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Mini Review

Modeling of Memrbane Processes for the Separation of Azeotropic Mixtures

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Abstract

The purpose of this work is to study the chemical technological processes for etherification processes, and a membrane unit for the separation of Ethyl Tert Butyl Ether (ETBE) and Ethanol mixture. A membrane system is examined to the separation of ETBE and ethanol. Calculation of vapor liquid equilibrium of the mixture system is done using UNIFAC model. The feasibility of the membrane integrated pervaporation process was evaluated by rigorous simulation and optimization using the Aspen Custom Modeler and Aspen Plus software packages.

Supporting Concepts: Etherification; ETBE; Membrane; Aspen Custom Modeler; Aspen Plus; UNIFAC; Modeling

Introduction

In recent years, ETBE have been producing higher than other oxygenate additives, because of less disadvantages. Another attractive feature of ETBE is that it can be produced using renewable material. In other words, part of the raw material in gasoline can be replaced with a renewable material. We simulated the different alternatives of ETBE process and compared. To purify the ETBE, the pervaporative separation of an ethanol/ETBE/hydrocarbon multicomponent mixture was studied and a phenomenological model including component activity influence to permeation process was developed that was used for the optimum design of a hybrid process. The methodology applied to the design of the hybrid process, allows the design of the structure of the process. Mathematical modeling and simulation of the membrane module have been performed using Aspen Custom Modeler and linked with Aspen Plus software to describe the overall process.

Modeling and simulation have become indispensable tools for engineers and researchers in synthesis, analysis and optimization of processes. Depending on the requirements of the model, different models with different complexities can be used, which differ greatly in predictive accuracy and determining the appropriate model parameters [1].

Membrane separation is one of the promising directions in the separation of multicomponent mixtures. The merits of this group of processes can be attributed to the fact that most of them are conducted at relatively low temperatures. This avoids additional energy consumption for heating and allows the separation of thermally unstable substances. During this process, the liquid passing through the membrane is removed as a vapor. The process of pervaporation is used in the dehydration of organic solvents, separation of mixtures of organic components and azeotropic mixtures. The developed mathematical model takes into account the activity of components in the multicomponent mixtures. In this purpose, additional calculations were made of the dependence of the molar fraction and the activity coefficient on the activity of components. Membrane transport follows Fick's law, with the permeant fugacity difference as the driving force.

Results and Discussion

For our study, a global transmembrane model based on the solution-diffusion theory was selected. It assumes equilibrium between the upstream liquid and the upstream membrane surface, and between the downstream vapor and its membrane side. Membrane transport follows Fick's law, with the permeant fugacity difference as the driving force. An intrinsic membrane property is the permeability (permeant flux times membrane thickness divided by permeant driving force) or the permeance (permeant flux divided by the permeant driving force). The latter magnitude is used for asymmetric or composite membranes for which the effective membrane thickness is not readily available [2].

The permeance of component *i* in the membrane, Q_i, is defined with regard to the flux J_i as:

$$J_i = Q_i \left(\hat{f}_i^{feed} - \hat{f}_i^{perm}\right) \approx Q_i \left(p_i^o \, x_i^{feed} \, \gamma_i - p_i^{perm}\right) \qquad \text{(Eq. 1)}$$

where $\hat{f}_i^{feed}$ and $\hat{f}_i^{perm}$ are the fugacities of component *i* in the feed mixture and in the permeate side of the membrane, respectively. The saturation vapor pressure (p_i^o) is obtained

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from the Antoine equation and the activity coefficients (γ_i) have been obtained using the UNIFAC-Dortmund model.

The activities of the components in the liquid phase are calculated as:

$$a_i = x_i \gamma_i \quad \text{(Eq. 2)}$$

In this work we have used the experimental data for the separation of ETBE/ethanol mixtures by pervaporation with PERVAP 2256 commercial membranes reported in previous papers by our research group. Those experimental data have now been incorporated into a model that describes the mass transport through the membrane as a function of the activity of the components and operating conditions. As reported by Ortiz et al. [3] the partial fluxes are a nonlinear function of the activity of the components, which means that the permeances are not constant but depend on the activity of the components. Therefore, taking into account the various semi-empirical models reported in literature, we have adjusted the ethanol permeability data to an equation that depends only on the activity of ethanol, as follows:

$$Q_{ethanol} = A_1 + B_1 * \left(a_{ethanol}\right)^{C_1} \quad \text{(Eq. 3)}$$

With regard to ETBE, we have found that its permeance can be described as a function of the activities of both ethanol and ETBE, as follows:

$$Q_{ETBE} = A_2 + B_2 * \left(a_{ethanol}\right) + C_2 * \left(a_{ETBE}\right) \quad \text{(Eq. 4)}$$

We have assumed that only two components (ethanol and ETBE) permeate through the membrane, while the rest of the components remain at the retentate side and do not permeate. This simplification was experimentally tested with the membrane PERVAP 2256 used to find the experimental data.

