

Modeling of a Hybrid Process Combining Zero-Gravity Distillation and Vapor Permeation

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Abstract. Process intensification comprises attractive concepts to develop more sustainable and efficient chemical production processes. Combining the process integration principle and equipment miniaturization provides a great potential for the design of chemical processes in a resource-efficient way. In this work, a model of a hybrid process combining small-scale distillation and vapor permeation was developed. The small-scale distillation process is represented by zero-gravity distillation. The distillate is further separated in a membrane unit. The overall process is considered based on the hydrodynamic analogy modeling concept which makes rigorous description of heat and mass transport possible. The developed model was used to simulate the separation of ethanol/water mixtures. Simulation studies were performed to investigate the influence of initial concentrations and dimensions of both separation units on the process efficiency.

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Introduction

To realize the vision of small-scale and modularized production plants, the development of small-scale separation units is necessary. This is particularly true for distillation, since it represents one of the most important separation operations accounting for 90-95% of the fluid separation techniques on an industrial scale [1]. The use of small-scale equipment offers great potential for process intensification, with enhanced mass transfer thanks to high surface-to-volume ratios and improved process safety due to small hold-ups. However, the stabilization of the phase interface between two fluids is a major obstacle. Therefore, small-scale fluid separation process equipment has not yet reached sufficient maturity for the application in production plants [2].

An interesting method to realize distillation processes in small equipment units is the so-called *zero-gravity distillation* (ZGD). Using the heat-pipe principle, the counter-current flow of the liquid and vapor phases can be established. In contrast to gravity in conventional distillation columns, capillary forces, for example arising in metal foams, are used to move the liquid phase. The pioneering study was published by Seok and Hwang [3]. They examined the distillation of methanol/ethanol and ethanol/water mixtures using the heat pipe principle. In their study, a glass tube with a fiberglass wick was used as the distillation unit. The feed was introduced in the middle of the glass tube, and the product streams were collected at the condenser and the evaporator. In parallel to the experimental study, Seok and Hwang [3] presented an analytical model, based on Darcy's law, and used the experimentally determined mass transfer coefficients to develop the species transfer model.

Zero-gravity distillation (ZGD) was further investigated by other research groups. Ramirez-Gonzalez et al. [4] reported a model for the zero-gravity distillation, which was based on the Young-Laplace equation and Darcy's law for fluid flow. The species transfer was described by the experimentally determined mass transfer coefficients. Tschernjaew et al. [5] proposed another approach, where the species transfer was determined by employing the Maxwell-Stefan equations for the multicomponent mixtures and did not entirely rely on the experimental parameters. Recently, Rieks et al. [6] presented a model for ZGD simulations with consideration of phase change phenomenon. Similar to [5], they used the hydrodynamic analogy (HA) concept to describe the liquid and vapor phases, without consideration of the phase change influence on the pressure and the impact of the distillation unit walls on the heat conductivity. A detailed HA-based model of ZGD was developed by Wende et al. [7]. Their treatment includes the feed stream as well as the distillate and bottom product streams into account. Furthermore, thermal conduction in the unit walls and the pressure change due to evaporation and condensation were considered. The model was validated using data from experimental measurements by Wende et al. [8].

Even though distillation is a very effective separation process, its applicability is restricted in some cases, e.g., for azeotropic mixtures. A distillation-based separation of such mixtures can only be realized by multiple columns operating at different pressure levels or using an additional component as an entrainer. Instead of using these methods,

which are costly in terms of equipment and energy, it is possible to combine distillation with a membrane separation process, e.g., vapor permeation or pervaporation.

Jonquière et al. [9] gave an overview of hybrid processes combining distillation and vapor permeation in industrial applications. They claimed that the main field of application for these methods is the separation of organic components and water. Also, some recent works dealt with this type of mixtures. For instance, Scharzec et al. [10] published a study on the separation of a ternary mixture tetrahydrofuran/methanol/water. They investigated a hybrid process of pervaporation and distillation using five different polymeric and inorganic membranes.

In all investigated processes, a high separation efficiency was achieved. Despite the potential of such hybrid processes for the separation of azeotropic mixtures, the commercialization of membrane assisted processes is still limited, because of the required large surface area of membranes and thus high capital costs [11].

The application of hybrid processes combining ZGD and vapor permeation appears to be advantageous for small-scale separations. Investment costs can be reduced with small equipment dimensions, while process efficiency increases due to high volume-to-surface ratios. Despite the potential of combining small-scale distillation and vapor permeation, no studies of this combination have been published so far. In this work, a model for the simulation of such a small-scale hybrid process combining ZGD and vapor permeation is proposed. The model includes the continuous ZGD unit with feed and products streams using metal foams as porous media. A vapor permeation unit is supplied with a polymeric membrane.

