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Screening of pervaporation membranes with the aid of conceptual models: An application to bioethanol production

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ABSTRACT

In this paper, we assess the performance of a given hydrophobic membrane from the conceptual design of a hybrid process formed by the hydrophobic membrane itself and the separation train located downstream. To this end, a single pervaporation experiment with a model ethanol–water mixture is needed to estimate the minimum area requirement of the hydrophobic membrane. Short-cut methods, on the other hand, can be used to estimate the minimum number of stages and reflux ratio of the distillation column. Estimation of the minimum area requirement for a hydrophilic membrane, which is considered to overcome the azeotropic composition, requires the integration of a spatially one-dimensional isothermal mass transfer model of the unit until the desired biofuel purity is achieved in the corresponding retentate stream.

The idea behind the approach is that the performance of a given membrane must be measured taking into account the overall hybrid process given that the hydrophobic membrane itself performs only a part of the desired separation.

The hybrid process is then assessed on the basis of a cost estimate using the minimum membrane areas of the two membrane units together with minimum number of stages and minimum reflux ratio of the distillation column among other structural and operating variables.

The outcome allows for the screening of pervaporation membranes, and yields valuable insights into the nature of the process as well as the constraints that a hybrid process may face. Membranes can be assessed based on their overall process performance by this method; only the subset of membranes presenting the best economic figures can be considered for a further analysis.

1. Introduction

Pervaporation is a well-known membrane based separation process with major applications in the dehydration of organic solvents, particularly those which form azeotropes with water (such as ethanol and isopropanol). The first systematic work on pervaporation was done by Binning et al. [1] at American Oil in the 1950s. They explained the mass transfer process through thin plastic films in terms of the solution-diffusion mechanism and emphasized the commercial potential for separating azeotropes and several organic mixtures. The process was not commercialized until 1982 when GFT (Gesellschaft fuer TrennTechnik GmbH, Germany) installed the first commercial pervaporation plant to deal with alcohol dehydration [2]. GFT has since installed more than 100 such plants.

One of the key issues in bioethanol fermentation is the inhibition that the fermentative microorganism (yeast) experiences by the product itself. As a consequence, a rather low ethanol concentration is reached in the final fermentation broth [3]. Several authors pointed out that this problem could be overcome by the use of a solvent removal technology like hydrophobic pervaporation [4–8]. Moreover, the performance of the fermentation unit may be improved due to an increase in the concentration of viable yeast cells through water removal via pervaporation and the use of more concentrated substrate solutions [9]. Additional benefits emerging from the integration of the fermentation with a pervaporation unit would be the switching of the operating mode of

