# Hybrid membrane-distillation processes

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This work focuses on modelling, simulation and process analysis of hybrid membrane separations namely on distillation and pervaporation. Such hybrid process can be applied for the separation of multicomponent azeotropic mixtures without the use of entrainer. Its application is illustrated by the separation of a non-ideal ternary mixture of acetone, isopropanol and water. The extended abstract describes the process simulator for pervaporation and vapour permeation. For the stand-alone membrane process the simulation results are in satisfactory agreement with the gained experimental data. A comparison of different model complexities is presented. The process analysis of the hybrid process shows the influence of decisive operational parameters on process performance and the economic potential of the hybrid process.

## 1. Introduction

Complex distillation steps and/or the use of an entrainer are required to separate azeotropic mixtures into pure components. Industrially applied processes are azeotropic, extractive and pressure-swing distillation. Another sophisticated process consists of distillation and membrane separation. Especially pervaporation (PV) and vapour permeation (VP) are very suitable for this application, because membranes the separation is very selective and is not limited by the vapour-liquid equilibrium. Therefore hybrid membrane processes have attracted much attention in recent years. Despite all advantages hybrid membrane processes are not yet established in chemical industry due to a rather short lifetime of membranes and the lack of process know-how.

## 2. Membrane separation

Besides high selectivity and compact design, PV and VP facilitate the simple integration into existing processes. Volatile components are separated by a non-porous membrane due to different sorption and diffusion behaviour. Consequently the separation is not limited by the vapour-liquid equilibrium which is the main advantage compared to common separation processes. The driving force is the gradient of the chemical potential which is generated by lowering the partial pressure of the most permeating component on the permeate side. Usually this is achieved by applying vacuum. The main difference between PV and VP is that the feed in VP is supplied as vapour whereas in PV the feed components change their aggregate state from liquid to vapour while permeating through the membrane. In PV the energy to vaporise the permeate is provided by the liquid feed stream. Therefore the liquid stream exits the membrane module at a decreased temperature.

Two main parameters characterise membrane separation processes: **membrane permeability** (permeability coefficient) and **membrane selectivity**. Membrane permeability is defined by Koros et al. (1996) as permeate flux $J_{i,Memb}$ per unit transmembrane driving force $\Delta DF_{i,Memb}$ per unit membrane thickness $\delta_{Memb}$.

$$P_{i,Memb} \equiv \frac{J_{i,Memb}}{\Delta DF_{i,Memb} \cdot \delta_{Memb}} \tag{1}$$

In general the thickness of the active membrane layer is not accessible. Therefore the term permeance is introduced which is defined as

$$Q_{i,Memb} \equiv \frac{J_{i,Memb}}{\Delta DF_{i,Memb}} \tag{2}$$

Membrane selectivity $a_{ij}$ characterises the ability of a membrane to separate two different components (i and j) of a mixture. Selectivity is defined as the ratio of membrane permeabilities or (for a given membrane) permeances (Wijmans, 2003):

$$\alpha_{ij} \equiv \frac{Q_{i,Memb}}{Q_{j,Memb}} \tag{3}$$

Further definitions of membrane specific terms are presented by Koros et al. (1996).

## 3. Hybrid membrane separation

The combination of pervaporation and distillation is focused on in this paper. This hybrid process uses the advantages of distillation and - at the same time - overcomes the limitations of distillation by the use of membrane separation. Depending on the thermodynamic properties of the mixture, the hybrid process offers multiple configuration options in order to combine membrane modules and distillation columns (Fig. 1). For the separation of close boiling mixtures the membrane is located in the side stream (Fig. 1a) to assist the separation in the column. Most investigations focus on the separation of non-ideal binary mixtures (Fig. 1b), e.g. purification of ethanol or isopropanol (IPA). The main purpose of the membrane unit is to overcome the azeotropic point of the top product. A further enrichment up to the desired product purity can be achieved with the membrane or with a second column.