Mathematical Model

In this section, the mathematical model of the hybrid process combining ZGD and vapor permeation is described. The model for the ZGD unit is based on the approach suggested by Wende et al. [7]. Here, we only focus on the most important aspects.

The ZGD unit is considered to be filled with a vapor-liquid system, as shown in Fig. 1. Both phases are binary mixtures containing the same two species. The liquid phase is embedded in the porous structure and covered by the vapor phase. The ZGD unit has an evaporator at the left side which is integrated into the ZGD unit. In contrast, the condenser at the right side operates externally. A feed stream is supplied at the bottom of the unit. The bottom product stream $\dot{B}$ is withdrawn from the liquid phase. The vapor stream leaving the unit at the right side is split. The one part is condensed and redirected in the ZGD unit as a reflux while the other part is further treated in a membrane unit.

The ZGD unit is modeled in a two-dimensional approximation in the xz -plane based on the HA concept [12]. The main idea of this concept is to replace the actual process fluid flow by relevant, simplified flow patterns. If such an analogy is adequate, a rigorous description of heat and mass transport becomes possible.

The capillary forces are assumed to be strong enough to immediately compensate any movement of the liquid-vapor interface due to evaporation and condensation. As a result, the vapor-liquid interface coincides with the boundary between the metal foam and the vapor phase, as shown in Fig. 1.

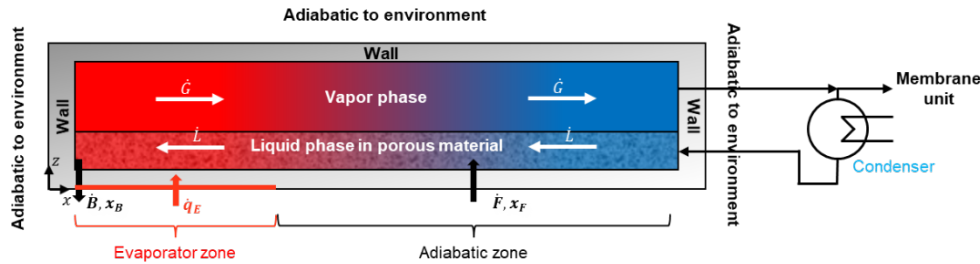


Fig. 1 Schematic presentation of the of the ZGD unit and its computational domain with the corresponding boundary conditions.

Both fluids are Newtonian, with constant fluid properties. The vapor phase flow is modeled as a steady and laminar creeping flow in x -direction. With these assumptions, the Navier-Stokes equation reads:

$$\frac{\partial^2 u_v}{\partial z^2} = \frac{1}{\mu_v} \cdot \frac{\partial p_v}{\partial x} \quad (1)$$

where u_v is the vapor-phase velocity, μ_v is its viscosity and p_v is the pressure of the vapor phase. As boundary conditions for Eq. (1) zero vapor velocity at the phase interface and the no-slip condition at the upper wall are applied. Darcy's law is used to describe the liquid flow inside the metal foam [13]:

$$-u_l = \frac{K}{\mu_l} \cdot \frac{\partial p_l}{\partial x} \quad (2)$$

with the liquid-phase velocity u_l , the liquid viscosity μ_l and the permeability of the metal foam K . Steady-state heat transfer equations are used for the vapor and liquid phase:

$$\rho_v u_v c_{p,v} \frac{\partial T_v}{\partial x} - \lambda_v \nabla^2 T_v = 0 \quad (3)$$

$$\rho_l u_l c_{p,l} \frac{\partial T_l}{\partial x} - \lambda_{l,eff} \nabla^2 T_l = 0 \quad (4)$$

Here, ρ_k is the density, T_k is the temperature and $c_{p,k}$ is the specific heat capacity for each phase, $k = \{l, v\}$. λ_v denotes the thermal conductivity of the vapor phase. The effective thermal conductivity $\lambda_{l,eff}$ in the liquid-solid region depends on the metal foam porosity. Bhattacharya et al. [14] proposed an experimentally validated correlation for the effective thermal conductivity. At the vapor-liquid phase interface the thermodynamic equilibrium relationship must be fulfilled. In the walls of the ZGD unit, only heat conduction occurs. Under such conditions the heat transport equation reads:

$$-\lambda_w \nabla^2 T_w = 0 \quad (5)$$

where λ_w is the thermal conductivity of the wall material and T_w is the temperature in the walls. The continuity condition of the heat fluxes normal to the wall surface has to be fulfilled at all unit walls. The boundary condition at the transition from the wall to the environment is a zero-gradient condition, as the unit is assumed to be adiabatic. At the lower wall, the heat flux for the evaporator is taken into account.

