MASS TRANSFER CHARACTERISTICS OF ISOPROPANOL PERVAPORATIVE DEHYDRATION THROUGH CMC-CA-01 MEMBRANE

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Pervaporation can subsitute conventional azeotropic distillation as an alternative dehydration process. Applying this technique, the azeotropic point of azeotrope can be exceeded without any additives under boiling temperature. The entire energy used for dehydration is substantially lower in comparison with azeotropic rectification, furthermore, this modern separation process without additives can be part of an enviromentally conscious technology. In the course of our experiments we described with the pervaporational behavior of isopropyl alcohol from experimental data of model solutions. At the Corvinus University of Budapest, Department of Food Engineering the matemathical modeling was carried out, using our earlier experimental data whith CMC-CA-01 membrane [1]. The aim of this calculations was the definition of the mass transfer properties of the membrane and development of design eqauations for industrial application. As the results are demonstrated, that membrane characteristic defined by resistance in series model provides fundamentals for technological design to industrial application and for the economical examination. And it also provides data for the process simulation of hybrid technology.

Keywords: pervaporation, isopropanol, membrane, modelling, dehydration

Introduction

Isopropyl alcohol is a solvent, which is widely used in chemical and pharmaceutical industry. It is used as an organic solvent in the pharmaceutical industry, in the process of esterification, and in electronics it is the cleaning agent of fine pieces. It is a well known phenomenon, that isopropyl alcohol composes azeotrope with water, which makes the recovery of water from industrial byproducts more difficult in conventional distillation [2]. The conventional industrial processes needs the application of further additives. In the course of azeotropic destillation they use di-isopropyl-ether, benzene or cyclohexane [3], and in case of extractive distillation ethylene-glycole as the carrier agent [4]. The advantage of pervaporation is that azeotrope can be separated simply whithout additives forming terner. In addition to applying this process in chemical industry, this method of dehdydration of isopropanol by pervaporation of azeotrope can be prepared to substitute the solvent for extraction of edible oils in edible oil processing industry. The isopropanol has the sufficient properties, although its oil absorbing capacity is lower than that of the hexane, it can not be neglected as an organic solvent in the process of extraction [5]. As the oil absorbing capacity of isopropanol is substantially higher than the azeotrope, its absolutization is very important, and it can be carried out economically by pervaporation [1]. The industrial application of this process can be justified by the technology- and cost-

efficiency of pervaporation. In the centre of the scientific and industrial development stands the hybrid separation technology. To reach the azeotropic point the technology based on the conventional distillation technique and the pervaporational dehydration is applied effectively in the branches of chemical industry [6]. A lot of researchers deal with the optimization of hybrid technology. The optimization is based on experimental results, which is followed by an optimization program on PC and process simulation using theoretical and half-empirical mathematical models, determining the parameters of the applied model [7]. However the characteristics of the applied membrane has to be known to put the pervaporation into process simulation environment [8].

The characteristic of pervaporation membrane can be evaluated from the view of capacity/permeability and the separation efficiency of the membrane. Permeate flux is the permeate pervaporated and condensed in the pervaporative system during time unit through the membrane surface.

$$J = \frac{m_P}{A \cdot \tau} \qquad (1)$$

Where:
   J – the permeate flux (kg/(m²h)),
   A – the membrane surface (m²),
   τ – the pervaporation time (h).

The selectivity shows in which the component, permeating through the membrane is enriched in comparison with the feed solution.

$$\beta_i = \frac{x_{P,i}}{x_{F,i}} \tag{2}$$

Where:

β_i – selectivity of (i) component (-),

$x_{F,i}$ – feed concentration of (i) component (kg/kg),

$x_{P,i}$ – permeate concentration of (i) component (kg/kg).

The separation factor shows how effectively the membrane can separate the two components.

$$\alpha_i = \frac{x_{F,i} \cdot (1 - x_{P,i})}{x_{P,i} \cdot (1 - x_{F,i})} \tag{3}$$

Where:

α_i – selectivity of membrane concerning to (i) component (-).

The pervaporation separation index describes the effectiveness of the process as overall effect of permpeate flux and separation factor.

$$PSI_i = J \cdot \alpha_i \tag{4}$$

Where:

PSI_i – pervaporation separation index of (i) component (kg/(m^{2}h)).