In this study, the temperature dependence of membrane permeance in the proposed mathematical model was described trough the Arrhenius-type equation (Eq. 5),

$$Q_{i,T} = Q_{i,\bar{o}} \exp\left(\frac{-E_{act,i}}{R\,T}\right) \quad \text{(Eq. 5)}$$

Experimental permeation data from Alonso-Davila [4] have been fitted to Eqs. 4.6-4.8 using the Aspen Custom Modeler (AspenTech) software tool, obtaining the estimated parameters that are reported in Table 1. The experimental data used to estimate the model parameters were obtained from laboratory-scale experiments performed under isothermal conditions.

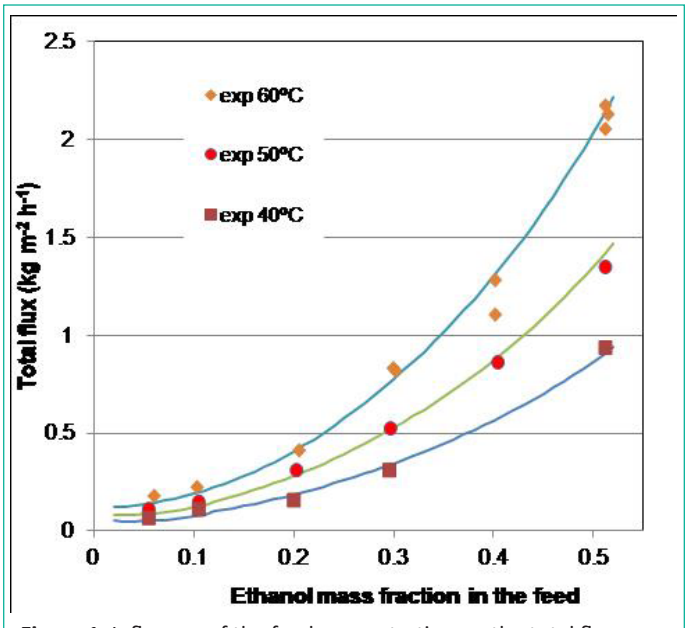

Figure 1: Influence of the feed concentration on the total flux through the Pervap-2256 membrane. The solid lines represent the predictions of the model.

Table 1: Parameters of the pervaporation model for EtOH/ETBE mixtures permeating through PERVAP 2256 membrane (65 ºC).

	Ethanol	ETBE	
		$X_{ETBE} > 0.78$	$X_{ETBE} < 0.78$
A_i	4.79×10^{-3}	8.61×10^{-3}	7.57×10^{-4}
B_i	0.186	-4.04×10^{-4}	-3.03×10^{-4}
C_i	8.208	-1.43×10^{-4}	-7.08×10^{-4}
$E_{act,i}$ (kJ mol^{-1})	- 3.35	- 3.91	

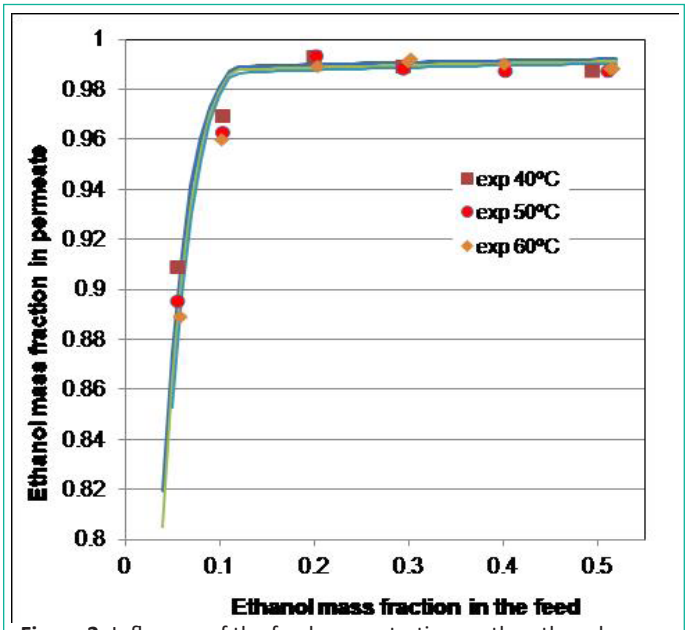

Figure 2: Influence of the feed concentration on the ethanol content in the permeate. The solid lines represent the predictions of the model.