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Nomenclature

A, A_{min}, a_{min}	membrane area (m^2), min = minimum
$a_{i,P}$	activity of component i in permeate
B	bottom flow rate (kmol/s)
D	distillate flow rate (kmol/s)
$E_{a,i}$	apparent activation energy of component i (J/mol)
EOS	equation of state
ΔT_{min}	minimum approach temperature in heat exchangers
Hyd+	hydrophilic
Hyd−	hydrophobic
J_i^{mass}	mass flux of component i through the membrane (g/(m^2 h))
J_i^{mol}	molar flux of component i through the membrane (kmol/(m^2 h))
L_F	feed flow rate leaving the fermentation unit (kmol/s)
$L_F^{infinite}$	36 kmol/s
L_R	retentate flow rate leaving the hydrophobic membrane (kmol/s)
LMTD	logarithmic mean temperature difference
M_i	molecular weight of component i
m_i^0	parameter for component i, mass-transfer model in Vier [41]
MINLP	mixed integer non-linear programming
N_i	parameter for component i, mass-transfer model in Vier [41]
NIST	National Institute of Standards and Technology
OC	overall cost (U$S/year)
OCp	overall cost of pervaporation unit (U$S/year)
OCvr	overall cost of vacuum-refrigeration system (U$S/year)
P_i^0	saturated vapor pressure of component i (kPa)
P_p	permeate pressure (kPa)
P^+	permeate flow rate leaving the hydrophilic membrane (kmol/s)
P^-	permeate flow rate leaving the hydrophobic membrane (kmol/s)
P_{high}	high operation pressure of the refrigeration cycle (kPa)
P_{low}	low operation pressure of the refrigeration cycle (kPa)
PSI	performance separation index
PSI_B	performance separation index for binary mixtures
PSI_M	performance separation index for multicomponent mixtures
R	universal gas constant (J/(mol K))
R, r	retentate flow rate leaving the hydrophilic membrane (kmol/s)
R_{min}	minimum reflux ratio of the distillation column
R_{op}	actual reflux ratio of the distillation column
T, T_{max}	temperature, max. working temp. of the hydrophilic membrane (K)
$T_{cooling}$	cooling temperature of the permeate stream
$T_{freezing}$	freezing point
x_B	mass or mole fraction of ethanol in B
x_D	mass or mole fraction of ethanol in D
x_L	mass or mole fraction of ethanol in the feed to the hydrophobic membrane
x_N	minimum feed composition for which a tangent pinch controls the separation
x_F	mass or mole fraction of ethanol in the feed to the column
x_{P+}	mass or mole fraction of ethanol in P^+
x_{P-}	mass or mole fraction of ethanol in P^-
x_P	feed pinch
x_R	mass or mole fraction of ethanol in R
x_{R-}	mass or mole fraction of ethanol in L_R
x_t	tangent pinch
x_i, y_i	retentate and permeate mole fractions in mass transfer models
$x_{ethanol}$, $y_{ethanol}$	ethanol liquid and vapor mole fractions in the diagram y versus x
VCRC	vapor-compression refrigeration cycle

Greek letters

α	selectivity factor
α_i	parameter for component i, mass-transfer model in Vier [41]
β	enrichment factor
γ_i	activity coefficient of component i
σ_{EtOH}^P	ethanol recovery in condensed permeate (%)

the fermentor from batch to continuous and the elimination of the beer column in the flowsheet of the conventional process [4,6].

For the production of biofuels, pervaporation can be applied to both the recovery of alcohols from fermentation broth and for the dehydration of the alcohols to meet fuel dryness specifications [9,10]. Huang et al. [11] performed a comprehensive review of feasible separation technologies in biorefineries. The mentioned authors include the hybrid process pervaporation–fermentation followed by ethanol dehydration via hydrophilic pervaporation among the technologies showing significant potential and great promise for further investigation, development and application.

Sukitpaneenit and Chung [12] present a comprehensive survey of various membrane materials ranging from polymers, inorganic membranes, and mixed-matrix or hybrid membranes available in the literature for ethanol recovery. A summary of the survey is shown in Fig. 9 of the mentioned paper. According to the mentioned authors, most polymeric membranes reported in previous studies have a relatively low selectivity with a wide range of permeation flux. Silicalite-1 or hydrophobic zeolite membranes exhibit both high selectivity and flux while the pervaporation performance of mixed-matrix or hybrid membranes, which are mostly silicalite-1/PDMS membranes, is spatially scattered in the transition gap between both respective materials. The authors also report results in terms of flux and separation factor for self-developed PVDF/nanosilica dual-layer hollow fibers. They achieved the target for the separation factor of 20 at a permeation flux of 1.1 kg/(m2 h) for a 5 wt.% ethanol feed solution at 50 °C.

In this context, the screening of hydrophobic membranes based on limited information is critical given that the selection task is often costly in time and resources. The product between flux and selectivity appears as the most obvious way to assess the performance of a given hydrophobic membrane. However, in order to fully understand the long-term performance in an integrated system, the analysis must be enhanced by incorporating information about the membrane stability and the influence of fermentation by-products on the separation of ethanol from water for long term experimental runs of a pervaporation module coupled to a laboratory bioreactor operated in a continuous fashion [4]. This is a costly and time-consuming task that should be reserved only for a limited number of membranes.

Several authors have been investigating the influence of fermentation by-products on flux and selectivity of different hydrophobic membranes. Chovau et al. [6] found, for example, that weak acids rendered the Pervap 4060 membrane from Sulzer Chemtech (Switzerland) more hydrophilic, resulting in an increase of water flux up to 48% and a reduction in ethanol permeate