Material and method

To modeling of the behavior of izpropil alcohol pervaporation is based on the results of the experiments of isopropanol water model solutions examined by ATRA et al. (1999) [1], which had feed concentration close to azeotropic composition. The experiments were carried out in a laboratory pervaporation equipment with CMC-CA-01 type membrane made by the Swiss CELFA MEMBRANTECHNIK firm. The feed was circulated over the 110 cm^2 active hydrophyl membrane surface at 45, 55, 65 °C temperature with 200 L/h recirculation bulk flow rate, while 30 mbar pressure was set on permeate side. The amount, and the compositon of the gained pervaporation products were measured, and the flux of permeate was determined from a 200 mL feed model solution in a five-hour interval

In the course of our experiments we calculated the characteristics of pervaporation from the entire, 25 hour pervaporation period.

Mathematical modeling of pervaporation

To describe the mass transfer of the membrane both the concentration and partial vapour pressure are suitable. However, in case of pervaporation, partial vapour pressure as a driving force characterises better for the process description [9].

$$J_i = Q_{OV,i} \cdot A \cdot (p_{L,i} - p_{G,i}) \tag{5}$$

Where:

J_i – mole stream of (i) component through the membrane [mol/s],

$Q_{OV,i}$ – overall mass transfer coefficient of (i) component with driving force of partial vapour perssure (mol/m^{2}Pas),

A – the membrane surface (m^2),

$p_{L,i}$ – partial vapour pressure of (i) component at feed side (Pa),

$p_{G,i}$ – partial vapour pressure of (i) component at permeate side (Pa).

$$p_{L,i} = \frac{c_{L,i} \cdot \gamma_i \cdot P_i^0}{\rho_L} \tag{6}$$

Where:

$c_{L,i}$ – molar concentration of (i) component at liquid side (mol/m^3)

γ_i – activity coefficient of (i) component at liquid side calculated by NRTL method [10],

P_i^o – saturated vapour pressure of (i) component (Pa) [11],

ρ_L – molar density of liquid (mol/m^3).

$$p_{G,i} = \frac{c_{G,i} \cdot P}{\rho_G} \tag{7}$$

Where:

$c_{G,i}$ – molar concentration of (i) component on permeate side (mol/m^3),

P – entire pressure of solution at permeate side (Pa),

ρ_G – molar density of vapour phase at permeate side (mol/m^3).

Assuming that the resistance at permeate side is negligible [7-9], the mass transfer through the membrane can be desribed by linear resistance model as follows [12]:

$$\frac{1}{Q_{OV,i}} = \frac{1}{Q_{M,i}} + \frac{1}{Q_{L,i}} \tag{8}$$

Where:

$Q_{OV,i}$ – overall mass transfer coefficient of (i) component with driving force of partial vapour perssure (mol/m^{2}Pas),

$Q_{L,i}$ – mass transfer coefficient of (i) component with driving force of partial vapour perssure at liquid side (mol/m^{2}Pas),

$Q_{M,i}$ – mass transfer coefficient of (i) component with driving force of partial vapour perssure in membrane (mol/m^{2}Pas).

The mass transfer coefficient of liquid side with the driving force of partial vapour pressure:

$$Q_{L,i} = \frac{\rho_{L,i}}{\gamma_i \cdot P_i^0} \cdot k_{L,i} \tag{9}$$

Where:

$k_{L,i}$ – mass transfer coefficient (i) component with driving force of concentration-difference at liquid side (m/s).

$$k_{L,i} = \frac{Sh \cdot D_{i,j}}{d_e} \qquad (10)$$

Where:

Sh – Sherwood-number,

$D_{i,j}$ – diffusivity of (i) component in (j) solvent by Wilke-Chang equation (m^2/s) [13],

d_e –equivalent diameter calculated by the geomethric relations of the membrane modul (m).

The Sherwood-number can be described with the equation below in case of laminar bulk flow [14]:

$$Sh = 1{,}85 \cdot \left[Re \cdot Sc \cdot \frac{d_e}{l} \right]^{\frac{1}{3}} \qquad (11)$$

$$Re = \frac{v_L \cdot d_e \cdot \rho_L}{\eta_L} \qquad (12)$$

Where:

v_L – flow rate of liquid/feed (m/s),

η_L – dynamic viscosity of liquid (Pas).

Results and evaluation

By similar settings, water fluxes on different temperatures become more dynamic if we rise feed concentration *(Fig. 1)*. Higher feed concentration results higher driving force, which helps favourable membrane permeation. Permeate yield also rises with temperature. On the one hand the liquid side partial pressure rising with temperature has strengthening effect on driving force due to the rise of saturation pressure, the water molecules diffuse more intensively on a higher temperature on the other hand. [15]. Flux values vary in the lowest range at 45 °C on CMC-CA-01 membrane, but there is no significant difference between 55 and 65 °C.