Steady-state transport equations are used to describe the species transport in the vapor and liquid phase:

$$\rho_v u_v \frac{\partial c_v}{\partial x} - D_v \nabla^2 c_v = 0 \quad (6)$$

$$\rho_l u_l \frac{\partial c_l}{\partial x} - D_{l,eff} \nabla^2 c_l = 0 \quad (7)$$

Here, c_v and c_l the concentrations of the light boiling component in the liquid and vapor phase, respectively. The diffusivity of the vapor phase is denoted by D_v . $D_{l,eff}$ denotes the effective diffusivity in the liquid-solid region [15]. As a boundary condition at the vapor-liquid phase, the thermodynamic equilibrium relationship is applied. At the transition between the walls and the fluid phases, a zero-gradient boundary condition is applied.

The total mass flow rates in the liquid phase $\dot{L}$ and vapor phase $\dot{G}$ are obtained by balancing the local interfacial mass fluxes $\dot{m}$ at an arbitrary x -position:

$$\frac{d\dot{L}}{dx} = -\dot{m} \cdot b \quad (8)$$

$$\frac{d\dot{G}}{dx} = \dot{m} \cdot b \quad (9)$$

with the internal unit width (without walls) b . The feed, bottom product and distillate streams are considered in the mass balance at the specific x -positions x_F , x_B , x_D where the streams are supplied to or removed from the unit (see Fig 2).

The vapor stream leaving the ZGD unit is further treated in a membrane unit. This unit consists of two horizontal microchannels and a hydrophilic polymeric membrane between them (Fig. 2). The membrane is made of polyvinyl alcohol (PVA) and polyacrylonitrile (PAN). In the permeate channel, the vacuum conditions are assumed. For this reason, the computational domain can be limited to the channel of the retentate and the membrane (red lines in Fig. 2). The membrane unit is isothermal and adiabatic with respect to the environment. Again, the vapor flow is modeled as a steady and laminar creeping flow. The corresponding equation for the velocity profile is given by Eq. (1). The no-slip condition is applied as boundary condition at the bottom wall and the membrane-vapor interface.

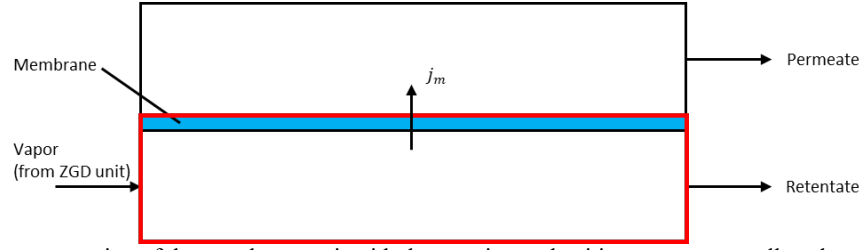


Fig. 2 Schematic representation of the membrane unit with the entering and exiting streams as well as the mass flow across the membrane; the red lines mark the computational domain.

The species flux across the membrane j_m is determined by the approach suggested by Meyer-Blumenroth [16]:

$$j_{i,m} = \frac{c_{t,m} \cdot D_{i,m}^T}{\bar{\gamma}_{i,m} \cdot \delta_m} \cdot \left[\frac{f_{i,F} - f_{i,P}}{f_i^0} \right] \quad (10)$$

Here, $f_{i,F}$ and $f_{i,P}$ are the fugacity of the species i in the feed and permeate, respectively, f_i^0 is the reference fugacity, $\bar{\gamma}_{i,m}$ is the activity coefficient averaged over the membrane thickness, δ_m is the membrane thickness and $c_{t,m}$ is the total mixture concentration. $D_{i,m}^T$ is the so-called thermodynamic diffusivity determined by the Nernst-Einstein equation. The fugacity is determined by the partial pressure of the component p_i , the molar concentration x_i and the activity coefficient γ_i :

$$f_i = \gamma_i \cdot x_i \cdot p_i \quad (11)$$

The temperature dependence of $D_{i,m}$ can be described by an Arrhenius approach [16]:

$$D_{i,m}(T) = D_{i,m}^0 \cdot \exp\left(-\frac{E_i}{R} \left(\frac{1}{T^0} - \frac{1}{T}\right)\right) \quad (12)$$

while $D_{i,m}^0$ and T^0 describe the reference state. $\bar{\gamma}_{i,m}$ is determined by averaging the local activity coefficient $\gamma_{i,m}$ of the feed and permeate side. The local activity coefficients are given by [16]:

$$\gamma_{i,m} = \exp\left[B_{ii} \left(1 - \left(\frac{f_{i,m}}{f_{i,m}^0} + B_{ij} \frac{f_{j,m}}{f_{j,m}^0}\right)\right)\right] \quad (13)$$

The species transfer model for the flux across the membrane contains four empirical parameters B_{ii} , B_{ij} , $D_{i,m}^0$ and E_i for a binary system.