Only few investigations exist dealing with the separation of ternary aqueous mixtures into pure components in one distillation column combined with a hydrophilic membrane unit located in the side stream of the column (Fig. 1c). These studies show the feasibility of this hybrid process and

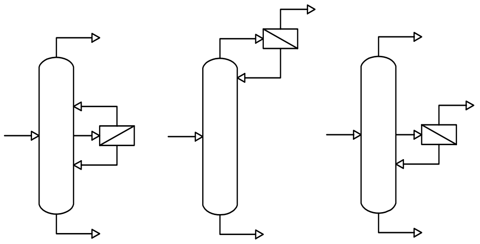

Fig.1: Hybrid process to separate a) close boiling, b) binary azeotropic and c) ternary mixtures (Hömmerich, 1998a)

that the operating conditions for the membrane separation can be more suitable as compared to other process configurations (Kuppinger et al., 2000).In this work, the application of this hybrid membrane process is illustrated by an industrially relevant non-ideal ternary mixture of acetone, isopropanol and water (Turton et al., 1998).

In contrast to stand-alone processes the design of hybrid processes with strong interactions between the two unit operations - due to recycle streams and non-idealities of the membrane separation - is very complex and therefore requires a distinctive process understanding and adequate models for both unit operations.

# 4. Modelling, simulation and model validation

A simulation tool for PV and VP was developed in the commercial simulation environment ASPEN Custom Modeler$^{TM}$ (ACM). Based on a detailed mathematical model, the tool allows for both feasibility studies and for extended phenomenology studies of a single unit operation or an entire hybrid processes with supplementary peripherals. The user can chose between different model complexities and can thus influence the accuracy of the simulation results directly.

## 4.1 Modelling of pervaporation and vapour permeation

The flexible model structure enables the choice of different modelling approaches to calculate the membrane permeance of each component (Table 1). Among them a short-cut approach with constant permeances, a temperature dependence represented by the Arrhenius equation and extended model approaches (Hömmerich, 1998), (Meyer-Blumenroth, 1989) are implemented to utilise different membrane materials, e.g. inorganic zeolithes or glassy and swelling polymeric membranes.

The following effects leading to a decrease of the driving force can be taken into account: feed and permeate pressure drop, temperature loss due to permeate vaporisation and phenomena like concentration and temperature polarisation. Additionally, different configurations like lumen and shell feed or co and counter current flow are possible. The implemented cost functions enable the evaluation of the economic benefits of the membrane separation compared to standard processes.

| **mass transport model** | **permeance $Q$** | |
|---|---|---|
| **short-cut model (SC)** | $Q_i^0$ | constant |
| **Arrhenius (AR)** | $Q_i^0 \cdot exp\left(-\frac{E_i}{R}\left(\frac{1}{T^0}-\frac{1}{T}\right)\right)$ | T-dependent |
| **Meyer-Blumenroth (MB)** | $\frac{\tilde{D}_i(T)}{\bar{\gamma}_i}$ | DF: activities |
| **Hömmerich (HÖ)** | $A_i^* \frac{b_i(T)\cdot a_i^F}{1+b_i(T)\cdot a_i^F}\cdot\frac{1}{\bar{a}_i}$ | DF: activities |
| **sorption/diffusion (SD)** | $\frac{\bar{c}_i(T)\cdot\bar{D}_i(T)}{\bar{f}_i}\cdot\frac{1}{\delta_M}$ | DF: fugacities |

Table 1: Various model approaches

## 4.2 Model simulation and validation

A capillary composite membrane with an active layer of polyvinyl alcohol (PVA) is applied for the experimental investigation. Two different module sizes, a so called pencil module (4 fibres, $A_{Memb}$= 18 cm²) and a big pencil module (10 fibres, $A_{Memb}$= 75 cm²) are used. PV and VP experiments with binary (IPA and water) and ternary mixtures (IPA, water and acetone) are carried out in a multipurpose lab-scale plant to determine relevant model parameters and to validate the developed simulation tool. The approach of Meyer-Blumenroth (MB) shows the best results to calculate the permeances gained experimentally. Additionally, all non-ideal effects are taken into account. The comparison of simulated and experimental permeate fluxes shows satisfactory agreement and is illustrated in Fig. 2.