However during the pervaporative process the concentration-polarisation of the accumulating molecules in the boundary-layer close to the membrane intensifies on every temperature. This has a counter-effect on mass transfer and it is presented in the variation of the entire mass transfer coefficient of water through the membrane *(Fig. 2)*. This effect leads to a rising resistance in the hydrodinamic boundary-layer at liquid side, which becomes more intense by lower feed concentraiton which means the end of pervaporative dehydration.

This can also be observed in case of water, in the variation of mass transfer coefficients, at liquid (feed) side with the driving force of concentration difference, as a function of pervaporation time *(Fig. 3)*.

It can be determined that the mass transfer coefficient of water at liquid side is higher with orders of magnitude than the overall and the membrane mass transfer coefficient regarding to values studied at different temperatures with the driving force of partial pressure *(Fig. 4)*. Thus it has no effect on overall mass transfer, and the function in pervaporative resistance in serial resistance model is negligible. It can be seen in Fig. 4, that the mass transfer coefficient of membrane is equal

to the overall mass transfer coeffcient, hereby the mass transfer is determined by the membrane and its structure in each case [16].
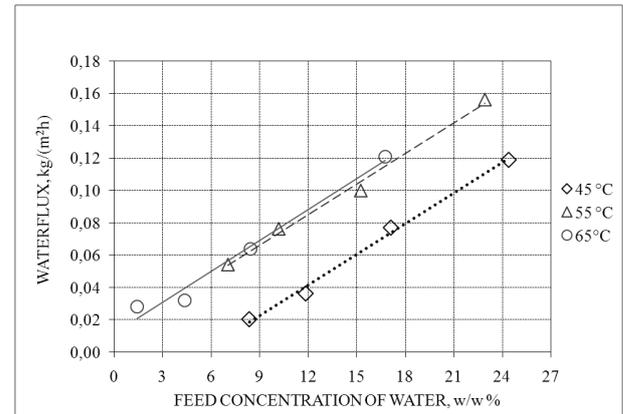

Figure 1: Water flux as a function of water content of feed at different temperatures
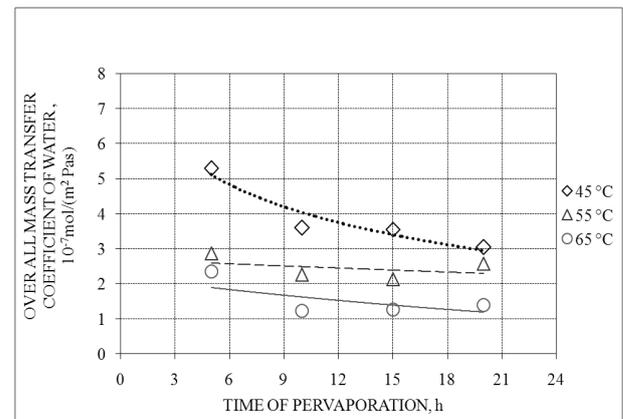

Figure 2: Overall mass transfer coefficient calculated for water as a function of pervaporation time
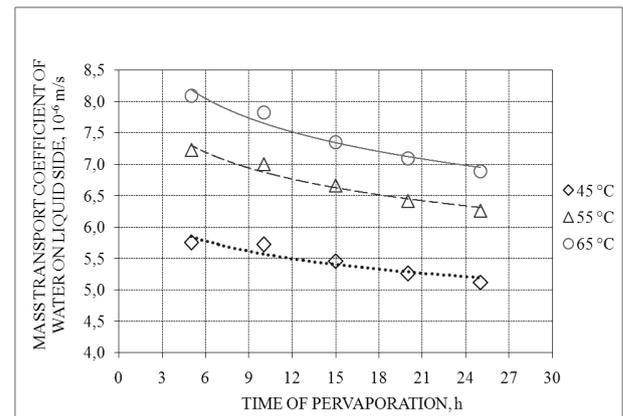

Figure 3: Mass transfer coefficient at liquid side as a function of pervaporation time with the driving force of concentration difference at different temperatures