Comparison of the experimental data [4] with the model data fitting (Eqs. 1-5) is shown in Figures 1 and 2.

In order to simulate the behavior of a pervaporation module at industrial scale, a mathematical model of a plate and frame membrane module was adapted from Luyben [5] where the above membrane performance model was incorporated. Steady state mass and energy balances were developed considering (i) plug-flow for the feed liquid stream, (ii) perfect mixing in the permeated vapor, (iii) negligible pressure drop within the module, (iv) negligible polarization effects and (v) negligible heat losses. For calculation purposes a discretization technique has been applied: the membrane module has been divided into a set of cells; five cells have been considered in each membrane module. The dynamic changes in composition and temperature of the retentate in each cell are described by means of ordinary differential equations. As heat resistances through the membrane are usually negligible, the temperature on the retentate and permeate sides in each cell are assumed to be equal. The molar holdup in each cell M_R is assumed constant, so the total molar balance is algebraic. Thus, the mass and energy balances are as follows:

(Eqs. 6-8)

$$\frac{dM_R}{dt} = 0 = F_{R,n-1} - F_{R,n} - F_{P,n}$$

$$M_R \frac{dh_{R,n}}{dt} = 0 = F_{R,n-1}\, h_{R,n-1} - F_{R,n}\, h_{R,n} - F_{P,n}\, H_{P,n}$$

$$M_R \frac{dz_{R,n,i}}{dt} = 0 = F_{R,n-1}\, z_{R,n-1,i} - F_{R,n}\, z_{R,n,i} - F_{P,n}\, z_{P,n,i}$$

where

$F_{R,n}$ = molar flowrate of the liquid retentate from cell *n* (kmol h^{-1})

$F_{P,n}$ = molar flowrate of vapor permeate from cell *n* (kmol h^{-1})

$h_{R,n}$ = molar enthalpy of liquid retentate in cell *n* (GJ $kmol^{-1}$)

$H_{P,n}$ = molar enthalpy of vapor permeate leaving cell *n* (GJ $kmol^{-1}$)

$z_{R,n,i}$ = mole fraction of component *i* in the liquid retentate in cell *n*.

$z_{P,n,i}$ = mole fraction of component *i* in the vapor permeate leaving cell *n*.

The permeate flowrate is the sum of the two components (ethanol and ETBE) fluxes times the membrane area (A_{mem}) as given by Eq. 9, and the composition of the permeate is given by the ratio of partial to total flux (Eq. 10).

$$F_{P,n} = A_{mem}\left(J_{n,ethanol} + J_{n,ETBE}\right) \quad \text{(Eq. 9)}$$

$$z_{P,n,i} = A_{mem} \times \frac{J_{n,i}}{F_{P,n}} \quad \text{(Eq. 10)}$$

The flux of component "*i*" in each cell is calculated using the following equation:

$$J_i = Q_i\left(z_{Ri}\,\gamma_i\,P_i^{sat} - z_{Pi}\,P_{permeate}\right) \quad \text{(Eq. 11)}$$

The temperature of the retentate is calculated from the known liquid enthalpy $h_{R,n}$ and the known retentate composition $Z_{R,n}$ using physical properties relationships.

The Aspen Custom Modeler (ACM) software is used to simulate the pervaporation process. Composition and temperature of the retentate and permeate streams are variables distributed along the module, which are computed by simultaneously solving the material and energy balances (Eqs. 6-8). To do this, the thermodynamic properties that are a function of temperature and composition need to be computed in each cell using subroutines specific in ACM software. Thus, properties such as activity coefficients, vapor pressure, density, heat capacity, and liquid and vapor enthalpies are calculated as variables distributed along the membrane module. In addition, the membrane permeances are also calculated in each cell using the equations of the proposed model (Eqs. 1-5) as a function of the activities and temperature. The differential and algebraic equations (Eqs. 6-11) for each cell and each module are incorporated in the Aspen Custom Modeler program. The ACM model is then exported to Aspen Plus software as a standalone module to integrate the pervaporation membrane module into global flowsheets. So we can evaluate diagrams with different configurations or different number of membrane modules, and analyze the influence of the recycling streams (recovered unreacted ethanol). Considering the commercially available pervaporation modules, a membrane area of 30 m^2 for each module was assumed. Permeating molecules are removed from the downstream surface of the membrane in the vapor phase, and the latent heat for the phase change is obtained from the sensible heat of the feed [6]. Thus, in PV cells a temperature drop will be observed between the feed inlet and the retentate outlet streams. Feed pressure has been chosen such that the feed to the PV modules is in the liquid state at the operating temperature (70 ºC).

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