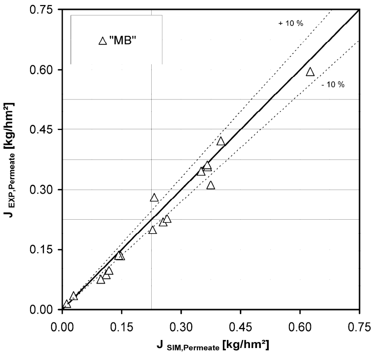

Fig.2: Simulated vs. experimentally gained permeate fluxes

### 4.3 Rate based modelling of distillation

For the theoretical investigation of the hybrid process, a mass transfer model for distillation has to be applied. Thus, a rate based model developed by Klöker et al. (2005) was accessed. The relevant models for the distillation column, membrane separation and peripherals are connected in the simulation environment ACM™.

## 5. Process analysis

The aim of this analysis in pilot and industrial scale is to gain detailed insights into process behaviour of the stand-alone process pervaporation and of the hybrid process consisting of distillation and pervaporation.

### 5.1 Pervaporation

If permeances in lab-scale plants are measured, operating and structural parameters are chosen in the way that non-idealities and mass transfer limitations in the module can be minimized or completely neglected. In most cases this approach cannot be applied to pilot or technical scale membrane modules due to boundary conditions like feed flow limitations. This results in rather complex interactions between module geometry, flow pattern, flow velocity, permeate flux, feed temperature and feed and permeate pressure. The effect of mass transfer resistance on module performance can be illustrated by module efficiency (Sommer, 2003), which is defined as the ratio of ideal and real flux:

$$\varsigma_{Module} \equiv \frac{J_{ideal}}{J_{real}} \tag{4}$$

While the efficiencies of lab scale modules are almost 100 % the efficiency of pilot or technical scale modules can decrease significantly. The influence of Reynolds number and, consequently, feed mass flow on the permeate flux for an ideal case is shown in Fig. 3a. There is a strong influence depending mainly on the grade of depleting the aqueous feed stream. Fig. 3b shows typical module efficiencies for an up-scaled module ($A_{Memb}$=1 m²). The temperature loss in the feed stream due to permeate vaporisation is the main reason for the low module performance at small Reynolds numbers. Depending on the feed mass flow and temperature, membrane areas up to 5 times higher than in ideal conditions are required. Therefore, it’s crucial to take all non-ideal effects into account for investigations of pilot and industrial scale hybrid processes.

### 5.2 Hybrid membrane process

The analysis of the hybrid membrane process is conducted in two scales. For the first, pilot scale, a 50 mm column is fed with 2 kg/h and equipped with 6 m structured packing type Sulzer BX; for the second, industrial scale, a column with a feed stream of 2290 kg/h is used. The relevant operating and structural parameters are optimized regarding the target value water removal (pilot scale), membrane area and product costs (industrial scale).

First simulation studies in pilot scale show that is necessary to introduce an internal recycle stream to obtain adequate module efficiencies as the side stream of the column is limited by internal liquid column flows.

Fig.4 shows the influence of operational parameters heat duty and side stream mass flow on water removal. The membrane area is set to 2 m². In a wide operating range it is possible to remove almost 98 % of the water fed to the column.

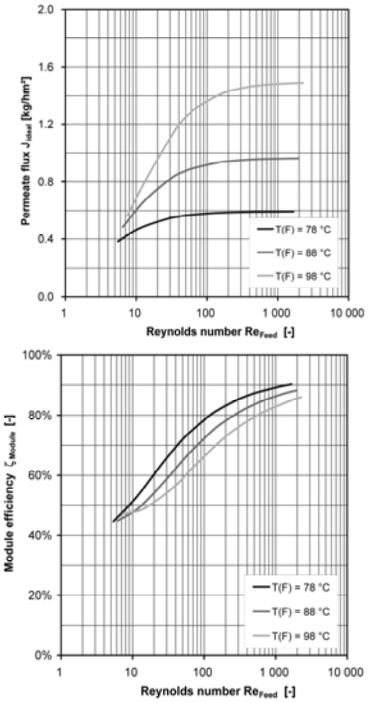

Fig.3: a) ideal - without
b) real - with driving
force reducing effects

For the industrial scale the influence of heat duty and side stream on membrane area and operational costs is illustrated in Fig. 5. The minimal required membrane area for the given separation task is found in the region of high heat duties and large mass flows (Fig. 5a). On the other hand, however, the cost optimum of the hybrid process is localised in a different operating region, namely at low heat duties (Fig. 5b).

