10 costs can be reduced of about 15% (fourth bar). The second and fifth bar show results for the optimised module geometry. The costs can be reduced by 12% and 31% respectively. An additional improvement of 13% and 37% (third and sixth bar) can be achieved by optimising the membrane selectivity.

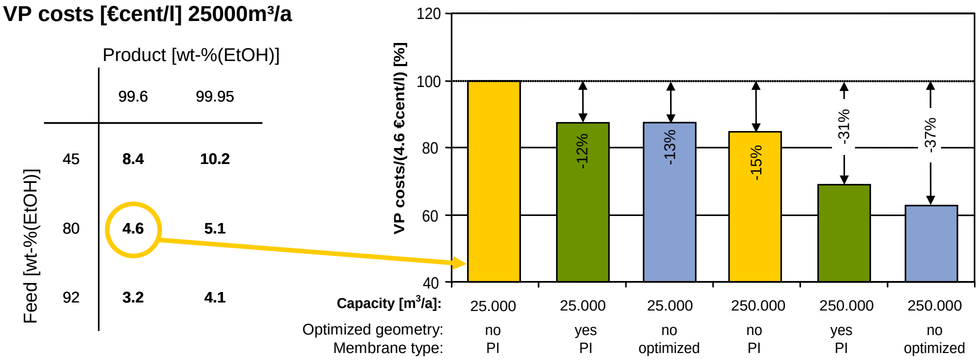


Figure 6 Summary of optimisation results for 25000 m³/a (table left) and comparison of different optimisation for 80 wt.-% to 99.6 wt.-% ethanol (bar diagram right)

5. Conclusion and Outlook

In this work different membrane assisted separation processes for the dehydration of ethanol have been investigated. The hybrid separation processes consist of distillation, adsorption and vapour permeation. These innovative combinations of different unit operations can overcome existing limitations and offers energy efficient and economic processes, due to arising synergy effects. For each unit operation rigorous mathematical models including peripheral devices are applied to perform a detailed process analysis. Finally an evolutionary algorithm is linked to the simulation tool to perform optimisation studies. In a process consisting of combination of vapour permeation and distillation feed and permeate pressure have a significant influence on membrane area and ethanol yield. Cost optimisation with respect to the feed, permeate pressure, and membrane selectivity have been performed. Finally a comparison of several optimisation results stress the potential of the hybrid separation process to achieve significant cost reduction by optimising operating conditions as well as structural parameters like module geometry and membrane selectivities.

In further studies a detailed comparison and evaluation of all process configurations should be performed. Additionally the alternative of the in-situ separation of ethanol from fermentation broth with pervaporation using a hydrophobic membrane [9] should be also considered.

Acknowledgements

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