All this phenomenon is a results of the favourable hydrodinamic conditions, which make prosperous circumstances. On the one part it affects favourably the mass transfer through the well-known material and hydrodynamic characteristics, on the other part the

continous intensive flux inpedes the formation of partition balance between boundary-layer and the membrane and lowers the degree of concentration polarisation, which rises the resistance at liquid side.
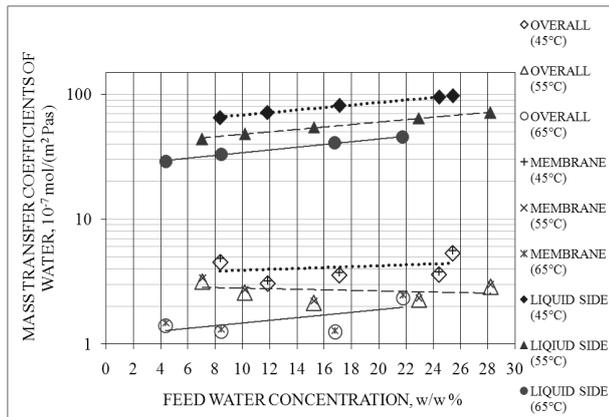

Figure 4: Coefficients in mass transfers a function of feed concentration at different temperatures
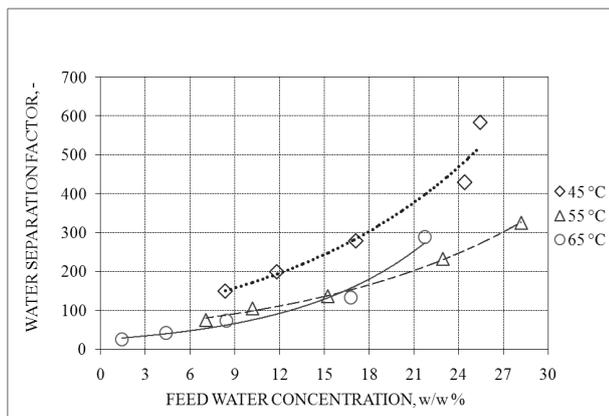

Figure 5: Separation factor of water as a function of feed concentration at different temperatures

The vapour phase containes more isopropanol through the progress in view of applied temperatures during dehydration experiments. This phenomenon can be noticed at every temperature which decreases the separation effeciency. All these reveal themselves in the decreasing tendency of separation factor in case of water. Water separating ability of the membrane is decreasing by the feed concentration *(Fig. 5).*

The phenomenon can be explained by the theory of "free volume" [17]. The polimer chaines setting up the membrane, on account of accelerating heat movement, create free volumes open for the diffusing molecules. The flexible volume enlargement decreases energy need to diffusive mass transfer, hereby enables faster movement of water molecules inside the membrane resulting in a mending pervaporative yield. At the same time all these facilitate the permeation of more undesired isopropyl-alcohol molecules lowering the efficiency of dehydration.

By the decreasing feed concentration the membrane selectivity and separation ability referred to water lowers by the reasons mentioned before. The pervaporation separation index follows a decreasing tendency as well,

however at a higher temperature it moves a in higher range because of the more favourable flux *(Fig. 6).*

Flux and separation coefficient changes opposite direction to the increase of temperature. Nevertheless, the degree of the change is higher in case of permeate flux, so because of its rising, the increase in pervaporation separation index can be noticed.
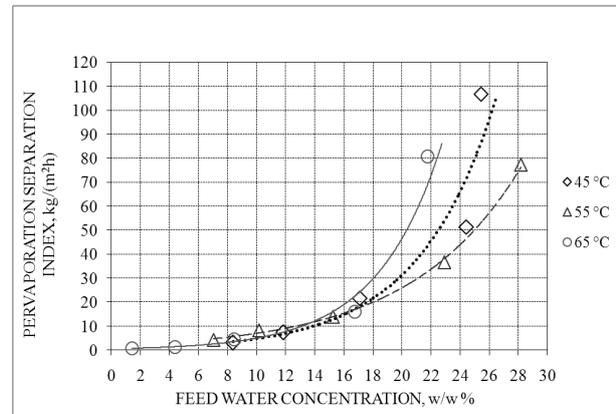

Figure 6: Pervaporation separation index of water as a function of feed at different temperatures

Conclusion

The characteristic of CMC-CA-01 type hydrophyllic pervaporation membrane defined by serial resistance model provides principles to mechanical, technological design and to the economical examination of the process for industrial application, together with provides model for the computerized process simulation of hybrid technology [17-22]. The proposed equations are suitable for optimization of the industrial process. The efficiency of dehydration decreases with feed concentration, so continous technology can be preferred. Rising the temperature gets better productivity of the process, however the selectivity and the separation factor decrease. So the energy investment into the pervaporation rises the yield of the process, but over a certain feed temperature the dehydration efficiency decreases. Regarding to the mass transfer characteristics and the connection among these, the liquid side resistance in the pervaporation process is negligible, so the pervaporative resistance is influenced by only the material and the structure of the membrane.

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