Nevertheless the investigated hybrid process is not yet competitive to common distillation processes. Equipped with the investigated high selective PVA membrane, the generated costs per ton of acetone are 1.8 times higher. The two main reasons are: high energy costs for permeate condensation due to expensive cooling brine and high specific membrane costs due to low permeate fluxes and a short membrane lifetime (2 years).

On the other hand, if the boundary conditions of the hybrid process change, because modified membranes can be applied (e.g. increased lifetime to 5 years, membrane costs per m² are cut in half, cooling water can be used), the hybrid process becomes very attractive.

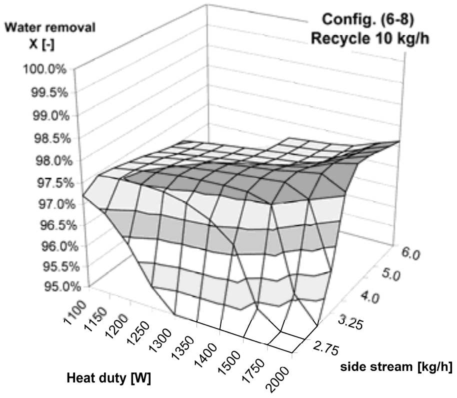

Fig.4: Influence of heat duty and side stream mass flow on water removal

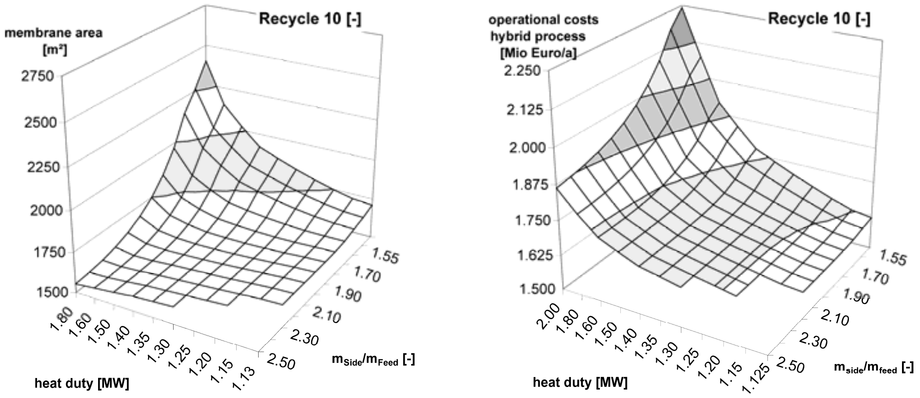

Fig.5: Industrial scale: influence of heat duty and side stream mass flow on a) required membrane area b) operational costs

Even a benefit of ~ 100 000 € per year can be achieved compared to the conventional distillation process.

## 6. Conclusion

In this work, a flexible and robust simulation tool for pervaporation and vapour permeation is presented. It has been developed in the simulation environment ASPEN Custom Modeler$^{TM}$. Various modelling approaches and different modelling complexities are implemented. Binary and ternary lab-scale pervaporation experiments have been performed to determine relevant model parameters and to validate the model. The agreement between simulation and experiment is satisfactory.

The hybrid membrane process has been analysed with detailed models for both unit operations and supplementary peripherals. All non-ideal effects have to be taken into account especially for the membrane separation. The influence of decisive operational parameters on dewatering (pilot scale) and on membrane area and operational costs (industrial scale) is illustrated. Even though this hybrid membrane process is not yet competitive, the benefits are very likely to prevail in the nearest future.

## 7. References

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