The mathematical model was implemented in the MATLAB® software. All equations were discretized with the finite difference method and solved sequentially and iteratively.

Results and Discussion

The combined distillation and vapor permeation is investigated. Fluid properties were taken from Linstrom and Mallard [17]. Diffusivities and equilibrium data were determined using the methods described by Poling et al. [18]. The parameters for the vapor permeation are published by Meyer-Blumenroth [16].

In this work, three different simulation cases are studied. The inner dimensions of the ZGD unit in Case 1 are a length of 300 mm, a height of 20 mm and a width of 50 mm. The vapor permeation unit dimensions are 5 mm in width, 5 mm in height and 50 mm in length. The feed concentration of ethanol is $x_{EtOH,F} = 0.4$. In Case 2, the ZGD unit length is 150 mm, while the width, height, feed concentration and the dimensions of the vapor permeation unit are the same as in Case 1. The dimensions of the vapor permeation unit are varied in Case 3. The length is 100 mm, while the width and height are the same as in Case 1 and 2. The ZGD unit dimensions are equal to those of Case 1. The ethanol feed concentration is $x_{EtOH,F} = 0.2$.

In Fig. 3 the results for the simulation of Case 1 are depicted. Fig. 3a shows the simulated concentration profile of ethanol (light boiling component) in the liquid phase of the ZGD unit. This profile reveals that the light boiling component is accumulated at the right side; accordingly, water is accumulated at the opposite side of the unit. In the bottom product, an ethanol mole fraction of 0.04 is obtained; in the distillate of the ZGD unit it is equal to 0.81. In Fig. 3b the concentration profile of water (heavy boiling component) in the membrane unit is shown. The exiting

stream has a residual water mole fraction of 0.015. At the entrance, the concentration of water decreases sharply in the membrane unit. This results in a high mass flux across the membrane. In the further course, the mass flux decreases, and the concentration runs up to the limit value of 0.015. This phenomenon can be explained by the decrease in the partial pressure of water and hence the driving force along the x-axis of the vapor permeation module.

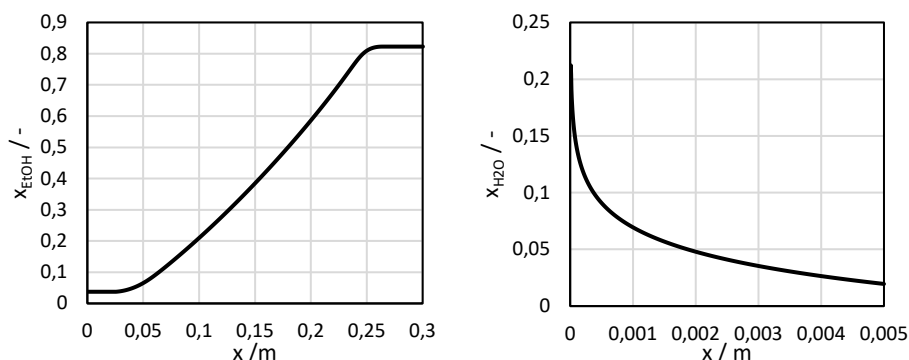


Fig. 3 Simulation results of the hybrid process: ethanol mole fraction in the liquid phase in the ZGD unit with a length of 300 mm (a); water mole fraction in the retentate of the membrane unit (b).

Fig. 4 shows the results of the simulations of Case 2. The numerically determined concentration profiles of ethanol in the liquid phase in ZGD unit are presented in Fig. 4a. The ethanol mole fraction in the distillate stream is 0.71, while in the bottom product stream, it is 0.16. Compared to Case 1, a lower separation efficiency is achieved. In Fig. 4b, the numerically obtained concentration profiles of the membrane unit are shown. The water mole fraction in the vapor stream from the ZGD unit is higher than in Case 1. Nevertheless, the membrane unit achieves a purity of an ethanol mole fraction of 0.985 in the exiting stream.

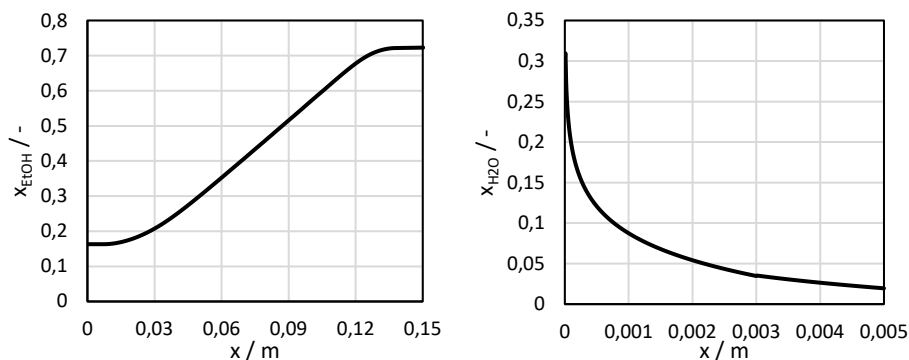


Fig. 4 Simulation results of the hybrid process: ethanol mole fraction in the liquid phase in the ZGD unit with a length of 150 mm (a); water mole fraction in the retentate of the membrane unit (b).

The simulation results of the hybrid process of Case 3 are presented in Fig. 5. In Fig. 5a, the numerically determined ethanol concentration profile is shown. For this mode, the ethanol concentration in the distillate stream of the ZGD unit is 0.78. In the bottom product pure water is obtained. The numerical results for the water mole fraction profile in the membrane unit are depicted in Fig. 5b. Again, the concentration of water decreases sharply at the entrance. Along the vapor permeation unit length, the water mole fraction flattens and reaches a limit value of 0.01 at the end. After the length 66 mm of the membrane unit, the species flux across the membrane is strongly attenuated.

The simulated hybrid processes with small-scale equipment achieve ethanol concentrations in the retentate of 0.985 in Case 1 and Case 2 and 0.99 in Case 3. These results are comparable to the values obtained in large-scale processes combining distillation and vapor permeation. Therefore, the combination of the two process integration principles miniaturization and using different separation unit operations, offers a high potential for efficient separation units for modularized plants and in the field of specialty chemicals and pharmaceuticals.

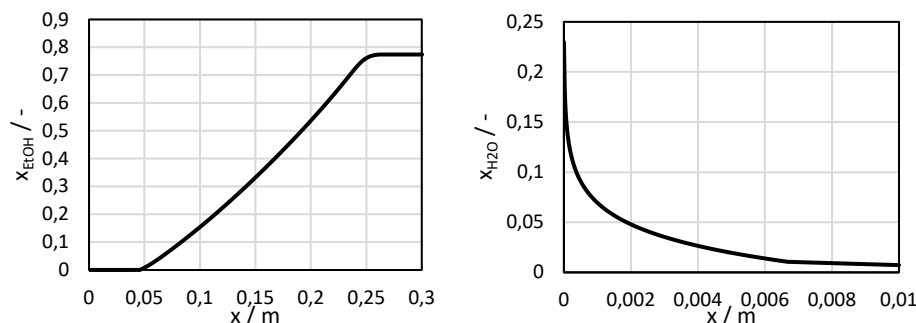


Fig. 5 Simulation results of the hybrid process: ethanol mole fraction in the liquid phase in the ZGD unit with a length of 300 mm and an ethanol feed concentration of 0.2 (a); water mole fraction in the retentate of the membrane unit (b).

Conclusions

A new model for the simulation of hybrid processes combining ZGD and vapor permeation based on the concept of the hydrodynamic analogy was developed. The model governs the coupled transport phenomena in the ZGD unit with feed stream and product withdrawal. Furthermore, the vapor permeation unit is included in the description. This unit consists of two horizontal microchannels and a hydrophilic polymeric membrane between them. The species transport across the membrane was described by the approach suggested by Meyer-Blumenroth [16].

Three different simulation studies were performed in which the dimensions of the units and the feed concentration were varied. The small-scale hybrid processes can be evaluated as a resource-efficient method with a high separation efficiency. The retentate reached an ethanol mole fraction of 0.985 in Case 1 and Case 2 and 0.99 in Case 3. Therefore, this process can be evaluated as efficient and has the potential to be used as an effective separation method in various fields, e.g., specialty chemicals.

As the next steps, simulation studies of aqueous mixtures containing different organic solvents, e.g., acetone or isopropanol, are planned.

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